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EQUATION OF STATE OF SOLIDS

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EQUATION OF STATE OF SOLIDS

BY

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ABSTRACT

In Section I an attempt is made to derive the degeneracy factor of Eyring's Significant Structure Theory for a particular model of a solid with vacant lattice sites. A form is obtained which differs from that obtained by Eyring and which gives results less satisfactory than Eyring's factor when compared with Hugoniot data.

In Section II some equilibrium Hugoniot states are calculated for a mixture of two materials and the formulae are applied to combinations of quartz-like and polyethylene-like materials. Gruneisen parameters are found to differ somewhat from those calculated with a simple mass-weighted mixing formula and, in general, the properties of the more compressible material tend to dominate. Some elastic calculations are made for various composite configurations. It is noted that conditions of uniaxial strain are violated, and that the relations between mean pressure and volume are sensitive to the boundary condition on the face of the composite. Some comments are made about deviations from equilibrium.

Conventional methods for reducing ultrasonic velocity data taken at high pressures require a priori knowledge of the compressibility as a function of pressure if elastic constants are to be calculated. In Section III an iterative procedure is outlined which makes it possible to determine the elastic constants provided only that ambient pressure values of thermal expansion coefficient, its temperature derivative, and specific heat at constant pressure are known. The method is applied to travel time measurements in NaCl and KCl made by Bartels and Schuele. The new procedure changes values of the elastic constants by about 1%.

Section IV extends the above iterative procedure to include data and constants for crystals of arbitrary symmetry. It is applied to calcite and rutite for illustration.

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PART I

EQUATION OF STATE FROM SIGNIFICANT STRUCTURE THEORY

C. T. Tung

Two computations have been made in attempts to improve the Significant Structure Theory described in Technical Summary Report No. 3. The theory requires at every P and T the computation of the "solid" part of the volume, V_s, before the liquid volume, V, can be determined. In Summary Report No. 3, V_s is computed from an extrapolation of the experimental solidus for argon. It appears logically superior to use the solid part of the partition function to compute V_s, even though this is out of the equilibrium range of the solid phase. The program was modified to accomplish this, but the results were unsatisfactory, apparently because the solid partition function is unsatisfactory for outside the equilibrium region.

In the Significant Structure Theory of liquids, a partiton function of a liquid is considered as three parts: solid partition function, degeneracy factor, and gas partition function. Two proportionality constants are introduced into the degeneracy factor of Eyring's model and they are determined by fitting the thermodynamic properties at normal conditions; it is doubtful that these two constants are really constant over a wide range of pressures and temperatures. To avoid this confusion and to search for a more realistic mathematical description of the degeneracy factor, we give an elementary derivation of this factor for simple liquids (such as argon, xenon, neon, krypton, etc.) based on some simple geometrical configurations.

Let us define the following:

$\phi(r)$ -- intermolecular potential of separation distance r.

V_s -- molar volume of solid.

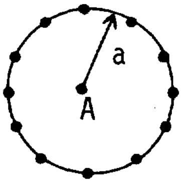
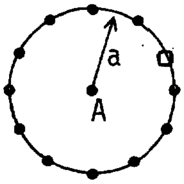
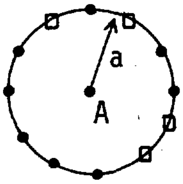
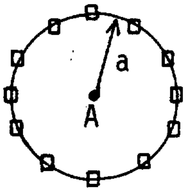
V -- molar volume of liquid.

$X = V_s/V$ -- probability for a site to be occupied by a molecule.

$Y = (V-V_s)/V$ -- probability for a site being empty (hole).
M -- coordination number (=12).
a -- nearest neighbor distance.

As far as a given atom A is concerned, the positional degeneracy of atom A is essentially determined by its nearest neighboring populations of atoms and holes. There are **thirteen types of geometrical configurations** as follows (actual picture being three-dimensional):

(· denoting atom and □ denoting hole)

type j =	0	1	j	12
configuration	 no hole adjacent to A	 1 hole adjacent to A	 j holes adjacent to A	 12 holes adjacent to A
P_j probability of jth type	$C_0^M X^M Y^0$	$C_1^M X^{M-1} Y^1$	$C_j^M X^{M-j} Y^j$	$C_M^M X^0 Y^M$
E_j total energy of atom A in jth type	E_o	$E_1 = E_o - \phi(a)$	$E_j = E_o - j\phi(a)$	$E_M = E_o - M\phi(a)$

E_o is the total energy of atom A when the first shell is completely filled.

Let us denote the averaged total energy of atom A over twelve configurations as $\overline{E}$. Then, we have

$$\begin{aligned}\overline{E} &= \sum_{j=0}^{12} P_j E_j = \sum_{j=0}^{12} C_j^{12} X^{12-j}[E_0 - j\phi(a)]Y^j \\ &= E_0 \sum_{j=0}^{12} C_j^{12} X^{12-j} Y^j - \phi(a) \sum_{j=1}^{12} jC_j^{12} X^{12-j} Y^j \\ &= E_0 (X + Y)^{12} - \phi(a) Y[\partial(X + Y)^{12}/\partial Y] \\ &= E_0 - 12Y\phi(a) = E_0 - 12\phi(a)(V - V_s)/V \qquad (1.1)\end{aligned}$$

Now, let us observe

$$\exp(-\overline{E}/kT) = [\exp(-E_0/kT)][\exp(+12\phi(a)(V - V_s)/VkT)].$$

Thus, we get

$$\text{positional degeneracy factor} = \exp[+12\phi(a)(V - V_s)/VkT]. \qquad (1.2)$$

If $|+12\phi(a)(V - V_s)/VkT| \ll 1$, we have

$$\text{positional degeneracy factor} = 1 + 12\phi(a)(V - V_s)/VkT. \qquad (1.3)$$

Here, nearest neighbor distance, a, can be expressed in terms of V_s by

$$a = (\sqrt{2}V_s/N)^{1/3},\text{ N being Avogadro's number.}$$

The validity of Eq. (1.2) or Eq. (1.3) is restricted to the condition that $\phi(a)$ be positive, since the positional degeneracy factor must always be greater than or equal to one.

Replacing Eyring's degeneracy factor, $g = 1 + n_h \exp[-aE_s V_s/(V-V_s)NkT]$, by Eq. (1.2), we calculate the Hugoniot. The results are less satisfactory than those obtained with the Eyring model, indicating that his factor summarizes effects other than the spatial degeneracy considered here.

PART II

COMPRESSION OF COMPOSITE MATERIALS

G. E. Duvall and S. M. Taylor, Jr.

2.1 INTRODUCTION

We define a composite material as one in which the physical properties vary from point to point, usually, but not necessarily, periodically. A lattice of mass points with interacting forces is an example of such a system, and the study of wave propagation in lattices is very old. Sir Isaac Newton studied the propagation of waves in a one-dimensional lattice as substitute for a continuous string. With mathematical tools available to him he found the lumped constant system to be simpler than the continuum. Sir William Hamilton also studied the one-dimensional lattice and found the equivalent of the Schroedinger solution, though it was not so concisely expressed since Bessel functions had not yet been invented. In the latter part of the nineteenth century Lord Baden-Powell and later Lord Kelvin used the one-dimensional lattice as a model for the study of optical dispersion.

In modern physical science and technology, problems of x-ray diffraction, electronic, mechanical and thermal properties of solids, E-M antennae design, and even astrophysics all hinge upon the effects of wave propagation in periodic or aperiodic structures or systems.

Problems in the present context vary somewhat from those conventionally associated with lattices because it is not always possible to ignore details of propagation within the components of the composite material and because problems of finite amplitude waves are often involved. This means that the dispersion phenomena which are associated with any lattice become more complicated and that the superposition of multiple disturbances is no longer permitted. In spectral terms this means that propagation velocity depends on both frequency and amplitude and that waves of a single arbitrary frequency cannot be propagated. In such circumstances it is sometimes helpful to consider and attempt to understand a very specific and well-defined simple problem, which may then serve as a base for the understanding of more complicated problems.

For this purpose we consider a half-space of the composite material and suppose that the free surface is subjected to a step-change in pressure or velocity normal to the surface. This state of pressure or velocity at the free surface is maintained indefinitely and we may inquire about the development and structure of the wavefront, deviations from conditions of uniaxial strain, and the equilibrium states in a region long after the wavefront has passed.

Simple as this problem is, its complete solution is still very ambitious and we confine ourselves for the present to questions about the equilibrium state, with some remarks about the developing wavefront.

2.2 EQUILIBRIUM COMPRESSION OF TWO FLUIDS

A. B. Wood many years ago considered a composite system consisting of small gas bubbles dispersed in water.[2.1] He argued that at low frequencies there should be local equilibrium of temperature and pressure amongst gas bubbles and water, that each should assume a volume appropriate to that pressure and temperature, and that the derivative of the resulting pressure-volume relation would accordingly give the sound velocity. To a first approximation the water could be assumed rigid, then the sound velocity is

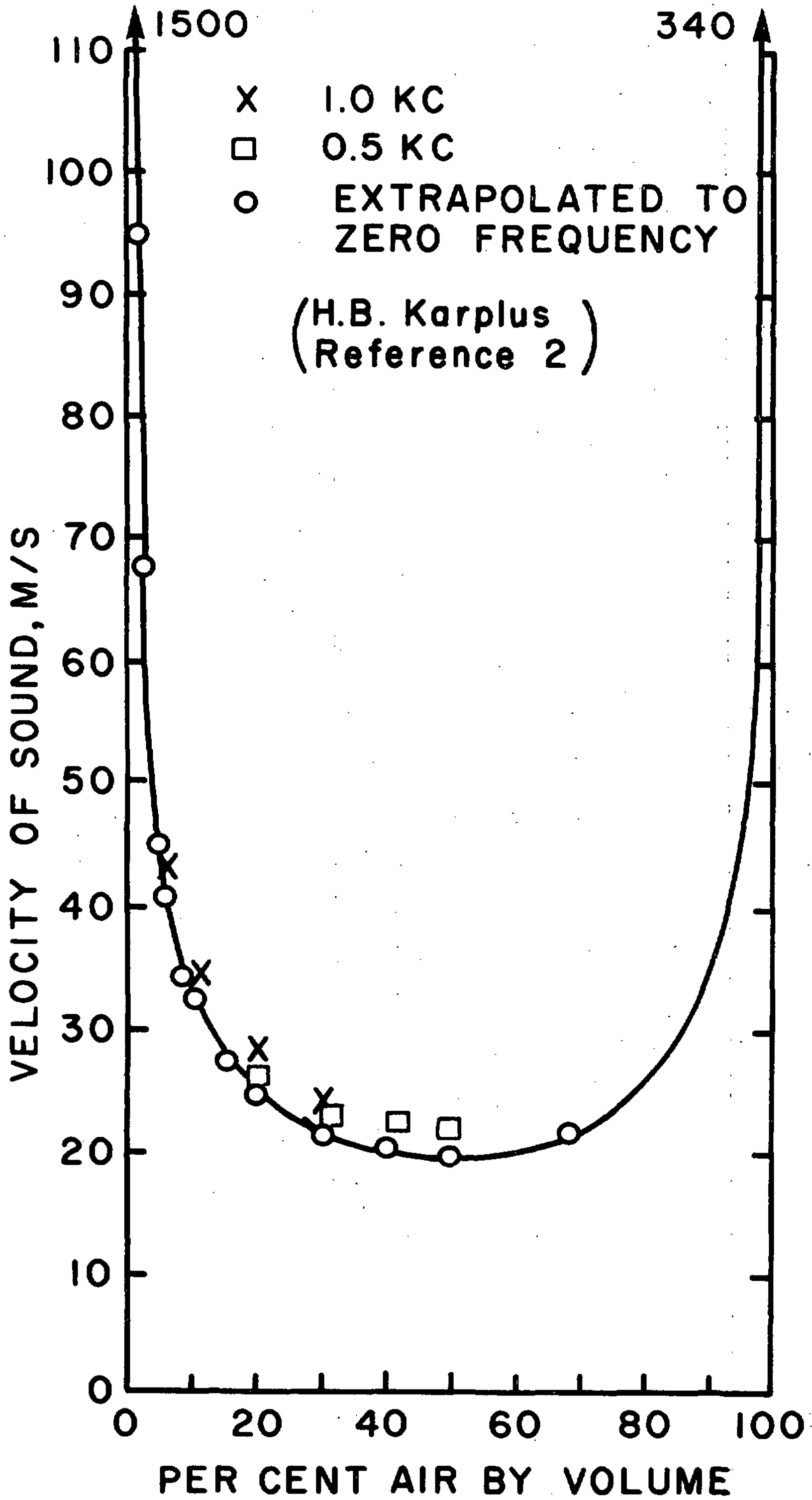
$$c \simeq (P/\rho_0 R)^{1/2}(1 + R) \tag{2.1}$$

where P is ambient pressure, ρ_0 = density of water and R is the volume ratio of gas to water at P and temperature T.

As would be expected, sound velocities predicted by Eq. (2.1) can be very low, as little as a few meters/second. Equation (2.1) has a broad minimum at R = 1 with c = 10 meters/sec when P = 1 bar, with c rising steeply for both large and small R (Fig. 2.1). H. B. Karplus, in work reported about ten years ago, refined Wood's model and tested it experimentally for considerable range of parameters.[2.2,2.3] His results are summarized in Fig. 2.1, taken from reference 2.2. The frequencies at which measurements were made were less than 10% of the mean resonant frequency of the bubbles, and he concluded that there was no significant frequency dispersion.

The principles on which Wood's model are based are well founded and can be extended to other materials. When a compression front passes over a mixture of two materials there will be an initial period in which stress equilibrium is being established. The duration of this period will be the order of several times the larger of the two numbers ℓ_i/c_i, i = 1, 2, where ℓ and c are characteristic dimension and sound velocity of the two components respectively. As a result of compression, each component will experience a temperature rise determined by the stress field and by its own material properties. Roughly speaking, when stress equilibrium has been established, temperatures T_1 and T_2 will exist in the two components. Neglecting convection and radiation, which will accelerate the process, these two temperatures will be equalized in a time the order of several times the larger of the two numbers $C_i\rho_i\ell_i^2/\kappa_i$, i = 1, 2, where C_i, ρ_i, ℓ_i, κ_i are specific heat, density, dimension and thermal conductivity of the ith component respectively. The time required for thermal equilibration is normally much greater than that required for stress equilibration. The ratio of the latter time to the former is the order of ℓ/Λ, where Λ is the scattering mean free path for phonons. Λ may range from a single lattice cell diameter in a disordered structure to grain size in a highly ordered structure.

Sufficiently far behind the front of the shock, then, we expect stress and temperature equilibrium to exist. If the materials be liquid, this reduces to equilibrium in P and T. In either liquid or solid case the thermodynamics of compression are appropriately described by the Gibbs functions of the two components and of the mixture. If interfacial energies are



VELOCITY OF SOUND
IN WATER CONTAINING AIR BUBBLES

Figure 2.1

negligible, we can disregard, for the present, the sizes and shapes of the components and consider only their mass fractions. Let λ be the mass fraction of component 2 and $1 - \lambda$ that of component 1. Then the Gibbs function for unit mass of the mixture is

$$G = (1 - \lambda)\, G_1 + \lambda\, G_2 \tag{2.2}$$

where subscripts "1" and "2" refer to the two components. Other thermodynamic functions are obtained as derivatives of Eq. (2.2):

specific volume: $$V = (\partial G/\partial P)_T \equiv G_P \tag{2.3}$$

$$= (1 - \lambda)V_1 + \lambda V_2 \tag{2.4}$$

specific entropy: $$S = -(\partial G/\partial T)_P \equiv -G_T \tag{2.5}$$

$$= (1 - \lambda)S_1 + \lambda S_2 \tag{2.6}$$

isothermal compressibility:

$$\beta = -(1/V)(\partial V/\partial P)_T = -G_{PP}/V \tag{2.7}$$

$$\beta V = (1 - \lambda)\beta_1 V_1 + \lambda \beta_2 V_2 \tag{2.8}$$

thermal expansion coefficient:

$$\alpha = (1/V)(\partial V/\partial T)_P = G_{PT}/V \tag{2.9}$$

$$\alpha V = (1 - \lambda)\alpha_1 V_1 + \lambda \alpha_2 V_2 \tag{2.10}$$

specific heat at constant pressure:

$$C_P = T(\partial S/\partial T)_P = -TG_{TT} \tag{2.11}$$

$$C_P = (1 - \lambda)C_{P1} + \lambda C_{P2} \tag{2.12}$$

G and its derivatives are assumed to be continuous, so the definitions in Eqs. (2.7), (2.9) and (2.11) lead to the following identities, which can be of use in evaluating experimental data:

$$G_{PPT} = -(\partial\beta V/\partial T)_P = (\partial\alpha V/\partial P)_T \tag{2.13}$$

$$G_{TTP} = -(1/T)(\partial C_p/\partial P)_T = (\partial(\alpha V)/\partial T)_P \tag{2.14}$$

In the application of Eqs. (2.2) - (2.12), we assume the thermodynamic properties of the two components to be known. These equations provide procedures for computing properties of the mixture.

