

LA-UR-14-26858

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Title: Molecular Solid EOS based on Quasi-Harmonic Oscillator approximation for phonons

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Intended for: Report

Issued: 2014-09-02

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MOLECULAR SOLID EOS BASED ON QUASI-HARMONIC OSCILLATOR APPROXIMATION FOR PHONONS

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September 1, 2014

Abstract

A complete equation of state (EOS) for a molecular solid is derived utilizing a Helmholtz free energy. Assuming that the solid is non-conducting, phonon excitations dominate the specific heat. Phonons are approximated as independent quasi-harmonic oscillators with vibrational frequencies depending on the specific volume. The model is suitable for calibrating an EOS based on isothermal compression data and infrared/Raman spectroscopy data from high pressure measurements utilizing a diamond anvil cell. In contrast to a Mie-Grüneisen EOS developed for an atomic solid, the specific heat and Grüneisen coefficient depend on both density and temperature.

Notation

Thermodynamic variables for EOS

V is the specific volume

T is the temperature

$F(V, T)$ is the Helmholtz free energy

$P(V, T) = -\partial_V F$ is the pressure

$S(V, T) = -\partial_T F$ is the specific entropy

$e(V, T) = F + T S$ is the specific internal energy

$C_V(V, T) = (\partial_T e)_V = T(\partial_T S)_V$ is the specific heat at constant volume

$\Gamma(V, T) = V (\partial_e P)_V$ is the Grüneisen coefficient

Variables for phonon spectrum

ν_i is phonon frequency for the i^{th} vibrational mode.

$\theta = h\nu/k_b$ is characteristic temperature for frequency ν

k_b is the Boltzmann constant (1.381×10^{-23} J/K)

h is the Planck constant (6.626×10^{-34} J s)

$\theta/[K] = 1.44 \tilde{\nu}/[\text{cm}^{-1}]$, spectrometry units of inverse wavelength $\tilde{\nu} = \nu/c$

R is the gas constant (8.314 J/mol·K)

\mathcal{M} is the molecular weight

n is the number of atoms per molecule

N_A is Avogadro number (6.022×10^{23} molecules per mole)

Other thermodynamic variables

$\rho = V^{-1}$ is density

$c = (\partial_\rho P)_S^{1/2}$ is isentropic sound speed

$K_T(V, T) = -V(\partial_V P)_T$ is isothermal bulk modulus

$K_S(V, T) = -V(\partial_V P)_S = \rho c^2$ is isentropic bulk modulus

$C_P(V, T) = (\partial_T [e + V P])_P = T(\partial_T S)_P$ is the specific heat at constant P

$\beta(V, T) = V^{-1}(\partial_T V)_P$ is coefficient of thermal expansion

Thermodynamic identities

$$\frac{C_V}{C_P} = \frac{K_T}{K_S} = 1 - \frac{\beta^2 T K_T}{\rho C_P} = 1 - \Gamma^2 \frac{C_V T}{V K_S} \quad (1)$$

For other identities, see for example [Menikoff & Plohr, 1989; App. A]. Note, however, that this reference uses K for compressibility which is reciprocal of the bulk modulus used for K here.

1 Introduction

Empirical equations of state (EOS) used for solids typically are of the Mie-Grüneisen form; see for example, [Menikoff, 2007; sec. 4.4]. A key simplifying property of the Mie-Grüneisen EOS is that the Grüneisen coefficient is a function of only V . This is compatible with the specific heat depending on only a single scaled temperature; that is, $C_V(V, T) = \tilde{C}(T/\theta(V))$ and $\Gamma = \Gamma(V) = -\frac{d \ln \theta}{d \ln V}$, see for example [Menikoff, 2012]. These properties for Γ and C_V are reasonable approximations for metals which form atomic crystals.

For a molecular crystal (such as an explosive) the approximations do not adequately account for the intra-molecular vibrational modes (optical phonons) which dominate the specific heat. The variation in the intra-molecular frequencies with density results in the Grüneisen coefficient and specific heat being functions of both density and temperature. The density and temperature dependence of the specific heat is especially important for the thermal reaction rate of an explosive.

The phonons can be accounted for utilizing a quasi-harmonic oscillator approximation; *i.e.*, each phonon corresponds to a quantum harmonic oscillator with frequency ν_i depending on V ; see [Born & Huang, 1954]. An atomic crystal has only acoustic phonons. Typically, a Debye model is used for the acoustic phonons.

An EOS model for a molecular crystal based on the quasi-harmonic oscillator approximation for each optical phonon has briefly been described before; see for example [Menikoff, 2007; sec. 4.3.4]. The purpose of this report is to present the details. The form of the model is suitable for calibrating a complete EOS based on isothermal compression data and infrared/Raman spectroscopy data from measurements utilizing a diamond anvil cell to achieve high pressure.

2 Free energy

It is convenient to specify a complete EOS in terms of the Helmholtz free energy. Based on a reference isotherm through an initial state (V_0, T_0) , the general form of the free energy (see for example, [Menikoff, 2012; Eq. (30)])

can be expressed as

$$F(V, T) = e_0 - T S_0 - \int_{V_0}^V dV' \left[P(V', T_0) + \frac{\Gamma(V', T_0)}{V'} C_V(V', T_0) (T - T_0) \right] - \int_{T_0}^T \frac{dT'}{T'} (T - T') C_V(V, T') , \quad (2)$$

where $e_0 = e(V_0, T_0)$ and $S_0 = S(V_0, T_0)$.

Due to the thermodynamic identity (see for example, [Menikoff, 2012; Eq. (31)]),

$$V [\partial_V C_V]_T = T [\partial_T (\Gamma C_V)]_V , \quad (3)$$

the specific heat and the Grüneisen coefficient are not fully independent. Integrating the identity yields

$$\Gamma(V, T) C_V(V, T) = \Gamma(V, T_0) C_V(V, T_0) + V \frac{\partial}{\partial V} \int_{T_0}^T \frac{dT'}{T'} C_V(V, T') . \quad (4)$$

Hence, $\Gamma(V, T)$ is determined by $\Gamma(V, T_0)$ and $C(V, T)$.

