Atomistic Simulations of Geomaterials
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# Phonons, QHA; Solutions

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## 1. Harmonic oscillator **YXFHYI**

In the HCl molecule the force constant is $k = 478$ N/m.

**Solution :**

(a) The reduced mass is

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} = \frac{1.008 \cdot 35.453}{1.008 + 35.453}\text{u} = 0.98\text{u} = 1.627 \cdot 10^{-27}\text{kg}$$

(b) The vibrational frequency is

$$\nu = \frac{1}{2\pi} \cdot \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \cdot \sqrt{\frac{478}{1.627 \cdot 10^{-27}} \frac{\text{N}}{\text{m} \cdot \text{kg}}} = 8.6254 \cdot 10^{13}\,\text{Hz}$$

and the corresponding corresponding wave-number

$$1/\lambda = \frac{8.6254 \cdot 10^{13}}{299\,792\,458} \frac{\text{s}}{\text{m}\,\text{s}} = 287704\frac{1}{\text{m}} = 2877\frac{1}{\text{cm}}$$

## 2. Heat capacity **DJ5828**

Using the partition function $Z = \frac{1}{1-e^{-\frac{\epsilon}{k_B T}}}$ of a single mode with energy $\epsilon = \hbar \cdot \omega_0$

(a) Show that the thermal energy of a single mode is $\langle E \rangle = \frac{\epsilon}{e^{\frac{\epsilon}{k_B T}}-1}$
Hint : $\langle E \rangle = k_B T^2 \cdot \frac{\partial \ln Z}{\partial T}$

(b) Show that its contribution to the heat capacity is $C_V = k_B \cdot \left[\frac{\epsilon}{k_B T}\right]^2 \frac{e^{\frac{\epsilon}{k_B T}}}{\left[e^{\frac{\epsilon}{k_B T}}-1\right]^2}$
Hint : $C_V = \frac{\partial \langle E \rangle}{\partial T}$

**Solution :**

(a) We calculate the thermal energy through the derivative of the partition function :

$$
\begin{aligned}
\langle E \rangle &= k_B T^2 \cdot \frac{\partial \ln Z}{\partial T} = k_B T^2 \cdot \frac{1}{Z} \cdot \frac{\partial Z}{\partial T} \\
&= k_B T^2 \cdot \frac{1}{Z} \cdot \frac{-1}{\left[1 - e^{-\frac{\epsilon}{k_B T}}\right]^2} \cdot \left(-e^{-\frac{\epsilon}{k_B T}}\right) \cdot \frac{\epsilon}{k_B T^2} \\
&= \frac{k_B T^2 \epsilon \, e^{-\frac{\epsilon}{k_B T}}}{k_B T^2} \frac{1 - e^{-\frac{\epsilon}{k_B T}}}{\left[1 - e^{-\frac{\epsilon}{k_B T}}\right]^2} \\
&= \epsilon \cdot \frac{e^{-\frac{\epsilon}{k_B T}} \cdot e^{\frac{\epsilon}{k_B T}}}{\left[1 - e^{-\frac{\epsilon}{k_B T}}\right] \cdot e^{\frac{\epsilon}{k_B T}}} \\
&= \frac{\epsilon}{e^{\frac{\epsilon}{k_B T}} - 1}
\end{aligned}
$$

(b) We calculate the contribution to the heat capacity through the derivative of the thermal energy :

$$
\begin{aligned}
C_V &= \frac{\partial}{\partial T} \frac{\epsilon}{e^{\frac{\epsilon}{k_B T}} - 1} \\
&= \epsilon \cdot (-1) \cdot \left[e^{\frac{\epsilon}{k_B T}} - 1\right]^{-2} \cdot e^{\frac{\epsilon}{k_B T}} \cdot \frac{\epsilon}{k_B T^2} \cdot (-1) \\
&= \frac{\epsilon e^{\frac{\epsilon}{k_B T}}}{k_B T^2 \cdot \left[e^{\frac{\epsilon}{k_B T}} - 1\right]^2} = k_B \cdot \left[\frac{\epsilon}{k_B T}\right]^2 \frac{e^{\frac{\epsilon}{k_B T}}}{\left[e^{\frac{\epsilon}{k_B T}} - 1\right]^2}
\end{aligned}
$$

## 3. Phonon Density of states MgO **QN9I65**

Setup a calculation for a phonon density of states for Mgo at 0 GPa and 290 K. Modify the provided input file for the `gulp-code` adding the unit cell (Space group $Fm\bar{3}m$, $a = 4.2$Å) and the temperature. Further information about the input files and instructive examples can be found on `http://gulp.curtin.edu.au`.

