Title: Complete Mie-Gruneisen Equation of State

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COMPLETE MIE-GRÜNEISEN EQUATION OF STATE

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Abstract

The Mie-Grüneisen equation of state (EOS) is frequently used in hydro simulations to model solids at high pressure (up to a few Mb). It is an incomplete EOS characterized by a Grüneisen coefficient, $\Gamma = -V\,(\partial_e P)_V$, that is a function of only V. Expressions are derived for isentropes and isotherms. This enables the extension to a complete EOS. Thermodynamic consistency requires that the specific heat is a function of a single scaled temperature. A complete extension is uniquely determined by the temperature dependence of the specific heat at a fixed reference density. In addition we show that if the domain of the EOS extends to $T = 0$ and the specific heat vanishes on the zero isotherm then Γ a function of only V is equivalent to a specific heat with a single temperature scale. If the EOS domain does not include the zero isotherm, then a specific heat with a single temperature scale leads to a generalization of the Mie-Grüneisen EOS in which the pressure is linear in both the specific energy and the temperature. Such an EOS has previously been used to model liquid nitromethane.

Notation

Thermodynamic quantities are denoted as follows: e is the specific internal energy, V is the specific volume, P is the pressure, T is the temperature, and S is the specific entropy. The specific heat at constant volume and Grüneisen coefficient are denoted by $C_V = (\partial_T e)_V$ and $\Gamma = V\,(\partial_e P)_V$, respectively. In addition, a summary of standard thermodynamic identities can be found, for example, in [Menikoff & Plohr, 1989; App. A].

1 Mie-Grüneisen EOS

In the first subsection, we specify the pressure, $P(V, e)$, for what is commonly known as the Mie-Grüneisen EOS. This is an incomplete EOS. In the second subsection, the general theory is presented for extending an incomplete EOS to a complete EOS. This involves determining a temperature $T(V, e)$ and an entropy $S(V, e)$, which are thermodynamically consistent; *i.e.*, satisfy the differential relation

$$\mathsf{d}e = -P\,\mathsf{d}V + T\,\mathsf{d}S\ . \tag{1}$$

In the third section, the theory is applied to extend the incomplete Mie-Grüneisen EOS to a complete EOS. The extension is not unique. There is a degree of freedom associated with the specific heat.

1.1 Incomplete form

The incomplete Mie-Grüneisen EOS is widely used in hydro simulations to model solids for pressures up to a few Mb. It has the form

$$P(V, e) = P_{\text{ref}}(V) + \frac{\Gamma(V)}{V}\Big(e - e_{\text{ref}}(V)\Big)\ . \tag{2}$$

The original motivation of this form utilized the zero temperature isotherm (cold curve) as the reference curve and identified the second term on the right side with the thermal contribution to the pressure. Hence, it is assumed that $\Gamma(V) > 0$.

A key property of the Mie-Grüneisn form for the pressure is that the Grüneisen coefficient is assumed to be a function of only V. As a consequence, the pressure is linear in e, and any curve parameterized by V,

$$P_{\text{ref}}(V) = P(V, e_{\text{ref}}(V)) \ ,$$

can be chosen as a reference curve. Common choices are a shock locus, an isentrope (constant entropy), or an isotherm (constant temperature). For a shock locus or an isentrope through the initial state (V_0, e_0) with pressure P_0 and temperature T_0, the reference energy can be expressed in terms of the reference pressure;

$$e_h(V) = e_0 + \tfrac{1}{2}(P_h(V) + P_0)(V_0 - V) \ , \tag{3a}$$

$$e_S(V) = e_0 - \int_{V_0}^{V} \mathsf{d}V' \, P_S(V') \ , \tag{3b}$$

for a reference Hugoniot or isentrope, respectively.

In order for the reference energy of an isotherm to be thermodynamically consistent, knowledge of the specific heat is needed. From the thermodynamic identity $(\partial_V e)_T = -(P - \Gamma \, C_V \, T/V)$,

$$e_T(V) = e_0 - \int_{V_0}^{V} \mathsf{d}V' \left[P_T(V') - \frac{\Gamma(V')}{V'} \, C_V(V', T_0) \, T_0 \right] \ .$$

Later in this subsection, we determine a scaling property of the specific heat, Eq. (15) below. The energy on the reference isotherm can then be expressed as

$$e_T(V) = e_0 - \int_{V_0}^{V} \mathsf{d}V' \left[P_T(V') - \frac{\Gamma(V')}{V'} \, C_V\Big(V_0, T_0/\phi(V')\Big) \, T_0 \right] \ . \tag{4}$$

where $\phi(V)$ is given by Eq. (7) below. Thus, only the temperature dependence of the specific heat at V_0 is needed.