Utilizing Eq. (3), the pressure can be expressed as

$$\begin{aligned} P(V, T) &= -(\partial_V F)_T \\ &= P(V, T_0) + V^{-1} \int_{T_0}^T dT' \Gamma(V, T') C_V(V, T') . \end{aligned} \quad (5)$$

This is compatible with the thermodynamic identity

$$(\partial_T P)_V = \Gamma C_V / V . \quad (6)$$

The specific entropy is given by

$$\begin{aligned} S(V, T) &= -(\partial_T F)_V \\ &= S(V, T_0) + \int_{T_0}^T \frac{dT'}{T'} C_V(V, T') , \end{aligned} \quad (7)$$

where the entropy on the reference isotherm is

$$S(V, T_0) = S_0 + \int_{V_0}^V dV' \frac{\Gamma(V', T_0)}{V'} C_V(V', T_0) . \quad (8)$$

This is compatible with the thermodynamic identities

$$(\partial_T S)_V = C_V/T , \quad (9)$$

$$(\partial_V S)_T = \Gamma C_V/V . \quad (10)$$

The specific energy is given by

$$\begin{aligned} e(V, T) &= F + T S \\ &= e(V, T_0) + \int_{T_0}^T dT' C_V(V, T') , \end{aligned} \quad (11)$$

where the energy on the reference isotherm is

$$e(V, T_0) = e_0 - \int_{V_0}^V dV' \left[P(V', T_0) - \frac{\Gamma(V', T_0)}{V'} C_V(V', T_0) T_0 \right] . \quad (12)$$

This is compatible with the thermodynamic identity

$$(\partial_V e)_T = -P + \Gamma C_V T/V . \quad (13)$$

These formulas show that a complete EOS is determined by two functions of one variable, $P(V, T_0)$, $\Gamma(V, T_0)$, and one function of two variables, $C_V(V, T)$. Moreover, this formulation is thermodynamically consistent; *i.e.*, obeys the differential relation $de = -P dV + T dS$.

If $C_V(V, T) \rightarrow 0$ as $T \rightarrow 0$, then the temperature integrals can be extended to $T_0 = 0$. Using the cold curve as a reference, $P_c(V) = P(V, 0)$, the free energy reduces to

$$F(V, T) = e_0 - \int_{V_0}^V dV' P_c(V') - \int_0^T \frac{dT'}{T'} (T - T') C_V(V, T') . \quad (14)$$

Moreover, the compatibility relation, Eq. (4) reduces to

$$\Gamma(V, T) C_V(V, T) = V \frac{\partial}{\partial V} \int_0^T \frac{dT'}{T'} C_V(V, T') . \quad (15)$$

Hence, $\Gamma(V, T)$ would be completely determined by $C_V(V, T)$. Furthermore, from the thermodynamic identity, Eq. (1), $K_T = K_S$ at $T = 0$. Consequently, $P_c(V)$ is both the $T = 0$ isotherm and the $S = 0$ isentrope.

For an electrically non-conducting solid, the specific heat is dominated by lattice excitations called phonons. The last term on the right hand side of Eq. (14) can be replaced by the phonon free energy; *i.e.*,

$$F(V, T) = e_0 - \int_{V_0}^V dV' P_c(V') + F_{ph}(V, T) . \quad (16)$$

Since the phonon model is defined by a free energy, it satisfies the compatibility relation, Eq. (3). Consequently, the free energy given by Eq. (2) with the phonon Γ and C_V is equivalent to the free energy given by Eq. (16), provided that

$$P(V, T_0) = P_c(V) + V^{-1} \int_0^{T_0} dT' \Gamma(V, T') C_V(V, T') , \quad (17)$$

$$S_0 = \int_0^{T_0} \frac{dT'}{T'} C_V(V_0, T') . \quad (18)$$

Utilizing a reference isotherm with $T_0 > 0$ facilitates calibrating the model to experimental data. The formulation can also be used with other thermal models whose domain does not include $T = 0$, such as that of a liquid.

3 Phonon free energy

We base the thermal component of the EOS on two approximations for the free energy of lattice vibrations. First, in the quasi-harmonic approximation each atom is assumed to be in a quadratic potential well centered at its equilibrium position within the crystal lattice, which depends only on V ; see for example, [Wallace, 2002; chpt. 3]. Second, the normal modes of the lattice vibrations, called phonons, are each treated as an independent quantum harmonic oscillator.

The phonon specific free energy can be expressed as

$$F_{ph}(V, T) = \frac{RT}{\mathcal{M}} \int d\omega g(\omega, V) \ln[1 - \exp(-\hbar\omega/k_b T)] , \quad (19)$$

where $\omega = 2\pi\nu$ is the angular phonon frequency, $g(\omega, V)$ is the density of phonon states, and \mathcal{M} is the molecular weight. The density of states is

the number of vibrational modes per unit frequency for a given specific volume V . An important property of a quantum harmonic oscillator is that the energy eigenstates are equally spaced; *i.e.*, $e_j = (j + \frac{1}{2})\hbar\omega$ for $j = 0, 1, 2, \dots$. The quantum zero-point energy, $\frac{1}{2} \int d\omega g(\omega, V) \hbar\omega$, is neglected since it is a function of only V and is accounted for in the reference isotherm. The term in the integrand $\ln[1 - \exp(-\hbar\omega/k_b T)]$ corresponds to $-\ln Z$, where $Z = \sum_{j=0}^{\infty} \exp(-e_j/k_b T)$ is the partition function for a single quantum oscillator.

To localize an excitation within a particular unit cell of the lattice, one needs to introduce the wave vector \vec{k} , and utilize eigenfunctions of the crystal Hamiltonian that have the form given by Blochs theorem

$$\psi(\vec{r}) = \exp[i\vec{k} \cdot \vec{r}]u(\vec{r}) , \quad (20)$$

where $u(\vec{r})$ is a periodic function on the crystal lattice. To avoid aliasing and obtain a unique decomposition, \vec{k} is restricted to the first Brillouin zone; *i.e.*, the unit cell in reciprocal lattice space. The energy eigenstates then determine vibrational frequencies that depend on the wave vector; *i.e.*, $\hbar\omega_j(\vec{k}) = e_j(\vec{k})$.

