Thermodynamics of Solids: Harmonic and Quasi-harmonic Approximations

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Outline

- Classical value of the heat capacity of solids (Dulong-Petit “law”, equipartition of the energy)

- Quick recap of Statistical Thermodynamics (canonical ensemble, partition function, independent degrees of freedom)

- The Harmonic Approximation for molecular vibrations

- Vibrations in solids: phonon dispersion

- Quantum models for the heat capacity of solids (Einstein's and Debye's models)

- Harmonic thermodynamic properties (convergence and limitations)

- The Quasi-harmonic Approximation (thermal expansion, P-V-T equation-of-state, constant-pressure properties, isothermal bulk modulus)
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In 1819, Dulong and Petit noted that the molar specific heat of all elementary solids is very nearly 6.

In 1831 Neumann extended this law to say that each atom in the solid contributes 6 cal/g mol K to the specific heat of the solid.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T$, °C</th>
<th>$c_v$, cal/g mole–°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0</td>
<td>6.00</td>
</tr>
<tr>
<td>Au</td>
<td>0</td>
<td>6.07</td>
</tr>
<tr>
<td>Cr</td>
<td>0</td>
<td>5.35</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>5.85</td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
<td>6.05</td>
</tr>
<tr>
<td>Sb</td>
<td>0</td>
<td>6.00</td>
</tr>
<tr>
<td>Graphite</td>
<td>0</td>
<td>1.82</td>
</tr>
<tr>
<td>Diamond</td>
<td>0</td>
<td>1.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T$, °C</th>
<th>$c_v/2$ or 3, cal/g mole–°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>28</td>
<td>6.27</td>
</tr>
<tr>
<td>CuO</td>
<td>22</td>
<td>5.20</td>
</tr>
<tr>
<td>KCl</td>
<td>23</td>
<td>6.20</td>
</tr>
<tr>
<td>CuS</td>
<td>25</td>
<td>5.95</td>
</tr>
<tr>
<td>PbO$_2$</td>
<td>24</td>
<td>5.17</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>15–99</td>
<td>5.61</td>
</tr>
<tr>
<td>ZnO</td>
<td>16–99</td>
<td>5.08</td>
</tr>
<tr>
<td>PbCl$_2$</td>
<td>0–20</td>
<td>6.08</td>
</tr>
</tbody>
</table>

If diamond is heated to relatively high temperatures, its specific heat also approaches 6 cal/g mol K.
Although these laws are by no means exact, they strongly suggest that some underlying physical principle might be responsible for the degree of success they enjoy.

Fig. 4.5 Temperature dependence of $c_v$ for many solids. $\Theta_{\text{Pb}} = 88$, $\Theta_{\text{Ag}} = 215$, $\Theta_{\text{KCl}} = 218$, $\Theta_{\text{Zn}} = 235$, $\Theta_{\text{NaCl}} = 287$, $\Theta_{\text{Cu}} = 315$, $\Theta_{\text{Al}} = 392$, $\Theta_{\text{CaF}_2} = 499$, $\Theta_{\text{C}} = 1860$. 

Combined data for:
Pb, Ag, KCl, Zn, NaCl, Cu, Al, CaF$_2$, and C
In 1871, **Boltzmann** showed how a classical model for a crystal based on the equipartition of the energy could provide a simple explanation to the Dulong-Petit law.

**Equipartition of the energy:**

*The original idea of equipartition was that, in thermal equilibrium, energy is shared equally among all of its various forms.*

*Each degree of freedom contributes with $\frac{1}{2} k_B T$ to the thermal internal energy of the system.*

For a classical harmonic oscillator, the total energy would be $H = H_{\text{kin}} + H_{\text{pot}} = \frac{p^2}{2m} + \frac{1}{2} a q^2$.

Equipartition therefore implies that in thermal equilibrium, the oscillator has average energy

$$\langle H \rangle = \langle H_{\text{kin}} \rangle + \langle H_{\text{pot}} \rangle = \frac{1}{2} k_B T + \frac{1}{2} k_B T = k_B T.$$
In 1871, Boltzmann showed how a classical model for a crystal based on the equipartition of the energy could provide a simple explanation to the Dulong-Petit law.