Isentropes play an important role in the theory. The energy on an isentrope through the state (V_0, e_1), which we label S_1, is determined by the ODE

$$(\mathsf{d}/\mathsf{d}V) e_S(V) = -P(V, e) \ , \tag{5}$$

with the initial condition $e_{S_1}(V_0) = e_1$. The value of S_1 is discussed in the next subsection. Substituting Eq. (2) yields

$$\frac{\mathsf{d}}{\mathsf{d}V} e_S(V) + \frac{\Gamma(V)}{V} e_S(V) = -\Big[P_{\text{ref}}(V) - \frac{\Gamma(V)}{V} e_{\text{ref}}(V) \Big] \ . \tag{6}$$

With the integrating factor

$$\phi(V) = \exp\Big[-\int_{V_0}^{V} \mathsf{d}V' \, \frac{\Gamma(V')}{V'}\Big] \ , \tag{7}$$

the ODE can be written as

$$\frac{\mathsf{d}}{\mathsf{d}V}\Big[\frac{e_S(V)}{\phi(V)}\Big] = -\frac{P_{\text{ref}}(V) - \frac{\Gamma(V)}{V} e_{\text{ref}}(V)}{\phi(V)} \ . \tag{8}$$

The solution can be expressed as

$$e_{S_1}(V) - e_{S_0}(V) = \phi(V)\,(e_1 - e_0) \ , \tag{9}$$

where the energy on the isentrope S_0 through the initial state (V_0, e_0) is given by

$$e_{S_0}(V) = \phi(V)\left[e_0 - \int_{V_0}^{V} \mathsf{d}V' \frac{P_{\text{ref}}(V') - \frac{\Gamma(V')}{V'} e_{\text{ref}}(V')}{\phi(V')}\right] \ .$$

Substituting $\Gamma/V = -(\mathsf{d}\phi/\mathsf{d}V)/\phi$ and integrating by parts, the energy on the initial isentrope can be re-expressed as

$$e_{S_0}(V) = e_{\text{ref}}(V) - \phi(V) \int_{V_0}^{V} \mathsf{d}V' \left[\frac{P_{\text{ref}}(V') + (\mathsf{d}e_{\text{ref}}/\mathsf{d}V)(V')}{\phi(V')}\right] \ . \tag{10}$$

When the reference curve is an isentrope, the integral vanishes.

The pressure on the isentrope S_1 is then determined by

$$P_{S_1}(V) = P_{S_0}(V) + \frac{\Gamma(V)}{V}\,\phi(V)\,(e_1 - e_0) \ , \tag{11}$$

where

$$P_{S_0}(V) = P_{\text{ref}}(V) + \frac{\Gamma(V)}{V}\left[e_{S_0}(V) - e_{\text{ref}}(V)\right] \tag{12}$$

is the pressure on the isentrope through the initial state. Since $\Gamma > 0$, the projection of isentropes onto the (V, P)-plane and the (V, e)-plane, do not cross.

We note in passing that a convex EOS is required for all physical shock waves to be entropy increasing and compressive. This means that all isentropes $P_S(V)$ are convex. It follows from Eq. (11) that $\frac{\Gamma(V)}{V}\,\phi(V)$ must be convex; *i.e.*, the derivative with respect to V is negative and the second derivative is positive. This places some restrictions on the form for $\Gamma(V)$. A simple sufficient condition is that $\Gamma(V)/V$ is monotonically increasing with decreasing V. The common choices $\Gamma =$ constant and $\Gamma/V =$ constant satisfy the requirement for convexity. Also, $P_{S_0}(V)$ needs to be convex. This may place additional restrictions on $\Gamma(V)$, depending on the reference curve.

Using thermodynamic identities, an alternate expression for the Grüneisen coefficient is

$$\Gamma = -(V/T)\,(\partial_V T)_S \ . \tag{13}$$

Consequently, the temperature on an isentrope is given by

$$T_S(V) = \phi(V)\,T_S(V_0) \ . \tag{14}$$

Since $\Gamma(V) > 0$, $\phi(V) > 0$ and monotonically increasing with decreasing V. Hence, the temperature on an isentrope increases with decreasing V. Moreover, isotherms do not cross in the (V,T)-plane.

