Thermal Energy at the Nanoscale
Homework - Week 3

Spring 2013

1. **Graphene ZA mode specific heat**

In the lectures, we obtained integral expressions for the specific heat of modes that can be approximated with a linear dispersion (Debye model) and constant dispersion (Einstein model). The ZA mode of graphene, which represents out-of-plane vibrations, is however closely approximated near the Brillouin zone center by a quadratic dispersion relation of the form $\omega = CK^2$ where C is a constant.

(a) Determine the maximum cutoff wavevector K_Q and the corresponding cutoff frequency ω_Q in terms of the unit cell density η_a.

(b) Obtain an integral expression for the specific heat of the ZA mode as a function of temperature.

The low temperature specific heat of graphene shows a linear dependence on temperature (see Figure 1) which then becomes quadratic for temperatures greater than 100 K. Can you explain this behavior based on your knowledge of the dispersion relation of graphene (see HW 2 for a plot) and the expression you have just obtained in this problem?

2. **Specific heat of metals**

Figure 2 shows experimental measurements of the heat capacity of potassium at low temperatures. The following temperature dependence is observed:

$$c_v/T = 2.08 + 2.57T^2$$

where c_v is in units of mJ/mol deg^2 and T is in K.

(a) Provide analytical expressions for the y-intercept and slope of the graph. Hint: Neglect optical phonon contribution to specific heat as the experimental data is provided for low temperatures.

(b) Assuming that the conduction electron density in potassium is $1.34{\times}10^{22}$ cm^{-3}, determine the Fermi energy of potassium. Note that the experimental data is expressed per mole of potassium, while the heat capacity expressions derived in the lecture are per unit volume. Assume the density and atomic mass of potassium are 0.862 g/cc and 39 amu. respectively.

(c) Potassium has a body-centered cubic (BCC) structure (1 atom per primitive unit cell) with an atomic density of $1.33{\times}10^{22}$ atoms/cc. Determine the Debye temperature of potassium assuming that the three acoustic branches are replaced by a single branch of uniform group velocity.

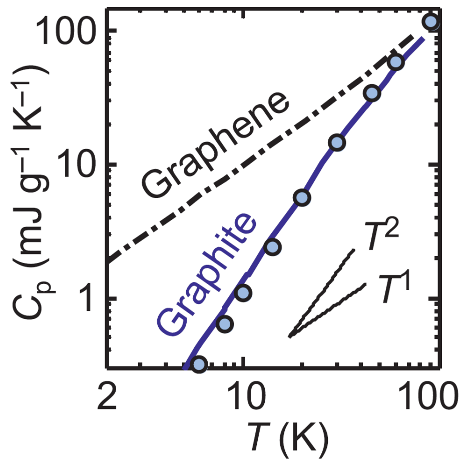

Figure 1: Temperature dependence of the specific heat of graphene and graphite. Figure originally published by Pop et al., MRS Bulletin, vol. 37, pp. 1273-1281, 2012.

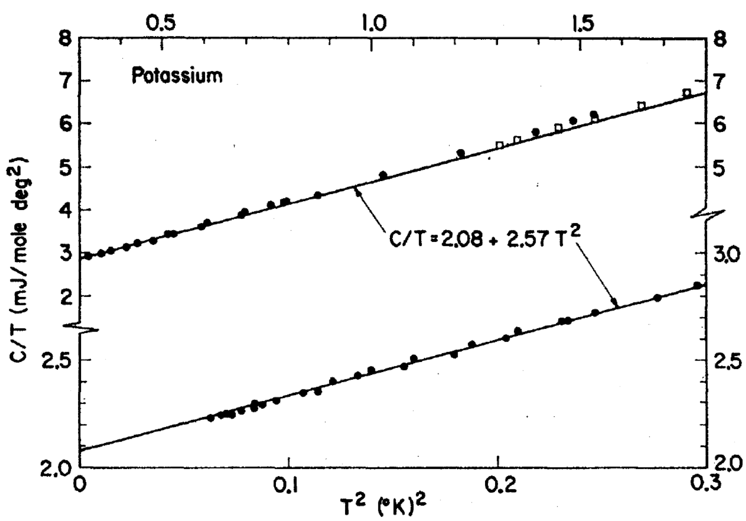

Figure 2: Temperature dependence of the specific heat of potassium and sodium. Figure originally published by Lien and Phillips, Physical Review, vol. 133, pp. A1370-A1377, 1964.

3. **Thermal conductivity from kinetic theory**

In the lecture, we obtained the thermal conductivity of a three dimensional material from kinetic theory. Perform a similar analysis for one and two dimensional materials to obtain the following generalized expression:

$$\kappa = \frac{1}{d} c_v v \Lambda$$

where d is the dimension and can take the values 1, 2 or 3. Also obtain an integral expression for the thermal conductivity and observe the temperature dependence at low temperatures. Assume that the velocity and mean free path are independent of temperature and carrier energy.

4. **Specific heat of a diatomic chain**

Consider the diatomic chain studied in week 1 with atomic masses m_1, m_2 ($m_2 > m_1$) and a uniform atom spacing of a. Also assume a uniform spring constant g between all adjacent atoms. In this problem, we calculate the specific heat of the diatomic chain using the Debye model for the acoustic branch and the Einstein model for the optical branch. Assume that the constant frequency ω_E in the Einstein model is an average of the minimum and maximum frequencies of the optical branch.

(a) Show that the ratio of Einstein and Debye temperatures can be expressed in terms of the mass ratio m_2/m_1 as shown below:

$$\frac{\theta_E}{\theta_D} = \frac{1}{\pi}\left(\sqrt{\frac{m_1}{m_2}} + \sqrt{\frac{m_2}{m_1}} + \sqrt{1 + \frac{m_2}{m_1}}\right)$$

(b) Calculate the normalized acoustic and optical phonon specific heats (normalized by $\eta_a k_B$) at normalized temperatures of $T/\theta_D = 0.2$, 1 and 2. Assume a mass ratio $m_2/m_1 = 2$. Also provide an intuitive explanation of your numerical results.

(c) Use the online CDF tool to understand the acoustic and optical contributions to the total specific heat as a function of temperature. Also observe how these contributions change with varying mass ratio. Again, provide a physical explanation for the trend in the curves with varying mass ratio.