Each atom in the solid can oscillate in three independent directions, so the solid can be viewed as a system of 3N independent simple harmonic oscillators, where N denotes the number of atoms in the lattice. Since each harmonic oscillator has average energy $k_B T$, the average total energy of the solid is $U = 3Nk_B T$.

By taking N to be the Avogadro number $N_A$, and using the relation $R = N_A k_B$, $U = 3RT$.

The constant volume specific heat is just the temperature derivative of the internal energy:

$$c_v = \frac{\partial U}{\partial T} = 3R = 5.972 \text{ cal/mol K}$$
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However, this law is inaccurate at lower temperatures, due to quantum effects.

\[ c_v = \frac{\partial U}{\partial T} = 3R = 5.972 \text{ cal/mol K} \]
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Statistical Thermodynamics (1)

Statistical Thermodynamics provides a link between a quantum-mechanical description of the microscopic states accessible to the fundamental constituents of matter and the thermodynamic properties of the macroscopic system.

It answers the following question:

“If particles (atoms, molecules, or electrons and nuclei) obey certain microscopic laws, what are the observable properties of a system containing a very large number of such particles?”

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Any macroscopic **thermodynamic measurement** takes a **finite time**, which is much **longer than** the typical **relaxation times of microscopic events** and thus measures a dynamical **time average** over a multitude of accessible microscopic states.

Two possible approaches to model such average macroscopic thermodynamic properties:

- **Solve the dynamics of the system**
  (time-dependent)

- **Build an “Ensamble” of system replicas**
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OFTEN IMPRACTICAL
The “ensamle” approach is valid under the **Ergodic Hypothesis (EH)**, which assumes that this system exhibits the same average properties in space as a single system exhibits in time:

\[
<X> = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau X(t) \, dt = \lim_{M \to \infty} \frac{1}{M} \sum_{i=1}^{M} X_i
\]

The EH implies that in its dynamical evolution during a very long time, the system “explores” all possible states:
Different kinds of “ensambles” can be defined:

**MICRO-CANONICAL ENSAMBLE**

*microcanonical ensemble:* Each system is isolated from the others by rigid, adiabatic, impermeable walls; $U$, $V$, and $N$ for each system are constants.

This ensamble is not very simply applicable to the systems we usually study in the laboratory, which are in thermal equilibrium with their surroundings, but it is centrally involved in molecular dynamics simulations.
Different kinds of “ensambles” can be defined:

**GRAND-CANONICAL ENSAMBLE**

*grand canonical ensemble:* Each system is separated by rigid, permeable, diathermal walls. $T$, $V$, and $\mu$ for each system are constants, but both energy and mass can be exchanged; this is like a canonical ensemble made up of leaky boxes.

Useful for treating interacting particles.
Statistical Thermodynamics (4)

Different kinds of “ensambles” can be defined:

**CANONICAL ENSAMBLE**

Each system is closed to the others by rigid, diathermal, impermeable walls; $T$, $V$, and $N$ for each system are constants, but energy can be exchanged — it is as though the systems were immersed in an isothermal bath.

It often provides the simplest theoretical treatment of systems of non-interacting particles and it is central to Monte Carlo simulations.
The **canonical ensemble** occurs when a system with fixed $V$ and $N$ is at constant temperature (connected to an infinite heat bath). In the canonical ensemble, the probability of each microstate $m$ is proportional to $\exp(-\beta E_m)$.

The probabilities are constrained because their sum over *all* microstates of the system must equal one. Therefore, we can immediately write that the probabilities must have this exact form:

$$\phi_m = \frac{\exp(-\beta E_m)}{\sum_n \exp(-\beta E_n)}$$

where the sum in the denominator is performed over all microstates in the system. This sum ensures the condition that $\sum_m \phi_m = 1$. 