The fact that $T_S(V)$ and $e_S(V) - e_{S_0}(V)$ both scale by the same factor, for all isentropes, is a consequence of the Grünesien coefficient being a function of only V. It implies that the specific heat satisfies the relation

$$C_V\Big(V,T\Big) = (\partial_T e)_V = \frac{(\partial_S e)_V}{(\partial_S T)_V} = C_V\Big(V_0, T/\phi(V)\Big) \ . \tag{15}$$

Typically, $C_V(V_0,T)$ is monotonically increasing with increasing temperature. The scaling then implies

$$\begin{aligned}(\partial_V C_V)_T &= -\frac{\mathsf{d}\phi/\mathsf{d}V}{\phi^2(V)}\Big(\partial_T C_V\Big)_V\Big(V_0, T/\phi(V)\Big)\\ &= \frac{\Gamma(V)}{V\,\phi(V)}\Big(\partial_T C_V\Big)_V\Big(V_0, T/\phi(V)\Big) > 0\,.\end{aligned} \tag{16}$$

The scaling of the specific heat will be used in a later subsection to construct a thermodynamically consistent complete EOS.

1.2 Extending to complete EOS

To obtain a complete EOS, the temperature $T(V,e)$ and entropy $S(V,e)$ need to be specified consistent with the thermodynamic relation, Eq. (1). This can be re-expressed as

$$\mathsf{d}S = (1/T)\,\mathsf{d}e + (P/T)\,\mathsf{d}V \ . \tag{17}$$

In order for S to be a perfect differential, the cross derivatives must be equal

$$\partial_V(1/T)_e = \partial_e(P/T)_V \ . \tag{18}$$

This can be re-expressed as a hyperbolic PDE for the scalar variable T

$$(\partial_V - P\partial_e)\,T = -(T/V)\,\Gamma \ . \tag{19}$$

The characteristic curves in the (V, e)-plane,

$$\mathsf{d}e_s/\mathsf{d}V = -P(V, e_s) \ , \tag{20}$$

are the same as the isentropes. On the characteristic curve, the temperature satisfies

$$\frac{\mathsf{d}T}{\mathsf{d}V} = -\frac{\Gamma}{V}\,T \ , \tag{21}$$

which is the same as the thermodynamic identity, Eq. (13). Hence on the characteristic curve $e_s(V)$, the temperature is given by

$$T_s(V) = T_s(V_0)\ \exp\biggl[-\int_{V_0}^{V} \mathsf{d}V'\,\frac{\Gamma\Bigl(V', e_s(V')\Bigr)}{V'}\biggr] \ . \tag{22}$$

This analysis leads to a general procedure for extending an incomplete EOS to a complete EOS. First, one selects a curve in the (V, e)-plane that crosses every isentrope exactly once. For illustrative purposes, we use the line $V = V_0$. On the selected curve, the specific heat C_V may be arbitrarily chosen. The temperature and entropy on the selected curve are determined by integrating ODEs from the thermodynamic relations. For example, $T(V_0, e)$ and $S(V_0, e)$ are determined by

$$\frac{\mathsf{d}}{\mathsf{d}e}\begin{pmatrix} T \\ S \end{pmatrix} = \begin{pmatrix} 1/C_V(V_0, T) \\ 1/T \end{pmatrix} \ , \tag{23}$$

with the initial conditions $T(V_0, e_0) = T_0$ and $S(V_0, e_0) = S_0$. Then given any point (V, e), the isentrope ODE (20) can be integrated to determine $e_s(V_0)$. Hence, from Eq. (23) we obtain $T(V_0, e_s)$ and $S(V_0, e_s)$. Using $T(V_0, e_s)$, Eq. (22) determines $T(V, e)$. Moreover, $S(V, e) = S(V_0, e_s)$. Thus, T and S are defined for all (V, e), and are thermodynamically consistent.

1.3 Complete form

For the incomplete Mie-Grüneisen EOS, the extension to a complete EOS can be greatly simplified because the isentropes are determined explicitly by Eqs. (7, 9, 14). A key point of the general theory is that all extensions are defined by specifying the specific heat at a fixed V_0. Conversely, specifying $C_V(V_0, T)$ uniquely determines the extension.

