

ANEOS Code Modification: Thermal model adjustment parameter

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Abstract

This document describes changes to the ANEOS equation of state package to include a parameter for adjustment of the Debye thermal model used for the solid and liquid phases. The original ANEOS had hard-coded a Dulong-Petit limit for the thermal term in the Helmholtz free energy (Thompson & Lauson, 1974). These changes are implemented into the version of ANEOS that includes the molecular gas feature (Melosh, 2007) and the ability to incorporate both a melt curve and high-pressure phase transition (Collins & Melosh, 2014). A new ANEOS model for forsterite has been developed using the heat capacity adjustment feature and constraints from recently obtained data at high pressures and on the vapor curve (Stewart et al., submitted).

1 The ANEOS Model

A wide-ranging equation of state (EOS) describes the thermodynamic surface of a material as a function of density, ρ , and temperature, T . ANEOS separates the Helmholtz free energy, F , into three terms:

$$F(\rho, T) = F_c(\rho, T) + F_{th}(\rho, T) + F_e(\rho, T). \quad (1)$$

The cold term, F_c , includes the contributions that do not depend on temperature; the thermal term, F_{th} , includes the temperature-dependent parts of the interatomic forces; and the electronic term F_e includes the ionization energies at high temperatures. ANEOS uses a formula for the thermal term that spans the free energy of the condensed phase and the free energy of the gas by using the parameter ψ . ψ is a term that represents how closely the material corresponds to an ideal gas. The original formula is described in Thompson and Lauson (1974) and discussed at length in Melosh (2007). It was modified to include a critical point adjustment parameter b in Thompson (1990) and expanded to include molecular gas by Melosh (2007). In the interpolated region, the current expression for the thermal free energy is given by:

$$F_{th}(\rho, T) = N_0 k T \left\{ \left[3 \ln \left(1 - e^{-\theta/T} \right) - \mathcal{D}_3(\theta/T) \right] + \frac{3}{2} \frac{1}{b} \ln (1 + \psi^b) \right\}, \quad (2)$$

$$\psi(\rho, T) = Z_m \frac{C_{13} \rho^{2/3} T}{\theta^2}, \quad (3)$$

$$C_{13} = \frac{N_0^{5/3} h^2}{2\pi k} \exp \left\{ \frac{2}{3} \sum_l \frac{N_l}{N_0} \ln \left(\frac{N_l}{N_0^{5/2} M_l^{3/2}} \right) \right\} \quad (4)$$

When the temperatures are large and/or the densities are low, ψ is large and the right hand term in Eq. 2 dominates and the free energy approaches an ideal gas. N_0 is the average number of atoms per gram; k is the Boltzmann constant; T is temperature; θ is the density-dependent Debye temperature; \mathcal{D}_3 is the third order Debye function; ρ is density; Z_m is the multiplicative factor to incorporate the free energy of molecules from Melosh (2007); N_l is the number of atoms with atomic mass M_l ; and h is Planck's constant. The adjustment parameter b is used to lower the critical point. The input variable is C_{62} and $b = 1 - C_{62}$. The value is typically set to 0.5. Several input variables are needed for the molecular gas model; see Melosh (2007).

The density-dependent Debye temperature is related to the Grüneisen parameter by

$$\Gamma = \frac{\rho}{\theta} \frac{d\theta}{d\rho}. \quad (5)$$

The ANEOS Grüneisen formulation is discussed in more detail below.

Because ANEOS was designed to be run during a hydrocode calculation, there is an option to simplify the Debye function to the high-temperature limit. The full

Debye function is used when the input value of θ_0 is negative. The simplified function is used when the input value is positive. Then, the interpolated free energy term is given by:

$$F_{th}(\rho, T) = N_0 kT \left\{ \left[3 \ln \left(\frac{\theta}{T} \right) - 1 \right] + \frac{3}{2} \frac{1}{b} \ln (1 + \psi^b) \right\}. \quad (6)$$

Debye theory describes the phonon contribution to the specific heat capacity in a solid. In the liquid region, the ANEOS free energy is the sum of the solid free energy plus a contribution from melting. Thus, the interpolation expression for F_{th} applies to both the solid and liquid phases.

In Equation 2, the Debye function approaches the Dulong-Petit limit of $3N_0 kT$ at high temperatures. However, shock experiments have shown that the heat capacities in silicate liquids varies substantially from the Dulong-Petit limit (Hicks et al., 2006; Root et al., 2018). The phonon model cannot be generalized easily for molecular liquids (e.g., Bolmatov et al. (2012)).