The classical analog is instructive; a periodic lattice of molecules in which the motion is governed by Newtons law with a force field consisting of springs connecting neighboring atoms. The lattice vibrations correspond to the normal modes, for which the displacement of each atom is proportional to $\exp[i(\vec{k} \cdot \vec{r} - \omega t)]$. To leading order, the solution to the equations of motion satisfy a dispersion relation for the vibrational frequencies, $\omega(\vec{k})$. For a crystal containing a mole of molecules, there are $3nN_A$ normal modes. Since N_A is very large, \vec{k} can be regarded as continuous. This motivates utilizing the density of states to account for the distribution of frequencies.

The phonon spectrum $\omega(\vec{k})$ splits into acoustic and optical branches; see for example [fig. 17, Kittel, 1967] or [fig. 3.3, Poirier, 1991]. In effect, for a given molecular vibrational mode, \vec{k} gives rise to a phase shift between atoms in neighboring unit cells. Since the atoms are all coupled through the force field, the motion in neighboring unit cells can affect the mode frequency.

For the three acoustic branches $\omega_i(k) \rightarrow c_i k$ as $k \rightarrow 0$, where the c_i are the acoustic speeds; one longitudinal mode and two transverse modes. Each of the $3n - 3$ optical branches is associated with a specific vibrational mode of the molecule, and typically has a narrow band of frequencies in the range

of infrared light. Typically, the Debye model is used for the three acoustic modes. We later show that except for very low temperatures the Debye model specific heat can be approximated by a harmonic oscillator phonon mode with an effective frequency proportional to the Debye temperature.

We approximate the density of states with the sum of Dirac δ -functions; *i.e.*, $g(\omega, V) = \sum_{i=1}^{3n} \delta(\omega - \omega_i(V))$. The density of states is normalized such that each vibrational frequency corresponds to a mole of molecules. The phonon free energy can then be written in terms of the free energy of harmonic oscillators,

$$F_{ph}(V, T) = \mathcal{M}^{-1} \sum_{i=1}^{3n} F_{ho}(V, T; \nu_i) . \quad (21)$$

It follows that the thermodynamic variables for each mode are additive; *i.e.*,

$$S_{ph}(V, T) = \mathcal{M}^{-1} \sum_{i=1}^{3n} S_{ho}(V, T; \nu_i) , \quad (22a)$$

$$e_{ph}(V, T) = \mathcal{M}^{-1} \sum_{i=1}^{3n} e_{ho}(V, T; \nu_i) , \quad (22b)$$

$$C_{V,ph}(V, T) = \mathcal{M}^{-1} \sum_{i=1}^{3n} C_{V,ho}(V, T; \nu_i) , \quad (22c)$$

$$P_{ph}(V, T) = \mathcal{M}^{-1} \sum_{i=1}^{3n} P_{ho}(V, T; \nu_i) . \quad (22d)$$

From the thermodynamic identities

$$(\partial_T S)_V = C_V/T ,$$

$$(\partial_V S)_T = \Gamma C_V/V ,$$

the Grüneisen coefficient can be expressed as

$$\Gamma(V, T) = \frac{V(\partial_V S)_T}{T(\partial_T S)_V} = - \frac{V}{T} \left(\frac{\partial T}{\partial V} \right)_S . \quad (23)$$

It follows that Γ is the specific heat weighted average of the mode Γ_i , or

$$\Gamma(V, T) C_V(V, T) = \sum_{i=1}^{3n} \Gamma_{ho}(V, T; \nu_i) C_{V,ho}(V, T; \nu_i) . \quad (24)$$

3.1 Quantum-harmonic oscillator

For each mode, the free energy per mole corresponds to that of a quantum harmonic oscillator,

$$F_{ho}(V, T; \nu) = RT \ln\left(1 - \exp[-\theta(V)/T]\right) , \quad (25)$$

where $\theta(V) = h\nu(V)/k_b$ is the characteristic temperature associated with the frequency $\nu(V)$. The entropy, energy, specific heat per mole and the pressure (P_{ho}/\mathcal{M}) are given by

$$S_{ho}(V, T)/R = -\ln\left[1 - \exp(-x)\right] + \frac{x \exp(-x)}{1 - \exp(-x)} , \quad (26a)$$

$$e_{ho}(V, T)/(R\theta) = \frac{\exp(-x)}{1 - \exp(-x)} , \quad (26b)$$

$$C_{V,ho}(V, T)/R = \left[\frac{x}{1 - \exp(-x)}\right]^2 \exp(-x) , \quad (26c)$$

$$\Gamma_{ho}(V) = -d\ln\theta/d\ln V , \quad (26d)$$

$$P_{ho}(V, T) = \frac{\Gamma_{ho}(V)}{V} e_{ho}(V, T) , \quad (26e)$$

where $x = \theta(V)/T$. Since $R = N_A k_b$, the average number of excitation per molecule is $e_{ho}/(N_A h\nu) = e_{ho}/(R\theta)$. At $T = \theta$, $x = 1$ and $e_{ho}/(R\theta) = 0.58$; *i.e.*, on average slightly more than $\frac{1}{2}$ an excitation per molecule. We note that Γ_{ho} is a function of only V . Nevertheless, from Eq. (24), the Grüneisen coefficient Γ is a function of both V and T .

The limiting properties of these variables are as follows. As $T \rightarrow 0$,

$$\begin{aligned} x &\rightarrow \infty , \\ S_{ho} &\rightarrow 0 , \\ e_{ho} &\rightarrow 0 , \quad C_{V,ho} \rightarrow 0 . \end{aligned}$$

The limit $S \rightarrow 0$ is known as Nernst theorem (or the third law of thermodynamics). It implies that the $S = 0$ isentrope coincides with the $T = 0$ isotherm. This requires that $C_V \rightarrow 0$. Consequently, zero temperature is unattainable experimentally. Hence, the need for a formulation based on a reference isotherm with $T_0 > 0$.

