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Atomistic Simulations of Geomaterials
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Phonons, QHA

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1. Harmonic oscillator — YXFHYI

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

(a) Calculate the reduced mass $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$ of the HCl molecule in SI units (kg).

$$m_{\mathrm{H}} = 1.008\,\mathrm{u},\ m_{\mathrm{Cl}} = 35.453\,\mathrm{u},\ \mathrm{u} = 1.6605402^{-27}\mathrm{kg}$$

(b) Calculate the vibrational frequency ν of the HCl molecule in SI units (Hz) and the corresponding wave-number $\frac{1}{\lambda}$ (in cm^{-1}).

$$\nu = \frac{1}{2\pi} \cdot \sqrt{\frac{k}{\mu}}$$

and

$$1/\lambda = \frac{\nu}{c} \text{ where } c = 299\,792\,458\frac{\mathrm{m}}{\mathrm{s}}$$

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 : $C_V = \frac{\partial \langle E \rangle}{\partial T}$

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 $Fm3m$, $a = 4.2$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 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, λ 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 ν is

$$E = h \cdot \nu$$

where h is Planck's constant.

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

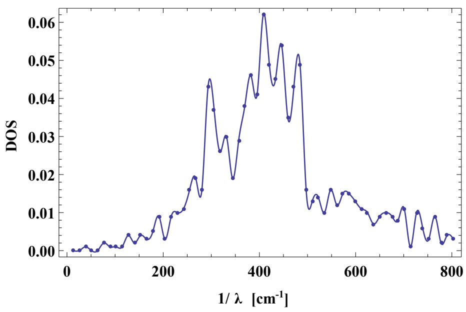
$$403\,\mathrm{cm}^{-1}\ .$$

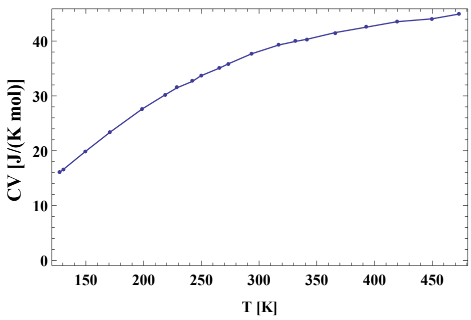
(a) Calculate the heat capacity C_V at 300 K of one degree of freedom (in meV/K and $J/(mol \cdot K)$).
Heat capacity for a single mode :

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

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

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

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

(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

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