

At 0°K , ignoring zero-point vibrations, the resultant internal potential energy for non-alkali metals is

$$E_p = a \exp[b(1-X^{1/3})] - cX^{-1/3}$$

where $X = V/V_0$, the dimensionless volume, and a, b, c are constants. The first term corresponds to repulsion due to overlap of electron shells on the ions. The second term accounts for Coulomb interaction and for exchange interaction among conduction electrons.

Thermal energy is accounted for in a quasi-harmonic approximation. A Debye model gives the Helmholtz energy as

$$F = E_p + Nk_B T \left\{ \frac{9}{8} \frac{\theta_D}{T} + 3 \ln \left[1 - \exp\left(-\frac{\theta_D}{T}\right) \right] - D \left(\frac{\theta_D}{T} \right) \right\}$$

where $D\left(\frac{\theta_D}{T}\right)$ is the Debye function,

$$D\left(\frac{\theta_D}{T}\right) = \frac{3T^3}{\theta_D^3} \int_0^{\theta_D/T} \frac{z^3 dz}{e^z - 1},$$

N is the number of unit cells in the solid, and k_B is Boltzmann's constant. From $P = -\left(\frac{\partial F}{\partial V}\right)_T$ we have

$$P = P_p + \frac{\gamma}{V} Nk_B \left[\frac{9}{8} \frac{\theta_D}{T} + 3 \ln \left[1 - \exp\left(-\frac{\theta_D}{T}\right) \right] - D\left(\frac{\theta_D}{T}\right) \right]$$

where γ is the Gruneisen parameter (Eq. (1)) and the potential pressure is

$$P_p = A X^{-2/3} \exp[b(1-X^{1/3})] - K X^{-4/3}.$$

Note that this is a Mie-Gruneisen equation of state,

$$P = P_p(V) + \frac{\gamma}{V} E_T.$$

We have a single experimental compression curve and two unknown functions $P_p(V)$ and $\gamma(V)$. One way to handle this is to express the Gruneisen parameter as a function of the potential pressure. The model chosen for this was the Dugdale-MacDonald formula,

$$\gamma(V) = -\frac{V}{2} \frac{\partial^2(P_p V^{2/3})}{\partial V^2} \bigg/ \frac{\partial(P_p V^{2/3})}{\partial V} - \frac{1}{3}.$$

A constant δ may be added to make $\gamma(V)$ agree at room conditions with the thermodynamic value (Eq. (1)). In a review article on the Gruneisen equation of state, Royce (1971) concludes that the Dugdale-MacDonald formula is the best choice for non-alkali metals.

Two basic assumptions were made in using shock data to generate an equation of state:

1. Experimental values of P , V , E belong to states of thermal equilibrium.
2. The solid is considered a fluid with a hydrostatic shock pressure, ignoring strength effects.

In silver this seems reasonable as its Hugoniot elastic limit is estimated at 1.2 kbar (Sec. III.C).

In the classical limit $T \gg \theta_D$, the Debye function may be expanded to give

$$P = P_p(x) + \frac{3RT}{MV_0} \frac{\gamma}{X} \left[1 + \frac{1}{20} \frac{\theta_D^2}{T^2} \right]$$

where M is the gram molecular weight, R the gas constant, and V_0 the reference specific volume. Temperature is determined from

$$E = E_p(X) + \frac{3RT}{M} \left[1 + \frac{1}{20} \frac{\theta_D^2}{T^2} \right]$$