To provide some flexibility in fitting the liquid region, I introduced an adjustment parameter to the thermal energy term, f_{cv} , so that the free energy is given by:

$$F_{th}(\rho, T) = N_0 kT \left\{ f_{cv} \left[3 \ln (1 - e^{-\theta/T}) - \mathcal{D}_3(\theta/T) \right] + \frac{3}{2} \frac{1}{b} \ln (1 + \psi^b) \right\}, \text{ or} \quad (7)$$

$$F_{th}(\rho, T) = N_0 kT \left\{ f_{cv} \left[3 \ln \left(\frac{\theta}{T} \right) - 1 \right] + \frac{3}{2} \frac{1}{b} \ln (1 + \psi^b) \right\}. \quad (8)$$

The value is entered in V44 of the ANEOS input deck. The value of f_{cv} adjusts the high-temperature heat capacity limit for the Debye function to $3f_{cv}N_0 kT$. Note that deviating from the Dulong-Petit limit generally decreases the accuracy of the thermal model for the solid phase.

This modified version of ANEOS has been used to updated the EOS for forsterite (Mg_2SiO_4). A summary of these changes and the forsterite EOS results is presented in (Stewart et al., submitted). The forsterite ANEOS parameters are available on <https://github.com/ststewart/>.

2 Derivation of the Thermodynamic Variables

To implement the simplified thermal free energy, Eq. 8, the section of ANEOS1.f for the ‘liquid/solid-vapor interpolation region’ was replaced with the following equations.

$$P_{th} = \rho^2 \left(\frac{\partial F_{th}}{\partial \rho} \right)_T \quad (9)$$

$$= \rho^2 N_0 kT 3f_{cv} \frac{\partial \ln(\theta/T)}{\partial \rho} + \rho^2 \frac{3}{2} \frac{N_0 kT}{b} \frac{1}{1 + \psi^b} \left[\frac{2}{3} \frac{b\psi^b}{\rho} (1 - 3\Gamma) \right] \quad (10)$$

$$= \rho N_0 kT 3f_{cv} \Gamma + \rho N_0 kT \frac{\psi^b}{1 + \psi^b} (1 - 3\Gamma). \quad (11)$$

The derivatives of ψ and θ are given by:

$$\frac{\partial \psi}{\partial \rho} = \frac{2}{3} \frac{\psi}{\rho} (1 - 3\Gamma) \quad (12)$$

$$\frac{\partial \psi}{\partial T} = \frac{\psi}{T} \quad (13)$$

$$\frac{\partial (\ln(\theta/T))}{\partial \rho} = \frac{\Gamma}{\rho} \quad (14)$$

$$\frac{\partial(\ln(\theta/T))}{\partial T} = -\frac{1}{T}. \quad (15)$$

$$E = F + TS = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \quad (16)$$

$$E_{th} = -T^2 \left[3f_{cv} N_0 k \left(-\frac{1}{T} \right) + \frac{3}{2} N_0 k \frac{\psi^{b-1}}{1+\psi^b} \frac{\partial \psi}{\partial T} \right] \quad (17)$$

$$= 3f_{cv} N_0 k T - \frac{3}{2} N_0 k T \frac{\psi^b}{1+\psi^b} \quad (18)$$

$$S_{th} = \left(-\frac{\partial F_{th}}{\partial T} \right)_\rho \quad (19)$$

$$= -3f_{cv} N_0 k \ln(\theta/T) - N_0 k T 3f_{cv} (-1/T) + N_0 k f_{cv} - \quad (20)$$

$$\frac{3}{2b} \frac{\psi^{b-1}}{1+\psi^b} \frac{\psi}{T} N_0 k T - N_0 k \frac{3}{2b} \ln(1+\psi^b) \quad (21)$$

$$= N_0 k \left[4f_{cv} - 3f_{cv} \ln \left(\frac{\theta}{T} \right) + \frac{3}{2} \left(\frac{1}{b} \ln \left(\frac{1}{1+\psi^b} \right) - \frac{\psi^b}{1+\psi^b} \right) \right] \quad (22)$$

$$C_v = \left(\frac{\partial E_{th}}{\partial T} \right)_V = -T \frac{\partial^2 F_{th}}{\partial T^2} \quad (23)$$

$$= \frac{E_{th}}{T} - \frac{3}{2} N_0 k b \left(\frac{\psi^b}{1+\psi^b} \right) + \frac{3}{2} N_0 k b \left(\frac{\psi^b}{1+\psi^b} \right)^2 \quad (24)$$

$$\frac{\partial P_{th}}{\partial T} = \frac{P_{th}}{T} + \rho N_0 k (1-3\Gamma) b \left[\left(\frac{\psi^b}{1+\psi^b} \right) - \left(\frac{\psi^b}{1+\psi^b} \right)^2 \right] \quad (25)$$

$$\frac{\partial P_{th}}{\partial \rho} = \frac{P_{th}}{\rho} + 3f_{cv} \rho N_0 k T \frac{d\Gamma}{d\rho} - 3\rho N_0 k T \left(\frac{\psi^b}{1+\psi^b} \right) \frac{d\Gamma}{d\rho} + \quad (26)$$

$$\frac{2}{3} N_0 k T b (1-3\Gamma)^2 \left[\left(\frac{\psi^b}{1+\psi^b} \right) - \left(\frac{\psi^b}{1+\psi^b} \right)^2 \right] \quad (27)$$

The simplified Debye function has the side effect of leading to negative entropies at low temperatures. Thus, this version of the model is not suitable for low temperature applications. This problem can be avoided by calculating the full Debye function.