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The **Canonical Partition Function**

Here, since we are in the canonical ensemble, we define a **canonical partition function**:

\[
Q(T, V, N) \equiv \sum_{\text{all } n \text{ at } V, N} \exp(-\beta E_n)
\]

Here, \( Q \) is a function of \( T, V, \) and \( N \) because \( V \) and \( N \) specify the list of microstates used in the sum, and \( T \) provides a value of \( \beta \). Using \( Q \), we can then easily write that the microstate probabilities are given by:

\[
\varphi_m = \frac{\exp(-\beta E_m)}{Q}
\]
The **Canonical Partition Function**

Why is it so important to give this normalizing factor its own variable and name? As we commented previously, partition functions relate to thermodynamic potentials. We can start to see this for $Q$ by computing the average energy in the canonical ensemble:

$$
\langle E \rangle = \sum_n \varrho_n E_n \\
= \frac{1}{Q} \sum_n E_n \exp(-\beta E_n)
$$

Notice, however, that the expression in the sum looks similar to $Q$ except that there is a factor for the microstate energy. In fact, this sum can be written in terms of a derivative of $Q$:

$$
\langle E \rangle = \frac{1}{Q} \left(-\frac{dQ}{d\beta}\right) \\
= -\frac{d \ln Q}{d\beta}
$$

$$
F(T, V, N) = -k_B T \ln Q(T, V, N)
$$

Helmholtz free energy
If we can compute the canonical partition function $Q$, then we can obtain the Helmholtz free energy $F$, which is a fundamental thermodynamic potential of the system. From that, we can obtain all other thermodynamic properties.

$$
\langle E \rangle = \frac{1}{Q} \left( - \frac{dQ}{d\beta} \right) = - \frac{d \ln Q}{d\beta}
$$

$$
F(T,V,N) = -k_B T \ln Q(T,V,N)
$$
Different Degrees of Freedom

What if we can write the energy function as a sum of two different terms, depending on mutually exclusive subsets of the total set of degrees of freedom? This might look like:

\[ E(\text{all DOF}) = E_1(\text{DOF subset 1}) + E_2(\text{DOF subset 2}) \]

DOF subset 1, DOF subset 2 mutually exclusive

In this case, for the canonical ensemble, we can write:

\[ Q(T, V, N) = \sum_{\text{DOF subset 1}} \sum_{\text{DOF subset 2}} e^{-\beta E_1(\text{DOF subset 1}) - \beta E_2(\text{DOF subset 2})} \]
\[ = \sum_{\text{DOF subset 1}} \sum_{\text{DOF subset 2}} e^{-\beta E_1(\text{DOF subset 1})} e^{-\beta E_2(\text{DOF subset 2})} \]
\[ = \left[ \sum_{\text{DOF subset 1}} e^{-\beta E_1(\text{DOF subset 1})} \right] \left[ \sum_{\text{DOF subset 2}} e^{-\beta E_2(\text{DOF subset 2})} \right] \]
\[ = Q_1(T, V, N) Q_2(T, V, N) \]

This derivation shows that any time the energy function can be split into multiple terms involving different degrees of freedom, the partition function can be factored into separate partition functions for each degree of freedom subset.

For energy functions which are linearly separable in the system degrees of freedom, the canonical partition function can be written as a product of canonical partition functions for the individual components of the energy function.
Different Degrees of Freedom

By considering the electronic, rotational, translational and vibrational degrees of freedom as independent, the canonical partition function can be factorized as:

\[ Q_{\text{tot}} = Q_{\text{tra}} \times Q_{\text{rot}} \times Q_{\text{ele}} \times Q_{\text{vib}} \]

So that

\[ \log Q_{\text{tot}} = \log Q_{\text{tra}} + \log Q_{\text{rot}} + \log Q_{\text{ele}} + \log Q_{\text{vib}} \]

For an ideal solid, there are no translational and rotational degrees of freedom, so the partition function reduces to:

\[ Q_{\text{tot}} = Q_{\text{ele}} \times Q_{\text{vib}} \]

Let us briefly discuss the electronic degrees of freedom.
Different Degrees of Freedom

Given that the energy separation among electronic energy levels is much larger than the thermal energy, the electronic contribution to the partition function is negligible:

\[ Q_{\text{ele}} = \sum_j e^{-\frac{e_j}{k_B T}} \]

\[ = e^{-\frac{e_0}{k_B T}} + e^{-\frac{e_1}{k_B T}} + \cdots \]

\[ \approx 1 \]

\[ \Delta E_{\text{ele}} \gg k_B T \]

And thus:

\[ Q_{\text{tot}} = Q_{\text{vib}} \]
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Molecular Vibrations (Harmonic)