If the compression front envisioned in this problem ever achieves what can be described as a steady profile, then the jump conditions can be applied to relate the equilibrium state behind the front to that ahead. The thermodynamics of compression are then summarized in the Rankine-Hugoniot Equation,

$$E = E_0 + (1/2)(P + P_0)(V_0 - V), \tag{2.15}$$

and in the first and second laws of thermodynamics. Differentiating Eq. (2.15), we have

$$dE = (1/2)(V_0 - V)dP - (1/2)(P + P_0)dV = TdS - PdV$$

or

$$TdS = (1/2)(V_0 - V)dP + (1/2)(P - P_0)dV \tag{2.16}$$

Expressing both V and S in terms of P and T, as in Eqs. (2.3) and (2.4) we obtain for the equation of the Hugoniot in the T, P plane:

$$dT = dP[(V_0 - V) - \beta V(P - P_0) + T\alpha V]/[2C_p - \alpha V(P - P_0)] \tag{2.17}$$

Integration of Eq. (2.17) makes it possible to evaluate any thermodynamic parameter in the equilibrium compressed state, provided $G_1(P,T)$, $G_2(P,T)$ and λ are known.

The Gruneisen parameter Γ and sound velocity c are readily obtained from the above expressions. From the definition of sound velocity:

$$c^2 = -V^2(\partial P/\partial V)_S = -V^2/[(\partial V/\partial P)_S], \tag{2.18}$$

$$(\partial V/\partial P)_S = (\partial V/\partial T)_P + V(\partial T/\partial P)_S$$

$$= -\beta V + T\alpha^2V^2/C_P \tag{2.19}$$

Substituting (2.19) into (2.18) yields

$$c^2 = V^2/(\beta V - T\alpha^2V^2/C_P) \tag{2.20}$$

The Gruneisen parameter is calculated in similar fashion:

$$\Gamma = (V/C_V)(\partial P/\partial T)_V = V\alpha/C_V\beta \tag{2.21}$$

Since $$C_V = C_P - \alpha^2VT/\beta,$$

Eq. (2.21) becomes

$$\Gamma = \alpha V^2/(\beta VC_P - \alpha^2V^2T). \tag{2.22}$$

In computing c and Γ for the mixture, V, αV, βV and C_P are to be determined from Eqs. (2.4), (2.8), (2.10) and (2.12), then substituted into Eqs. (2.20) and (2.22).

In illustrating the above relations and procedures, we would like to say that we had created Gibbs functions for two substances which were consistent with all available experimental data and had all of the proper limiting behavior. Unfortunately we can't. What we have done is to create rather conventional descriptions of a quartz-like material and a polyethylene-like material and use these to illustrate the effects of varying λ on the above parameters. The following assumptions were made for each material:

$$P_i(V,T) = P_i(V,T_0) + b_i C_{Vi}(T - T_0), \quad i = 1,2 \tag{2.23}$$

$$C_{Vi} = \text{constant} \tag{2.24}$$

$$b_i = \Gamma_i/V_i = \text{constant} \tag{2.25}$$

$$P_i(V,T_0) = \frac{1}{\gamma_{io}\beta_{io}}\left[\left(\frac{V_{io}}{V_i}\right)^{\gamma_{io}} - 1\right] \tag{2.26}$$

$$T_0 = 293°\text{K}.$$

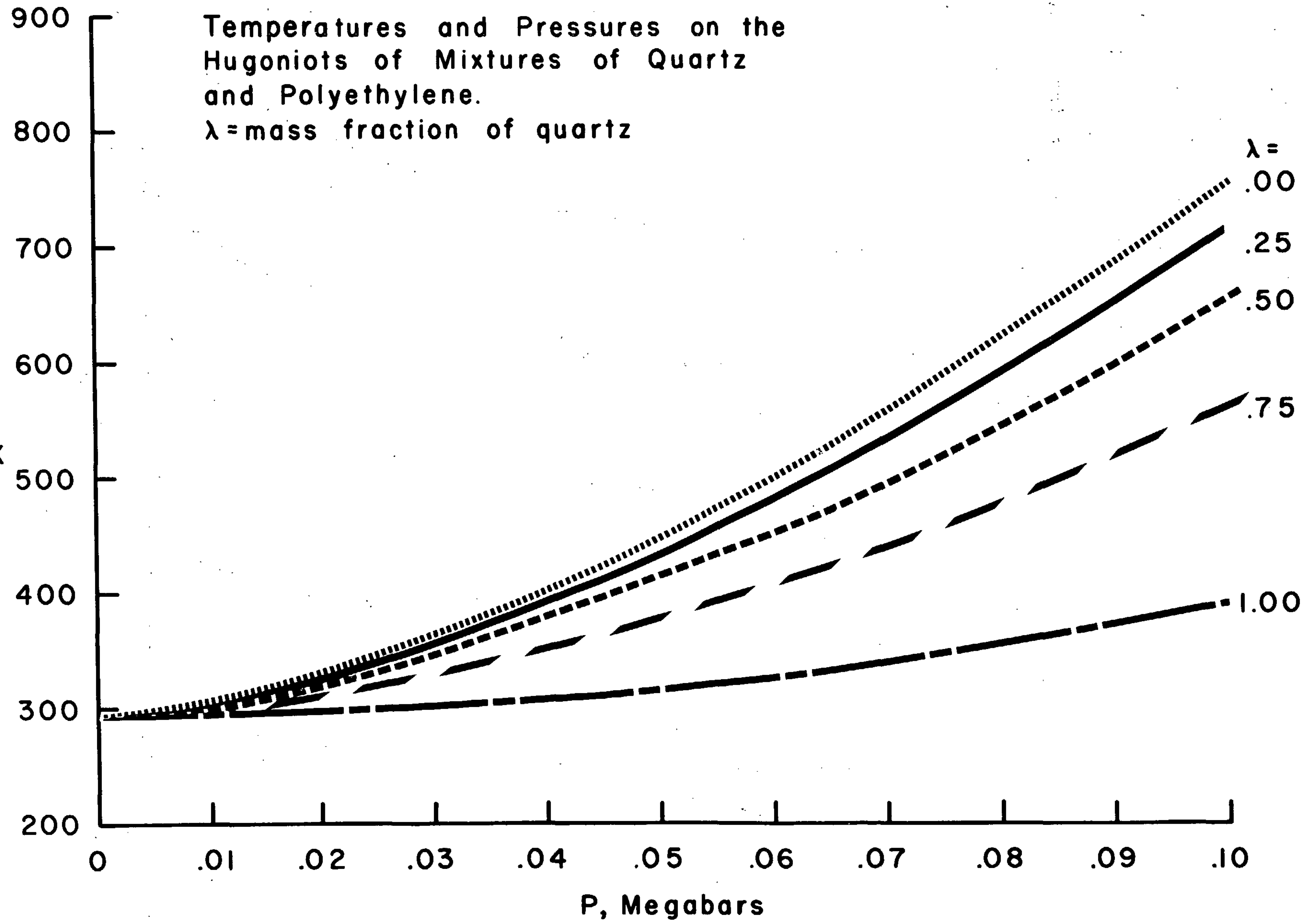
The following constants were used:

	Polyethylene	Quartz
i	1	2
b_i, g/cc	.3887	.7832
C_{Vi}, Mbcc/g°	1.436×10^{-5}	$.56 \times 10^{-5}$
V_{io}, cc/g	1.035	.378
γ_{io}	10.2	5.58
β_{io}, Mb^{-1}	19.31	2.70

The results of computations are shown in Figs. 2.2 - 2.6. Most are not particularly remarkable. Figure 2.2 shows that temperature along the Hugoniot increases very rapidly when a little polyethylene is added to quartz, and that the rate of change of temperature decreases as the amount of polyethylene increases. This is the kind of effect to be expected when a compressible material is added to a relatively incompressible one. The nearly linear change in V/V_0 for fixed P shown in Fig. 2.3 shows that volume is but little affected by temperature changes on the Hugoniot, again as expected. In Fig. 2.4 the Gruneisen parameter, computed from Eq. (2.22), is compared for $\lambda = 0.50$ with a simple mass-weighted average:

$$\Gamma = (1 - \lambda)\Gamma_1 + \lambda\Gamma_2 \tag{2.27}$$

Figure 2.2



Temperatures and Pressures on the Hugoniots of Mixtures of Quartz and Polyethylene.
λ = mass fraction of quartz

Figure 2.3

Pressures and Volumes on the Hugoniots of Mixtures of Quartz and Polyethylene.
λ = mass fraction of quartz.

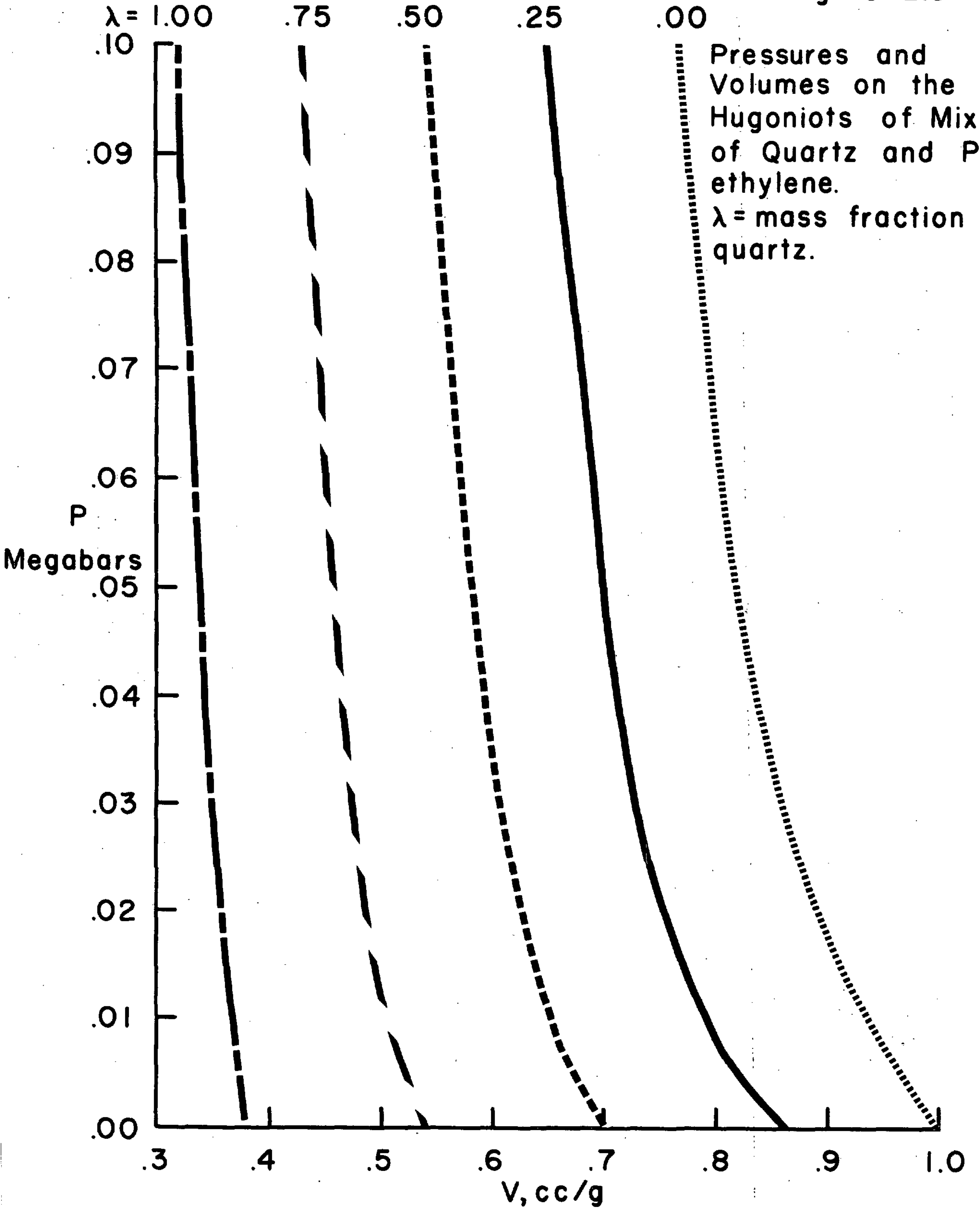
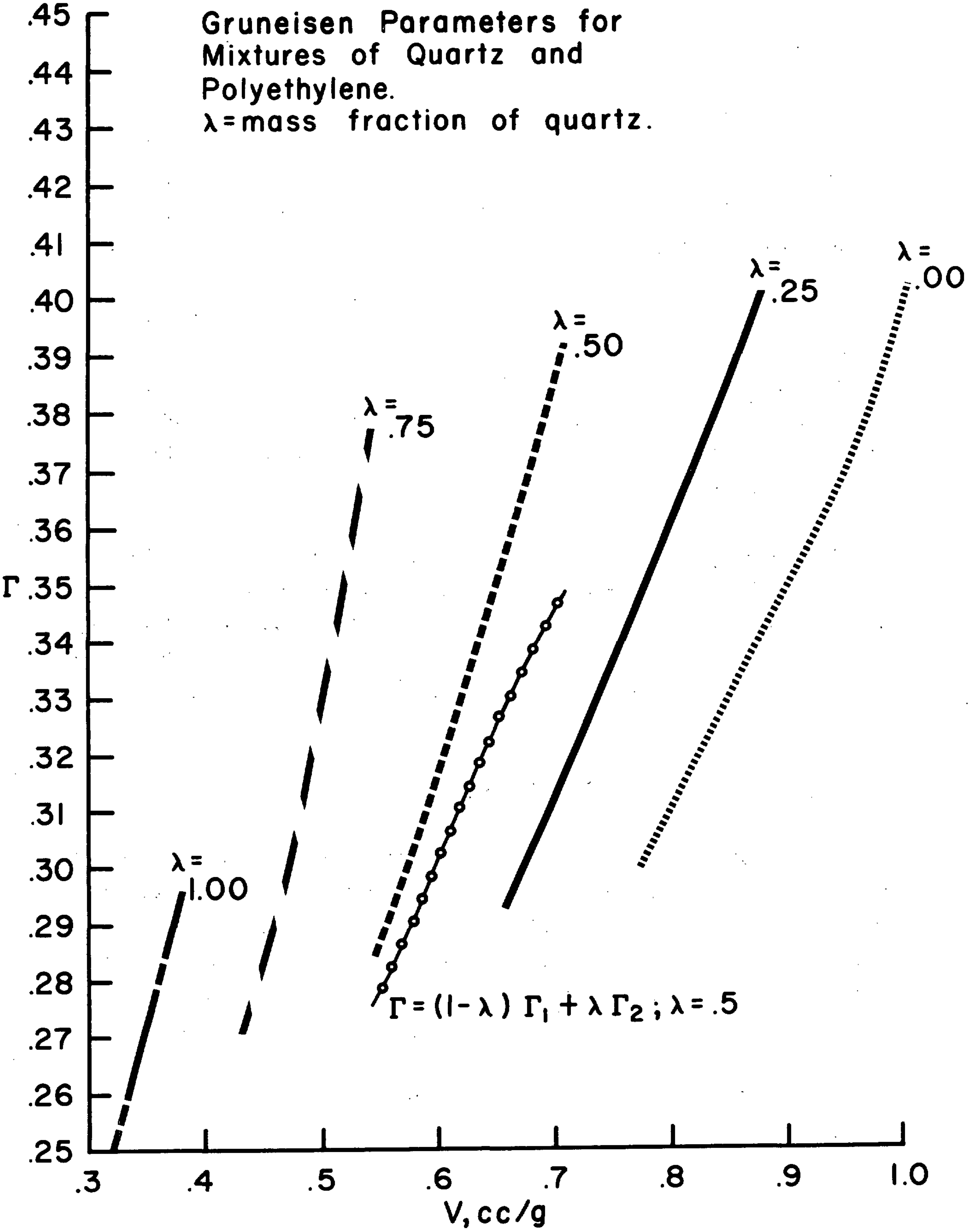


Figure 2.4



Gruneisen Parameters for Mixtures of Quartz and Polyethylene.
λ = mass fraction of quartz.

Figure 2.5 shows perhaps the most interesting result. Although Γ/V is assumed constant for each component, the resultant for the mixture is quite strongly volume dependent; the mass weighted average values differ appreciably from the correct values. Sound velocities, shown in Fig. 2.6, change almost linearly with λ.

