Introduction

At high temperatures the internal energy of a crystal lattice can be obtained from the equipartition of energy theorem. Each particle can oscillate in three directions so that 1 mole of the solid can be treated as $3N_A$ oscillators. Each oscillator has two degrees of freedom which we can identify with kinetic and potential energy. The equipartition theorem states that the energy associated with each degree of freedom is $\frac{1}{2}k_BT$. The internal energy per mole of solid is thus

$$U = 3N_A \times \frac{1}{2}k_BT \times 2 = 3RT \quad (1)$$

so that the molar specific heat at constant volume is

$$C_v = \left. \frac{\partial U}{\partial T} \right|_v = 3R. \quad (2)$$

This result, first presented by Dulong and Petit (1819), applies to all solids if the temperature is high enough for the solid to behave classically.

Experimentally, it is observed that $C_v$ is less than $3R$ at low temperatures, approaching zero at absolute zero. In 1912, Peter Debye introduced a quantum mechanical model which provided a good approximation to the observed heat capacity for solids over a wide range of temperatures. At low temperature, only the long wavelength vibrational modes of the lattice are populated. He assumed that these could be approximated by treating the lattice as a continuum so that the density of modes with wavevector $k$ could be given by

$$D(k) = \frac{3V}{2\pi^2}k^2 \quad (3)$$

where $V$ is the volume of the crystal. The population of a mode with wavevector $k$ is given by the Bose-Einstein distribution,

$$n_k = \left( e^{\beta\nu(k)} - 1 \right)^{-1} \quad (4)$$

where $\beta$ is the inverse temperature and $\nu(k) = kc_s/2\pi$ is the frequency for a mode of
wavevector \( k \) in a crystal in which the speed of sound is \( c_s \). In order to obtain the correct high temperature behaviour for a crystal containing \( N \) atoms in volume \( V \), only the lowest \( 3N \) modes were considered and the density of states was cut off at the mode with frequency

\[
\nu_D = c_s \left( \frac{3N}{4\pi V} \right)^{\frac{1}{3}}.
\]  

(5)

The Debye Temperature is defined as \( T_D = h\nu_D/k \). Within this model, the mean energy for \( n \) moles of the solid can be written as

\[
U = 3nRT F \left( \frac{T_D}{T} \right)
\]  

(6)

where the function \( F \) is given by the integral

\[
F(x) = \frac{3}{x^3} \int_0^x dy \frac{y^3}{ey - 1}.
\]  

(7)

The resulting form of the specific heat, \( C_v \), is shown in figure (1). At sufficiently high temperatures the internal energy approaches the classical value given by Eq (1). Note that substances which have a high Debye temperature show the greatest deviation from the classical result.

In this experiment you will determine the Debye temperatures of various metals (Cu, Zn, Sn, Al, Pb) by seeing how they depart from classical behaviour when cooled from room temperature to liquid nitrogen temperature (77 K).

**Procedure**

**Note that liquid nitrogen can cause severe cold burns and should be handled with care at all times.**

1. The apparatus consists of 3 styrofoam coffee cups stacked inside each other. Fill the innermost cup to within about 1 inch of the brim with liquid nitrogen. A copper cylinder placed inside the cups reduces nitrogen loss due to splashing. Take four or five pieces of each metal, wrap them in a small nylon bag and weigh them.

2. Calculate \( \Delta U_{class} \) for each metal.

3. Determine how much nitrogen is boiled off when the metal is added to it. There will be a significant loss due to evaporation, which can be taken into account using the
following method:

- Monitor the total weight (cup + nitrogen + metal) for about 2 minutes.
- **SLOWLY** lower the metal into the nitrogen — excessive bubbling and splashing can cause erroneous results. (How would such a problem affect the result?) Record the change in weight versus time while the nitrogen is being boiled off and for several minutes after everything has settled down. Plot a graph of weight vs. time to determine the amount of nitrogen which is lost due to the metal alone.

4. The heat given up to the nitrogen by the metal as it cools is

\[
\Delta Q = mL
\]  

(8)

where \( m \) is the mass of gas released and \( L = 2 \times 10^5 \text{ J.kg}^{-1} \) is the latent heat of vaporization. If your \( \Delta Q \) is greater than the classical value which you calculated above,
you probably weren’t careful enough when putting the metal into the liquid. You should repeat each measurement at least twice to check that your data is reproducible.

**Analysis**

Neglecting any volume change in the solid accompanying the drop in temperature, $\Delta Q$ is also equal to the change in internal energy of the metal, $U_i - U_f$. Thus (from Eq (6))

$$\Delta Q = 3nRT_i F \left( \frac{T_D}{T_i} \right) - 3nRT_f F \left( \frac{T_D}{T_f} \right)$$

(9)

where $T_i$ is the initial temperature of the metal, and $T_f$ is the final temperature. Solve Eq (9) and obtain the Debye temperature for each metal. Tabulated values of $T_D$ for various metals can be found in any solid state physics text.

1. Estimate $C_v$ for each metal at 77 K. Comment on the difference between these values and the classical (room temperature) value.

2. As can be seen from Eq (6), the Debye temperature can be related to the speed of sound in the crystal. What do your results tell you about the speed of sound in the metals you have studied?

**Reference**