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PH3500 Classical Physics   **Problem Set 7**   **23.10.2009**

The specific heat of solids

The temperature-dependence of the specific heat of a crystalline solid was one of the most important physical problems that contributed to the development of quantum theory in the early days. It turns out that this T-dependence is quite striking, especially at very low temperatures. We know now that there are in fact two distinct contributions to the specific heat of (metallic) crystalline solids at very low T – one due to the electron 'gas' in the metal, and the other due to collective vibrations of the lattice. The first is dominant at very low temperatures, and is **linear** in T; the second is proportional to T^3 at low temperatures (the "Debye T^3 law"), and rises thereafter to a saturation value. The electronic contribution requires treatment of the electron gas in terms of Fermi-Dirac (quantum) statistics, and will be taken up later. The lattice contribution can be computed – at least in the framework of a simplified model – using what we have learnt so far. The simplified model, called the **Einstein model**, truns out to have problems at very low T, and does not in fact yield the correct (T^3) behaviour ... but we shall see where the problem lies and comment on how Debye set matters right, in the solutions.

1. Let us regard the crystal of N atoms as a set of N independent harmonic oscillators in three dimensions. For simplicity, let us assume that there is just one natural frequency, ω. A full quantum mechanical treatment of the oscillator problem shows that a **linear** harmonic oscillator has discrete non-degenerate energy levels given by $\hbar\omega(n + \frac{1}{2})$, $n = 0, 1, 2, \ldots$ ad inf. In three dimensions, the oscillator has energy levels specified by three quantum numbers n_1, n_2, n_3 with energy $= \hbar\omega(n_1 + n_2 + n_3 + \frac{3}{2})$, where n_1, n_2, n_3 run over non-negative integers. Clearly, we can rewrite this as $\varepsilon_n = (n + \frac{3}{2})\hbar\omega$, $n = 0, 1, 2, \ldots$, but now each energy level ε_n is **degenerate**. Call the degeneracy factor g_n, and deduce what it is in terms of n. Taking the atoms of the lattice to be independent, and located at distinct positions, calculate the partition function of the solid (i.e., of the collection of N oscillators). You must show that

$$Z = \left[2\sinh(\beta\hbar\omega/2) \right]^{-3N} .$$

2. Hence show that the internal energy of the system is

$$U = \left(\frac{3N\hbar\omega}{2} \right) \coth\left(\frac{\hbar\omega}{2k_B T} \right) .$$

Sketch the variation of U/N with T. Identify and understand the physical significance of the limiting values of this quantity as $T \to 0$ and $T \to \infty$. What would you call 'high' and 'low' temperature limits in this problem?

3. Hence show that the specific heat C, the quantity that we want to compute, is given by

$$C = 2Nk_B \left(\frac{\xi}{\sinh \xi} \right)^2 , \quad \text{where } \xi = \hbar\omega/(2k_B T) .$$

Sketch the variation of C as a function of T. In particular, show that the above expression tends, as $T \to \infty$, to the constant value expected on the basis of the classical equipartition theorem for a collection of oscillators (the 'Dulong and Petit law' for this particular system).

4. **How** does C tend to zero as $T \to 0$? (Why should it tend to zero at all as $T \to 0$?) Why does this model fail to yield the experimentally correct T^3 variation of C as $T \to 0$?

5. From Z, you can write down the free energy $F = -k_B T \ln Z$ of the system. Do so, and then calculate the entropy of the solid using $S = -(\partial F/\partial T)$. (You could also use $S = (U - F)/T$, of course!). The answer is

$$S = 3Nk_B \left[\xi \coth \xi - \ln(2 \sinh \xi) \right]$$

where $\xi = \hbar\omega/(2k_B T)$ as defined earlier. **Show that $S \to 0$ as $T \to 0$, in accordance with the Nernst heat theorem.**