These results on variations of Γ and Γ/V with volume and with λ are worthy of particular note. Attempts have been made elsewhere to characterize multicomponent materials in terms of effective Γ's in such a way that the effective Γ turns out to be approximately equal to or less than that of the lower constituent. Experiments performed to check these calculations have produced pressures lower than calculated values by as much as 56 percent, indicating that the effective Gruneisen parameter was even lower than estimated. This result is contrary to those shown in Fig. 2.4; however, experiments were performed with slightly porous samples, and this fact calls the results into question.

The influence of varying Γ on the stress field has been the subject of extensive debate. It seems fairly certain that in some circumstances it can have a substantial effect. For that reason it is most appropriately calculated by the procedure given here when equilibrium conditions are expected. If they are not, it is of no significance anyway.

2.3 LOCAL DEVIATIONS FROM UNIAXIAL STRAIN

The feature of plane stress wave propagation in homogeneous materials which most clearly distinguishes it from other geometries is the exact maintenance of uniaxial strain; no material particle of a continuum undergoes any motion in a direction parallel to the wavefront. This is one of the first conditions to fail in a composite material, except in a special case discussed below.

To illustrate the point we consider several special cases:

Figure 2.5

Γ/V for Mixtures of Quartz and Polyethylene

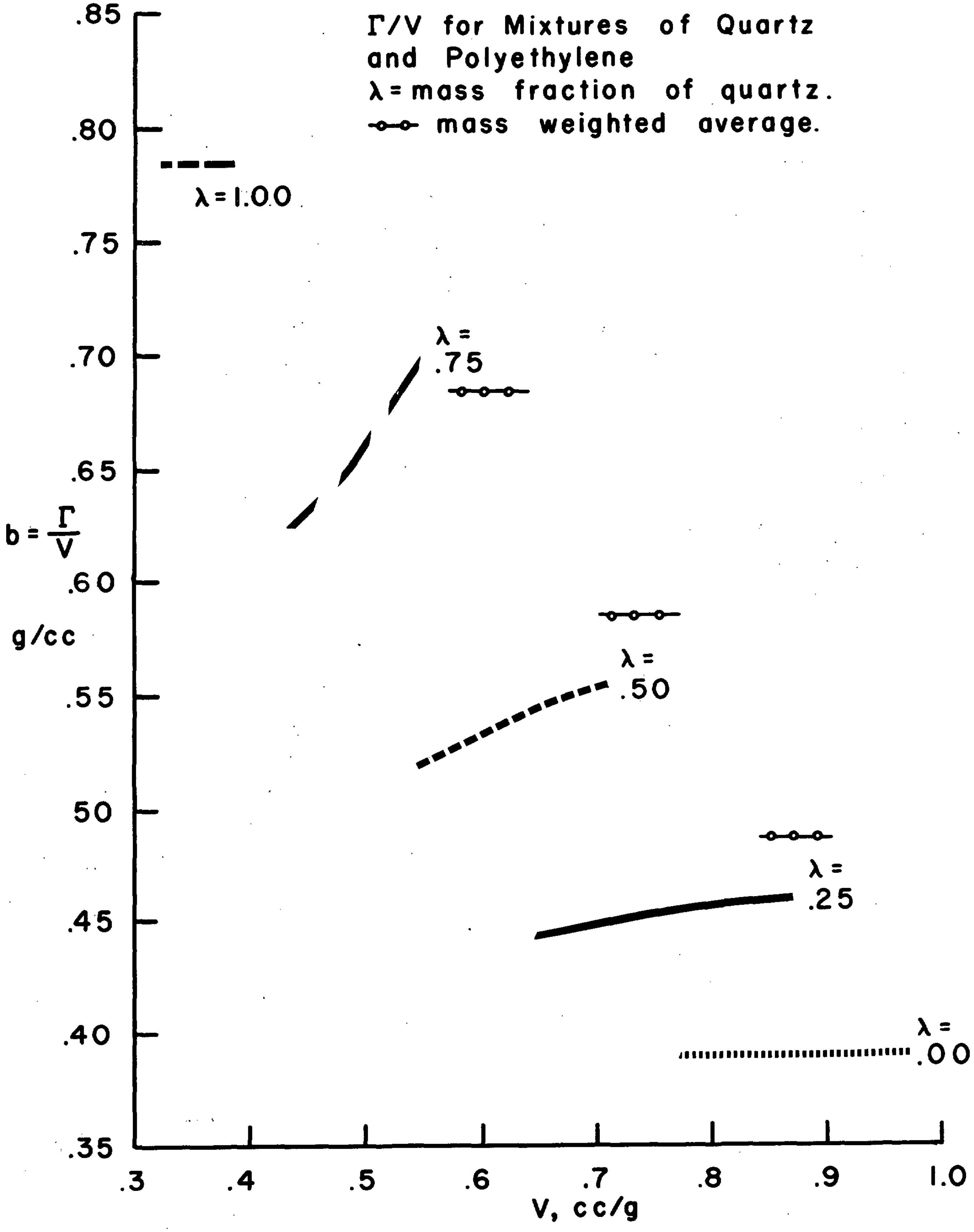
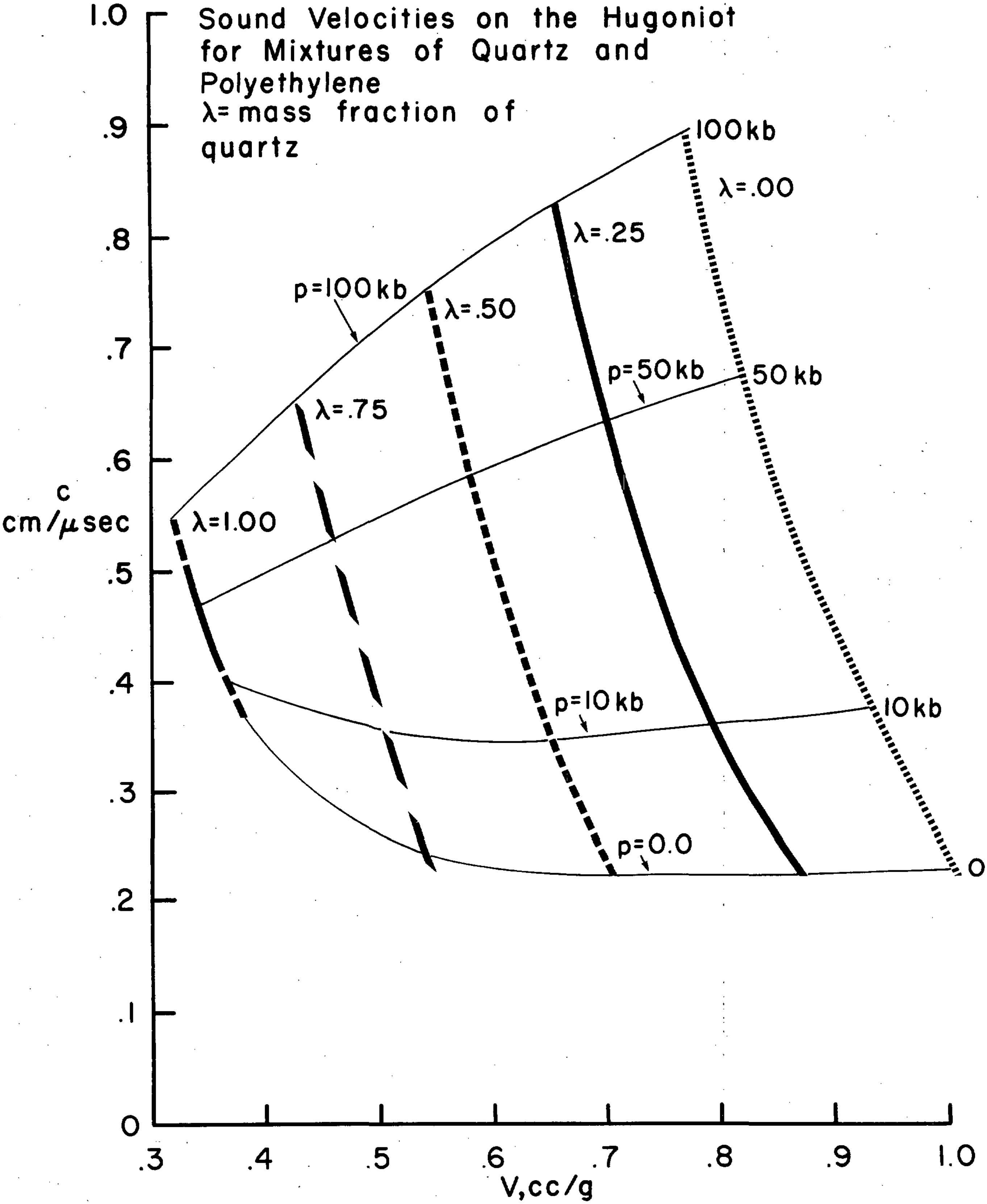


Figure 2.6



Sound Velocities on the Hugoniot for Mixtures of Quartz and Polyethylene
λ= mass fraction of quartz

2.3.1 Two Fluids; Slabs in Propagation Direction

The fluid structure is assumed to be symmetric so that on compression from x_0 to x the cell width, a_0, remains constant. The total specific volumes before and after compression are given by Eq. (2.4). Applying this to the system of Fig. 2.7 yields the relations

$$w_0 x_0 = V_2(P,T)\lambda$$

$$(a_0 - w_0)x_0 = V_1(P,T)(1 - \lambda)$$

$$wx = V_2(P + dP, T + dT)\lambda$$

$$(a_0 - w)x = V_1(P + dP, T + dT)(1 - \lambda)$$

If we choose x_0 so the mass of the cell is one gram, let $x - x_0 = dx$, $w - w_0 = dw$, $V_2(P + dP, T + dT) - V_2(P,T) = dV_2$, etc., the lateral strain resulting from compression dx is

$$\varepsilon_{y2} \equiv dw/w_0 = dV_2/V_2 - dV/V \tag{2.28}$$

$$\varepsilon_{y1} = -dw/(a_0 - w_0) = dV_1/V_1 - dV/V \tag{2.29}$$

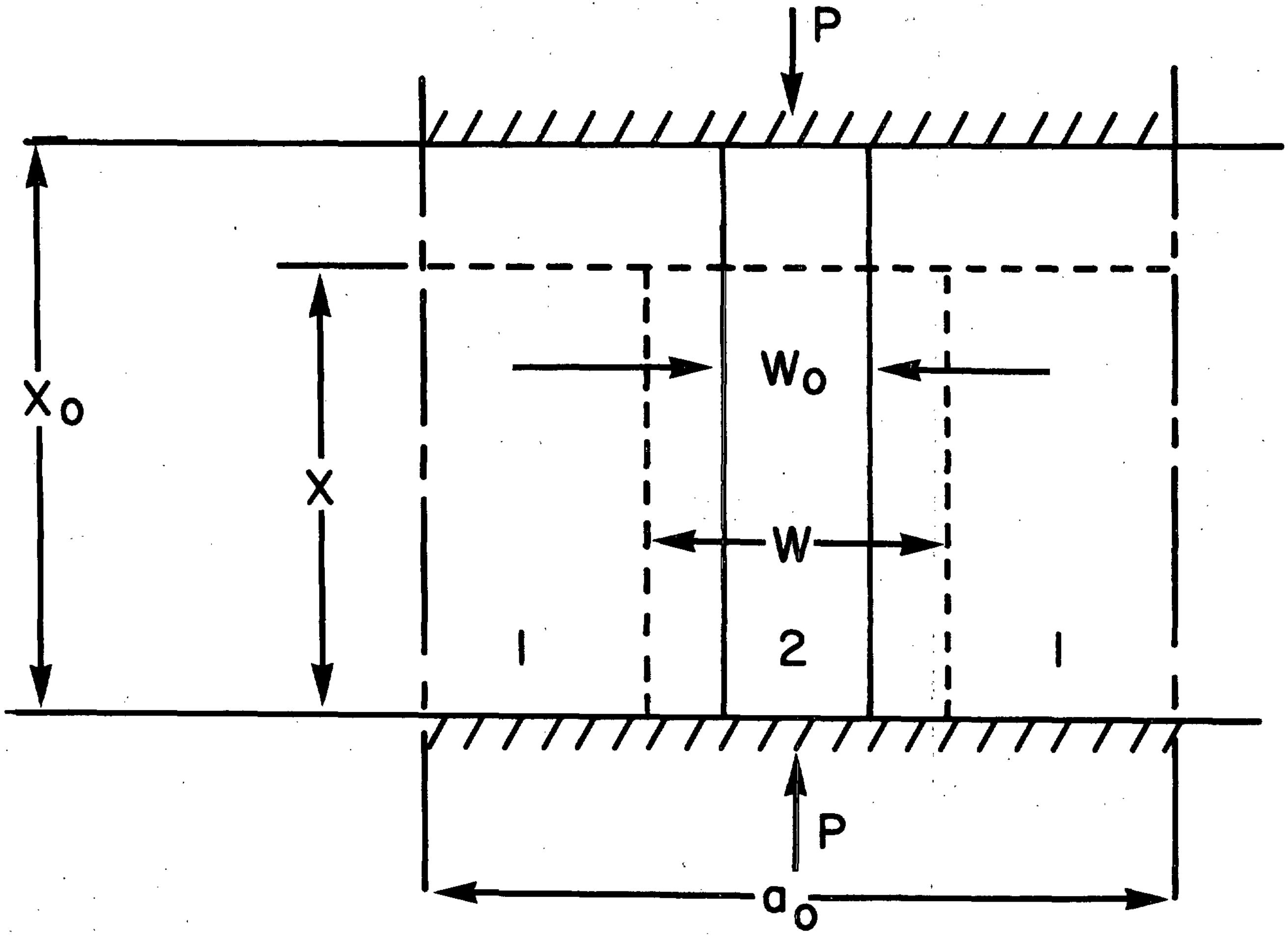
These satisfy the cell condition $\int_0^{a_0} \varepsilon_y dy = 0$.

2.3.2 Two Fluids; Slabs Parallel to Wave Front

In this case, shown in Fig. 2.8, lateral strain, ε_y, is identically zero, $dx = dV$, $dw = dV_2$.

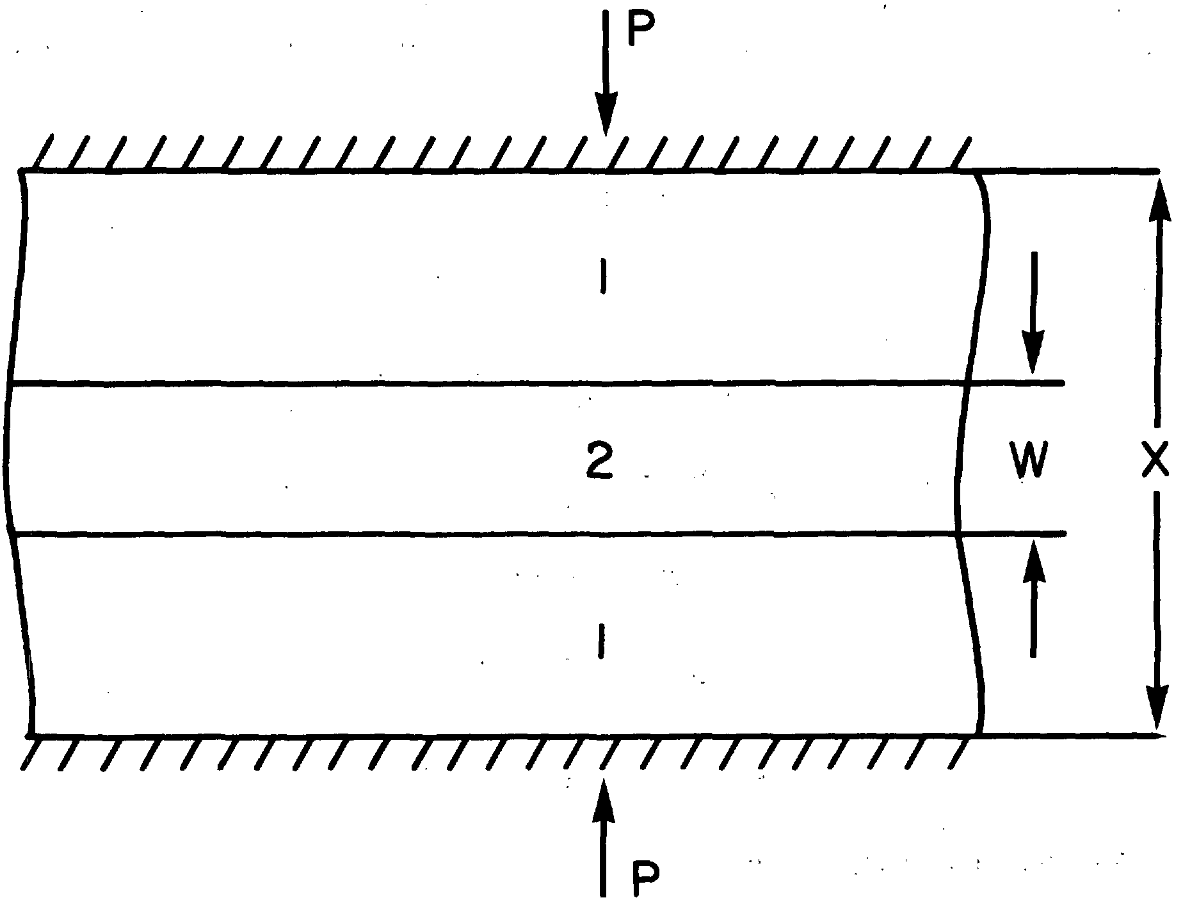
2.3.3 Two Fluids; Rods Normal to Wave Front

