3.2.5. Empirical equation of state

Because shock-compression experiments provide information on ε and v, we are led to consider preparing a complete description of a substance in terms of the entropy density function $s = \hat{s}(v, \varepsilon)$. The pressure and temperature are given in terms of the function $\hat{s}$ by the relations $p/\theta = \partial\hat{s}/\partial v$ and $1/\theta = \partial\hat{s}/\partial\varepsilon$. Elimination of θ from these equations give the equation

$$\partial\hat{s}/\partial v - p\partial\hat{s}/\partial\varepsilon = 0, \tag{3.5}$$

where $p = \hat{p}(v, \varepsilon)$. The function $\hat{p}(v, \varepsilon)$ would be determined over a certain domain of the (v, ε) plane if Hugoniot curves centered on several initial states were measured. With this function in hand, eq. (3.5) can be solved for the entropy density function $\hat{s}$.

From the form of eq. (3.5) we see that the total derivative of $\hat{s}$ vanishes along curves (called *characteristic curves*) in the (v, ε) plane having the slope $d\varepsilon/dv = -p(v, \varepsilon)$. Since $ds = 0$ along these curves, they are isentropes. The *shape* and *position* of the isentropes are thus obtained from a knowledge of Hugoniot curves centered on several initial states. To complete the determination of $\hat{s}$, it is necessary to specify the value of the entropy on each isentrope. This can be done if s is known along some data curve, say the atmospheric pressure isobar, that intersects the isentropes. When these data are specified, a unique solution $\hat{s}(v, \varepsilon)$ is obtained in the region of the (v, ε) plane where $\hat{p}$ is defined and which lies between the isentropes through the end points of the data curve. The great strength of this method is that it proceeds on the basis of the data, invoking no assumptions about the form of the equation of state. This feature is also its greatest liability in that no means of extrapolating the equation of state beyond the range of experimental data is suggested, nor is any connection to theoretical models provided.

Cowperthwaite and Blackburn [71C6] attempted to determine the equation of state of a silicone oil by this method, but were unsuccessful because the differences between Hugoniot curves centered on different initial temperatures were too small in comparison to the uncertainty in their measurement. Lysne and Hardesty [73L4] did carry out a successful determination of the equation of state of nitromethane, but found it necessary to extrapolate the results to pressures above the highest-lying isentrope through the initial data. The difficulties that these investigators experienced are general ones that have so far precluded further application of the method.

3.2.6. Theoretical equations of state

Equations of state based in varying degrees on fundamental considerations of atomic interaction are widely used to describe shock-compressed material. The majority of the work has been directed toward metals but alkali halides, rare gas solids, liquefied gases, and other substances have also been considered. The theories share the common assumption that the energy density (either the internal energy or the Helmholtz free energy) can be expressed as the sum of terms representing the effect of several independently functioning mechanisms. The most basic of these terms, called the potential energy density, represents the static interaction of the atoms or ions and, in the case of metals, the energy of the cold electron gas. A contribution representing the energy of zero-point oscillations is added to the potential energy density to obtain the cold-compression energy density function $\varepsilon_c(v)$ characterizing the behavior of the solid at absolute-zero temperature. At temperatures above absolute zero the thermal energy $\varepsilon_\theta(v, \theta)$ of lattice oscillations is added and at very high temperatures the electronic energy density $\varepsilon_e(v, \theta)$ representing effects of thermal excitation of conduction electrons becomes important. Each of these energy contributions gives rise to an associated pressure contribution according to the formula $p = -\partial\varepsilon/\partial v$. The various contributions

are discussed separately in the following sections. We do not take explicit account of the melting transition that may be expected to occur as a result of compression by sufficiently strong shocks, nor do we review models of the behavior of matter in the liquid state. These problems have been investigated at some length by direct computer simulation of atomic interactions. The results of some such calculations have been summarized by Grover [77G8] in terms of a scaling model.

Cold compression. Calculation of the cold-compression behavior of a substance can be begun by a priori assumption of the form of the interatomic potential, by first-principles determination of this potential, or by deducing it from Hugoniot data on the basis of assumptions about the other contributions to the total pressure. This latter approach is the most common by far, but a significant effort is being expended on more basic work, particularly with regard to metals.

When the cold-compression behavior is interpreted specifically in terms of atomic interactions, these interactions are represented by an effective pair potential. Early Soviet work often employed the Born–Mayer (exponential) repulsion potential combined with inverse power attractive potentials to model the interaction in metals and ionic crystals. Other investigators [65A2, 64P2, 70D2, 71Z2, 73R4, 74P1, 74R1] studying these materials, rare-gas solids, liquid hydrogen and an organic crystal, have followed this path or have used Morse, Lennard-Jones, or other potentials in a similar way. Ross [73R4] has shown a favorable comparison of an exponential-six potential fit to shock-compression data on solid argon with a potential inferred from molecular beam experiments. Following a somewhat different approach, Barnes [67B1, 78B2] has used a cold-compression curve based on a Morse attractive term fit to bulk modulus data and a repulsive term fit to results of a calculation based on the Thomas–Fermi model.

Zhdanov and Polyakov [75Z1, 76Z1, 76Z2] have approximated the compression behavior of several alkali halide crystals by a calculation in which the energy of the lattice is determined using Hartree–Fock wave functions for the free ions. These results, which are obtained without appeal to any shock-compression data, are used to calculate Hugoniot curves that are, in several cases, in quite reasonable agreement with observation for both low and high pressure phases of the materials. Hardy and coworkers [77H1, 77H2, 78B3] have developed an alternative model, but have not applied it in the regime of pressure and temperature achieved by shock compression.

Considerable effort has gone into prediction of the cold-compression behavior of metals. Pastine [67P1] and Pastine and Carroll [71P1] have discussed a calculation of the behavior of sodium and aluminum in which the cold energy function is constructed as the sum of terms representing the interaction potential of the atom cores (regarded as incompressible), and the ground state, Fermi, exchange, and correlation energies of the valence electrons. Approximate expressions for each of these terms are taken from the literature and their sum is a closed-form expression for the potential. The simplicity of this analysis lies in the fact that the core structure of the atom is held fixed, that the Fermi surface is taken to be spherical, and that the band structure of these materials had previously been determined as a function of lattice parameter. Detailed band-structure calculations of compression behavior have now been made in several cases [70R2, 74R1, 76R3, 77M1, 78M3, 79M2]. The potential of these solutions for providing insight into the behavior of matter and their unique capability for providing information about states not accessible to experimental observation (e.g., metallic hydrogen [77R2]) ensures that their importance will continue to increase in spite of the difficulty and expense of obtaining them. The importance and potential value of detailed theoretical studies of compressibility were pointed out by Royce [67R3, 71R2] and Al'tshuler and Bakanova [69A2] who showed how the atomic volume of a number of metallic solids bore a systematic relationship to their electronic configuration and how