DOS and Thermodynamics

Introduction

From experimental physics you should already be familiar with the different models used when analyzing heat capacity data. For the electronic contribution to the isochoric heat capacity C_V^{el}, the Sommerfeld model is commonly employed. In fact, this model is simply the standard expression for the heat capacity from thermodynamics,

$$C_V(T) = \left.\frac{\partial U}{\partial T}\right|_V , \tag{1}$$

evaluated for the internal energy of the free electron gas (see exercise sheet 2),

$$U = \int \mathrm{d}E\, E\, D(E) f(E) = \frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int \mathrm{d}E\, E^{3/2} f(E)\,. \tag{2}$$

The smearing function,

$$f(E) = \frac{1}{\mathrm{e}^{(E-\mu)/k_\mathrm{B}T} + 1}\,, \tag{3}$$

is known as Fermi-Dirac distribution and used when integrating over a DOS associated with fermions (electrons are fermions). The integral in Eq. (2) cannot be solved analytically. However, using the Sommerfeld expansion (see e.g. [1, Example 30.5], [2, Sec. 7.2.1] and [3, Sec. 3.3]), it can be approximated by

$$U = \text{const.} + \frac{\pi^2}{6} D(E_\mathrm{F})\,(k_\mathrm{B}T)^2 + \mathcal{O}(T^4) \tag{4}$$

and thus we find

$$C_V(T) \simeq \gamma T \quad \text{with} \quad \gamma = \frac{\pi^2}{3} k_\mathrm{B}^2\, D(E_\mathrm{F})\,. \tag{5}$$

for the heat capacity and Sommerfeld coefficient γ.

Tasks

1. Try to estimate the Sommerfeld coefficient γ for non-magnetic systems like aluminum (Al), sodium (Na), potassium (K) and silver (Ag) using GPAW.

   Compare your results with [2, Tab. 7.2]. You can find a similar table with mostly the same data also on Wikipedia: https://en.wikipedia.org/wiki/Electron_heat_capacity

   Hint:
   According to Eq. (2), you need to find $D(E_\mathrm{F})$. So first of all performing the ground state calculation as usual and let GPAW return the Fermi energy via the corresponding getter-function. Since

   ```
   en, dos = si.calc.get_dos(spin=0, npts=201, width=0.1)
   ```

   returns the DOS as an array of `npts` elements, we cannot determine $D(E_\mathrm{F})$ exactly, but only within the data points we have access to (ignoring the possibility of interpolation for now). Thus, we should look for the energy value nearest to E_F, find its index and use the latter on the `dos` array. You can find the index using

   ```
   idx = np.abs(en - ef).argmin()
   ```

   as in the previous lab.

2. For magnetic metals, the situation is again more complicated because the DOS is different for each spin channel compared to non-magnetic systems. You can try the spin-polarized version of the gamma-script on the bcc-iron system with:

```
cell = bulk("Fe", "bcc", 2.87, cubic=True)
cell.set_initial_magnetic_moments([2.2, 2.2])
```

3. In `/opt/share/dos_sommerfeld/`, you can find the DOS of several metals computed using a full-potential all-electron DFT-code. This kind of electronic structure program gives qualitatively better results compared to pseudopotential codes like GPAW for the price of a vastly increased computation time.

   The data is given as a 2D array, where the first column is the energy in Hartree units and relative to the Fermi energy. The second column holds the corresponding density of states in states per Hartree and per unit cell. In order to load such a file into python, you can use this snippet:

```
# load in the data file
data = np.loadtxt(filename)
# energy in eV
en = data[:, 0] * Hartree
# DOS in same unit GPAW uses
dos = data[:, 1] / Hartree
```

   See for yourself that the γ calculated from this data does not differ much from GPAW values.

Note: Don't forget to convert your γ into a unit that can be compared to the coefficients listed in the tables below:

$$\mathrm{DOS}\,[\mathrm{eV}^{-1}\,\text{formula unit}^{-1}] \times k_{\mathrm{B}}^2\,[\mathrm{eV}^2\mathrm{K}^{-2}] \quad \longrightarrow \quad \gamma\,[1\times10^{-3}\,\mathrm{J mol}^{-1}\mathrm{K}^{-2}]\,, \tag{6}$$

where mol is to be interpreted as "mole of formula unit".