Symmetry produces a rectangular cell, of dimensions y_0 by z_0,



Compression of Two Fluid Slabs Normal to Wave Front

Figure 2.7



Compression of Two Fluid Slabs Parallel to Wave Front

Figure 2.8

on the boundary of which the particle motion is normal to the plane of the paper (Fig. 2.9). Again choosing x_0 so as to produce a cell of unit mass, we have

$$x_0 y_0 z_0 = V$$

$$\pi a_0^2 x_0 = A_0 x_0 = \lambda V_2$$

$$(y_0 z_0 - A_0)x_0 = (1 - \lambda)V_1$$

After compression $x = x_0 + dx$, $a = a_0 + da$, $A = A_0 + dA$.

$$dx = dV/y_0 z_0$$

$$A_0 dx + x_0 dA = \lambda dV_2$$

$$(y_0 z_0 - A_0)dx - x_0 dA = (1 - \lambda)dV_1$$

The relative change in area of the rod is

$$dA/A_0 = (dV_2/V_2 - dV/V) \qquad (2.30)$$

If it remains circular in cross-section, the radial strain is

$$da/a_0 = dA/2A_0 \qquad (2.31)$$

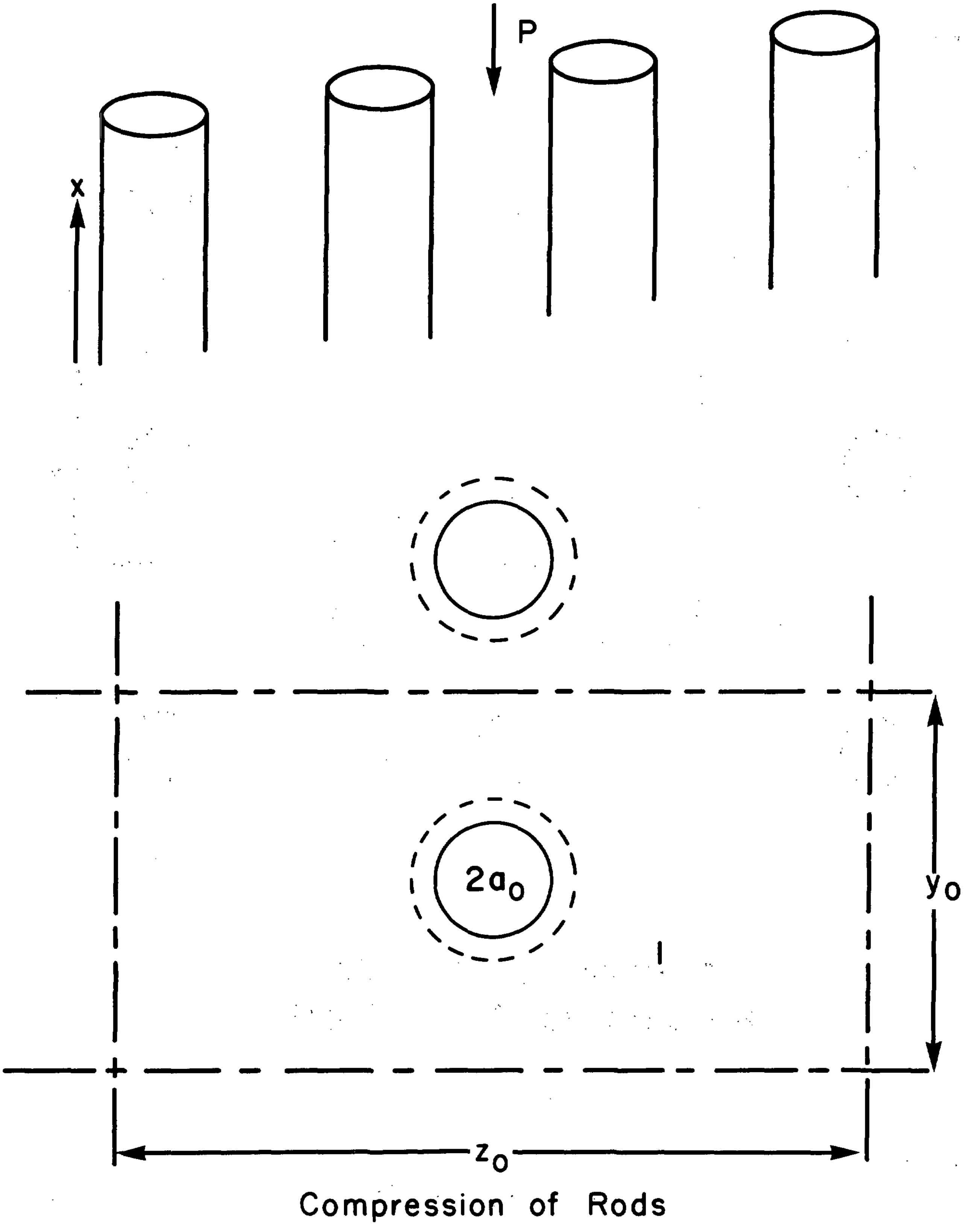
2.3.4 Two Fluids; Rods Parallel to Wave Front

The mass per unit length of the cell shown in Fig. 2.10 is

$$M = x_0 y_0/V.$$

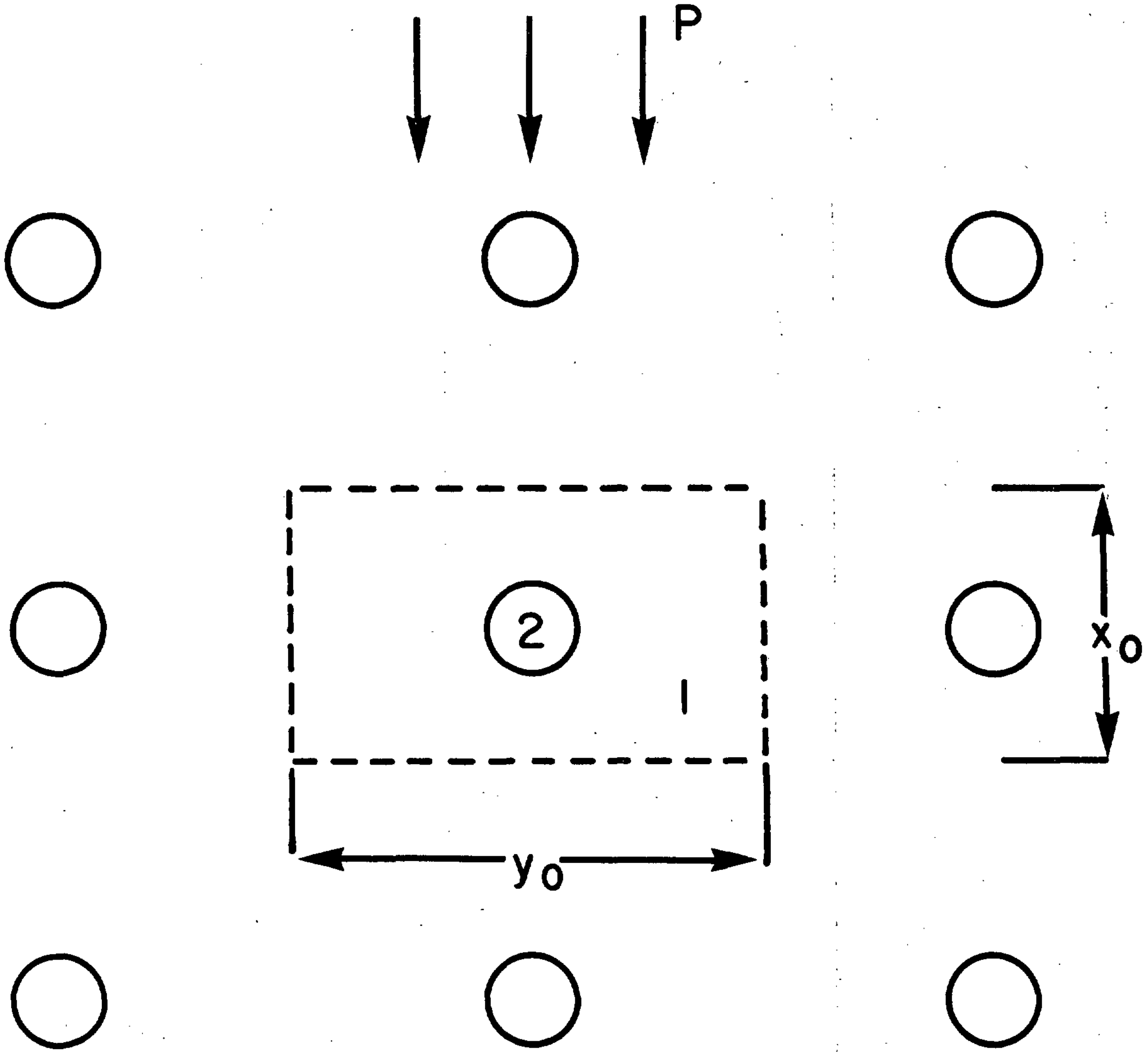
That of the cylinder is

$$M\lambda = A_0/V_2 = \pi a_0^2/V_2$$



Compression of Rods Normal to Wave Front

Figure 2.9



Compression of Rods
Parallel to Wave Front

Figure 2.10

When pressure P is applied as shown, the area of the rod changes by an amount $dA = M\lambda dV_2$; if it retains its circular cross-section the radial strain at its periphery is

$$da/a_o = dV_2/2V_2 \tag{2.32}$$

The same result is obtained if the rods are staggered so that the undistorted cell is hexagonal.

2.3.5 Elastic Slabs Normal to Wave Front[2.4]

In this case, shown in Fig. 2.11, it is not enough to apply a uniform pressure in the direction of compression. Instead we suppose the cell to be compressed by a rigid piston driven by a force F per unit length. Then the mean pressure acting over the cell is $\overline{p} = F/a_o$. Under the assumed conditions the x-displacement is the same for both components, so

$$\varepsilon_{x1} = \varepsilon_{x2} = dx/x_o$$

In the notation of Fig. 2.11 we define specific volumes V_1, V_2, V:

$$V = a_o x_o; \qquad (1 - \lambda)V_1 = (a_o - w_o)x_o; \qquad \lambda V_2 = w_o x_o$$

Differentiating these, we have

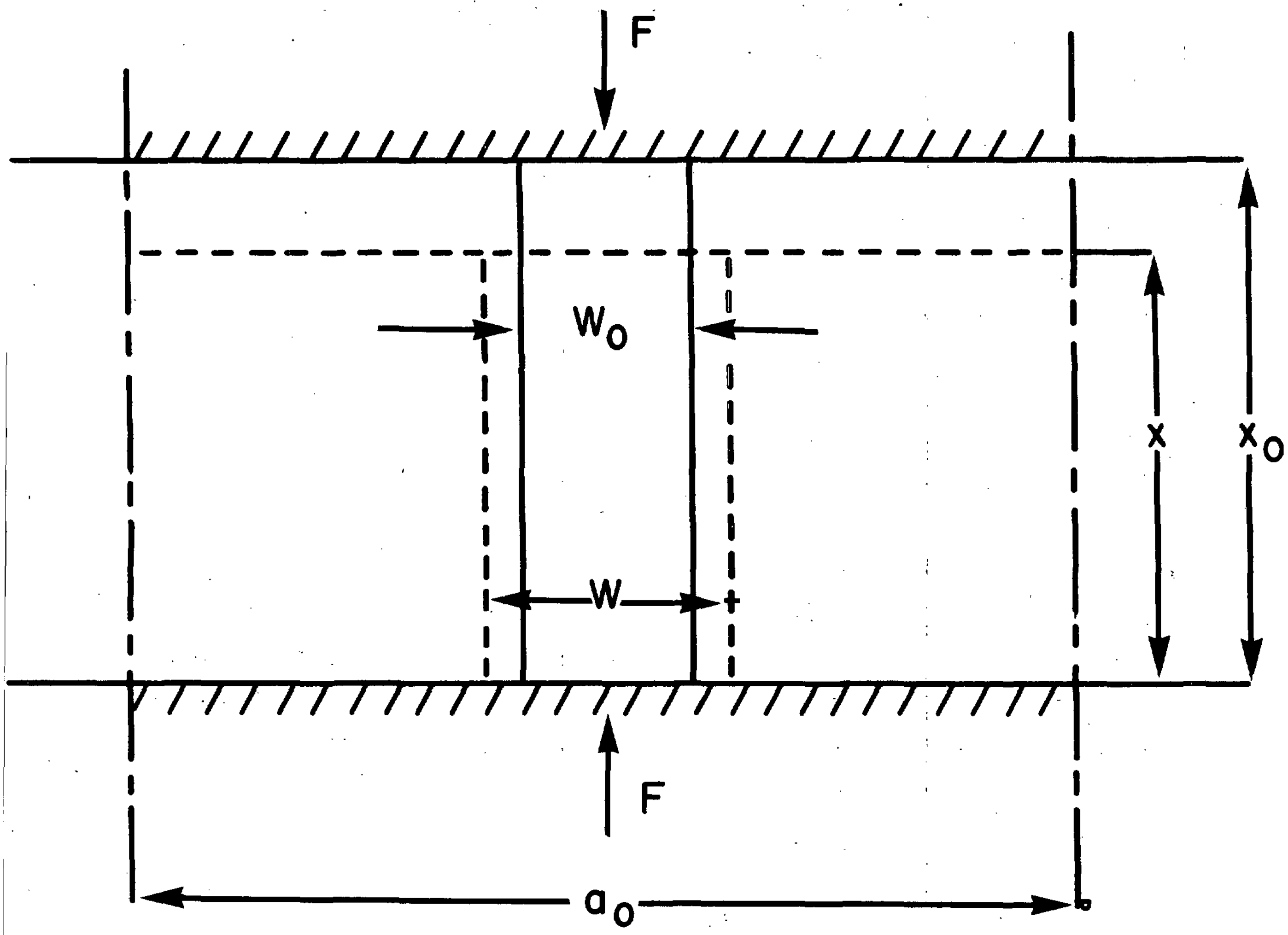
$$a_o dx = dV; \qquad w_o dx + x_o dw = \lambda dV_2; \qquad (a_o - w_o)dx - x_o dw = (1 - \lambda)dV_1$$