As previously noted, the specific heat satisfies a simple scaling relation, Eq. (15). This can be used to complete the Mie-Grünesen EOS as follows. First, determine the integrating factor $\phi(V)$ from Eq. (7) and the energy on the initial isentrope $e_{S_0}(V)$ from Eq. (10). Then the temperature and entropy at the state (V, e) are determined by applying the ODE (23) at fixed V; *i.e.*, integrate from $e_{S_0}(V)$ to e the ODE

$$\frac{\mathsf{d}}{\mathsf{d}e}\begin{pmatrix} T \\ S \end{pmatrix} = \begin{pmatrix} 1/C_V\big(V_0, T/\phi(V)\big) \\ 1/T \end{pmatrix} , \tag{24}$$

starting with the initial conditions $T = T_0\,\phi(V)$ and $S = S_0$.

A frequently used special case is for $C_V =$ constant. The integral can then be done explicitly. The result is

$$T(V, e) = T_0\,\phi(V) + \big[e - e_{S_0}(V)\big]/C_V \ , \tag{25a}$$

$$S(V, e) = S_0 + C_V\ \ln\left[1 + \frac{e - e_{S_0}(V)}{T_0\,C_V\,\phi(V)}\right] . \tag{25b}$$

Physically, $C_V = 0$ at $T = 0$. Consequently, this special case of an EOS with constant C_V should not be used at low temperature.

2 Free energy

It is instructive to express the complete Mie-Grüneisen EOS in terms of the Helmholtz free energy. The free energy is defined by

$$F(V, T) = e - T\,S \ . \tag{26}$$

The thermodynamic relation, Eq. (1), can be re-expressed as

$$\mathsf{d}F = -P\,\mathsf{d}V - S\,\mathsf{d}T \ . \tag{27}$$

We aim to construct F from the pressure on an isotherm, the specific heat and the Grüneisen coefficient.

Since entropy satisfies the relation

$$\mathsf{d}S = \frac{\Gamma\,C_V}{V}\,\mathsf{d}V + \frac{C_V}{T}\,\mathsf{d}T \ , \tag{28}$$

it can be expressed as

$$S(V,T) = S_0 + \int_{V_0}^{V} \mathsf{d}V'\,\frac{\Gamma(V',T_0)\,C_V(V',T_0)}{V'} + \int_{T_0}^{T} \mathsf{d}T'\,\frac{C_V(V,T')}{T'} \ . \tag{29}$$

Then from Eq. (27), the free energy can be written as

$$\begin{aligned} F(V,T) = e_0 - T_0\,S_0 - \int_{V_0}^{V} \mathsf{d}V'\,P(V',T_0) \\ - \int_{T_0}^{T} \mathsf{d}T' \left\{ S_0 + \int_{V_0}^{V} \mathsf{d}V'\,\frac{\Gamma(V',T_0)\,C_V(V',T_0)}{V'} + \int_{T_0}^{T'} \mathsf{d}T''\,\frac{C_V(V,T'')}{T''} \right\} \ . \end{aligned}$$

This can be re-expressed as

$$\begin{aligned} F(V,T) = e_0 - T\,S_0 - \int_{V_0}^{V} \mathsf{d}V' \left[P(V',T_0) + \frac{\Gamma(V',T_0)}{V'}\,C_V(V',T_0)\,(T-T_0) \right] \\ - \int_{T_0}^{T} \frac{\mathsf{d}T'}{T'}(T-T')\,C_V(V,T') \ . \end{aligned} \tag{30}$$

We note that the integrals require $C_V(V,T)$ but only $\Gamma(V,T_0)$. This is because the specific heat and the Grüneisen coefficient are not fully independent.

Evaluating

$$\partial_V(\partial_T\partial_T F) = \partial_T(\partial_T\partial_V F)$$

leads to the compatibility condition [Sheffield & Duvall, 1983]

$$V\,[\partial_V C_V]_T = T\,[\partial_T(\Gamma\,C_V)]_V \ . \tag{31}$$

Integrating with respect to T yields

$$\Gamma(V,T)\,C_V(V,T) = \Gamma(V,T_0)\,C_V(V,T_0) + V\,\frac{\partial}{\partial V}\int_{T_0}^{T} \frac{\mathsf{d}T'}{T'}\,C_V(V,T') \ . \tag{32}$$

