prediction of changes in this electronic configuration with pressure was correlated to observations of compressibility.

It is generally agreed that the behavior of matter at very large compressions (more than about fivefold) is satisfactorily described by corrected variants of the Thomas–Fermi theory [72K2, 76K2]. Unfortunately, there is a large gap between the twofold or threefold compressions that are experimentally accessible and those for which this theory is likely to be useful. Soviet workers [77A1], particularly, have assumed that this gap can be bridged by relatively straightforward interpolations. Other workers, noting that effects of the shell structure of atoms are often apparent at the limit of the experimental range, argue that a succession of electronic transitions must precede the collapse of the atomic structure to the state modeled by the Thomas–Fermi theory. If this is the case, the interpolation will have to be guided by detailed electronic calculations (see, for example, [77G1, 79M2]).

Thermal energy and pressure. The internal energy of a solid is mostly that of cold compression but thermal energy, in this case associated with oscillatory motion of the atoms, cannot be neglected. As an example, we note that when copper is subjected to a 100 GPa shock, 13 per cent of this pressure is of thermal origin. At 1500 GPa the thermal pressure is about one-half the total. The thermal energy is a much larger fraction of the total in each case. As more compressible substances are considered, thermal effects increase in importance and can dominate the response of highly compressible substances at the limit of the experimentally accessible range of pressures.

Analysis of thermal effects proceeds by direct numerical simulation of the motion of large arrays of atoms (see, e.g., [67R2, 70H3, 74R1, 78W2]), by detailed lattice-dynamic analyses (see, e.g., [70H3, 74D1]), by application of cell models (see, e.g., [70D2, 70H3, 73R4]) or, most often, by rather pragmatic application of the Mie–Grüneisen theory. The Mie–Grüneisen equation, $p_\theta = (\gamma/v)\varepsilon_\theta$, is a relation between the thermal energy ε_θ and the thermal pressure of a solid. The coefficient γ, called Grüneisen's parameter, is defined thermodynamically by the relation $\gamma = v(\partial p/\partial \varepsilon)|_v$ or, as in Grüneisen's theory, in terms of the way in which the frequencies of quasi-harmonic lattice oscillations vary with compression. This latter interpretation leads to the conclusion that γ is a function of v alone, and it is this result that forms the substance of the theory. Various aspects of the Mie–Grüneisen theory as its relates to the present subject are discussed by Knopoff and Shapiro [69K6], Zharkov and Kalinin [71Z2], Royce [71R1], and Romain and coworkers [76R2, 77M5].

A thermodynamic measure of Grüneisen's parameter is readily obtained at atmospheric pressure by substituting compressibility, specific heat, and thermal expansion data into an appropriate form of the thermodynamic definition. Measurements at smaller specific volumes can, in principle, be made by means of shock compression of porous samples or by multiple shock experiments, as discussed previously. Accurate determination of γ has proven difficult, however, because the thermal pressure to which γ is related is too small in comparison to the cold pressure to be measured accurately at small compressions, while interpretation of observations at large compression are complicated by effects of anharmonicity and electronic excitation not included in the Mie–Grüneisen model. The errors of determination of Grüneisen's parameter by shock-compression experiments are not less than ± 10 per cent. Under the circumstances, a rough fit to the data is adequate and the relation $\gamma(v)/v$ = constant, where the constant is evaluated from atmospheric-pressure data, has proven quite satisfactory [68M2, 76N1]. Since the thermal pressure is small at low compressions, a crude estimate of γ is adequate for such purposes as extraction of an isotherm from Hugoniot data.

The importance of Grüneisen's parameter, and the difficulty of determining it experimentally, have led to widespread use of theoretical models. Since $\gamma(v)$ is related to oscillations of atoms in the same force field giving rise to the cold pressure, it is to be expected that it will be related to the function $p_c(v)$. Three models, called the Slater–Landau, Dugdale–MacDonald, and Vahchenko–Zubarev or free-volume models relating $\gamma(v)$ to the cold-compression moduli have been proposed (see, e.g., [71R1]). These models are in serious disagreement at small compressions but converge on one another as the compression is increased. None of the models (nor the formula γ/v = constant) has been demonstrated to be accurate at large compressions. If a relation between $\gamma(v)$ and $p_c(v)$ is adopted, both functions can be evaluated from Hugoniot data. Such calculations have been made by McQueen and Marsh [60M1], Al'tshuler et al. [60A1], and Keeler [72K3], and various methods of obtaining these functions have been discussed by Takeuchi and Kanamori [66T1], Shapiro and Knopoff [69S3], Zharkov and Kalinin [71Z2], and O'Keeffe [70O1, 73O1].

When the thermal pressure and cold pressure are added to give the total pressure $p = p_c(v) + [\gamma(v)/v]\varepsilon_\theta$, an incomplete equation of state relating p, v, and ε $(= \varepsilon_c + \varepsilon_\theta)$ is obtained. This relation has been found to be valid near the Hugoniot curve and is sufficient for the calculation of the recompression Hugoniot curves and expansion isentropes needed for interpretation of experimental observations [70M1].

A complete equation of state is obtained by combining the Mie–Grüneisen pressure–energy relation with the Debye relation between thermal energy and temperature. Usually the classical-limit value is adequate and we have $\varepsilon_\theta = C_v\theta$, where the specific heat C_v takes the value $3R$ with R being the gas constant. When this relation is used, the thermal pressure is given by $p_\theta = (3R/v)\gamma\theta$ and the necessity of having an accurate value of γ if temperatures are to be estimated from pressure measurements is apparent.

Effects of anharmonicity and electronic excitation. At elevated temperatures the Grüneisen model must be modified to take account of anharmonicity of the lattice vibrations and thermal excitation of conduction electrons. When a substance is heated to a significant fraction of its melting temperature, the amplitude of the crystal lattice oscillations becomes large enough to destroy the accuracy of the quasi-harmonic approximation. In most cases where the heating is by shock compression, the temperature at which this effect becomes pronounced is increased over its usual value because of the increase in the melting temperature caused by the compression (the increase in the repulsive potential restricts the motion of the atoms). The cases in which anharmonic effects are especially important are those where the shock heating is anomalously large relative to the specific volume, as in the case of shock-compressed porous substances.

In the quasi-harmonic approximation the thermal pressure is given by $(\gamma/v)C_v\theta$. The fourth-order anharmonic theory (see, e.g., [71Z2]) yields a correction term proportional to θ^2. This term can simply be added to the quasi-harmonic thermal pressure, or can be incorporated into γ, yielding a "temperature-dependent Grüneisen parameter". In early Soviet work [62A1, 62K1, 63A1] high-temperature effects were taken into account by using an empirical interpolation between values $\gamma = \gamma_0$ and $C_v = 3R$ appropriate for a solid under normal conditions and the values $\gamma = \frac{2}{3}$ and $C_v = \frac{3}{2}R$ appropriate for an ideal gas. This reduction of γ and C_v is equivalent to assuming that the vibrational frequencies of the lattice increase with increasing temperature [65A2]. Pastine [67P1, 68P1], in a slightly different formulation, has also made use of the idea that anharmonic effects can be taken into account by allowing the mode frequencies to increase with increasing temperature.

When the temperature of shock-compressed material reaches several thousand kelvins, the