For small dx:

$$\varepsilon_{y2} \equiv dw/w_o = dV_2/V_2 - \varepsilon_x; \qquad \varepsilon_x = dx/x_o$$

$$\varepsilon_{y1} = -dw/(a_o - w_o) = dV_1/V_1 - \varepsilon_x$$

$$\varepsilon_{z1} = \varepsilon_{z2} = 0$$



Compression of Elastic Slabs
Normal to Wave Front

Figure 2.11

Assuming Hooke's law with Lame constants L_1, μ_1, L_2, μ_2:

$$\sigma_{x1} = L_1 dV_1/V_1 + 2\mu_1 \varepsilon_x$$

$$\sigma_{y1} = (L_1 + 2\mu_1) dV_1/V_1 - 2\mu_1 \varepsilon_x$$

$$\sigma_{z1} = L_1 dV_1/V_1$$

$$\sigma_{x2} = L_2 dV_2/V_2 + 2\mu_2 \varepsilon_x$$

$$\sigma_{y2} = (L_2 + 2\mu_2) dV_2/V_2 - 2\mu_2 \varepsilon_x$$

$$\sigma_{z2} = L_2 dV_2/V_2$$

In addition we have the relations

$$dV = \lambda dV_2 + (1 - \lambda) dV_1$$

$$\sigma_{y1} = \sigma_{y2}$$

$$\sigma_{x1}(1 - \lambda) V_1 + \sigma_{x2} \lambda V_2 = -F x_o$$

Define

$$\mathcal{V}_1 = (1 - \lambda) V_1; \qquad \mathcal{V}_2 = \lambda V_2; \qquad \alpha = L + 2\mu$$

$$Q = \alpha_1/\mathcal{V}_1 + \alpha_2/\mathcal{V}_2$$

Then the above equations yield the following:

$$dV_1/V_1 = \varepsilon_x [1 + (L_2 - L_1)/\mathcal{V}_1 Q] \tag{2.33}$$

$$dV_2/V_2 = \varepsilon_x [1 - (L_2 - L_1)/\mathcal{V}_2 Q] \tag{2.34}$$

$$\varepsilon_{y1} = \varepsilon_x (L_2 - L_1)/\mathcal{V}_1 Q \tag{2.35}$$

$$\varepsilon_{y2} = -\varepsilon_x(L_2 - L_1)/V_2Q \tag{2.36}$$

$$\sigma_{x1} = \varepsilon_x[\alpha_1 + L_1(L_2 - L_1)/V_1Q] \tag{2.37}$$

$$\sigma_{y1} = \varepsilon_x[L_1 + \alpha_1(L_2 - L_1)/V_1Q] \tag{2.38}$$

$$\sigma_{z1} = L_1\varepsilon_x[1 + (L_2 - L_1)/V_1Q] \tag{2.39}$$

$$\sigma_{x2} = \varepsilon_x[\alpha_2 + L_2(L_1 - L_2)/V_2Q] \tag{2.40}$$

$$\sigma_{y2} = \varepsilon_x[L_2 + \alpha_2(L_1 - L_2)/V_2Q] \tag{2.41}$$

$$\sigma_{z2} = L_2\varepsilon_x[1 + (L_1 - L_2)/V_2Q] \tag{2.42}$$

To a first approximation, waves will be transmitted down the slab with velocities given by

$$c_1^2 = \mathrm{V}_1\partial\sigma_{x1}/\partial\varepsilon_x = [\alpha_1 + L_1(L_2 - L_1)/V_1Q]\mathrm{V}_1 \tag{2.43}$$

$$c_2^2 = \mathrm{V}_2\partial\sigma_{x2}/\partial\varepsilon_x = [\alpha_2 + L_2(L_1 - L_2)/V_2Q]\mathrm{V}_2 \tag{2.44}$$

For comparison, the velocity of waves on a thin plate in air is given by

$$c_p^2 = (\alpha - L\xi)/\rho \tag{2.45}$$

where

$$\text{Poisson's ratio} = \xi/(1 + \xi)$$

ξ plays the same role in extension of a plate with $\varepsilon_z = 0$ as Poisson's ratio in extension of a bar. Comparing Eqs. (2.43) and (2.44) with (2.45) shows that effective values of ξ can be defined for each component:

$$\xi_{1\ \mathrm{eff}} = (L_1 - L_2)/V_1Q \tag{2.46}$$

$$\xi_{2\ \mathrm{eff}} = (L_2 - L_1)/V_2Q \tag{2.47}$$

If, for example, $L_2 > L_1$, $\xi_{1\text{ eff}} < 0$ and component "1" contracts laterally when $F > 0$. As $L_1 \rightarrow 0$, $\xi_{2\text{ eff}} \rightarrow \xi_2 = L_2/\alpha_2$, and component "2" becomes an unsupported plate. When $L_2 = L_1$, uniaxial strain exists.

If components 2 and 1 have large and small moduli, respectively, compression in the x-direction produces a resolved shear stress, $\sigma_{x2} - \sigma_{y2}$, in 2 which will ultimately lead to structural failure of 2. A non-zero modulus in component 1 delays failure of 2 when loading is increased. For example, let failure occur when

$$\phi \equiv (\sigma_x - \sigma_y)^2 + (\sigma_x - \sigma_z)^2 + (\sigma_y - \sigma_z)^2 = 2k^2 \tag{2.48}$$

Then for an unsupported plate with given ε_x

$$\phi_p = 4\mu^2\varepsilon_x^2[1 + \xi^2 + (1 + \xi)^2]. \tag{2.49}$$

When $\xi = \xi_{\text{eff}}$, $\phi \equiv \phi_{\text{eff}}$; when $\xi = 0$, uniaxial strain obtains and $\xi = 0$, $\phi = \phi_o$. Then when $L_2 > L_1$

$$\phi_o \leq \phi_{2\text{ eff}} \leq \phi_p.$$

Failure then occurs for a value of σ_x less than the failure value in uniaxial strain and greater than that for an unsupported plate. Under the same conditions, $\xi_{1\text{ eff}} < 0$ and $\phi_{1\text{ eff}} < \phi_o$, so the value of σ_x at which failure of 1 occurs is greater than for uniaxial strain.

The net result of all this is that waves in the softer component will travel faster than in uniaxial strain, those in the stiffer component will travel more slowly than in uniaxial strain, and that there will, in general, be two cusps in the (p_x,V) or (σ_x,ε_x) curve for the composite due to elastic failure of the components.

The above discussion has been cast in terms of linear elastic materials for convenience and because the results are explicit. The results are readily generalized if ε and σ are replaced by $d\varepsilon$ and $d\sigma$, respectively.

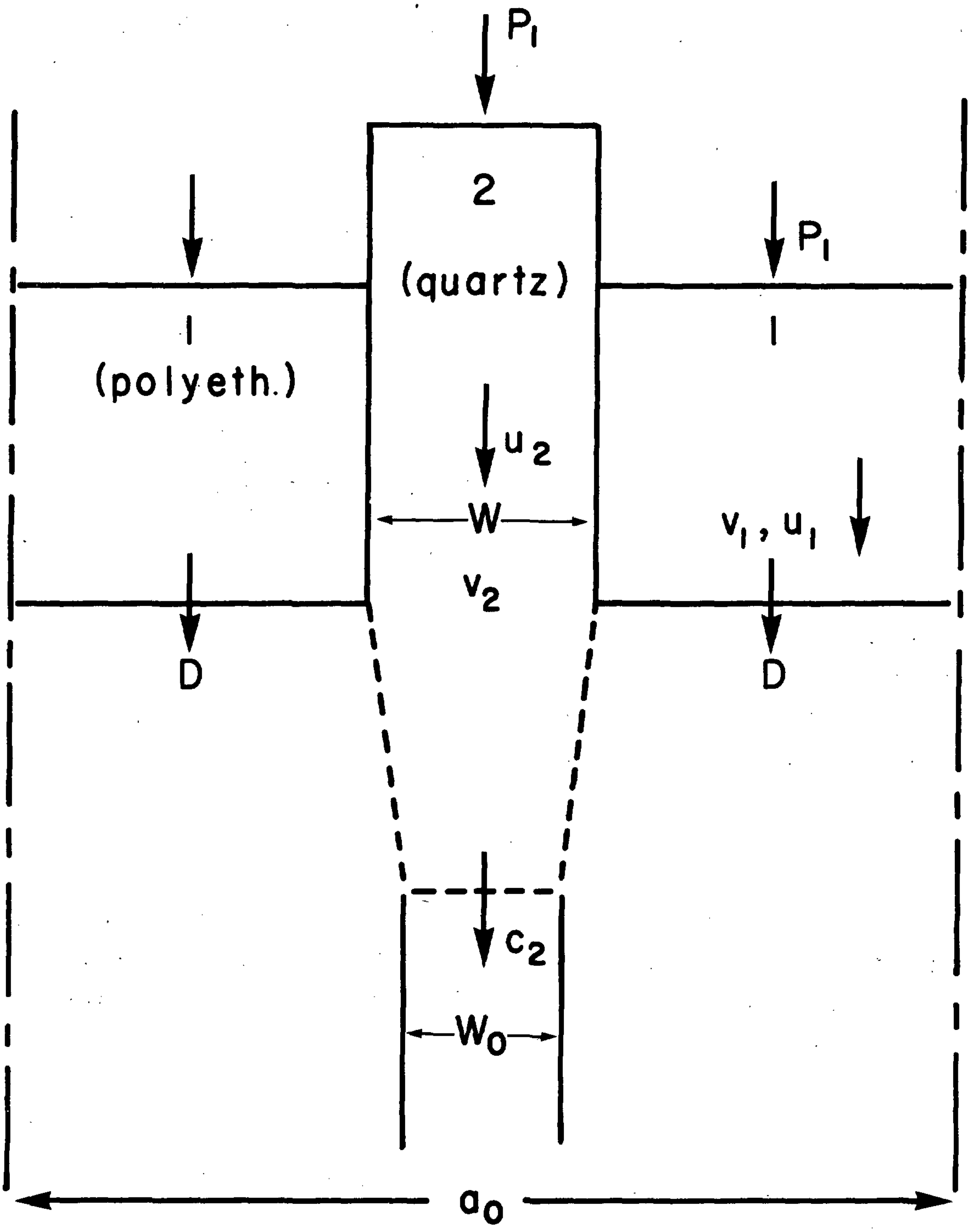
2.4 DEVIATIONS FROM EQUILIBRIUM

As stated in Section 2.2, thermal equilibration takes longer than stress equilibration. The time required depends upon dimensions and materials; and in many real and experimental situations, thermal equilibrium will not be reached. Fortunately wave propagation is sometimes insensitive to thermal effects, unless they produce phase transitions or chemical reactions. In any exceptional cases which must be treated, the effects can be bounded by assuming isothermal compression on the one hand and adiabatic on the other.

For inert, fixed inhomogeneities, stress equilibration time $\sim \alpha \ell / c$, $1 < \alpha < 10$, will usually be a reliable guide. If the inhomogeneities are not inert or are not fixed, a new set of rules applies. The most notable example is in the effect of dislocations on precursor decay. The mechanics of any such case must be examined in detail in order to make any estimate of equilibration time. Another practical example of such a case is that of a granular material in which small grains may slide over one another under the influence of shear forces and friction.

There is another manner in which the usual concepts of equilibration, discussed in Sections 2.2 and 2.3, may be violated: In Fig. 2.11 an element of a cell is assumed to be compressed uniformly by a rigid piston so that ε_x is the same for each component. If, in fact, a real x-travelling shock were being produced, one component would be compressed more than the other, resulting in relative motion at the interfaces and in different stress conditions from those obtained in Section 2.3.5, unless the shock were too weak to break the interface bond.

Consider, for example, alternate slabs of quartz and polyethylene in the geometry of Fig. 2.12. A uniform pressure, p_1, is applied to the top of the column and held there. Wave propagation velocity in quartz is greater than in polyethylene, so waves in the center slab outrun those on the sides. A true steady state is never reached. However a kind of equilibrium may be achieved. The compression wave causes the quartz slab to expand, radiating



Non-Equilibrium Compression

Figure 2.12

energy into the polyethylene ahead of the polyethylene wave front. This tends to inhibit the rate of propagation of energy in quartz. If we suppose that this effect is great enough, we may assume the jump conditions to be approximately satisfied across a wavefront travelling down the cell with velocity D in both components. Then the jump conditions for mass and momentum become

$$\rho_{oi} u_{oi} D = \rho_i y_i (D - u_i) \tag{2.50}$$

$$p_1 y_i = \rho_{oi} y_{oi} D u_i \tag{2.51}$$

$$i = 1,2; \quad y_{o1} = a_o - w_o, \quad y_{o2} = w_o$$

$$y_1 = a_o - w, \quad y_2 = w$$

Define $\mathcal{V}_1 \equiv (a_o - w)x_1$, $\mathcal{V}_2 \equiv wx_2$, where x_1 and x_2 are the respective lengths in "1" and "2" of elements which originally had lengths x_o. Define x_o so that the mass of the undisturbed cell of volume $x_o a_o$ is unity. Then the jump conditions can be summarized in the relation

$$\mathcal{V}_1/\mathcal{V}_2 = (1 - \lambda)x_1(x_o - x_1)/\ x_2(x_o - x_2) \tag{2.52}$$

If we examine the stress and strain in the compressed region, we get a set of relations identical to those set forth in Section 2.3.5, except that $\sigma_{x1} = \sigma_{x2} = -p_1$ and $\varepsilon_{x1} \neq \varepsilon_{x2}$. This leads to the following results for the linear elastic case:

$$-\varepsilon_{x1}/p_1 = [(\alpha_1\alpha_2 - L_1L_2)\mathcal{V}_2 + \mathcal{V}_1(\alpha_2^2 - L_2^2)]/D \tag{2.53}$$

$$\varepsilon_{y1}/p_1 = \mathcal{V}_2(\alpha_2L_1 - \alpha_1L_2)/D \tag{2.54}$$

$$\sigma_{x1} = -p_1 \tag{2.55}$$

$$-\sigma_{y1}/p_1 = [L_2\mathcal{V}_2(\alpha_1^2 - L_1^2) + L_1\mathcal{V}_1(\alpha_2^2 - L_2^2)]/D \tag{2.56}$$

$$-(\sigma_{x1} - \sigma_{y1})/p_1 = 4\mu_1\mu_2(L_1 V_2/\nu_1 + L_2 V_1/\nu_2)/D$$

$$= -2\mu_1\varepsilon_{x1}(1 + \xi_{1\ \mathrm{eff}})/p_1 \tag{2.57}$$

where

$$D = \alpha_2 V_2(\alpha_1^2 - L_1^2) + \alpha_1 V_1(\alpha_2^2 - L_2^2)$$

ν = Poisson's ratio

$$\xi_{1\ \mathrm{eff}} = V_2(\alpha_2 L_1 - \alpha_1 L_2)/[V_2(\alpha_1\alpha_2 - L_1 L_2) + V_1(\alpha_2^2 - L_2^2)] \tag{2.58}$$

The analogous quantities for component 2 are obtained by interchanging the indices "1" and "2", except on p_1. Under the assumed conditions the maximum resolved shear stress, $(\sigma_x - \sigma_y)/2$, is the same for both components.

The effects of changing the boundary condition are best displayed by comparing values of ξ_{eff} from Eqs. (2.47) and (2.58):

λ =	0	.25	.50	.75	1.00
$\xi_{2\ \mathrm{eff}}$ (Eq. 2.47)	.0344	.0341	.0334	.0316	0
$\xi_{2\ \mathrm{eff}}$ (Eq. 2.58)	-.5932	-.590	-.583	-.563	0

μ_1 = .0116 Mb, μ_2 = .452 Mb

1 - polyethylene, 2 - quartz

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PART III

AN ITERATIVE PROCEDURE TO ESTIMATE THE VALUES OF ELASTIC CONSTANTS OF A CUBIC SOLID AT HIGH PRESSURES FROM SOUND WAVE VELOCITY MEASUREMENTS

Dattatraya P. Dandekar

3.1 INTRODUCTION

An investigator attempting to determine the variation of elastic constants of solids with pressure by ultrasonic measurements on new (or even well known) materials may find that the needed compressibility measurements are either unavailable or if available are unreliable. Cook's method enables one to obtain an estimate of the values of the elastic constants of a solid at high pressure without a priori knowledge of the compressibility of the substance.[3.1] In developing the estimating procedure Cook assumed that the parameter Δ(P) (c.f. General Notation and Analysis, Eq. (3.5)), remained constant with pressure. The value of Δ(P) at any pressure P is given by its magnitude at one atmosphere. Ruoff[3.2] extended the results of Cook in the case of cubic solids by presenting an estimating procedure which permitted the parameter Δ(P) to vary with pressure. This was done by expressing Δ(P) in a power series expansion given by (3.1):

$$\Delta(P) = \Delta(P{=}1) + P\left(\frac{\partial\Delta(P)}{\partial P}\right)_{P\to 1} + \frac{P^2}{2}\left(\frac{\partial^2\Delta(P)}{\partial P^2}\right)_{P\to 1} + \ldots \tag{3.1}$$

where the quantities on the right-hand side of (3.1) are evaluated at one atmosphere.

Even so the lack of relevant data in the case of most materials limits one to the first derivative of Δ(P). This is easily seen by differentiating Δ(P) with respect to pressure P. The present work develops an iterative procedure to estimate the values of the elastic constants of cubic solids at high pressure which differs from the one developed by Ruoff with respect to the assumptions regarding (i) the pressure derivative of the thermal volume expansion coefficient at a temperature T, (ii) the temperature derivative of the volume thermal expansion coefficient at a pressure P, and (iii) the estimation procedure for $\Delta(P)$. It is shown here that no assumptions regarding (i) and (ii) are necessary in order to estimate the elastic constants of cubic solids at higher pressures provided the ultrasonic measurements are made as a function of pressure at more than two temperatures. This enables one to compute a more realistic estimate of elastic constants of cubic solids as a function of pressure.

The size, density and elastic constants of a material specimen change with the application of pressure. Concomitant changes are observed in the value of the resonant or null frequencies of a standing wave and also in the measurement of travel-time for a pulse between flat parallel faces of the specimen. The analysis presented in this paper refers to frequency measurements but is equally valid for the travel-time measurements of an elastic wave propagated in a medium.