As $T \rightarrow \infty$,

$$\begin{aligned} x &\rightarrow 0 , \\ S_{ho} &\rightarrow R \ln(T/\theta) , \\ e_{ho} &\rightarrow R T , \quad C_{V,ho} \rightarrow R . \end{aligned}$$

Consequently, the total specific heat approaches the limit

$$C_{V,ph} = \mathcal{M}^{-1} \sum_{i=1}^{3n} C_{V,ho}(V, T; \nu_i) \rightarrow 3n \cdot (R/\mathcal{M}) . \quad (27)$$

This is known as the law of Dulong and Petit, or the classical limit in which all the phonon modes are completely saturated.

4 Molecular solid EOS model

Substituting the phonon specific heat and Grüneisen coefficient into the formulae in section 2 leads to a model EOS for a molecular crystal. The pressure and energy can be written as follows:

$$P(V, T) = P(V, T_0) + \mathcal{M}^{-1} \sum_{i=1}^{3n} \frac{\Gamma_i(V)}{V} [e_i(V, T) - e_i(V, T_0)] , \quad (28a)$$

$$e(V, T) = e(V, T_0) + \mathcal{M}^{-1} \sum_{i=1}^{3n} [e_i(V, T) - e_i(V, T_0)] , \quad (28b)$$

where

$$e(V, T_0) = e_0 - \int_{V_0}^V dV' \left[P(V', T_0) - \mathcal{M}^{-1} \sum_{i=1}^{3n} \frac{\Gamma_i(V')}{V'} C_{V,i}(V', T_0) T_0 \right] , \quad (29a)$$

$$e_i(V, T) = R \theta_i(V) \frac{\exp(-\theta_i(V)/T)}{1 - \exp(-\theta_i(V)/T)} , \quad (29b)$$

$$\Gamma_i(V) = - \frac{d \ln \theta_i}{d \ln V} , \quad (29c)$$

$$C_{V,i}(V, T) = R \left[\frac{\theta_i(V)/T}{1 - \exp(-\theta_i(V)/T)} \right]^2 \exp(-\theta_i(V)/T) . \quad (29d)$$

Thus, the model is specified by a reference isotherm, $P(V, T_0)$, and the characteristic temperatures of the phonons, $\theta_i(V)$ for $i = 1, \dots, 3n$. These quantities can be measured experimentally. However, some constraints are necessary for the model to be well behaved. For example, from Eq. (28a), continuity of the pressure on an isotherm $T \neq T_0$ requires that $\Gamma_i(V)$ is continuous for all modes. This in turn requires the phonon frequencies and their first derivatives to be continuous.

For completeness, we note that the total specific heat is given by

$$C_V(V, T) = \mathcal{M}^{-1} \sum_{i=1}^{3n} C_{V,i}(V, T) , \quad (30)$$

and the Grüneisen coefficient by

$$\Gamma(V, T) = \frac{\sum_{i=1}^{3n} \Gamma_i(V) C_{V,i}(V, T)}{\sum_{i=1}^{3n} C_{V,i}(V, T)} . \quad (31)$$

With the aid of the thermodynamic identity Eq. (13) applied to each phonon mode, the isothermal bulk modulus can be expressed as

$$\begin{aligned} K_T(V, T) = & K_T(V, T_0) + \mathcal{M}^{-1} \sum_{i=1}^{3n} \frac{[\Gamma_i(V)]^2}{V} \cdot [\tilde{e}_i(V, T) - \tilde{e}_i(V, T_0)] \\ & - \mathcal{M}^{-1} \sum_{i=1}^{3n} V \frac{d}{dV} \left(\frac{\Gamma_i(V)}{V} \right) \cdot [e_i(V, T) - e_i(V, T_0)] , \end{aligned} \quad (32)$$

where $K_T(V, T_0) = -V \frac{\partial}{\partial V} P(V, T_0)$ and $\tilde{e}_i(V, T) = e_i(V, T) - C_{V,i}(V, T) T$.

Thermodynamic stability requires $K_T \geq 0$. Since $C_{V,i}$ is monotonically increasing with T , for $T > T_0$,

$$e_i(V, T) - e_i(V, T_0) < C_{V,i}(V, T) (T - T_0) < C_{V,i}(V, T) T - C_{V,i}(V, T_0) T_0 . \quad (33)$$

Consequently, the second term on the right hand side of Eq. (32) proportional to Γ_i^2 is negative. In fact from Eq. (29b) and Eq. (29d), it can be shown that $\tilde{e}_i(V, T)$ is monotonically decreasing with T and bounded;

$$-\frac{1}{2} R \theta_i(V) \leq \tilde{e}_i(V, T) \leq 0 . \quad (34)$$

Therefore, at high temperature, the third term in Eq. (32) proportional to $e_i(V, T)$ needs to be positive. Hence, $\frac{d}{dV} (\Gamma_i(V)/V) < 0$, which places a

constraint on how the phonon frequencies can vary with V . For $T < T_0$, $K_T < 0$ could be regarded as a van der Waal loop and regularized with a Maxwell construction. This may apply for $V > V_0$, in which case the van der Waal loop could be associated with sublimation; *i.e.*, break down of the assumption of a single phase solid EOS model.

Continuity of K_T requires both Γ_i and its derivative are continuous. Hence, from Eq. (29c), continuity of the first and second derivatives of the mode frequencies. A discontinuity in K_T is physically possible. In fact, this occurs at phase boundaries, and leads to splitting of rarefaction waves. A discontinuity in the second derivative of some mode frequency would have a similar effect on rarefaction waves. However, for large molecule with many modes, a kink in the derivative of any one mode frequency would have only a small effect on Γ and K_T .