If the domain extends to $T_0 = 0$, which requires, as is physically, that the specific heat vanishes at $T = 0$, then Γ is determined by C_V. Consequently with $T_0 = 0$, Eq. (30) for the free energy simplifies to

$$F(V,T) = e_0 - \int_{V_0}^{V} \mathsf{d}V'\, P_c(V') - \int_0^T \frac{\mathsf{d}T'}{T'} (T - T')\, C_V(V,T') \;, \tag{33}$$

where P_c is the cold curve, *i.e.*, $T = 0$ isotherm. It follows from Eqs. (26, 27) that the entropy, energy and pressure are given by

$$S(V,T) = -\partial_T F \quad = \int_0^T \frac{\mathsf{d}T'}{T'}\, C_V(V,T') \;, \tag{34}$$

$$e(V,T) = F + T\,S = e_0 - \int_{V_0}^{V} \mathsf{d}V'\, P_c(V') + \int_0^T \mathsf{d}T'\, C_V(V,T') \;, \tag{35}$$

$$P(V,T) = -\partial_V F \quad = P_c(V) + \int_0^T \frac{\mathsf{d}T'}{T'} (T - T')\, \partial_V C_V(V,T') \;. \tag{36}$$

Substituting the compatibility relation, Eq. (31), and integrating by parts, the pressure can be expressed as

$$P(V,T) = P_c(V) + V^{-1} \int_0^T \mathsf{d}T'\, \Gamma(V,T')\, C_V(V,T') \;. \tag{37}$$

This is consistent with the thermodynamic identity $(\partial_T P)_V = \Gamma\, C_V / V$.

To summarize, F is determined by a reference temperature T_0 and three functions; $P(V,T_0)$, $\Gamma(V,T_0)$ and $C_V(V,T)$. Due to the compatibility condition, Eq. (31), only $\Gamma(V,T_0)$ and not $\Gamma(V,T)$ can be specified. Alternatively, if the domain extends to $T_0 = 0$ and $C_V(V,0) = 0$ then the cold curve $P_c(V)$ and $C_V(V,T)$ are sufficient to determine F.

2.1 Mie-Grüneisen EOS

For the Mie-Grüneisen EOS, the compatibility condition, Eq. (31), reduces to a hyperbolic PDE for the scalar variable C_V;

$$V\, \partial_V C_V - \Gamma(V)\, T\, \partial_T C_V = 0 \;. \tag{38}$$

The characteristic curve in the (V,T)-plane is determined by the ODE

$$\frac{\mathsf{d}T}{\mathsf{d}V} = -\frac{\Gamma(V)}{V}\, T \;.$$

Therefore, the characteristic curve through the point (V_0, T_0) is $T = T_0\, \phi(V)$, where $\phi(V)$ is given by Eq. (7), and corresponds to an isentrope. On the characteristic curve, C_V is a constant. Hence, the specific heat has the form derived in the previous section, Eq. (15). Moreover, the specific heat is a function of only entropy.

The free energy for the Mie-Grüneisen EOS can be written as

$$F(V,T) = e_0 - \int_{V_0}^{V} \mathsf{d}V'\, P_c(V') - \theta(V) \int_0^{T/\theta(V)} \frac{\mathsf{d}\widetilde{T}}{\widetilde{T}} \Big[T/\theta(V) - \widetilde{T}\Big]\, \widetilde{C}_v(\widetilde{T}) \ , \tag{39a}$$

where

$$\theta(V) = \theta(V_0) \exp\Big[- \int_{V_0}^{V} \mathsf{d}V'\, \Gamma(V')/V'\Big] \ , \tag{39b}$$

$$\widetilde{C}_v(\widetilde{T}) = C_V\Big(V, \theta(V)\, \widetilde{T}\Big) \ . \tag{39c}$$

The function $\theta(V)$ can be thought of as a temperature, and $\widetilde{T} = T/\theta(V)$ as dimensionless. In effect, $\theta(V)$ is a temperature scale and plays an analogous role in scaling the specific heat as the Debye temperature used in the Debye model for the specific heat of a solid. We note that $\phi(V) = \theta(V)/\theta(V_0)$, and $C_V(V_0, T) = C_V(V, \phi(V)\, T)$. Since the specific heat scales with the ratio of θ, we may take $\theta(V_0) = 1\,\mathrm{K}$. It serves to keep track of the dimensions. To summarize, with $T_0 = 0$ as the reference temperature, a complete Mie-Grüneisen EOS is determined by three functions; $P_c(V)$, $\Gamma(V)$ and $\widetilde{C}_v(\widetilde{T}) = C_V\Big(V_0, \theta(V_0)\, \widetilde{T}\Big)$.