3.2 GENERAL NOTATION AND ANALYSIS

By a solid we always refer to a cubic solid. Even though the quantities dealt with here refer to a pressure P and a temperature T, for simplicity the relevant suffix for the temperature is dropped from the general notation.

$\rho(P)$:	the density of the material at pressure P
$\beta(P)$:	volume-expansion coefficient of the material at pressure P
$C_p(P)$:	specific heat at constant-pressure of the material at pressure P
$B^S(P)$:	adiabatic bulk modulus of the material at pressure P
$B^T(P)$:	isothermal bulk modulus of the material at pressure P

$\chi^T(P)$: isothermal compressibility of the material at pressure P

$L(J,P)$: the thickness of the specimen used in the measurement of the Jth velocity mode at pressure P

$\lambda(P) = \dfrac{L(J,P_1)}{L(J,P)}$: $P_1 < P$; $P_1 = 1 = 1$ atm or 1 bar, only in the case of cubic material

$V(J,P)$: the Jth velocity mode in the material at pressure P

$\tau(J,P)$: the travel-time for the Jth velocity mode at pressure P

$F(I,J,P)$: the Ith null frequency observed for the Jth velocity mode in the material at pressure P

$N(I,J,P)$: the number of 1/2 wavelengths in the specimen corresponding to $F(I,J,P)$

$\tau(I,J,P)$: the travel-time in the specimen corresponding to $F(I,J,P)$

$IMP(J,P)$: mechanical impedance of quartz transducer for Jth velocity mode at pressure P

$K(I,J,P)$: $IMP(J,P)$/mechanical impedance of the material corresponding to $\tau(I,J,P)$

$V(1,P)$: longitudinal velocity in the (100) direction at pressure P

$V(2,P)$: shear velocity in the (100) direction at pressure P

$V(3,P)$: longitudinal velocity in the (110) direction at pressure P

We need only know any three independent velocity modes in order to obtain the three elastic constants of a solid. In this paper the resonant frequencies measured as a function of pressure for the longitudinal modes of propagation in the (100) and (110) directions and the shear mode of propagation in the (100) direction have been used.[3.3]

We also assume the following:

(i) The temperature dependence of the volume, or the linear expansion coefficient at a temperature T and one atmosphere is known;

(ii) the specific heat at temperature T and one atmosphere is known; and

(iii) $\left(\frac{\partial\beta(P)}{\partial T}\right)_P \approx \left(\frac{\partial\beta(P_1)}{\partial T}\right)_{P_1}$, where $P \geq P_1$, holds.[3.4]

Then the procedure outlined below can be used to estimate the elastic constants of solids at higher pressures, without reference to a priori knowledge of the compressibility of the substance.

The relation between the adiabatic bulk modulus and $V^2(J,P)$, $(J = 1,3)$, in a cubic solid may be written as

$$B^S(P) = (1/3) \times \rho(P)\{4 \times V^2(3,P) - 4 \times V^2(2,P) - V^2(1,P)\} \qquad (3.2)$$

Relation (3.1), expressed in terms of $L(J,P_1)$, $\tau(J,P)$, $\lambda(P)$ and $\rho(P_1)$, is given as relation (3.3):

$$B^S(P) = (1/3)\rho(P_1) \times \lambda(P) \times \left\{\frac{4 \times L^2(3,P_1)}{\tau^2(3,P)} - \frac{4 \times L^2(2,P_1)}{\tau^2(2,P)} - \frac{L^2(1,P_1)}{\tau^2(1,P)}\right\} \qquad (3.3)$$

where $\rho(P) = \lambda^3(P) \times \rho(P_1)$.

By the definition of isothermal bulk modulus we obtain

$$B^T(P) = -\mathrm{Vol.}\,(P)\left(\frac{\partial P}{\partial\,\mathrm{Vol.}\,(P)}\right)_T = \rho(P)\left(\frac{\partial P}{\partial\rho(P)}\right)_T = \frac{\lambda(P)}{3}\left(\frac{\partial P}{\partial\lambda(P)}\right)_T \qquad (3.4)$$

where $\mathrm{Vol.}\,(P) \equiv 1/\rho(P)$. If

$$\Delta(P) = \frac{\beta^2(P) \times B^S(P) \times T}{\rho(P) \times C_p(P)} \qquad (3.5)$$

where temperature T is in degrees Kelvin, then

$$B^T(P) = \frac{B^S(P)}{[1 + (P)]}. \qquad (3.6)$$

Using Williams and Lamb's[3.5] method of ultrasonic wave velocity measurements as modified by Colvin,[3.6] transit time for the various wave propagations is obtained from the following relations:

$$N(I,J,P) = \text{Integer}\left\{\frac{F(I,J,P)}{\Delta F(I,J,P)} - 0.5 - K(I,J,P)\right\} \tag{3.7}$$

$$\tau(I,J,P) = \frac{N(I,J,P) + 0.5}{2 \times F(I,J,P)} - \frac{K(I,J,P)}{2}\left\{\frac{1}{F(R,J,P)} - \frac{1}{F(I,J,P)}\right\} \tag{3.8}$$

In the above expressions $K(I,J,P)$ may be written as

$$K(I,J,P) = \frac{IMP(J,P)}{\rho(P) \times V(J,P)} = \frac{IMP(J,P) \times \tau(J,P)}{\rho(P_1) \times \lambda^2(P) \times L(J,P_1)} \tag{3.9}$$

where $IMP(J,P)$ is the mechanical impedance of the transducer for the Jth velocity mode at pressure P.

It is evident from relation (3.8) that if the measurements are made near $F(R,J,P)$ any error in the estimation of $\tau(I,J,P)$ due to inaccurate knowledge of $K(I,J,P)$ becomes negligible.

By integrating relation (3.4) we obtain

$$\lambda(P) = \lambda(P_1) \times \exp.\left[\frac{P - P_1}{3 \times B^T(P)}\right] \tag{3.10}$$

Two things should be noted regarding the derivation of (3.10) from (3.4): (i) in the definition of isothermal bulk modulus at a pressure P, one could obtain its value by either decreasing or increasing the pressure slightly; and (ii) when integrating (3.4) it must be remembered that it is implied in the definition of $B^T(P)$ that it remains constant over the range of integration P_1 to P. In expression (3.10) it is implied that the isothermal bulk modulus of a substance at pressure P has been obtained by decreasing the pressure from P to P_1. The expression for $\lambda(P)$ as derived above differs from that obtained by following either Cook's or Ruoff's procedures. The expression for $\lambda(P)$ that will be obtained by following Cook's or Ruoff's procedure may be given by

$$\lambda(P) = 1 + \frac{1}{\rho(1)\, L^2(1)} \int_1^P [1 + \Delta(P)]$$

$$\left(\frac{4}{\tau^2(3,P)} - \frac{4}{\tau^2(2,P)} - \frac{1}{\tau^2(1,P)}\right)^{-1} dP \qquad (3.11)$$

where $L(J,1) = L(1)$, and $[1 + \Delta(P)]$ is a constant in Cook's method and equals $[1 + \Delta(1)]$ but is a variable in Ruoff's method.

This expression (3.11) for $\lambda(P)$ is arrived at by expressing $B^T(P)$ in terms of $\rho(1)$, $L(1)$, $\tau(J,P)$, and $\Delta(P)$ with the help of Eqs. (3.3) and (3.6), and integrating (3.4). Hence, $\lambda(P)$ in (3.11) can be determined if the value of $\Delta(P)$ can be estimated. Ruoff[3.2] estimates the value of $\Delta(P)$ from relation (3.1) by means of thermodynamic relations. For example, to evaluate $(\partial\Delta(P)/\partial P)_T$, we would rewrite $B^S(P)$ as

$$B^S(P) = \rho(P) \times \frac{L^2(P)}{\tau^2(P)} \qquad (3.12)$$

where $L^2(P)/\tau^2(P)$ is an abbreviation for the coefficient of $\rho(P)$ in Eq. (3.2). Then $\Delta(P)$ in (3.5) may be written as

$$\Delta(P) = \frac{\beta^2(P) \times T \times L^2(P)}{\tau^2(P) \times C_p(P)} \qquad (3.13)$$

and the logarithmic derivative of $\Delta(P)$ yields

$$\frac{1}{\Delta(P)}\left(\frac{\partial\Delta(P)}{\partial P}\right)_T = \frac{2}{\beta(P)}\left(\frac{\partial\beta(P)}{\partial P}\right)_T + \frac{2}{L(P)}\left(\frac{\partial L(P)}{\partial P}\right)$$

$$- \frac{2}{\tau(P)}\left(\frac{\partial\tau(P)}{\partial P}\right)_T - \frac{1}{C_p(P)}\left(\frac{\partial C_p(P)}{\partial P}\right) \qquad (3.14)$$

From thermodynamics, we know that

$$\left(\frac{\partial\beta(P)}{\partial P}\right)_T = - \left(\frac{\partial\chi^T(P)}{\partial T}\right)_P \qquad (3.15)$$

and

$$\left(\frac{\partial C_P(P)}{\partial P}\right)_T = -\frac{T}{\rho(P)}\left\{\left(\frac{\partial \beta(P)}{\partial T}\right)_P + \beta^2(P)\right\} \tag{3.16}$$

Hence, in the limit as P → 1, the expression (3.14) reduces to

$$\frac{1}{\Delta(1)}\left(\frac{\partial \Delta(P)}{\partial P}\right)_{T,P\to 1} = -\frac{2}{\beta(1)}\left(\frac{\partial \chi^T(P)}{\partial T}\right)_{P\to 1} - \frac{2}{3}\chi^T(1)$$

$$-\frac{2}{\tau(1)}\left(\frac{\partial \tau(P)}{\partial P}\right)_{T,P\to 1} + \frac{T}{\rho(1)\,C_P(P)}\left\{\left(\frac{\partial \beta(P)}{\partial T}\right)_{P\to 1} + \beta^2(1)\right\}. \tag{3.17}$$

Thus the magnitude of the first derivative of $\Delta(P)$ in the limit as P → 1 may be determined if $(\partial\chi^T(P)/\partial T)_{P=1}$, $(\partial\beta(P)/\partial T)_{P=1}$, $\beta(1)$, and $C_P(1)$ are known a and the value of $\Delta(P)$ may be approximated at a pressure P by

$$\Delta(P) = \Delta(1) + P\left(\frac{\partial \Delta(P)}{\partial P}\right)_{P\to 1,T} \tag{3.18}$$

Similarly the higher derivatives of $\Delta(P)$ may be evaluated if the relevant thermodynamic data are available.

The expression for $\lambda(P)$ in the new method, i.e. relation (3.10) desdescribed in this paper, is seen to differ from the earlier two works for two reasons. In their works, (i) $\lambda(P)$ is defined as $L(J,1)/L(J,P)$, and (ii) $\Delta(P)$ is estimated by a different procedure.

The quantities measured or known are $\rho(1)$, $L(J,1)$, $F(I,J,P)$ or $\tau(J,P)$, P and T. For quartz transducers, IMP(J,P) and F(R,J,P) can be obtained safely to 4000 bars and from room temperature to 90°K from the work of McSkimin and Andreatch.[3.7] This information is not required if the ultrasonic measurements are of the travel-times. $\beta(P)$ is usually known only as a function of temperature at one atmosphere. However, the variation in the elastic constants with temperature at pressure P provides one with the temperature derivative of the isothermal compressibility. And from relation

(3.15) one may obtain $\beta(P)$ at temperature T if $\beta(P)$ is known at one atmosphere and temperature T. In a normal substance where $P_1 \leq P$,

$$\left(\frac{\partial \chi^T(P)}{\partial T}\right)_P \leq \left(\frac{\partial \chi(P_1)}{\partial T}\right)_{P_1} \tag{3.19}$$

holds. So, to assume that

$$-\left(\frac{\partial \beta(P)}{\partial P}\right)_T \simeq \left(\frac{\partial \chi^T(P_1)}{\partial T}\right)_{P_1 = 1} \tag{3.20}$$

ensures that the value of $\Delta(P)$ obtained from (3.5) is underestimated. If ultrasonic measurements are made as a function of pressure at more than one temperature, a better estimate of $(\partial \chi^T(P)/\partial T)_P$ may be obtained by simply incorporating $(\partial \chi^T(P)/\partial T)_P$ as an additional parameter to be iterated according to the scheme presented in Figure 3.2. Where such information is unavailable (3.19) or (3.20) may be used. Similarly the computation of $C_P(P)$ from relation (3.16) by assuming

$$\left(\frac{\partial \beta(P)}{\partial T}\right)_T \simeq \left(\frac{\partial \beta(P_1)}{\partial T}\right)_{P_1 = 1} \tag{3.21}$$

implies that the resulting values of $C_P(P)$ from relation (3.16) will also be underestimated. However, the resultant error in the estimated value of $\Delta(P)$ due to the intrinsic underestimation of $\beta(P)$ and $C_P(P)$ is likely to be small, up to 3-4 kilobars for most materials. Thus everything in expression (3.5) except $B^S(P)$ and $\rho(P)$ is either known or may be approximated with reasonable accuracy.

The iterative procedure described below is that presented in Figure 3.1, because we feel that the understanding of the procedure given in Figure 3.2 will be facilitated by an understanding of the simpler procedure. Thus the iterative procedure described assumes that relations (3.20) and (3.21) hold.

At P = 1 atmosphere, all the quantities involved are known; no iteration is required to estimate the required elastic constants of solids.

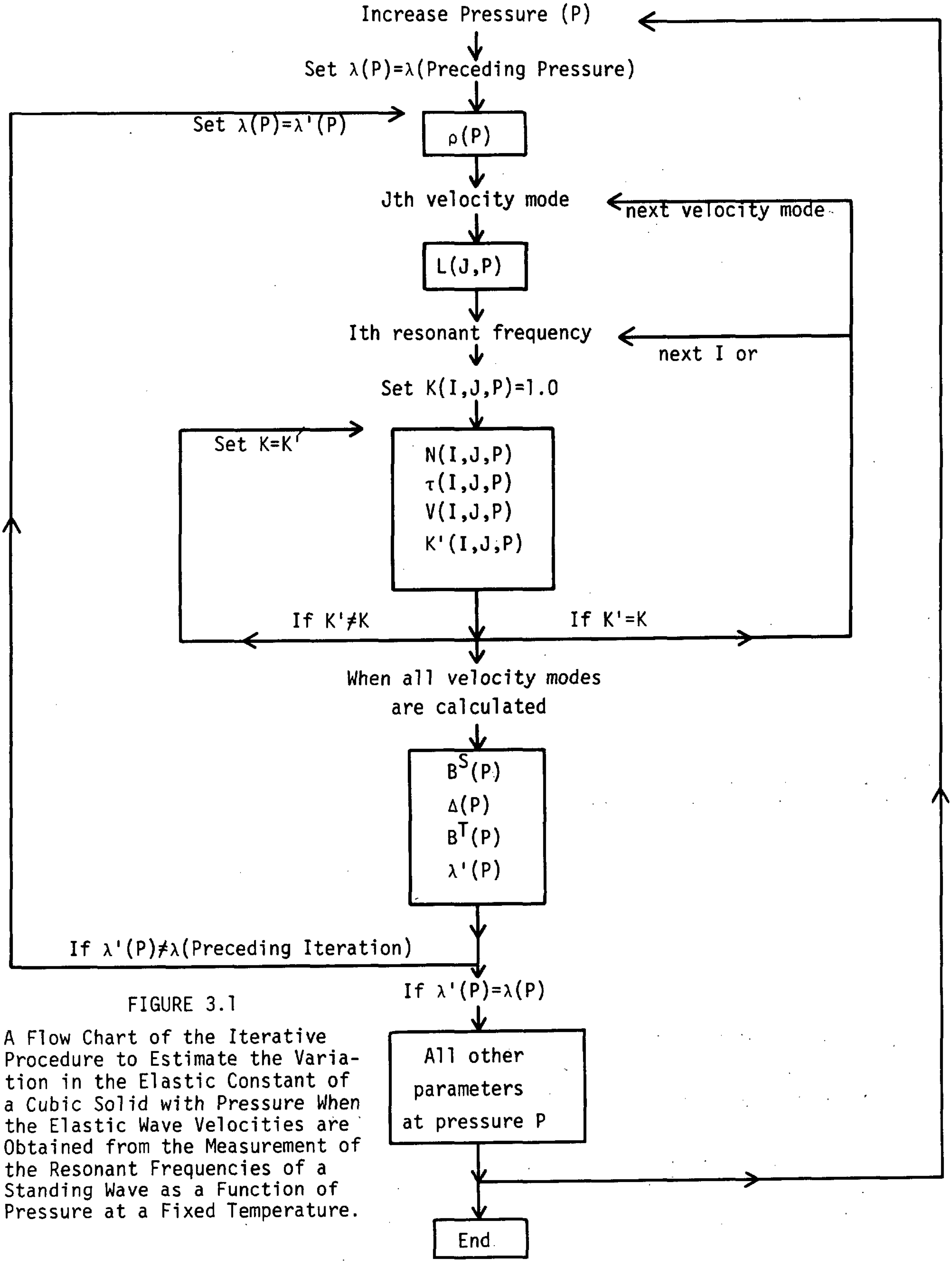

FIGURE 3.1

A Flow Chart of the Iterative Procedure to Estimate the Variation in the Elastic Constant of a Cubic Solid with Pressure When the Elastic Wave Velocities are Obtained from the Measurement of the Resonant Frequencies of a Standing Wave as a Function of Pressure at a Fixed Temperature.