The **Harmonic Approximation** assumes a truncation of the nuclear potential at second-order (**quadratic form**) and implies that the nuclear motion can be described in terms of $3N - 6(5)$ independent quantum harmonic oscillators:

$$W_{\alpha i, \beta j}^{\Gamma} = \frac{H_{\alpha i, \beta j}^{0}}{\sqrt{M_{\alpha} M_{\beta}}} \quad \text{with} \quad H_{\alpha i, \beta j}^{0} = \left( \frac{\partial^{2} E}{\partial u_{\alpha i}^{0} \partial u_{\beta j}^{0}} \right)$$

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Crystals contain a huge number of atoms, which implies a huge number of vibrational degrees of freedom.

\[ 3N \text{ vibrational DOF} \]

but now \( N \to \infty \)

It seems impractical...
We can start by describing the relative motion of atoms in the reference cell:

By translational invariance we would have (all lattice cells in phase):

We will see that this corresponds to fully neglecting phonon dispersion.
Atoms in different lattice cells can vibrate with a certain phase shift with respect to each other (phonon dispersion).
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\[
\lambda_{\min} = 2d
\]

or equivalently

\[
\lambda_{\min} = 2\pi / \lambda
\]

Wave-vector \( k = 2\pi / \lambda \)

or equivalently

A point in the first Brillouin zone
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In 1907, Einstein showed how the quantization concept that explained Planck's distribution law for blackbody radiation also explained the low-temperature behavior of the heat capacities of the solid elements:

**The Einstein model of crystals** assumes the following:

1) Each direction of each atom gives an independent harmonic oscillator, such that there are $3N$ oscillators.
2) The frequencies of all of the harmonic oscillators are the same, equal to $\nu$. 

![Graph and molecular structure](image)
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Einstein's Model for the Specific Heat

In 1907, Einstein showed how the quantization concept that explained Planck's distribution law for blackbody radiation also explained the low-temperature behavior of the heat capacities of the solid elements:

The Einstein model of crystals predicts a vanishing heat capacity as the temperature approaches absolute zero. This is quantum behavior and contrasts classical models, for which the heat capacity of a monatomic crystal is always $3k_B$.

\[ c_v(T, V) = 3k_B \left( \frac{\hbar v}{k_B T} \right)^2 \left( \frac{\hbar v}{e^{\frac{\hbar v}{k_B T}} - 1} \right)^2 \]
Debye's Model for the Specific Heat

In 1912, Debye develops his model for estimating the phonon contribution to the specific heat in solids. He basically assumes a linear dependence of phonon frequencies on wave-vector $k$:

The Debye model of crystals correctly predicts the experimentally-observed $T^3$ dependence of the heat capacity in crystals at low temperatures, and demonstrates the origins of this behavior in terms of quantum mechanics.
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How can we compute the actual phonon dispersion? We follow a direct space approach:
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How large should the supercell be?

The larger the better, until convergence is reached.

The Hessian of the supercell is built: \( V_{ai,bj}^g = \frac{\partial^2 E}{(\partial u_{ai}^0 \partial u_{bj}^g)} \)
We need to solve the harmonic Schrödinger equation for the nuclear motions. The usual way is to factorize it into separate ones, each associated to a wavevector $k$. The Hessian matrix is Fourier transformed into a set of dynamical matrices:

$$W_{ij}^k = \frac{1}{\sqrt{M_i M_j}} \sum_g \exp(\mathbf{i} \mathbf{k} \cdot \mathbf{g}) V_{ij}^g$$

that are then diagonalized:

$$(U^k)^\dagger \mathbf{W}^k U^k = \Lambda^k$$

The elements of the diagonal matrix $\Lambda^k$ provide the vibrational frequencies of the phonons with wavevector $k$, while the columns of the eigenvectors matrix give the corresponding normal coordinates:

$$q_i^k = \frac{1}{\sqrt{L^3}} \sum_{j=1}^{3N} \sqrt{M_j} U_{ji}^k \sum_g \exp(\mathbf{i} \mathbf{k} \cdot \mathbf{g}) x_i^g$$
According to standard lattice dynamics, the total harmonic Hamiltonian of a crystal is then expressed as:

\[
\hat{H} = \sum_{i,k} \hat{H}_i^k \quad \text{with} \quad \hat{H}_i^k = \frac{\sqrt{\lambda_i^k}}{2} \left[ -\frac{\partial^2}{\partial (\xi_i^k)^2} + (\xi_i^k)^2 \right]
\]