Finally, thermodynamic identities determine the isentropic bulk modulus, specific heat at constant pressure and the coefficient of thermal expansion;

$$K_S = K_T + (\Gamma^2/V) C_V T , \quad (35)$$

$$C_P = (K_S/K_T) C_V , \quad (36)$$

$$\beta = \Gamma C_V / (V K_T) . \quad (37)$$

An additional continuity constraint on Γ_i is needed for rarefaction waves to be smooth; *i.e.*, the characteristic speed $u + c$ varies smoothly, where u is the particle velocity and $c = (V K_S)^{1/2}$ is the isentropic sound speed. Along a rarefaction, the change in the characteristic speed can be expressed as [see Menikoff & Plohr, 1989; Eqs. (3.23) and (3.24)]

$$d(u + c) = \mathcal{G} \frac{dP}{\rho c} , \quad (38)$$

$$\begin{aligned} \mathcal{G} &= \frac{V^3 (\partial^2 P / \partial V^2)_S}{2 c^2} = \frac{1}{c} \left(\frac{\partial \rho c}{\partial \rho} \right)_S \\ &= \frac{1}{2} \left[1 - \frac{V}{K_S} \left(\frac{\partial K_S}{\partial V} \right)_S \right] . \end{aligned} \quad (39)$$

\mathcal{G} is known as the fundamental derivative of fluid dynamics, and must be positive for shock waves to be compressive and rarefaction waves to be expansive. It follows from Eqs. (35) and (32) that the second derivative of Γ_i needs to be continuous in order for \mathcal{G} to be continuous.

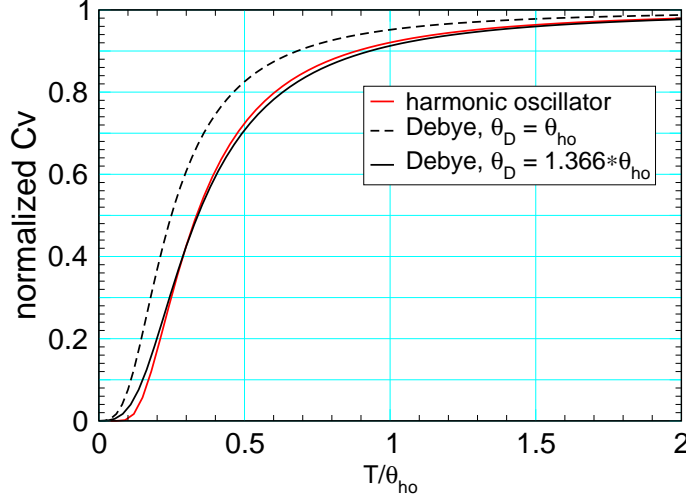


Figure 1: Normalized specific heat. Red curve is C_V/R for the harmonic oscillator model. Black curves are $C_V/(3R)$ for the Debye model. θ_{ho} and θ_D are respectively the characteristic temperatures for the harmonic oscillator and Debye model.

The normalized phonon mode specific heat, Eq. (29d), is shown in figure 1. For comparison, the specific heat for the acoustic modes from the Debye model is also shown. We note that the Debye specific heat can be approximated by the specific heat of a harmonic oscillator by a simple scaling of the characteristic temperature; *i.e.*, $\theta_{ho} = 0.732 \theta_D$. The largest difference is at very low temperature. For $T > 0.2 \theta_{ho}$, the acoustic specific heat is well approximated by a phonon mode specific heat. Typically, the Debye temperature is low and at ambient temperature the acoustic contribution to the specific heat is nearly saturated.

Hydro codes typically use the pressure as a function of (V, e) since the equations for hydrodynamics express the conservation of mass and energy. To utilize Eq. (28a), an iterative algorithm, such as Newton's method, is required to solve Eq. (28b) for T . Since the thermal term of P and e are expressed as a sum of $3n$ terms each of which involves an exponential, evaluating $P(V, e)$ is computationally expensive. Alternatively, the model can be used to generate an EOS table. The advantage is that evaluating the pressure from a table is independent of the complexity of the model. The trade-off is loss of accuracy due to interpolation; especially for derivatives needed to calculate the sound speed.

4.1 Remarks

In contrast to the Mie-Grüneisen EOS, the Grüneisen coefficient for the molecular model, Eq. (31), is a function of both V and T . Typically, the higher frequencies have a smaller mode Γ_i . Increasing temperature increases the specific heat, and consequently the relative weight of the higher frequencies. Hence, for fixed V , one can expect $\Gamma(V, T)$ to decrease as the temperature is increased. More generally, in the low temperature limit, $\Gamma(V) = \Gamma_1(V)$ is the lowest frequency mode, presumably the acoustic modes. In the high temperature limit, $\Gamma(V) = (3n)^{-1} \sum_i \Gamma_i(V)$ is the average over all modes.

For the Mie-Grüneisen model, the thermal pressure relative to the T_0 isotherm is $P_{therm} = \frac{\Gamma(V)}{V} [e - e(V, T_0)]$. In contrast, the thermal pressure for the molecular model can be expressed as

$$P_{therm} = \mathcal{M}^{-1} \sum_{i=1}^{3n} \frac{\Gamma_i(V)}{V} [e_i(V, T) - e_i(V, T_0)] \quad (40a)$$

$$= \frac{\langle \Gamma(V, T) \rangle_{T_0}}{V} [e(V, T) - e(V, T_0)] \quad (40b)$$

where the temperature averaged effective Grüneisen coefficient is

$$\langle \Gamma(V, T) \rangle_{T_0} = \frac{\sum_{i=1}^{3n} \Gamma_i(V) [e_i(V, T) - e_i(V, T_0)]}{\sum_{i=1}^{3n} \int_{T_0}^T dT' C_{V,i}(V, T')} . \quad (40c)$$

As $T \rightarrow T_0$, formally $\langle \Gamma(V, T) \rangle_{T_0} = 0/0$. Applying l'Hôpital's rule gives Eq. (31). However, in general $\langle \Gamma(V, T) \rangle_{T_0} \neq \Gamma(V, T)$ whenever Γ is a function of T . We expect the temperature averaged effective Grüneisen coefficient to decrease as T increases.

When all the mode Γ_i are equal, it follows from Eq. (31) that the Grüneisen coefficient depends only on V ; *i.e.*, the molecular EOS model reduces to the standard Mie-Grüneisen model. Moreover, from Eq. (29c), the mode frequencies can be expressed as $\theta_i(V) = \frac{\theta_i(V_0)}{\theta_0} \theta(V)$, where

$$\theta(V) = \theta_0 \exp \left[- \int_{V_0}^V dV \Gamma(V)/V \right] , \quad (41)$$

and $\theta_0 = 1$ K merely sets the temperature unit.