Solution:
Sommerfeld coefficient from GPAW DOS:

```
import numpy as np
from ase.units import mol, kJ, kB
from ase.build import bulk
from gpaw import GPAW, PW

# define a function to calculate gamma from DOS @ E_Fermi
def find_gamma(dos_fermi):
    # use equation (5) from exercise sheet
    gamma = (np.pi**2) / 3 * (kB**2) * dos_fermi
    # convert to 10^(-3) J / (mol * K^2)
    gamma = gamma * (mol / kJ * 1e6)
    return gamma

# -- decide for a system --
# cell = bulk("Na", "bcc", 4.28)
# cell = bulk("K", "bcc", 5.32)
# cell = bulk("Al", "fcc", 4.05)
cell = bulk("Ag", "fcc", 4.09)
```

```python


# -- spin-unpolarized version --
cell.calc = GPAW(xc="PBE", mode=PW(600), kpts=(8, 8, 8), spinpol=False, txt=None)
etot = cell.get_potential_energy()
ef = cell.calc.get_fermi_level()
en, dos = cell.calc.get_dos(width=0.2, npts=1001)
idx = np.abs(en - ef).argmin()
dosef = dos[idx]
# we have to manually add a factor of 2 to take spin degeneracy into account
gamma = find_gamma(2 * dosef)
print("spin unpolarized:")
print("\tEF: {:.3f}  DOS@EF: {:.3f}  gamma: {:.3f}".format(ef, dosef, gamma))


# -- spin-polarized version --
cell.calc = GPAW(xc="PBE", mode=PW(600), kpts=(8, 8, 8), spinpol=True, txt=None)
etot = cell.get_potential_energy()
ef = cell.calc.get_fermi_level()
# get DOS for each spin channel
en, dos0 = cell.calc.get_dos(spin=0, width=0.2, npts=1001)
en, dos1 = cell.calc.get_dos(spin=1, width=0.2, npts=1001)
# for systems without any magnetic moment, both DOS should be equal
if np.allclose(dos0, dos1) is True:
    print("DOS for spin 0 and 1 match exactly")
else:
    print("system has magnetic moment so DOS do not match")
# find gamma for each spin channel
gamma = []
for spin, dos in enumerate([dos0, dos1]):
    idx = np.abs(en - ef).argmin()
    dosef = dos[idx]
    g = find_gamma(dosef)
    gamma.append(g)
    print("spin", spin)
    print("\tEF: {:.3f}  DOS@EF: {:.3f}  gamma: {:.3f}".format(ef, dosef, g))

# add up both gammas
print("\n\tgamma_tot: {:.3f}".format(gamma[0] + gamma[1]))
```

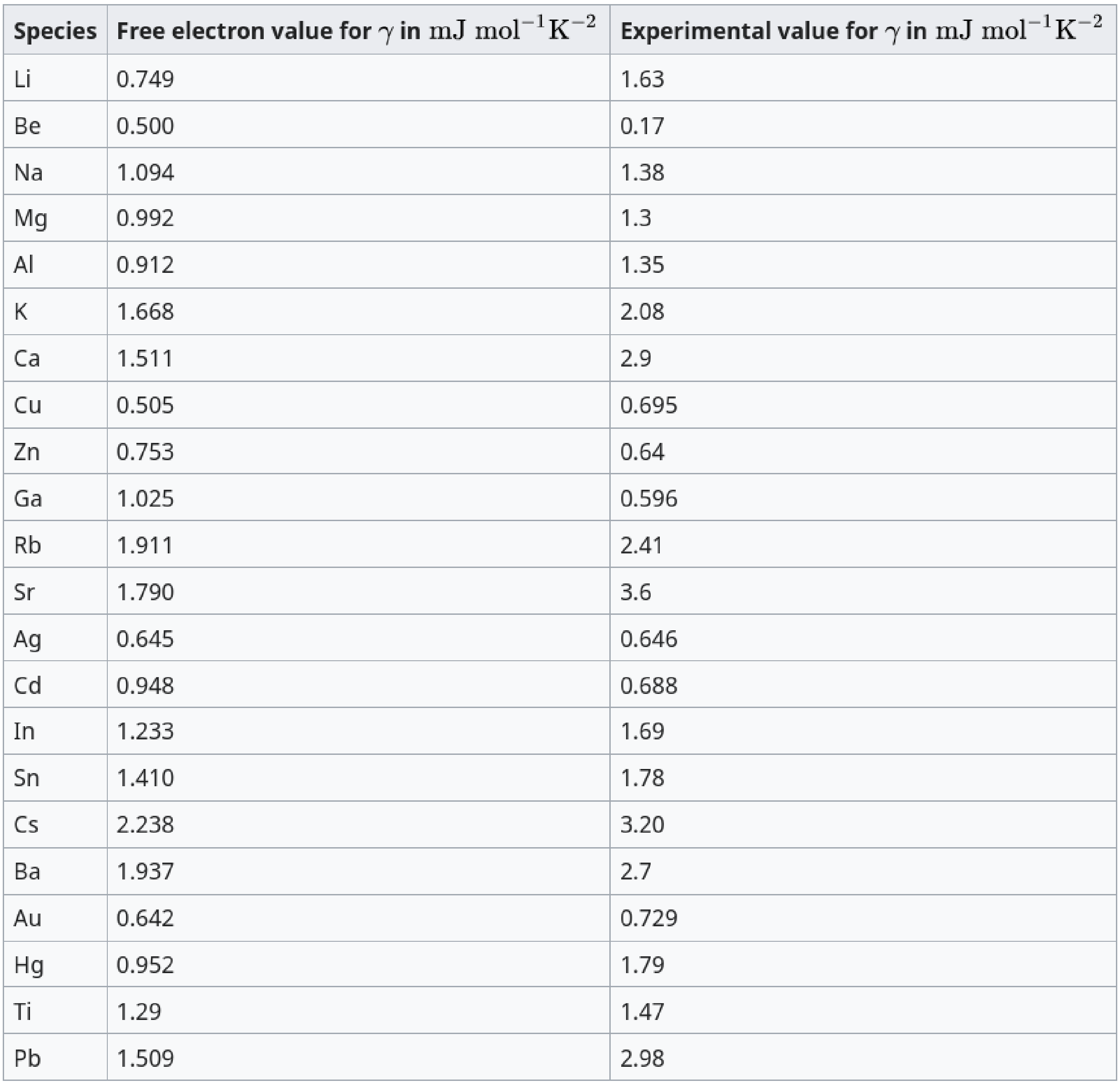
Sommerfeld coefficient from ELK DOS:

```python
import numpy as np
import matplotlib.pyplot as plt
from ase.units import Hartree, kB, mol, kJ
from scipy.integrate import trapezoid

# load data with numpy and store as 2D-array
data = np.loadtxt("TDOS.OUT")
# energy unit in ELK is Hartree, so convert to eV
en = data[:, 0] * Hartree
dos = data[:, 1] / Hartree
# Fermi energy is shifted to 0 in ELK
ef = 0
# find energy array index nearest to Fermi energy
idx = abs(en - ef).argmin()
# integrate DOS up to Fermi level for testing -> #valence electrons
n = trapezoid(dos[: idx + 1], en[: idx + 1])
print("DOS integral up to Fermi energy: {:.3f}".format(n))
plt.plot(en, dos)
# find D(E_F) corresponding to energy index for E_F
dosef = dos[idx]
gamma = (np.pi**2) / 3 * (kB**2) * dosef
# convert to mJ/mol/K^2
gamma *= mol / kJ * 1e6
print("gamma [mJ/mol/K^2] = {:.3f}".format(gamma))
# mark Fermi level and x-axis and draw plot to screen
plt.axvline(x=ef, lw=1, c="k", ls="--")
plt.axhline(y=0, lw=1, c="k")
plt.show()
```