The entropy, energy and pressure can readily be obtained:

$$S(V,T) = -\partial_T F \quad = \int_0^{T/\theta(V)} \frac{\mathsf{d}\widetilde{T}}{\widetilde{T}}\, \widetilde{C}_v(\widetilde{T}) \ , \tag{40}$$

$$e(V,T) = F + T\,S = e_0 - \int_{V_0}^{V} \mathsf{d}V'\, P_c(V') + \theta(V) \int_0^{T/\theta(V)} \mathsf{d}\widetilde{T}\, \widetilde{C}_v(\widetilde{T}) \ , \tag{41}$$

$$P(V,T) = -\partial_V F \quad = P_c(V) - \frac{\mathsf{d}\theta}{\mathsf{d}V} \int_0^{T/\theta(V)} \mathsf{d}\widetilde{T}\, \widetilde{C}_v(\widetilde{T}) \ . \tag{42}$$

Substituting Eqs. (39b, 41) into Eq. (42) yields

$$P(V,T) = P_c(V) + \frac{\Gamma(V)}{V} \Big[e(V,T) - e(V,0)\Big] \ , \tag{43}$$

which is the Mie-Grüneisen form for the pressure with the $T = 0$ isotherm as the reference. Moreover, from Eq. (40), the entropy is a function of the scaled temperature $T/\theta(V)$.

The last term in Eq. (41) can be thought of as the thermal energy. It factors into the product of two functions; $\theta(V)$ and a function of $T/\theta(V)$. Since entropy is monotonically increasing function of $T/\theta(V)$, the function can be inverted to obtain the scaled temperature as a function of entropy. Consequently, the energy as a function of V and S can be written in the form

$$\tilde{e}(V,S) = e_0 - \int_{V_0}^{V} \mathsf{d}V'\, P_c(V') + \theta(V)\chi(S) \;, \tag{44}$$

where $\chi(S) = \int_0^{T/\theta(V)} \mathsf{d}\widetilde{T}\, \widetilde{C}_v(\widetilde{T})$. In fact, Grinfeld [2011] has derived the complete Mie-Grüneisen EOS utilizing $\tilde{e}(V,S)$ as a thermodynamic potenial. He showed that Γ a function of only V implies the energy has the form given in Eq. (44). We note that our analysis began by computing the difference in energy of two isentropes, Eq. (9). This follows directly from the form of $\tilde{e}(V,S)$.

Finally, in passing, we note that the differential thermodynamic relation for the entropy, Eq. (28), implies

$$\Big(\partial_V - \frac{T\,\Gamma}{V}\,\partial_T\Big)\partial_T F = 0 \;. \tag{45}$$

When Γ is a function of only V, the solution to the PDE has the form given in Eq. (39a). This could be used to provide an alternate derivation of the complete Mie-Grüneisen EOS.

3 Single temperature scale EOS

For the Mie-Grüneisen EOS we have seen that when Γ is a function of only V, the specific heat and entropy are functions of a single scaled temperature variable. It is natural to ask whether the converse is true: Is Γ a function of only V if either S or C_V is a function of a single scaled temperature variable. We next show that the converse is true for S but not necessarily for C_V.

Suppose that $S(V,T) = \widetilde{S}(\widetilde{T})$ where $\widetilde{T} = T/\theta(V)$. Moreover, we assume that $\widetilde{S}(\widetilde{T})$ is a monotonic function and hence is invertible; *i.e.*, $\widetilde{T}$ is a function of S. The specific heat can be expressed as

$$C_V(V,T) = T(\partial_T S)_V = \widetilde{T}\mathsf{d}\widetilde{S}/\mathsf{d}\widetilde{T} \; . \tag{46}$$

Hence, the specific heat is a function of only S.

An alternate form of the compatibility condition, Eq. (31), is

$$C_V^2\,(\partial_S \Gamma)_V = V\,(\partial_V C_V)_S \; . \tag{47}$$

It can be proved [Davis, 2000] by evaluating

$$\partial_V(\partial_S\partial_S\, e) = \partial_S(\partial_V\partial_S\, e) \; . \tag{48}$$

It follows that if C_V is a function of only S then Γ is a function of only V. Therefore, if S is a function of a single scaled temperature variable then Γ is a function of only V.