The specific heat, Eq. (30), can then be expressed as

$$C_V(V, T) = \mathcal{M}^{-1} \sum_{i=1}^{3n} \tilde{C} \left(\frac{\theta_0}{\theta_i(V_0)} \cdot \frac{T}{\theta(V)} \right), \quad (42)$$

$$\tilde{C}(x^{-1}) = R \left[\frac{x}{1 - \exp(-x)} \right]^2 \exp(-x). \quad (43)$$

Hence, when the Γ_i are all equal, C_V reduces to a function of a single scaled temperature, $T/\theta(V)$.

5 High pressure phonon spectrum

Infrared absorption and Raman scattering measurements are used to determine the molecular vibrational spectrum, which we identify with the phonon frequencies. Diamond anvil cell (DAC) experiments are about the only technique that can compress a solid to high pressures and maintain the pressure long enough to perform the spectrum measurements. The best example of the extent to which the vibrational spectrum can be determined is the recent paper by [Bowden *et al.*, 2014] which reports on an extensive series of experiments carried out for TNT that determined the pressure dependence of the frequencies up to 14 to 20 GPa for almost all of the $3n - 6 = 57$ intramolecular vibrational modes; *i.e.*, excluding the molecular translation and rotational modes, which for a solid are low frequency acoustic and libration modes.

This is the type of data needed to calibrate the molecular solid EOS model of the previous section. Here we discuss general issues related to determining the spectrum and utilizing the available data to determine the specific heat and Grüneisen coefficient needed for the EOS model.

The measured infrared absorption and Raman scattering spectrum from DAC experiments show peaks, some sharp others spread out and overlapping. The peaks represent excited states of the crystal associated with the molecular vibrational frequencies. The width of the peaks are related to the relaxation times of the vibrational states. The relaxation times can be calculated using several techniques, see for example, [Piryantinski *et al.*, 2007], [Pereverzev and Sewell 2011], [Pereverzev *et al.*, 2013] and [Pereverzev *et al.*, 2014]. A crude estimate of the line width can be obtained using the

uncertainty principle, $\Delta e \Delta t \geq 0.5 \hbar$ and some simplifying assumptions. For $\Delta e = \hbar \Delta \nu$ and a scattering time Δt of a few vibrational periods (*i.e.*, proportional to $1/\nu$), the width of the peak would be $\delta \nu / \nu$ of a few percent. The width is increased by thermal broadening, and strain gradients within the sample. The gradients arise from stress concentrations at the contacts between the small crystallites compressed within the working volume of the DAC. The random orientation and anisotropic stress-strain response of the crystal also contribute to the gradients.

We note that the momentum transfer from infrared absorption or Raman scattering imparts to a molecule a very small velocity and negligible kinetic energy. For example, the momentum transferred by a photon ($\hbar \nu / c$) with $\lambda^{-1} = \nu / c = 1000 \text{ cm}^{-1}$ to a TNT molecule ($M = 227 \text{ g}/(\text{mole} \cdot N_A)$) would give the molecule a velocity $u = \hbar \nu / (M c) = 1.7 \times 10^{-7} \text{ nm/ps}$, and the ratio of the kinetic energy compared to the photon energy of $\hbar \nu / (2 M c^2) \approx 10^{-12}$. Consequently, the momentum can be neglected.

Two additional complications arise from the crystal structure. First, the crystal symmetry can result in selection rules for which some phonon modes do not couple to light scattering, and hence do not show up in the measured spectrum. Second, there can be more than one molecule in the unit cell. For example, the stable structure of TNT at ambient conditions is monoclinic, space group $P2_1/a$, and has 8 molecules per unit cell; see [Vrcelj *et al.*, 2003].

With z molecules per unit cell and n atoms per molecule, there are in principle $3z \cdot n$ phonon modes. Most but not all of the molecular vibrations are z -fold degenerate. Near degeneracy may contribute to the width of the peak in the measured spectrum. Also some peaks split or new ones arise as the sample is compressed. This may be an indication of strain gradients breaking the degeneracy or affecting the symmetry, and hence the selection rules.

To account for the additional modes, the model equations for P and e , Eq. (28) and Eq. (29a), need to be modified. The sum over the modes $\sum_{i=1}^{3n}$ is extended to the sum over all mode frequencies with a weight factor; *i.e.*, $\sum_i W t_i$, where the weight factor is the degeneracy of a frequency divided by z , in order that $\sum_i W t_i = 3n$.

To help identify the vibrational modes and their degeneracy, density functional theory (DFT) computations are used. The calculated frequencies correspond to the vibrational modes for a molecular gas. A gas molecule has

$3n - 6$ vibrational modes; *i.e.*, of the total $3n$ modes, 3 degrees of freedom correspond to translation and 3 to rotation of the molecule as a whole rather than vibrational modes. For a solid, the translational modes are replaced by the acoustic phonon modes previously discussed. The molecular rotations correspond to low frequency modes ($\nu < 3$ THz or $\tilde{\nu} < 100$ cm⁻¹) called librations that occur in molecular dynamics simulations; see [Pereverzev *et al.*, 2013]. The librations are similar to hindered rotors which are groups of atoms whose rotational amplitude is limited by neighboring molecules, see [McClurg, 1996]. Since the librations involve interactions between molecules, the low frequency modes set the time scale for excited molecules to thermally equilibrate with the lattice; typically about 1 ps.

An additional complication arises for some crystals such as TNT. Within the unit cell, two molecular conformations occur [Vrcelj *et al.*, 2003]. DFT computations for each conformation [Clarkson *et al.*, 2003] are used to determine the degeneracy of the frequencies in the measured spectrum [Bowden *et al.*, 2014]. This yields a weight factor of either 1 or $\frac{1}{2}$ for the mode degeneracy.

DAC experiments have been used to measure both density and phonon frequencies along an isotherm. The results are typically reported as $P(V, T_0)$ and $\nu_i(P)$. The mode Grüneisen coefficient, can be calculated using the chain rule;

$$\Gamma_i(V) = \frac{K_T(V, T_0)}{\nu_i(P(V, T_0))} \cdot \frac{d\nu_i}{dP}(P(V, T_0)) , \quad (44)$$

where K_T is the isothermal bulk modulus. The bulk modulus is calculated by fitting the (V, P) data to an analytic form (such as a Birch-Murnaghan function), and then taking the analytic derivative of the fitting form; *i.e.*,

$$K_T(V, T_0) = -V \frac{dP(V, T_0)}{dV} . \quad (45)$$

The fitting form serves to smooth the data.

