Notes for Lecture 9

Quantum statistical mechanics (preview)

Now, we discuss the formalism of the statistical mechanics from the quantum mechanical point of view.

In the quantum regime, the energy quantum has a much more significant effect than in the semi-classical treatment that we have been mostly employing so far would have us to believe. Also, the quantum entanglement has an important consequence: that is, the nature of particles, i.e., whether particles are fermions or bosons, starts to matter tremendously.

9.1 Einstein phonons, continued

The simple example of Einstein phonons (Section 8.5) already gives a good taste of these important aspects.

First, as $T \to 0$ (Eq. 8.63), $C_V \to 0$. Note that this is what one expects from the third law of thermodynamics (point 1 of page 16 of LN 2). The equipartition theorem (Eq. 6.49) predicts a T-independent heat capacity[1]

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{Q_d}{2} k_B \qquad \text{Du-Long Petit law} \tag{9.1}$$

contradicting the third law.

[1] $Q_d = 2$ for a single simple harmonic oscillator, since the Hamiltonian $= \frac{1}{2m}p^2 + \frac{1}{2}kx^2$ has two quadratic terms.

Second, the entropy $S = (E - F)/T$ can be calculated directly from Eqs. 8.58 and 8.59 (and using, of course, $F = -k_B T \log Z$),

$$S = \frac{1}{T}\big(\hbar\omega + \hbar\omega n_P(\omega) + k_B T \log n_P(\omega)\big) \tag{9.2}$$

$$\rightarrow \begin{cases} k_B \log\left(\frac{k_B T}{\hbar\omega}\right) & T \rightarrow \infty \quad (\text{i.e., } \frac{k_B T}{\hbar\omega} \rightarrow \infty) \\ k_B \beta\hbar\omega e^{-\beta\hbar\omega} \rightarrow 0 & T \rightarrow 0 \quad (\text{i.e., } \frac{k_B T}{\hbar\omega} \rightarrow 0) \end{cases} \tag{9.3}$$

So, at high temperature, the equipartition theorem is seen to be in action, in the following way. First of all, the energy is $k_B T$. And, the above expression for S makes it clear that $\frac{k_B T}{\hbar\omega}$ is the number of states available per oscillator under consideration. Why is this? The number of states for a microcanonical ensemble (i.e., a fixed value of E) can be calculated as the binomial coefficient as $\Omega(E) = \binom{N+M-1}{N-1}$, where N is the number of oscillators (identical but distinguishable since they are all fixed in space)[2], and $M = \frac{E}{\hbar\omega} = N\frac{k_B T}{\hbar\omega}$ is the total number of oscillation quanta. In the limit of $M \gg N$ (classical limit), one can see that this binomial coefficient goes to $\Omega(E) \approx \left(\frac{M}{N}\right)^N = \left(\frac{k_B T}{\hbar\omega}\right)^N$. So, indeed, $\frac{k_B T}{\hbar\omega}$ is $\Omega(E)$ per oscillator.

At low temperature, we see that S shows a **thermally activated behavior** in an Arrhenius law form, $\exp\left(-\frac{E_s}{k_B T}\right)$, where E_s is an energy scale of the problem, which in this case is the oscillation quantum, $\hbar\omega$. This is consistent with the same activated behavior seen for the heat capacity (Eq. 8.63)[3].

We shall see that the following general insight go a long way in guiding us for our exploration of quantum systems.

For a quantum system with an energy scale E_s, the equipartition theorem is valid if $k_B T \gg E_s$, while the system shows a manifestly quantum behavior, i.e., a thermally activated behavior with a small $e^{-\frac{E_s}{k_B T}}$, if $k_B T \ll E_s$.

For the Einstein phonon problem, the activated behavior guarantees that the entropy vanishes. This demonstrates **the third law of thermodynamics**[4]. Related to this is the above discussion of the heat capacity, which must also vanish as $T \rightarrow 0$.

[2] Note that the situation here is analogous to those in Sections 8.4.2 and 8.4.3. There, we saw that the problem breaks down to a single magnetic moment problem when using the Gibbs ensemble (constrained H). Here, the problem breaks down to a single oscillator problem when using the canonical ensemble (constrained T). On the other hand, in the micro-canonical ensemble for the current problem (conserved E), the whole system must be considered. This is analogous to the situation in Section 8.4.3, where a conserved M was involved.

[3] And, of course, that result for C_V can be easily re-derived from our expression of S, using $C_V = T\frac{\partial S}{\partial T}$ and $T\frac{d\beta}{dT} = -\beta$.

[4] However, for the phonon system, the exact manners in which the entropy and the heat capacity

Clearly, the entropy of the semi-classical ideal gas, Eq. 6.46, does not vanish as $T \to 0$, either! Based on the insight gained above, we expect that once we examine energy scales of the ideal gas problem more properly, this issue will be resolved. We shall do so, soon, in an upcoming lecture.

Another insight can be already learned, if we take a look at the function $n_P(\omega)$ again.

$$n_P(\omega) = \frac{1}{\exp(\beta\hbar\omega) - 1} \tag{8.60}$$

This function is the so-called **Planck distribution function**. What it represents is clearly the "thermal quantum number" of the oscillator, since $E = \left(n_P + \frac{1}{2}\right)\hbar\omega$ (Eq. 8.59).

> A simple harmonic oscillator quantum is a particle. More specifically, it is a boson, with zero chemical potential ($\mu = 0$). $n_P(\omega)$ represents the average number of thermally excited bosons, and is equivalent to the **occupation number** for the bosonic state at $\hbar\omega$.

The last part of this makes it clear that the Planck distribution function is a special case ($\mu = 0$)[5] of the Bose-Einstein distribution function $n_{BE}(\omega) = \frac{1}{\exp(\beta(\hbar\omega - \mu)) - 1}$. Why is μ zero? It is because the number of phonons is *fundamentally unrestricted*. An easy way to see this logic is through Section 7.5. In that section, it becomes clear that β is simply a Lagrange multiplier introduced when the energy is allowed to fluctuate but the average energy must be constrained. The chemical potential μ (or rather $-\beta\mu$) comes as an additional Lagrange multiplier, if the total number of particles is allowed to fluctuate, *independently of* the energy, while its average value is constrained. That the number of particles is independent of the total energy for electrons (fermions) or Helium atoms (^{4}He: bosons) is quite obvious[6]. However, the number of oscillation quanta that can be excited is clearly dependent on energy alone, and is therefore fundamentally unrestricted. There is no additional Lagrange multiplier to introduce, as there is no constraint, and thus no μ.

vanish as $T \to 0$ are not obtained correctly by the Einstein model. The behavior is captured properly by "Debye's T^3 law," to be covered soon.

[5] So, the classical limit for Einstein phonons does *not* correspond to $\mu \to -\infty$ (Eq. 8.8), since $\mu = 0$ by definition. The same is true for photons. In any case, the classical limit as $n \to \infty$ (large quantum number) or, equivalently, $\hbar \to 0$ is always applicable.

[6] This is, of course, because we are assuming low energy scale physics, in the following sense. If one studies high energy physics that is much higher than the mass-energy (mc^2) of particles such as electrons or Helium atoms, then the number of those particles *will* be dependent on energy, and, therefore, *will* be unrestricted!

Apart from the particular value of μ, the fact that the oscillation quantum is a boson is easy to understand: clearly many oscillation quanta can coexist! So, without really being aware of it, we have included the effect of quantum statistics in this simple example of Einstein phonons!