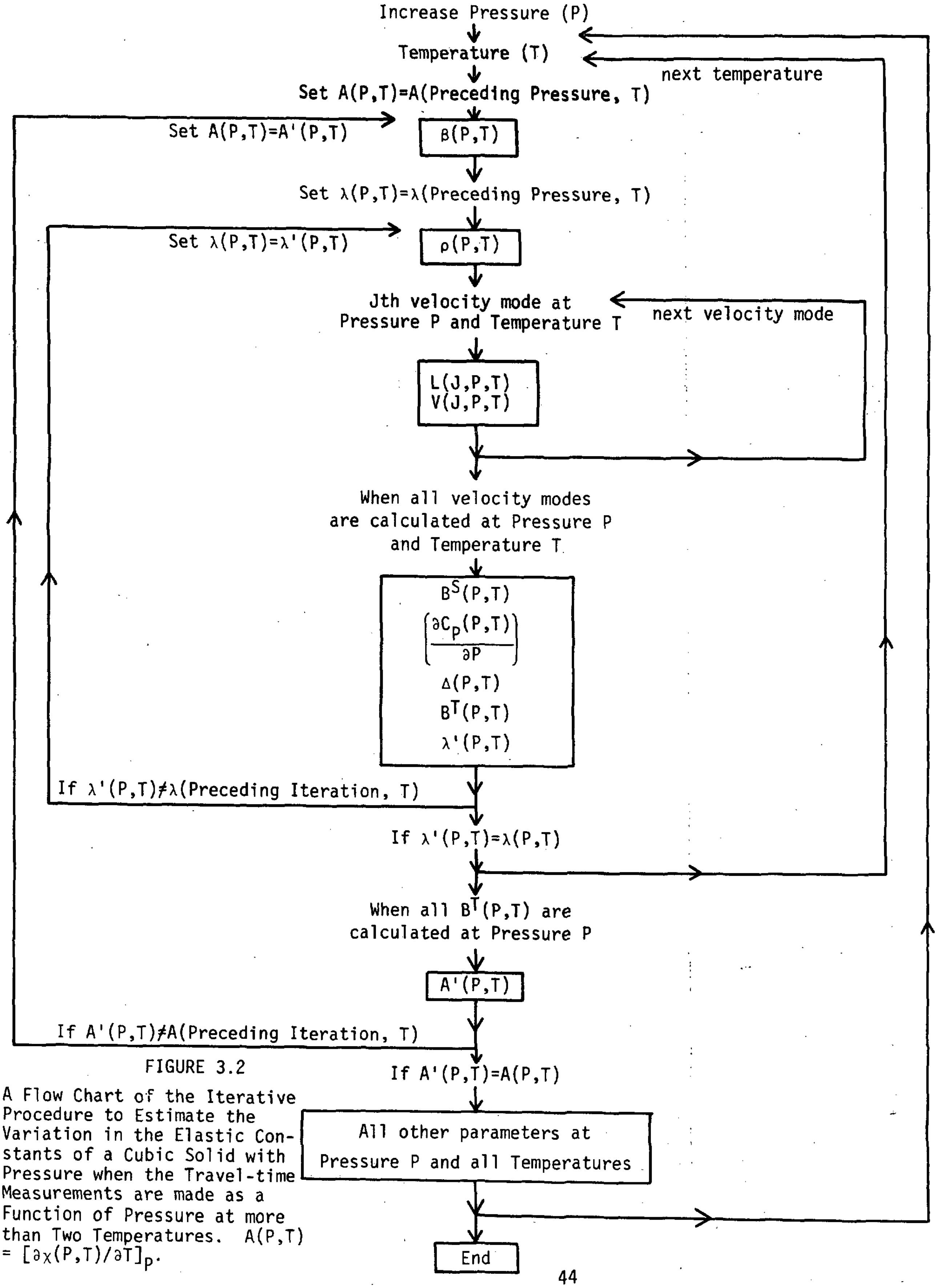

FIGURE 3.2

A Flow Chart of the Iterative Procedure to Estimate the Variation in the Elastic Constants of a Cubic Solid with Pressure when the Travel-time Measurements are made as a Function of Pressure at more than Two Temperatures. $A(P,T) = [\partial\chi(P,T)/\partial T]_P$.

At the next higher pressure all the fundamental quantities in the relations (3.3), (3.5), (3.6), (3.7), (3.8), (3.9), and (3.10), except $\lambda(P)$ and K(I,J,P) are known. The procedure developed here involves a two stage iteration, one at the level of pressure and the other on the Ith null frequency of the Jth mode. We set $\lambda(P) = \lambda(\text{preceding pressure})$ and K(I,J,P) = 1 and estimate N(I,J,P) and $\tau(I,J,P)$ and K(I,J,P). If the value of K(I,J,P) thus obtained agrees with the previously assigned value we compute N(I,J,P) for the (I + 1)th frequency. If this value of K(I,J,P) does not agree with the previously assigned value these values of N(I,J,P) and $\tau(I,J,P)$ are corrected by setting K(I,J,P) equal to the value obtained last, and iterating all over again. This is repeated till two consecutive estimates of K(I,J,P) are the same. A similar computation is performed for all the velocity modes. By interpolation, from these $\tau(I,J,P)$'s one obtains values corresponding to F(R,J,P), each of which is called $\tau(J,P)$. These $\tau(J,P)$'s in turn are used to obtain V(J,P) which together with $\rho(P)$ yield an estimate of $B^S(P)$, $\Delta(P)$, $B^T(P)$, and finally $\lambda(P)$. If the value of $\lambda(P)$ thus obtained agrees with the previously assigned value, the estimates of $B^S(P)$ and $B^T(P)$ are correct. If this value of $\lambda(P)$ does not agree with the previously assigned value these $B^S(P)$ and $B^T(P)$ are corrected by means of setting $\lambda(P)$ equal to the value of $\lambda(P)$ obtained last and iterating all over again. This is repeated till two consecutive estimates of $\lambda(P)$ are the same. Once this is known all other elastic constant parameters may be obtained. This iterative procedure is sketched diagramatically in Figure 3.1.

Table 3.1 displays the estimates of the pressure derivatives of the adiabatic and isothermal bulk moduli of NaCl and KCl at 295° and 195°K obtained from the above mentioned iterative procedure. The required travel time data as a function of pressure for this computation were reconstructed from the pressure derivatives of the travel-time for the various elastic wave velocities given in the paper of Bartels and Schuele.[3.8] All other ancillary data used were also taken from reference 3.8. It may be seen that the estimates of the pressure derivatives of the bulk moduli of NaCl and KCl obtained in the present work for pressures ranging up to 1.7 kb differ slightly from those obtained by Bartels and Schuele. However, such differences may become significant at higher pressures. It should be noted further that the iterative

TABLE 3.1

The Pressure Derivative of the Adiabatic and Isothermal Bulk Moduli of NaCl and KCl as Obtained by Bartels and Schuele (B and S), and as Obtained in the Present Work (D) from the Data of Bartels and Schuele.

	Bulk Modulus	
	B and S	D
NaCl		
295°K		
Adiabatic	5.27	5.33
Isothermal	5.35	5.38
195°K		
Adiabatic	5.13	5.18
Isothermal	5.20	5.23
KCl		
295°K		
Adiabatic	5.34	5.36
Isothermal	5.41	5.44
195°K		
Adiabatic	5.34	5.36
Isothermal	5.41	5.43

procedure outlined in the present work may be easily applied to determine the variation in the elastic constants of an isotropic solid.

Figure 3.2 is the schematic representation of the iteration procedure when the travel-time measurements are made as a function of pressure at more than two temperatures.

We are in the process of developing a variant of this iterative procedure designed to estimate the elastic constants of a non-cubic solid as a function of pressure.

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3.3 Change in the choice of independent velocity modes merely changes the expression for the adiabatic bulk modulus in expression (3.2).

3.4 Assumption (iii) need not be made if ultrasonic measurements are made as a function of pressure at more than two temperatures.

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PART IV

AN ITERATIVE SCHEME TO ESTIMATE THE VALUES OF ELASTIC CONSTANTS OF A SOLID AT HIGH PRESSURES FROM SOUND WAVE VELOCITY MEASUREMENTS

Dattatraya P. Dandekar

4.1 INTRODUCTION

In Section III we presented an iterative procedure to estimate the values of elastic constants of cubic and isotropic solids at high pressures from sound wave velocity measurements under the assumption that the concomitant compressibility measurements are unknown. This procedure resembled procedures developed by Cook[4.1] and Ruoff[4.2] with regard to the use of the principle of self-consistent integration but differed from both with regard to the assumption of the variation in $\Delta(P,T)$, defined as $\beta^2(P,T) \times T/\chi^S(P,T) \times \rho(P,T) \times C_p(P,T)$, with pressure and temperature and also with regard to the method of estimating $\Delta(P,T)$. This work presents a similar procedure which permits estimation of the values of elastic constants of a noncubic crystalline solid at high pressures from measurements of sound wave velocities. The iterative scheme presented here is a general one. When the ultrasonic measurements are made as a function of pressure at more than two temperatures no restrictive assumptions are required. However, when such measurements are made as a function of pressure at only one temperature, two additional assumptions become necessary before the iterative procedure can be applied.

These two assumptions are:

(i) The temperature derivatives of the linear compressibilities of a solid are independent of pressure.

(ii) The temperature derivatives of the linear thermal expansion coefficients are independent of pressure.

If measurements are made at two temperatures, assumption (ii) is required.

For simplicity of presentation the analysis presented refers to measurements of the transit time of an elastic wave propagated in an anisotropic medium rather than to measurements of resonant frequency. Since application of pressure changes the density, size and elastic properties of a solid, which is reflected by a concomitant change in the transit time of an elastic wave propagated in the solid, the change in transit time with pressure contains all the desired information about the changes brought about in a solid due to the application of pressure.

4.2 CONVENTIONS AND NOTATIONS

The elastic constants of a solid may be represented by reference to any Cartesian coordinate system (x,y,z). However, it is convenient to refer them to a system of coordinates having some relation to the crystal axes (a,b,c). In this work, whenever applicable the relationship between the Cartesian coordinate system (x,y,z) and the crystal axes (a,b,c) is the one adopted by the IRE Standards Committee.[4.3] The number of elastic constants (C_{ijkt}) necessary to characterize the elastic property of a solid depends upon the crystal class to which the solid belongs. The subscripts of these constants were contracted to (C_{pq}) by following the usual convention of writing the subscript ij, kt = 11, 22, 33, 23, 12, 12 by p, q = 1, 2, 3, 4, 5, 6 so as to represent these C_{pq} by a 6x6 matrix, denoted by $[C_{pq}]$. The corresponding 6x6 matrix of the elastic compliances S_{pq} may be obtained from C_{pq} by using the matrix relation between them, namely

$$[C_{pq}] \times [S_{pq}] = [\ I\ ] \tag{4.1}$$

where [I] is a 6x6 unit matrix. The C_{pq} matrices for different crystal classes may be found in reference 4.4.

4.2.1 Notation

P: Pressure

T: Temperature

$\rho(P,T)$:	Density of a solid at pressure P and temperature T
$\chi(\ell,m,n,P,T)$:	Linear compressibility of the solid in the direction whose direction cosines are given by ℓ, m, and n at P and T
$\beta(\ell,m,n,P,T)$:	Linear thermal expansion coefficient of the solid in the direction whose direction cosines are given by ℓ, m, and n at P and T
$\chi(P,T)$:	Volume compressibility of the solid at P and T
$\beta(P,T)$:	Volume thermal expansion of the solid at P and T
$L(\ell,m,n,J,P,T)$:	Width of the specimen used to measure the Jth velocity mode in the solid in the direction such that ℓ, m, n are the direction cosines at P and T
$\tau(\ell,m,n,J,P,T)$:	Transit time of the Jth wave velocity mode corresponding to $L(\ell,m,n,J,P,T)$
$V(\ell,m,n,J,P,T)$:	The Jth velocity in the solid in the direction whose direction cosines are ℓ, m, and n at P and T
$\lambda(\ell,m,n,J,P,T)$:	$\dfrac{L(\ell,m,n,J,P_1,T)}{L(\ell,m,n,J,P,T)}$ where $P_1 < P$, and P_1 equal to unity indicates one atmosphere pressure
$C_p(P,T)$:	Specific heat of the solid at constant P and T

The superscripts T and S attached to a quantity indicate its isothermal and adiabatic value respectively.

4.3 PRELIMINARIES

The various relations used in the iterative procedure to be described originate either in the theory of elastic wave propagation in a solid or in thermodynamic theory. These general relations are presented with brief introductory remarks drawn from the two theories and appended only to clarify the material of this paper.

4.3.1 Relations Obtained from the Theory of Elastic Wave Propagation

The elastic constants of a solid are determined by measuring the velocities with which elastic waves are propagated along several directions in the solid. The number of velocity measurements needed to understand the elastic property of the solid depends on the crystallographic class to which it belongs. Christoffel's equations (e.g. Eq. (4.2)), which are applicable to any crystalline system, give the relationship between measured velocities and elastic constants. In general, for a plane wave propagated in a crystal having direction cosines ℓ, m, n, the three possible wave velocities V may be found in terms of the elastic constants C_{pq} from the roots of Christoffel's equations.

$$\begin{vmatrix} A_{11} - \rho V^2 & A_{12} & A_{23} \\ A_{12} & AA_{22} - \rho V^2 & A_{23} \\ A_{13} & A_{23} & A_{33} - \rho V^2 \end{vmatrix} = 0 \tag{4.2}$$

where

$$A_{ij} = \ell^2 C_{1i1j} + m^2 C_{2i2j} + n^2 C_{3i3j} + m(C_{1i2j} + C_{2i1j}) + \ell n(C_{1i3j} + C_{3i1j}) + mn(C_{2i3j} + C_{3i2j}) \tag{4.3}$$

It follows that ρV^2 is related to C_{ijkt} in a manner which is determined by the direction in which a wave is propagated. Three different velocities of propagation imply that the three displacement vectors associated with these velocities are mutually perpendicular and hence independent. Usually the three waves are mixed; one is predominantly longitudinal and the other two are predominantly shear. Pure waves may be propagated only in a few special crystallographic directions. The location of the pure mode directions in crystals of various symmetries have been investigated exhaustively by Borgnis[4.5] and Brugger.[4.6]

4.3.2 Thermodynamic Relations

These relations serve two purposes:

(i) To evaluate the pressure derivatives of the specific heat and the linear thermal expansions in the three principal directions of the solid at pressure P and temperature T, and

(ii) To convert the adiabatic quantities into their isothermal counterparts at pressure P and temperature T.