Next we assume that the specific heat scales with a single temperature,

$$C_V(V,T) = \widetilde{C}_v\Big(T/\theta(V)\Big) \; . \tag{49}$$

This implies

$$\partial_V C_V = -(\theta'/\theta)\, T\, \partial_T C_V \tag{50}$$

where $\theta' = (\mathsf{d}/\mathsf{d}V)\theta$. Substituting into the compatibility condition, Eq. (31). leads to the equation

$$-\,[V\theta'/\theta]\partial_T C_V = \partial_T(\Gamma\, C_V) \; . \tag{51}$$

Integrating in T then gives

$$\Big[\Gamma(V,T) - g(V)\Big]\, C_V(V,T) = \Big[\Gamma(V,T_0) - g(V)\Big]\, C_V(V,T_0) \; , \tag{52}$$

where $g(V) = -V\,\theta'(V)/\theta(V)$. If the domain extended down to $T_0 = 0$ and $\widetilde{C}_v(0) = 0$, then $\Gamma = g(V)$ and we would obtain a Mie-Grüneisen EOS.

The cold curve is in the solid phase. For a liquid phase, the EOS model domain would not include the zero isotherm. In fact, specific heat scaling has been applied to liquid nitromethane by Winey *et al.* [2000]. In this case,

$$\Gamma(V,T) = g(V) + \Big[\Gamma(V,T_0) - g(V)\Big]\, \frac{\widetilde{C}_v(T_0/\theta(V))}{\widetilde{C}_v(T/\theta(V))} \; . \tag{53}$$

Hence, Γ is a function of both V and T. Typically, $C_V \to$ constant for large T. In this case Γ would become a function of only V at high temperatures. However, the limiting Γ would not be $g(V)$. Hence, the Mie-Grüneisen relation between Γ and the temperature scale $\theta(V)$ would not hold.

The free energy for the scaled temperature model is

$$\begin{aligned} F(V,T) = e_0 - T\,S_0 - \int_{V_0}^{V} \mathsf{d}V' \Big[P(V',T_0) + \frac{\Gamma(V',T_0)}{V'}\, C_V(V',T_0)\,(T-T_0) \Big] \\ - \theta(V) \int_{T_0/\theta(V)}^{T/\theta(V)} \frac{\mathsf{d}\widetilde{T}}{\widetilde{T}} \Big[T/\theta(V) - \widetilde{T} \Big]\, \widetilde{C}_v(\widetilde{T}) \ , \qquad (54) \end{aligned}$$

The entropy, energy and pressure are then given by

$$S(V,T) = S(V,T_0) + \int_{T_0/\theta(V)}^{T/\theta(V)} \frac{\mathsf{d}\widetilde{T}}{\widetilde{T}}\, \widetilde{C}_v(\widetilde{T}) \ , \qquad (55)$$

$$e(V,T) = e(V,T_0) + \theta(V) \int_{T_0/\theta(V)}^{T/\theta(V)} \mathsf{d}\widetilde{T}\, \widetilde{C}_v(\widetilde{T}) \ , \qquad (56)$$

$$\begin{aligned} P(V,T) = P(V,T_0) \, + \frac{g(V)}{V}\Big[e - e(V,T_0) \Big] \\ + \frac{\Gamma(V,T_0) - g(V)}{V}\, C_V(V,T_0)\,(T-T_0) \ . \end{aligned} \qquad (57)$$

where

$$S(V,T_0) = S_0 + \int_{V_0}^{V} \mathsf{d}V' \, \frac{\Gamma(V',T_0)}{V'}\, C_V(V',T_0) \ , \qquad (58)$$

$$e(V,T_0) = e_0 - \int_{V_0}^{V} \mathsf{d}V' \Big[P(V',T_0) - \frac{\Gamma(V',T_0)}{V'}\, C_V(V',T_0)\, T_0 \Big] \ . \qquad (59)$$

It is noteworthy that for fixed V, the pressure is linear in both e and T. This is somewhere between a Mie-Grüneisen model of a solid for which the pressure is linear in e, and an ideal gas for which the pressure is linear in T.

Another class of models in which Γ is a function of both V and T can be formulated in terms of a specific heat that is a function of several scaled temperature variables; see for example Menikoff [2007]. This is suited to a molecular crystal, for which the temperature scales are related to the optical phonon frequencies.

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