The updated equation using the full Debye function, Eq. 7, is given by

$$F_{th}(\rho, T) = N_0 k T \left\{ f_{cv} \left[3 \ln \left(1 - e^{-\theta/T} \right) - \mathcal{D}_3(\theta/T) \right] + \frac{3}{2} \frac{1}{b} \ln(1+\psi^b) \right\}, \quad (28)$$

The family of Debye functions is given by

$$\mathcal{D}_n(x) = \frac{n}{x^n} \int_0^x \frac{y^n}{e^y - 1} dy. \quad (29)$$

The derivative of the Debye function can be expressed using the Bernoulli function, \mathcal{B} ,

$$x \mathcal{D}'_n(x) = n (\mathcal{B}(x) - \mathcal{D}_n(x)), \text{ where} \quad (30)$$

$$\mathcal{B}(x) = \frac{x}{e^x - 1}. \quad (31)$$

The ANEOS Debye function returns the third order Debye function ($n = 3$) and two intermediate functions, D_2 and D_S :

$$\mathcal{D}_3(\theta/T) = \frac{3}{(\theta/T)^3} \int_0^{\theta/T} \frac{y^3}{e^y - 1} dy \quad (32)$$

$$D_2(\theta/T) = \ln(1 - e^{-(\theta/T)}) \quad (33)$$

$$D_S(\theta/T) = 3 \left(\mathcal{D}_3(\theta/T) - \frac{\theta/T}{e^{\theta/T} - 1} \right) \quad (34)$$

Then, the derivative of the third order Debye function is given by

$$\frac{d\mathcal{D}_3(x)}{dy} = \frac{-D_S}{x} \frac{dx}{dy}. \quad (35)$$

We will drop the subscript 3 in the rest of this section. The derivatives of the Debye function with respect to temperature and density are

$$\frac{\partial \mathcal{D}(\theta/T)}{\partial T} = \frac{D_S}{T} \quad (36)$$

$$\frac{\partial \mathcal{D}(\theta/T)}{\partial \rho} = -\frac{\Gamma}{\rho} D_S. \quad (37)$$

$$(38)$$

Similarly, the derivatives of the first thermal term can be expressed simply as

$$\frac{\partial (\ln(1 - e^{-\theta/T}))}{\partial T} = -\frac{1}{3T} (3\mathcal{D} - D_S) \quad (39)$$

$$\frac{\partial (\ln(1 - e^{-\theta/T}))}{\partial \rho} = \frac{\Gamma}{3\rho} (3\mathcal{D} - D_S). \quad (40)$$

The thermal contributions to the thermodynamic variables are:

$$P_{th} = \rho^2 \left(\frac{\partial F_{th}}{\partial \rho} \right)_T \quad (41)$$

$$= 3f_{cv} N_0 k T \rho \Gamma \mathcal{D} + N_0 k T \rho (1 - 3\Gamma) \left(\frac{\psi^b}{1 + \psi^b} \right) \quad (42)$$

$$E_{th} = F + TS = -T^2 \frac{\partial}{\partial T} \left(\frac{F_{th}}{T} \right) \quad (43)$$

$$= 3f_{cv} N_0 k T \mathcal{D} - \frac{3}{2} N_0 k T \frac{\psi^b}{1 + \psi^b} \quad (44)$$

$$S_{th} = \left(-\frac{\partial F_{th}}{\partial T} \right)_\rho \quad (45)$$

$$= N_0 k \left[4f_{cv} \mathcal{D} - 3f_{cv} D_2 + \frac{3}{2} \left(\frac{1}{b} \ln \left(\frac{1}{1 + \psi^b} \right) - \frac{\psi^b}{1 + \psi^b} \right) \right] \quad (46)$$

$$C_v = \left(\frac{\partial E_{th}}{\partial T} \right)_V = -T \frac{\partial^2 F_{th}}{\partial T^2} \quad (47)$$

$$= \frac{E_{th}}{T} + 3f_{cv} N_0 k D_S - \frac{3}{2} N_0 k b \left(\frac{\psi^b}{1 + \psi^b} \right) + \frac{3}{2} N_0 k b \left(\frac{\psi^b}{1 + \psi^b} \right)^2 \quad (48)$$