The solutions of the partial harmonic oscillator Schrödinger equation are:

\[
\hat{H}_i^k \mathcal{H}_{m_i^k} = \varepsilon_{m_i^k} \mathcal{H}_{m_i^k} \quad \varepsilon_{m_i^k} = \left( m_i^k + \frac{1}{2} \right) \frac{\sqrt{\lambda_i^k}}{2\pi} \quad \text{and} \quad \mathcal{H}_{m_i^k} = N_{m_i^k} e^{-\frac{(\xi_i^k)^2}{2}} \mathcal{H}_{m_i^k}
\]

Eigenvectors and eigenvalues of the total harmonic Schrödinger equation for the nuclear motion are then completely characterized:

\[
\Psi_M(\mathcal{R}) = \prod_{i,k} \mathcal{H}_{m_i^k} \left[ (\lambda_i^k)^{\frac{1}{4}} q_i^k \right] ;
\]

\[
E_M = \sum_{i,k} \varepsilon_{m_i^k}
\]

where \( M \) assigns the level of excitation of all vibrational modes (phonons):

\[
M = \{ \ldots, m_1^k, \ldots, m_{3N}^k, \ldots \}
\]
The partition function takes the form:

$$Q(T) = \sum_M e^{-\frac{E_M}{k_B T}} \quad \text{or, equivalently} \quad Q(T) = \prod_{i,k} Q_i^k(T) \quad \text{with} \quad Q_i^k(T) = \sum_{m_i^k=0}^{\infty} e^{-\frac{\epsilon_i^k}{k_B T}}$$

By substituting this expression into the statistical-thermodynamic definitions of the thermodynamic functions we get:

$$S(T) = k_B \sum_{k_p} \left[ \frac{\hbar \omega_{k_p}}{k_B T} \log \left(1 - e^{-\frac{\hbar \omega_{k_p}}{k_B T}} \right) \right]$$

$$E(T) = \sum_{k_p} \frac{\hbar \omega_{k_p}}{2} \left[ 1 + \frac{1}{e^{\frac{\hbar \omega_{k_p}}{k_B T}} - 1} \right]$$

$$C_V(T) = \sum_{k_p} \frac{(\hbar \omega_{k_p})^2}{k_B T^2} \left[ \frac{\hbar \omega_{k_p}}{e^{\frac{\hbar \omega_{k_p}}{k_B T}} - 1} \right]$$
Harmonic Thermodynamic Properties

Harmonic Thermodynamic Properties

Specific Heat

Entropy

AE, J. Maul, R. Demichelis and R. Dovesi,

Specific Heat


Diamond

Corundum

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Drawbacks of the Harmonic Approximation

Within standard quantum-chemical techniques, one has to describe the Lattice Dynamics of the system:

**HARMONIC APPROXIMATION**

- Spectroscopic properties (IR and Raman spectra);
- From phonon density of states, Inelastic Neutron Scattering (INS) spectra;
- Thermodynamic properties such as Entropy and constant-volume Specific Heat;
- Anisotropic Displacement Parameters (ADPs) and EXAFS Mean Square Relative Displacements (MSRD)
- Debye-Waller and Dynamic X-ray Structure Factors
- ....

**BUT...**

- No lattice thermal expansion;
- Elastic constants independent of temperature;
- Equality of constant-pressure and constant-volume specific heats;
- Infinite thermal conductivity;
- ...
Beyond the Harmonic Approximation

Within standard quantum-chemical techniques, one has to describe the **Lattice Dynamics** of the system:

**EXPLICIT ANHARMONIC TREATMENT**

- Phonon-phonon couplings explicitly computed;
- VSCF, VPT, VCI, TOSH, ...

**QUASI-HARMONIC APPROXIMATION**

- Introduces an explicit dependence of phonon frequencies on volume;
- Allows to evaluate thermal expansion;
- Allows to compute constant-pressure specific heat;
- Allows to compute isothermal and adiabatic bulk moduli;
- ...