The bulk modulus can increase significantly with pressure. For example, at room temperature, $K_T(15 \text{ GPa})/K_T(1 \text{ atm}) \sim 15$ for TNT. Consequently, if $d\nu_i/dP$ is constant, $\Gamma_i(V)$ would not be constant. In contrast to the typical assumption for atomic solids that $\Gamma(V)/V = \text{constant}$, the mode Γ_i for the high frequencies tends to start off low at ambient pressure and then increase with pressure, at least initially.

Measured phonon frequencies typically range from a low of about 100 cm^{-1} ($\theta = 140 \text{ K}$) to a high of about 3200 cm^{-1} ($\theta = 4600 \text{ K}$). The highest frequencies typically correspond to hydrogen stretch modes of H-C or H-N or H-O bonds. The low frequencies are difficult to measure. The ones corresponding to librations may not be in the measured spectrum.

For the specific heat, figure 1 shows that a mode is half saturated at $T \approx \frac{1}{3} \theta$, and 92 % saturated at $T = \theta$. Consequently, at room temperature (300 K), modes with $\theta < 900 \text{ K}$ or frequencies $\tilde{\nu} < 625 \text{ cm}^{-1}$ would be at least half saturated and contribute significantly to the specific heat. Low frequency modes that are not in the measured spectrum would be fully saturated and contribute R per mole to the specific heat. All the low frequencies need to be accounted for to get the specific heat correct.

The specific heat C_V from the phonon spectrum can be checked against the measured value at the ambient state (room temperature and atmospheric pressure) of the specific heat at constant pressure C_P . The thermodynamic identity

$$\frac{C_V}{C_P} = \frac{K_T}{K_S} = 1 - \frac{\beta^2 T K_T}{\rho C_P} \quad (46)$$

can be used to correct for the difference between C_P and C_V . Either the measured sound speed c , which determines the isentropic bulk modulus, $K_S = \rho c^2$, or the measured coefficient of thermal expansion, β , can be used. For a solid, C_V is typically a few per cent less than C_P .

All phonon modes, including the saturated ones, contribute to the Grüneisen coefficient. One way to account for low frequency modes not in the measured spectrum is to lump them together and fit their collective mode Γ such that Eq. (31) gives for $\Gamma(V_0, T_0)$ the value obtained from the thermodynamic identity

$$\Gamma = \beta c^2 / C_P \quad (47)$$

with the measured values of the coefficient of thermal expansion, sound speed and heat capacity C_P .

Finally, we note that the mode frequencies can be used within the simpler Mie-Grüneisen EOS to incorporate part of the temperature dependence of the specific heat. It is thermodynamically consistent to use a C_V that is a function of a single scaled-temperature variable with a Grüneisen coefficient depending on only V . Thus, the specific heat for the Mie-Grüneisen model

can be specified by

$$C_{V,MG}(V, T) = C_V(V_0, T/\phi(V)) , \quad (48a)$$

$$\phi(V) = \exp\left[\int_{V_0}^V dV' \Gamma(V')/V'\right] , \quad (48b)$$

with $C_V(V_0, T)$ defined by Eq. (22c) and Eq. (29d). The specific heat for the Debye model is also of this form, and has been used as a fitting form in which the Debye temperature is treated as a fitting parameter. This has the right qualitative behavior. However, $C_V(V, T)$ would only be accurate for $V = V_0$.

6 Extensions

Two extensions to increase the domain of applicability of the EOS model are discussed next. They represent extrapolations of the free energy beyond the data for the phonon spectrum. The aim is to preserve thermodynamic properties of interest, and thereby limit the loss of accuracy inherent when extrapolating the molecular solid functional form we are using for the free energy.

6.1 Solid-liquid phase transition

One of the applications of a molecular EOS is to an explosive. Some explosives, notably TNT, only have a significant reaction rate above the melting temperature. Therefore, it is important that the thermal component of an EOS account for the latent heat of melting. This requires incorporating a solid-liquid phase transition in the EOS model.

We assume that the phase boundary is defined by a melt curve, $P_m(T)$, and that the solid and liquid saturation boundaries are specified by the functions $V_s(T)$ and $V_\ell(T)$, respectively. We further assume that $\frac{dP_m}{dT} > 0$ and that $V_s(T) < V_\ell(T)$. The idea is to use the molecular solid free energy, $F_s(V, T)$, for $V < V_s(T)$, and to construct a liquid free energy, $F_\ell(V, T)$, by extrapolating the functional form for F_s to the region $V > V_\ell(T)$ such that the thermodynamic constraints at the phase boundary are satisfied.

Along an isotherm in the mixed region, $V_s(T) < V < V_\ell(T)$, the free energy varies linearly with V between the values on the solid and liquid saturation boundary; *i.e.*,

$$F_{mix}(V, T) = \frac{[V_\ell(T) - V]F_s(V_s(T), T) + [V - V_s(V, T)]F_\ell(V_\ell(T), T)}{V_\ell(T) - V_s(T)} . \quad (49)$$

On the phase boundary, thermodynamic consistency requires that the pressure and the Gibbs free energy, $G = F + PV$, of the solid and liquid are equal; *i.e.*,

$$P_m(T) = P_s(V_s(T), T) = P_\ell(V_\ell(T), T) , \quad (50a)$$

$$G_s(P_m(T), T) = G_\ell(P_m(T), T) . \quad (50b)$$

To build in the solid-liquid phase transition, we define the liquid free energy in terms of the molecular solid fitting form based on the phonon spectrum

$$F_\ell(V, T) = F_s(V - \Delta V(T), T) - P_m(T) \Delta V(T) , \quad (51a)$$

$$\Delta V(T) = V_\ell(T) - V_s(T) . \quad (51b)$$

The liquid pressure is

$$P_\ell(V, T) = -\partial_V F_\ell = P_s(V - \Delta V(T), T) . \quad (52)$$

By construction, for a given value of T , both the pressure and the Gibbs free energy match on the solid and liquid saturation boundaries. We note that F_s utilizes the harmonic oscillator approximation for the phonon modes. In the liquid regime, anharmonicity is expected to become important.