And the pressure derivatives are:

$$\frac{\partial P_{th}}{\partial T} = \frac{P_{th}}{T} + 3f_{cv} N_0 k \rho \Gamma D_S + \quad (49)$$

$$\rho N_0 k (1 - 3\Gamma) b \left[\left(\frac{\psi^b}{1 + \psi^b} \right) - \left(\frac{\psi^b}{1 + \psi^b} \right)^2 \right] \quad (50)$$

$$\frac{\partial P_{th}}{\partial \rho} = \frac{P_{th}}{\rho} + 3f_{cv}\rho N_0 k T \mathcal{D} \frac{d\Gamma}{d\rho} - 3f_{cv} N_0 k T \Gamma^2 D_S - \quad (51)$$

$$3\rho N_0 k T \left(\frac{\psi^b}{1 + \psi^b} \right) \frac{d\Gamma}{d\rho} + \quad (52)$$

$$\frac{2}{3} N_0 k T b (1 - 3\Gamma)^2 \left[\left(\frac{\psi^b}{1 + \psi^b} \right) - \left(\frac{\psi^b}{1 + \psi^b} \right)^2 \right] \quad (53)$$

3 Implementation Details

3.1 Input Parameters

There are 3 new input parameters: f_{cv} , QCC1 and QCC6. These are entered in positions V44, V45 and V46 in the ANEOS input deck. f_{cv} is dimensionless. QCC1 defines the low density (g cm^{-3}) to drop the solid terms in the Helmholtz free energy. QCC6 defines the large value of ψ (dimensionless) to transition to a pure gas. When $f_{cv} > 1$, QCC1 may need to be lowered from a default value and QCC6 may need to be raised above the default value. If V44-V46 are not entered (zero values), then the default values correspond to the unmodified ANEOS: $f_{cv} = 1$, QCC1= $10^{-10} \text{ g cm}^{-3}$, and QCC6= 10^5 .

3.2 Modifications to ANEOS2.f

```
C      Transfer heat capacity adjustment parameters from input file
      ACK(IT+88)=UI(44) !FCV
      ACK(IT+89)=UI(45) !QCC1 - low density cutoff for solid terms
      ACK(IT+90)=UI(46) !QCC6 - psi value at switch to pure gas treatment
```

3.3 Modifications to ANEOS1.f

```
C      Terms added to adjust heat capacity
      QCC1=1.D-10                ! original parameter value
      QCC6=1.D5                  ! original parameter value
      FCV=ONE                    ! initialize the thermal adjustment parameter to default 3Nk limit.
      IF(ACK(L+89).GT.ZERO) THEN ! If entered, use it
        QCC1 = ACK(L+89)
      ENDIF
      IF(ACK(L+90).GT.ZERO) THEN ! If entered, use it
        QCC6 = ACK(L+90)
      ENDIF
      IF(ACK(L+88).GT.ZERO) THEN ! If no entry, then default to ONE to use 3Nk limit.
        FCV = ACK(L+88)          ! Heat capacity adjustment parameter. Enter 1 to multiply by 3
      ENDIF
```

The updated code for the simplified Debye function is:

```
PN=FCV*THREE*RHO*FTT*GAMMA+
&      FTT*RHO*X3*(ONE-THREE*GAMMA)
EN=FCV*THREE*FTT-THALF*FTT*X3
SN=FT*(FOUR*FCV-FCV*THREE*LOG(THETA/T)+
&      THALF*(LOG(X2)/BB-X3))
CVN=EN/T-THALF*FT*BB*(X3-X3*X3)
DPDT=PN/T+BB*FT*RHO*(ONE-THREE*GAMMA)*(X3-X3*X3)
```

```

DPDR=DPDR+PN/RHO+FCV*THREE*FTT*RHO*GAMP-
&      FTT*RHO*X3*THREE*GAMP+
&      TWO*BB*FTT*X6*X6*X3*(ONE-X3)/THREE

```

The updated code for the full Debye function is:

```

PN=FCV*THREE*RHO*FTT*GAMMA*DFUNC+
&      FTT*RHO*X3*(ONE-THREE*GAMMA)
EN=FCV*THREE*FTT*DFUNC-THALF*FTT*X3
SN=FT*(FOUR*FCV*DFUNC-FCV*THREE*D2+
&      THALF*(LOG(X2)/BB-X3))
CVN=EN/T+THREE*FCV*FT*DS-THALF*FT*BB*X3*(ONE-X3)
DPDT=PN/T+THREE*FCV*FT*RHO*GAMMA*DS+
&      BB*FT*RHO*(ONE-THREE*GAMMA)*(X3-X3*X3)
DPDR=PN/RHO+FCV*THREE*FTT*RHO*GAMP*DFUNC-
&      THREE*FCV*FTT*GAMMA*GAMMA*DS-
&      FTT*RHO*X3*THREE*GAMP+
&      TWO*BB*FTT*X6*X6*X3*(ONE-X3)/THREE+DPDR

```

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