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- ...
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The harmonic expression for the Helmholtz free energy is retained and an explicit dependence of vibration frequencies on volume is introduced:

\[
F_{QHA}(T, V) = U_0(V) + F_{vib}^{QHA}(T, V)
\]

\[
F_{vib}^{QHA}(T, V) = E_0^{ZP}(V) + k_B T \sum_{k_j} \ln \left( 1 - e^{-\frac{h\omega_{k_j}(V)}{k_B T}} \right)
\]

The equilibrium volume \( V(T) \) at any temperature \( T \) is obtained by minimizing \( F \). A thermal expansion coefficient is defined as:

\[
\alpha_V(T) = \frac{1}{V(T)} \left( \frac{\partial V(T)}{\partial T} \right)_{P=0}
\]
QHA: Validity Domain

Is the QHA valid at all temperatures? **Generally NOT.** It depends on the system and on pressure.

Is the QHA valid at all temperatures? Generally NOT. It depends on the system and on pressure.

Is the QHA valid at all temperatures? Generally NOT. It depends on the system and on pressure.

Structural and Elastic Properties


Isothermal bulk modulus:

\[ K(T) = V(T) \left( \frac{\partial^2 F_{\text{QHA}}(V; T)}{\partial V^2} \right)_T \]
Structural and Elastic Properties

Diamond

TABLE I. Equilibrium volume of the primitive cell, $V_0$ (in Å$^3$), and bulk modulus, $K_0$ (in GPa), of diamond at zero pressure and temperature, as computed with different Hamiltonians and compared with experimental values.$^{30,76}$ Data in parentheses are obtained by neglecting ZPM effects. The lattice parameter is given by $a_0 = (4V_0)^{1/3}$.

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<th>Exp.</th>
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Structural and Elastic Properties


Corundum Al$_2$O$_3$
Anisotropic Thermal Expansion


Forsterite Mg$_2$SiO$_4$
Combining Temperature and Pressure

\[ P(V; T) = -\frac{\partial F_{\text{QHA}}(V; T)}{\partial V} = -\frac{\partial U_0(V)}{\partial V} - \frac{\partial F_{\text{vib}}^{\text{QHA}}(V; T)}{\partial V} \]

In The Earth’s Mantle:

Pressures up to ~140 GPa

Temperatures between ~800 K and 1200 K

Crust
Upper mantle
Mantle transition zone
Lower mantle
D”layer
Outer core
Inner core
Combining Temperature and Pressure

Corundum $\text{Al}_2\text{O}_3$


Forsterite $\text{Mg}_2\text{SiO}_4$

Combining Temperature and Pressure

\[ K_S = K_T + \frac{\alpha V^2 VTK_T^2}{C_V} = K_T \times \frac{C_P}{C_V} \]

Adiabatic bulk modulus

**Corundum Al\(_2\)O\(_3\)**


**Forsterite Mg\(_2\)SiO\(_4\)**

P-V-T Relation

**P-V-T**

AE, J. Maul, R. Demichelis and R. Dovesi,
P-V-T Relation

In situ X-ray diffraction:


Forsterite Mg$_2$SiO$_4$
The QHA allows to compute constant-pressure thermodynamic quantities:

\[ C_P(T) - C_V(T) = \alpha_V^2(T)K(T)V(T)T. \]

J. Maul, I. M. G. Santos, J. R. Sambrano and AE
Constant-pressure Specific Heat

Constant-pressure Specific Heat

Specific Heat

\[ C_v, C_p \text{ (J mol}^{-1}\text{K}^{-1}) \]

Entropy

\[ S \text{ (J mol}^{-1}\text{K}^{-1}) \]

\[ T \text{ (K)} \]


Corundum

Diamond

A. Erba MSSC2016 Torino (Italy), September 2016
Thank you for your kind attention.
Thermal Features of Molecular Crystals

Active pharmaceutical ingredients
High energy-density materials
Materials for non-linear optics

Molecular crystals still represent a challenge to state-of-the-art quantum-chemical methods

Urea:
Intra-molecular covalent interactions
Intra-chain electrostatic interactions
Inter-/Intra-chain H-bonds
Dispersive interactions

Grimme's DFT-D3 TZVP basis sets

Anisotropic thermal expansion via quasi-harmonic calculations
Anisotropic thermo-elasticity via quasi-static calculations
Thermodynamic properties via harmonic and quasi-harmonic calculations

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Thermal Expansion

Anisotropic Thermal Expansion

Thermodynamics

**Specific Heat**

\[ C_V - C_P \text{ (J mol}^{-1}\text{K}^{-1}) \]