Taking the derivative with respect to T of Eq. (51), yields the change in entropy

$$\Delta S(T) = S_\ell(V_\ell(T), T) - S_s(V_s(T), T) , \quad (53a)$$

$$= \frac{dP_m}{dT} \cdot \Delta V(T) . \quad (53b)$$

This is equivalent to the Claudius-Clapyron relation

$$\frac{dP_m}{dT} = \frac{\Delta S}{\Delta V} . \quad (54)$$

It follows that the specific energy of the liquid is

$$\begin{aligned} e_\ell(V, T) &= F_\ell + T S_\ell \\ &= e_s(V - \Delta V(T), T) + \left[T \frac{dP_m}{dT} - P_m(T) \right] \Delta V(T) . \end{aligned} \quad (55)$$

The last term would need to be added to Eq. (28b) for the specific energy in the liquid regime. It would contribute to the specific heat but not Eq. (28a) for the pressure.

The latent heat of the phase transition is $L = \Delta H$, where $H = e + PV$ is the enthalpy. It can be expressed as

$$L(T) = T \Delta S(T) , \quad (56a)$$

$$= T \frac{dP_m}{dT} \cdot \Delta V(T) . \quad (56b)$$

Thus, the measured values of the melt curve and the latent heat determine ΔV . The isotherms of the solid and $P_m(T)$ determine $V_s(T)$. Consequently, extending the solid EOS to account for the solid-liquid phase transition requires only $P_m(T)$ and $L(T)$.

6.2 Expansion region, $V > V_0$

Two issues arise with extending the molecular solid fitting form, Eq. (28), to the expansion regime. First is the choice of a reference curve for $V > V_0$. Second is that with increasing V the vibrational frequencies $\nu_i \rightarrow \text{constant}$ in order for C_V to be a function of only T , and so that the vibrational modes do not contribute to the thermal pressure.

It is natural to consider two cases based on the critical isotherm. Above the critical temperature, T_c , isotherms do not distinguish between the liquid and vapor phases. Below the critical temperature isotherms cross the liquid-vapor phase boundary.

6.2.1 Above critical isotherm

The domain $T > T_c$, excludes the liquid-vapor phase transition and greatly simplifies extrapolating the EOS into the expansion region. It is then natural to use the melt temperature at V_0 for T_{ref} of the reference isotherm.

For large V , isotherms should behave like that of an ideal gas. For the reference isotherm,

$$P_{\text{ref}}(V) \rightarrow (R/\mathcal{M})T_{\text{ref}}/V \quad \text{as } V \rightarrow \infty. \quad (57)$$

For the EOS to extrapolate smoothly, $P_{\text{ref}}(V)$ needs to match the values of P , dP/dV and d^2P/dV^2 at (V_0, T_{ref}) from the liquid isotherm defined in previous subsection.

The optical frequencies $\nu_i(V)$ need to approach a constant at some finite value V_* . Moreover, the constant should correspond to the vibrational frequencies for an isolated molecule; such as obtained from a DFT computation. This results in $\Gamma_i(V) = 0$ for $V > V_*$. Hence, the vibrational modes contribute to the specific heat but not the thermal pressure. The continuity constraints on ν_i and its derivatives discussed in section 4 apply at both V_0 and V_* .

For the three modes corresponding to rotations of the molecule, the limiting frequency ν_i should have a characteristic temperature $\theta_i \ll T_{\text{ref}}$ in order that the specific heat of each mode saturates at $\frac{1}{2}R/\mathcal{M}$.

For the three acoustic modes, each frequency needs to satisfy

$$\Gamma_i(V) = -V d \ln \nu_i / dV \rightarrow \frac{2}{3}. \quad (58)$$

Hence $\nu_i(V) \propto V^{-2/3} \rightarrow 0$ as $V \rightarrow \infty$, and $C_{V,i} \rightarrow \frac{1}{2}(R/\mathcal{M})$.

In the limit $V \rightarrow \infty$ only the acoustic modes have a non-zero Γ_i . From Eq. (31), $\Gamma(T) \rightarrow (R/\mathcal{M})/C_V(T)$. This is consistent with Eq. (57). Thus, the limiting behavior of the mode frequencies results in the molecular model EOS approaching an ideal gas EOS.

6.2.2 Below critical isotherm

Below the critical isotherm, the EOS model needs to account for the mixed liquid-vapor region. One approach is that used in the construction of a SESAME EOS table. The cold curve ($T_{\text{ref}} = 0$) is used as the reference curve. The model neglects sublimation; *i.e.*, the solid-vapor phase boundary. $P_{\text{ref}}(V)$ is constructed with a van der Waal loop starting at V corresponding to the value of the liquid saturation boundary at $P = 0$. The initial part of the van der Waal loop has $P_{\text{ref}} < 0$.

The same consideration as in previous subsection apply to extrapolating the mode frequencies. This determines the thermal component of the EOS. From Eq. (32), the isothermal bulk modulus increases with temperature. At some finite temperature, it is positive along the entire isotherm. Thus van der Waal loops occur only for a limited range of temperatures. Applying the Maxwell construction to eliminate the van der Waal loops, then defines the mixed liquid-vapor region.

An EOS with a liquid-vapor mixed region may be problematic for fluid flow simulations since they tacitly assume a single phase; *i.e.*, the thermodynamic state is characterized with only (V, e) . The use of the average density, $\rho = 1/V$, implies a material is homogeneous, and hence intimately mixed. At pressures well below the critical point, vaporization typically is associated with a large change in volume; *i.e.*, $V_{\text{liq}}(P) \ll V_{\text{vap}}(P)$. For many applications, this results in the liquid and vapor being phase separated, which would require a two-phase flow formulation. A single-phase fluid description would not have the correct wave properties when the material is in the mixed region.

Acknowledgement

The author thanks Eric Chisolm for his careful proof reading and suggestions to improve the clarity of the presentation.

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