(a) Run the gulp calculation typing `gulp < example_mgo.gin > example_mgo.got`

(b) Read out the following quantities from the output :

i. Zero point energy

ii. Entropy

iii. Heat capacity (constant volume) per formula unit.

(c) Compare with the experimental value of the heat capacity of $37.11 \frac{\mathrm{J}}{\mathrm{mol \cdot K}}$.

(d) From the density of states (DOS) determine visually an average vibrational wave number (in $\mathrm{cm}^{-1}$). Calculate its frequency in Hz and its energy in eV.
Hint : Remember that

$$c \cdot T = \lambda$$

where $c$ is the speed of light of a wave, $\lambda$ its wavelength and $T$ the time for one oscillation, i.e. the frequency is $\nu = 1/T$. Furthermore the energy of a particle with frequency $\nu$ is

$$E = h \cdot \nu$$

where $h$ is Planck's constant.

**Solution :**

(b) The quantities are

i. Zero point energy 0.647 eV

ii. Entropy 0.000960 eV/K

iii. Heat capacity $C_V = 136.735 \frac{\mathrm{J}}{\mathrm{mol \cdot K}}$, per unit cell of 8 atoms, i.e. 4 formula units

$$C_V = \frac{136.735}{4} \frac{\mathrm{J}}{\mathrm{mol \cdot K}} = 34.1825 \frac{\mathrm{J}}{\mathrm{mol \cdot K}}$$

(c) The deviation from the experimental value is $\frac{34.18-37.11}{37.11} = -8\%$.

(d) Visually we determine an average vibrational wave number of 430 $\mathrm{cm}^{-1}$. Its frequency is

$$\nu = \frac{c}{\lambda} = c \cdot 430 \cdot 100\mathrm{m}^{-1} = 12.891 \cdot 10^{12}\,\mathrm{Hz}$$

this corresponds to the energy of

$$\epsilon = \nu \cdot h = 0.0533\,\mathrm{eV}$$

## 4. Heat capacity of MgO from one mode 4TCCTL

We will approximate the heat capacity of MgO using one representative vibrational vibrational mode with energy $\epsilon = 0.05$ eV corresponding to a wave number of

$$403\,\mathrm{cm}^{-1}\ .$$

(a) Calculate the heat capacity $C_V$ at 300 K of one degree of freedom (in meV/K and $\mathrm{J/(mol \cdot K)}$).
Heat capacity for a single mode :

$$C_V = k_B \cdot \left[\frac{\epsilon}{k_B T}\right]^2 \frac{e^{\frac{\epsilon}{k_B T}}}{\left[e^{\frac{\epsilon}{k_B T}} - 1\right]^2}$$

(b) Calculate the heat capacity $C_V$ at 300 K of one formula unit MgO (in meV/K and $\mathrm{J/(mol \cdot K)}$).

**Solution :**

(a) We insert the quantities into the given expression and obtain

$$\begin{aligned}\frac{\epsilon}{k_BT} &= \frac{0.05\,eV}{k_B\cdot 300} = 1.93276\\ e^{\frac{\epsilon}{k_BT}} &= e^{1.93276} = 6.90853\\ \Rightarrow\ C_V &= k_B\cdot[1.93276]^2\frac{6.90853}{[6.90853-1]^2} = 0.739235\cdot k_B = 0.0637021\,\mathrm{meV/K}\end{aligned}$$

This corresponds to

$$C_V = 0.0637021\,\mathrm{meV/K}\cdot 1.602176620898\cdot 10^{-19}\,\mathrm{J/eV}\cdot 6.02214179\cdot 10^{23}\,\mathrm{1/mol} = 6.14632\,\mathrm{J/(K\cdot}$$

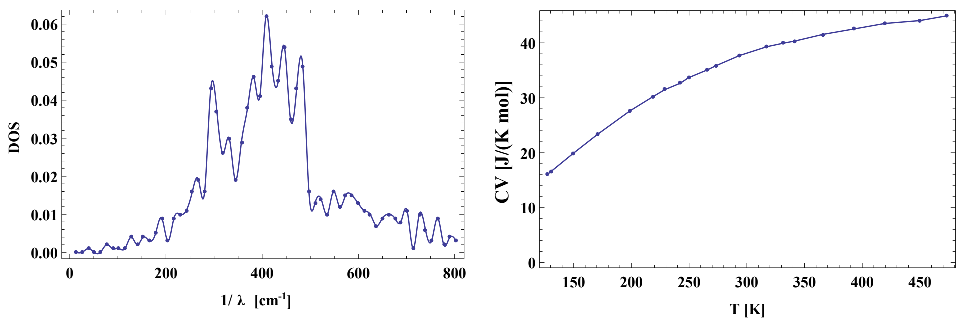
(b) The formula unit consists of 2 atoms with 3 degrees of freedom each, therefore the total heat capacity is