System	Symmetry	a	γ_{GPAW}	γ_{ELK}	γ_{theor}	γ_{exp}
Na	bcc	4.28	0.995	1.193	1.094	1.38
K	bcc	5.32	1.411	1.858	1.668	2.08
Al	fcc	4.05	0.863	0.770	0.912	1.35
Ag	fcc	4.09	0.706	0.670	0.645	0.65
Fe (nom)	bcc	2.87	9.115	-	-	-
Fe (afm)	bcc	2.87	6.505	-	-	-
Fe (fm)	bcc	2.87	2.566	1.856	0.498	4.98

Table 1: Ab initio calculated Sommerfeld coefficients for some metals. The lattice constant a is given in angstrom, whereas γ is tabulated in units of $1 \times 10^{-3}\,\mathrm{Jmol^{-1}K^{-2}}$. The free electron (theor) and experimental γ-values are taken from Fig. 1. GPAW calculations have been performed using the PBE functional, a $\boldsymbol{k}$-grid of $8\times8\times8$, $E_{\text{cut}} = 600\,\text{eV}$, 1001 DOS points and a smearing width of $0.2\,\text{eV}$.



Species	Free electron value for γ in $\mathrm{mJ\ mol^{-1}K^{-2}}$	Experimental value for γ in $\mathrm{mJ\ mol^{-1}K^{-2}}$
Li	0.749	1.63
Be	0.500	0.17
Na	1.094	1.38
Mg	0.992	1.3
Al	0.912	1.35
K	1.668	2.08
Ca	1.511	2.9
Cu	0.505	0.695
Zn	0.753	0.64
Ga	1.025	0.596
Rb	1.911	2.41
Sr	1.790	3.6
Ag	0.645	0.646
Cd	0.948	0.688
In	1.233	1.69
Sn	1.410	1.78
Cs	2.238	3.20
Ba	1.937	2.7
Au	0.642	0.729
Hg	0.952	1.79
Ti	1.29	1.47
Pb	1.509	2.98

Figure 1: Comparison between free electron model γ_{theor} and experimental Sommerfeld coefficients γ_{exp}. (src: https://en.wikipedia.org/wiki/Electron_heat_capacity)

References

[1] Stephen J. Blundell and Katherine M. Blundell. *Concepts in Thermal Physics*. Auflage: 0002. Oxford ; New York: Oxford University Press, U.S.A., Nov. 2009. ISBN: 978-0-19-956210-7.

[2] Rudolf Gross and Achim Marx. *Festkörperphysik*. 2., aktualisierte Auflage. Berlin ; Boston: De Gruyter, 2014. ISBN: 978-3-11-035869-8.

[3] Giuseppe Grosso. *Solid State Physics*. Auflage: 2. Auflage. Amsterdam: Elsevier Ltd, Oxford, 2013. ISBN: 978-0-12-385030-0.