**Entropy**

\[ S \text{ (J mol}^{-1}\text{K}^{-1}) \]


A. Erba MSSC2016 Torino (Italy), September 2016
Thermo-elasticity

\[ C_{vv} = \frac{1}{V_0} \frac{\partial^2 \varepsilon_0}{\partial \varepsilon_v \partial \varepsilon_u} \]
Thermo-elasticity

**HARMONIC**

\[ C_{vu} = \frac{1}{V_0} \frac{\partial^2 \mathcal{E}_0}{\partial \epsilon_v \partial \epsilon_u} \]

**CORRECT**

\[ C_{vu}(T) = \frac{1}{V(T)} \frac{\partial^2 F(T, V)}{\partial \epsilon_v \partial \epsilon_u} \]
Thermo-elasticity

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ADIABATIC CORRECTION

\[ C_{vu}^S(T) = C_{vu}^T(T) + \frac{TV(T)\lambda_v(T)\lambda_u(T)}{C_V(T)} \]
Thermo-elasticity

**HARMONIC**

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Exp. 60 293 K (S) | 11.7 | 54.0 | 6.2 | 10.7 | 9.2 | 10.6 | 11.1 |
Exp. 59 298 K (S) | 23.5 | 51.0 | 6.2 | -0.5 | 7.5 | 0.5 | 11.2 |
Exp. 58 298 K (S) | 21.7 | 53.2 | 6.3 | 8.9 | 24.0 | 0.5 | 11.6 |


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Thermo-elasticity

**HARMONIC**

\[ C_{vu} = \frac{1}{V_0} \frac{\partial^2 \mathcal{E}_0}{\partial \varepsilon_v \partial \varepsilon_u} \]

**QUASI-STATIC**

\[ C_{vu}(T) = \frac{1}{V(T)} \frac{\partial^2 \mathcal{E}_0}{\partial \varepsilon_v \partial \varepsilon_u} \]

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Thermo-elasticity

**HARMONIC**

\[ C_{vu} = \frac{1}{V_0} \frac{\partial^2 E_0}{\partial \epsilon_v \partial \epsilon_u} \]

**QUASI-STATIC**

\[ C_{vu}(T) = \frac{1}{V(T)} \frac{\partial^2 E_0}{\partial \epsilon_v \partial \epsilon_u} \]

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A. Erba MSSC2016 Torino (Italy), September 2016
Thermo-elasticity

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<td><strong>293 K (S)</strong></td>
<td><strong>11.9</strong></td>
<td><strong>67.0</strong></td>
<td><strong>8.5</strong></td>
<td><strong>12.5</strong></td>
<td><strong>8.4</strong></td>
<td><strong>15.6</strong></td>
<td><strong>11.7</strong></td>
</tr>
<tr>
<td><strong>PBE-D3</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 K</td>
<td>16.7</td>
<td>73.2</td>
<td>9.9</td>
<td>17.5</td>
<td>10.9</td>
<td>22.0</td>
<td>16.5</td>
</tr>
<tr>
<td>293 K (T)</td>
<td>10.9</td>
<td>64.2</td>
<td>8.3</td>
<td>12.1</td>
<td>7.7</td>
<td>15.8</td>
<td>11.2</td>
</tr>
<tr>
<td><strong>293 K (S)</strong></td>
<td><strong>12.7</strong></td>
<td><strong>66.1</strong></td>
<td><strong>8.3</strong></td>
<td><strong>13.9</strong></td>
<td><strong>9.6</strong></td>
<td><strong>15.8</strong></td>
<td><strong>11.8</strong></td>
</tr>
</tbody>
</table>

Exp. \textsuperscript{60} 293 K (S) | 11.7 | 54.0 | 6.2 | 10.7 | 9.2 | 10.6 | 11.1 |
Exp. \textsuperscript{59} 298 K (S) | 23.5 | 51.0 | 6.2 | -0.5 | 7.5 | 0.5 | 11.2 |
Exp. \textsuperscript{58} 298 K (S) | 21.7 | 53.2 | 6.3 | 8.9 | 24.0 | 0.5 | 11.6 |


A. Erba MSSC2016 Torino (Italy), September 2016
Thank you for your kind attention.