$$C_V = 6\cdot 6.14632\,\mathrm{J/(K\cdot mol)} = 36.88\,\mathrm{J/(K\cdot mol)}$$

or in eV/K per formula unit

$$C_V = 6\cdot 0.0637021\,\mathrm{meV/K} = 0.382213\,\mathrm{meV/K}$$

## 5. Heat capacity of MgO from DOS **SWGB6B**




Here we will approximate the heat capacity of MgO using the vibrational DOS in the Range of 12 to 800 cm$^{-1}$. The corresponding DOS is given electronically. Using your preferred computing environment (Excel, matlab, python, etc.) calculate the heat capacity of MgO as a function of T in the range of 150 to 450 K.

(a) Calculate the contribution of each mode

$$C_V(\epsilon_\mu, T) = k_B\cdot\left[\frac{\epsilon_\mu}{k_BT}\right]^2\frac{e^{\frac{\epsilon_\mu}{k_BT}}}{\left[e^{\frac{\epsilon_\mu}{k_BT}}-1\right]^2}$$

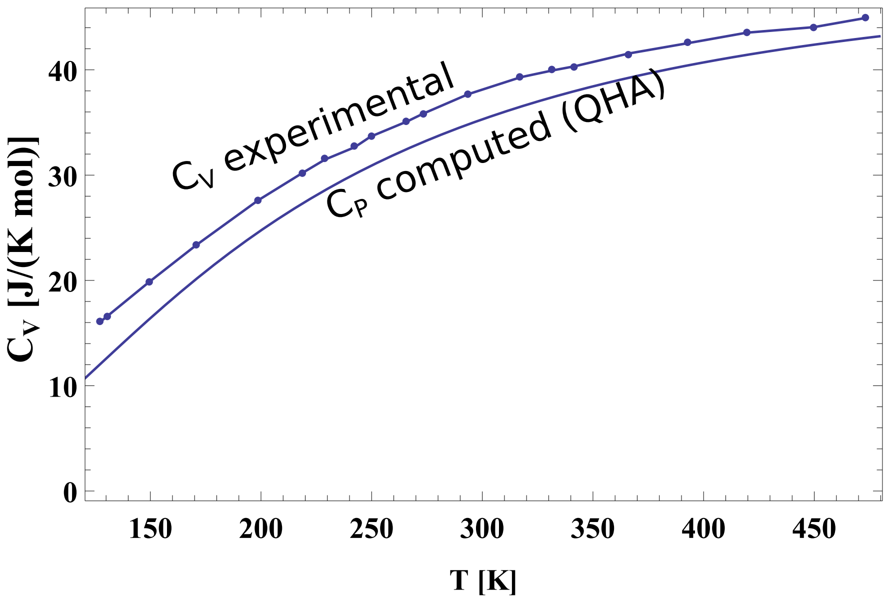
(b) Add up the contributions including the correct weighting to obtain the total heat capacity (corresponding to one mode)

$$C_V = \sum_\mu w_\mu\cdot C_V(\epsilon_\mu, T)$$

(c) Multiply by the number of freedoms per unit cell $N = N_{\text{at}} \cdot 3$ and compare with the experimental values at

| T [K] | $C_P$ [J/(mol · K)] |
|---|---|
| 149.1 | 19.7895 |
| 293.6 | 37.6846 |
| 449.8 | 44.0527 |

**Solution :**




We compute

| T [K] | $C_V$ [J/(mol · K)] |
|---|---|
| 149.1 | 6.24218 |
| 293.6 | 34.8153 |
| 449.8 | 42.3848 |

This corresponds an underestimation by 18, 8 and 4%.

**Physical constants :**

- Planck's constant $h = 6.62607004081 \cdot 10^{-34}$ J · s, or $h = 4.13566766225 \cdot 10^{-15}$ eV · s.
- Speed of light $c = 299792458$ m/s
- Electron Volt $eV = 1.602176620898 \cdot 10^{-19}$ J
- Boltzmann constant $k_B = 8.617330350 \cdot 10^{-5}$eV/K
- $6.02214179 \cdot 10^{23}$ particles per mol