The adiabatic and isothermal elastic compliances are related by

$$S^S_{ijkt}(P,T) - S^T_{ijkt}(P,T) = -\beta_{ij}(P,T)\,\beta_{kt}(P,T)\cdot T/C_p(P,T) \times \rho(P,T) \qquad (4.4)$$

When expressed in our notation the following relation between $\chi^S(\ell,m,n,P,T)$ and $\chi^T(\ell,m,n,P,T)$ results.

$$\chi^T(\ell,m,n,P,T) = \chi^S(\ell,m,n,P,T) + \frac{\beta(P,T) \times T}{\rho(P,T) \times C_p(P,T)}$$

$$\{\beta(1,0,0,P,T)\ell^2 + \beta(0,1,0,P,T)m^2 + \beta(0,0,1,P,T)n^2\} \qquad (4.5)$$

where

$$\beta(P,T) \equiv \beta(1,0,0,P,T) + \beta(0,1,0,P,T) + \beta(0,0,1,P,T) \qquad (4.6)$$

and

$$\chi(\ell,m,n,P,T) = (S_{11} + S_{12} + S_{13})^{\,2} + (S_{12} + S_{22} + S_{23})m^2$$

$$+ (S_{13} + S_{23} + S_{33})n^2 \qquad (4.7)$$

Equation (4.5) may also be written as

$$\chi^T(\ell,m,n,P,T) = \chi^S(\ell,m,n,P,T) + \Delta(\ell,m,n,P,T) \qquad (4.8)$$

where

$$\Delta(\ell,m,n,P,T) = \frac{\beta(P,T) \times T}{\rho(P,T) \times C_p(P,T)} \{\beta(1,0,0,P,T)^{\,2}$$

$$+ \beta(0,1,0,P,T)m^2 + \beta(0,0,1,P,T)n^2\}$$

From the definition of isothermal linear compressibility, we have

$$\chi^T(\ell,m,n,P,T) = -\frac{1}{L(\ell,m,n,P,T)}\left(\frac{\partial L(\ell,m,n,P,T)}{\partial P}\right)_T$$

$$= \frac{1}{\lambda(\ell,m,n,P,T)}\left(\frac{\partial \lambda(\ell,m,n,P,T)}{\partial P}\right)_T \qquad (4.9)$$

Since the subscript J has no significance in the above relation, it has been omitted from $L(\ell,m,n,J,P,T)$. By integrating Eq. (4.9) with respect to pressure, we obtain

$$\lambda(\ell,m,n,P,T) = \lambda(\ell,m,n,P_1,T) \times \exp\{(P-P_1)\ \chi^T(\ell,m,n,P,T)\} \qquad (4.10)$$

The above integration is performed by assuming that the compressibility is determined by reducing the pressure from P to P_1 and by taking into account the definition (4.8) which implies $\chi^T(\ell,m,n,P,T)$ remains constant in the range of integration P to P_1. Again the temperature derivative of linear compressibility is related to the pressure derivative of the linear thermal expansion of a material by

$$\left(\frac{\partial \chi^T(\ell,m,n,P,T)}{\partial T}\right)_P = -\left(\frac{\partial \beta(\ell,m,n,P,T)}{\partial P}\right)_T \qquad (4.11)$$

and the pressure derivative of specific heat may be written as

$$\left(\frac{\partial C_p(P,T)}{\partial P}\right)_T = -\frac{T}{\rho(P,T)}\left\{\beta^2(P,T) + \left(\frac{\partial \beta(P,T)}{\partial T}\right)_P\right\} \qquad (4.12)$$

The use of the above set of relations enables one to estimate the values of the elastic constants of a solid at high pressure without a priori knowledge of the compressibility of the substance.

4.4 GENERAL ITERATIVE SCHEME

In general the iterative scheme proposed here attempts to obtain self-consistent estimates of $\lambda(\ell,m,n,P,T)$ in the three principal directions, i.e.

$\lambda(1,0,0,P,T)$, $\lambda(0,1,0,P,T)$ and $\lambda(0,0,1,P,T)$ at pressure P and temperature T. The iterative procedure presented below assumes the following:

(i) The temperature dependence of the linear expansion coefficients are known at one atmosphere.

(ii) The value of specific heat is known as a function of temperature at one atmosphere.

(iii) An adequate number of velocity measurements are made to extract information about elastic properties of the solid as a function of pressure at more than one atmosphere.

Then, at P = 1 and within the experimental range of temperature, all the quantities in the above set of 12 relations are known; no iteration is required to estimate the values of the elastic constants of a solid as a function of temperature at one atmosphere.

At the next higher pressure all the quantities except $\lambda(\ell,m,n,P,T)$ in the above set of relations are known. The procedure developed here involves a three-stage iteration in order to yield a self-consistent estimate of not only the elastic constants but also of pressure and temperature derivatives of the linear thermal expansion and of the specific heat at pressure P and temperature T. The three stages of iteration are done at the levels of pressure, temperature and the three principal directions of the solid. To initiate the procedure, we set

$$\left(\frac{\partial\chi^T(\ell,m,n,P,T)}{\partial T}\right)_P = \left(\frac{\partial\chi^T(\ell,m,n,P_1,T)}{\partial T}\right)_{P_1} \tag{4.13}$$

and

$$\left(\frac{\partial\beta(\ell,m,n,P,T)}{\partial T}\right)_P = \left(\frac{\partial\beta(\ell,m,n,P_1,T)}{\partial T}\right)_{P_1} \tag{4.14}$$

where P_1 is the preceding value of pressure. These enable us to compute $\beta(\ell,m,n,P,T)$ and $C_p(P,T)$.

Next we set

$$\lambda(\ell,m,n,P,T) = \lambda(\ell,m,n,P_1,T) \tag{4.15}$$

With this assumption, we compute $\rho(P,T)$ from the relation

$$\frac{1}{\rho(P,T)}\left(\frac{\partial\rho(P,T)}{\partial P}\right)_T = \chi^T(P,T)$$

$$= \chi^T(1,0,0,P,T) + \chi^T(0,1,0,P,T) + \chi^T(0,0,1,P,T) \tag{4.16}$$

and $L(\ell,m,n,P,T)$; these with the known values of $\tau(\ell,m,n,J,P,T)$ enable us to estimate $C^S_{pq}(P,T)$ from Eqs. (4.2). The use of relations (4.1), (4.4), (4.11) and (4.12) together with assumptions (4.13) and (4.14) provides estimates of the values of $S^T_{pq}(P,T)$. From these estimates of $S^T_{pq}(P,T)$ we obtain $\chi^T(\ell,m,n,P,T)$, which in turn by relation (4.10) yields a new estimate of $\lambda(\ell,m,n,P,T)$. If the new values of $\lambda(\ell,m,n,P,T)$ in the three principal directions agree with their respective values assumed at the beginning of the iteration, the estimated values of the elastic constants are correct and consistent with the assumptions represented by relations (4.13) and (4.14). If these values of $\lambda(\ell,m,n,P,T)$ do not agree with the previously assumed values, the iteration is repeated with these new values of $\lambda(\ell,m,n,P,T)$ as starting values, and all the quantities are recalculated. This process is repeated until two successive estimates of $\lambda(\ell,m,n,P,T)$ in the three respective principal directions are equal in magnitude at the pressure P and a temperature T. This whole iteration procedure is carried out at the pressure P and at all the temperatures at which travel-time measurements are made. When all the elastic constants of a solid are estimated in the above manner at the pressure P as a function of temperature, we obtain new estimates of $[\partial\chi^T(\ell,m,n,P,T)/\partial T]_P$ and $[\partial\beta(\ell,m,n,P,T)/\partial T]_P$. If these new values of $[\partial\chi^T(\ell,m,n,P,T)/\partial T]_P$ and $[\partial\beta(\ell,m,n,P,T)/\partial T]_P$ in the three principal directions agree with their respective assigned values at the beginning of the iteration, the estimated values of the elastic constants at the pressure P and all the temperatures are correct. If these new values of $[\partial\chi^T(\ell,m,n,P,T)/\partial T]_P$ and/or $[\partial\beta(\ell,m,n,P,T)/\partial T]_P$ do not agree with their previously assigned values, the iterative procedure is repeated with these new values as the starting point. Such a procedure is repeated until two consecutive estimates of $[\partial\chi^T(\ell,m,n,P,T)/\partial T]_P$ and $[\partial\beta(\ell,m,n,P,T)/\partial T]_P$ agree with their respective initial values in all the three principal directions. The iterative procedure described above is represented by a flow chart in Figure 4.1.

The net outcome of the above-mentioned procedure is to yield (i) values of the elastic constants as functions of pressure and temperature, (ii) values of the partial temperature and pressure derivatives of the linear thermal expansion coefficient as functions of pressure and temperature, and (iii) the pressure derivative of the specific heat as a function of temperature. If, however, the transit times of the elastic waves in a solid are measured as functions of pressure at only one temperature, then values of the elastic constants of the solid may be estimated at high pressures (i) by interpreting P_1 in relations (4.13) and (4.14) to signify the preceding pressure at which these quantities are known, and (ii) by omitting the iterations on $[\partial\chi^T(\ell,m,n,P,T)/\partial T]_P$ and $[\partial\beta(\ell,m,n,P,T)/\partial T]_P$ in the above scheme.

Table 4.1 gives two sets of values of the elastic constants of calcite with pressure at 298°K. Both are based on the data of reference 4.7, but the one labelled "D" was obtained without iteration, using Bridgman's value for compressibility; the other was obtained from the present iterative procedure in conjunction with the required thermodynamic data. The sources of these thermodynamic data are indicated under the table. These two sets of estimates of C_{ij} of calcite are in good agreement. A similar calculation performed on the ultrasonic data of rutile is shown in Table 4.2.

We are in the process of analyzing the relevant ultrasonic data on several crystalline solids.

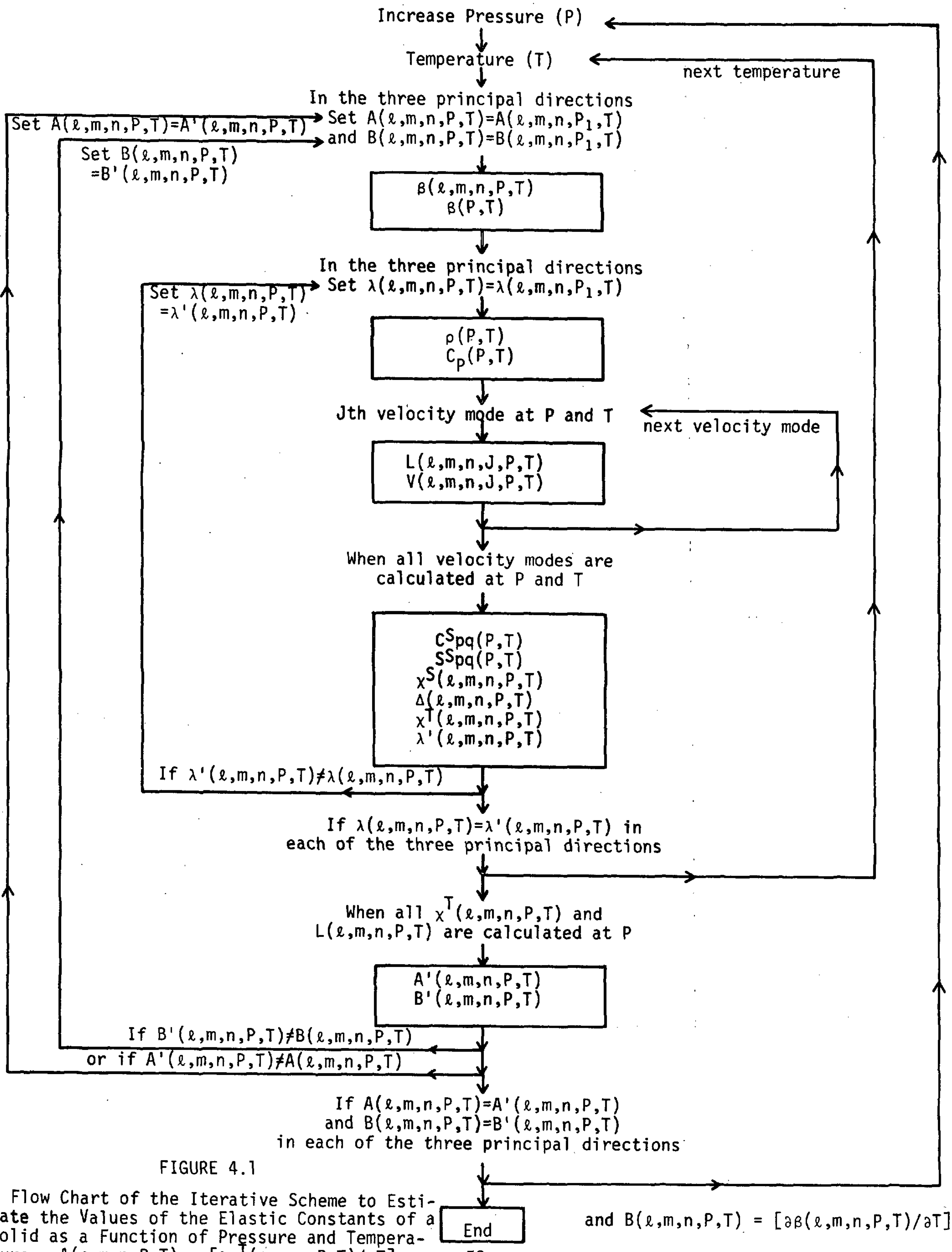

FIGURE 4.1

A Flow Chart of the Iterative Scheme to Estimate the Values of the Elastic Constants of a Solid as a Function of Pressure and Temperature. $A(\ell,m,n,P,T) = [\partial\chi^T(\ell,m,n,P,T)/\partial T]_P$ and $B(\ell,m,n,P,T) = [\partial\beta(\ell,m,n,P,T)/\partial T]_P$.

TABLE 4.1

Adiabatic Elastic Constants (in units of 10^{11} dyn/cm^2) of Calcite with Pressure at 298°K as Obtained by Dandekar[4.7] (D) and as Obtained by the Iterative Procedure (IP) from the same Ultrasonic Data.

Pressure Kbar	C_{11}		C_{33}		C_{44}		C_{66}		C_{14}		C_{13}	
	D	IP	D	IP	D	IP	D	IP	D	IP	D	IP
	±0.05		±0.05		±0.02		±0.07		±0.06		±0.33	
0.001	14.626	14.626	8.531	8.531	3.405	3.405	4.328	4.328	-2.076	-2.076	5.076	5.076
2.0	14.650	14.651	8.526	8.527	3.453	3.453	4.335	4.336	-2.078	-2.080	5.190	5.179
4.0	14.674	14.676	8.522	8.522	3.468	3.468	4.342	4.343	-2.101	-2.100	5.419	5.402
6.0	14.697	14.700	8.518	8.516	3.449	3.448	4.349	4.350	-2.137	-2.138	5.757	5.734

Sources of the values of thermodynamic parameters:

Thermal Expansion Coefficients: R. K. Kirby, J. Res. NBS, A, Phys. Chem. 71A, 363 (1967).

Specific Heat Value: J. S. Arthur, J. Appl. Phys. 21, 732 (1950).

Temperature Derivatives of the Compressibilities at 1 atm, Ref. 4.1.

TABLE 4.2

Adiabatic Elastic Constants (in kilobars) of Single Crystal Rutile with Pressure at 298°K Obtained by Manghanani[4.8] (M) and by Iterative Procedure (IP) from Manghanani's Data.

Pressure Kbar	C_{11}		C_{33}		C_{44}		C_{66}		C_{12}		C_{13}	
	M	IP	M	IP	M	IP	M	IP	M	IP	M	IP
0.001	2714.3	2714.3	4839.5	4839.5	1244.3	1244.3	1947.7	1947.7	1779.6	1779.6	1495.7	1495.7
1.25	2722.4	2722.4	4849.9	4850.8	1245.7	1245.2	1955.7	1955.7	1791.0	1791.0	1502.0	1503.4
2.50	2730.5	2730.4	4860.3	4862.1	1247.1	1246.3	1963.8	1963.7	1802.3	1802.3	1508.3	1509.6
5.00	2746.7	2746.6	4881.2	4884.7	1249.8	1248.4	1979.9	1979.7	1825.1	1825.1	1520.8	1522.2
7.50	2762.8	2862.8	4902.0	4907.3	1252.6	1250.5	1996.0	1995.9	1847.8	1847.8	1533.4	1534.8

Sources of the values of thermodynamic parameters:

Thermal Expansion Coefficients: R. K. Kirby, M. Res. NBS, A, Phys. Chem. 71A, 363 (1967).
Specific Heat Value: J. S. Arthur, J. Appl. Phys. 21, 732 (1950).
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13. ABSTRACT

In Section I an attempt is made to derive the degeneracy factor of Eyring's Significant Structure Theory for a particular model of a solid with vacant lattice sites. A form is obtained which differs from that obtained by Eyring and which gives results less satisfactory than Eyring's factor when compared with Hugoniot data.

In Section II some equilibrium Hugoniot states are calculated for a mixture of two materials and the formulae are applied to combinations of quartz-like and polyethylene-like materials. Gruneisen parameters are found to differ somewhat from those calculated with a simple mass-weighted mixing formula and, in general, the properties of the more compressible material tend to dominate. Some elastic calculations are made for various composite configurations. It is noted that conditions of uniaxial strain are violated, and that the relations between mean pressure and volume are sensitive to the boundary condition on the face of the composite. Some comments are made about deviations from equilibrium.

Conventional methods for reducing ultrasonic velocity data taken at high pressures require a priori knowledge of the compressibility as a function of pressure if elastic constants are to be calculated. In Section III an iterative procedure is outlined which makes it possible to determine the elastic constants provided only that ambient pressure values of thermal expansion coefficient, its temperature derivative, and specific heat at constant pressure are known. The method is applied to travel time measurements in NaCl and KCl made by Bartels and Schuele. The new procedure changes values of the elastic constants by about 1%. Section IV extends the above iterative procedure to include data and constants for crystals of arbitrary symmetry. It is applied to calcite and rutite for illustration.

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