Notes for Lecture 11

Quantum statistical mechanics

The puzzles of the heat capacity at low temperature and the black body radiation were the driving forces that gave birth to the quantum mechanics, early in the last century. Here, we begin to apply the formalism[1] that we developed in the last lecture note.

The puzzles that broke the dam of the development of quantum mechanics arose from the equipartition theorem (page 9 of lecture note 7). The essence of the equipartition theorem is that the energy is simply proportional to T, with the proportionality constant determined by the total quadratic degrees of freedom of the system. So, one expects that

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{V,N} = \frac{Q_d}{2} k_B \qquad (11.1)$$

in the notation of Eq. 7.34. However, experiments do not support this. While many materials do show nearly constant heat capacity near room temperature, its value is often less than that given by this equation. In such a case, the heat capacity will reach another plateau at higher temperature. More detrimental was the fact that at low temperatures (made accessible by the refrigeration technology rapidly developed at the turn of the last century) the heat capacity was not constant at all. It showed a severe reduction as the temperature was lowered, and it vanishes at T becomes very low.

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[1] As noted loosely during lectures several times, it would be a mistake, however, to think that the foundation of the statistical mechanics is a settled matter. For example, according to an on-going local theory research (J M Deutsch 2010, New J. Phys. 12 075021, "Thermodynamic entropy of a many-body energy eigenstate") a globally pure state can induce heat exchanges between subsystems and a well-defined thermodynamic entropy in a small subsystem, suggesting the importance of the entanglement entropy.

Note that this vanishing of the heat capacity at low T *is* consistent with, and in fact is *required* by, the third law of thermodynamics (page 16 of LN 2). The semi-classical statistical mechanics is utterly unable to explain the third law of thermodynamics, as we already noted (Eq. 7.8 and the discussion below it).

In order to explain these puzzles, the full quantum mechanics is necessary, as we will show now.

11.1 Single oscillator

Here, we consider a simple harmonic oscillator problem. We consider a single mode with a natural frequency ω. This is a model for photons or phonons. For phonons, we know what is oscillating – we know the medium – but for photons, we just do not know what the medium is. In the next lecture, we will consider the physical origin of phonons more deeply.

From the elementary quantum mechanics, we know that

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{11.2}$$

is the energy eigenvalues for this system.

11.1.1 Detour on the origin of the partition function

Now, what is the partition function? The answer is already given in Eq. 10.30. However, since this is the first time to evaluate it in quantum statistical mechanics, let us figure out how it arises from the density matrix formalism. From the consideration of the canonical ensemble in contact with a reservoir, we know that the probability associated with each microstate in a canonical ensemble is given by $\propto \exp(-\beta E_\alpha)$. So, the density matrix is given by

$$\rho = \sum_\alpha \frac{\exp(-\beta E_\alpha)}{Z} \left|\Psi_\alpha\right\rangle \left\langle\Psi_\alpha\right| \tag{11.3}$$

where Z is defined as the probability normalization constant, as it should be. By taking the trace of the density matrix with the energy eigenstate basis $|\Psi_\beta\rangle$, we get

$$\begin{aligned} \mathrm{tr}\,\{\rho\} &= \frac{\sum_{\alpha,\beta} \exp(-\beta E_\alpha)\,\langle \Psi_\beta |\, \Psi_\alpha\rangle \,\langle \Psi_\alpha |\, \Psi_\beta\rangle}{Z} && (11.4)\\ &= \frac{\sum_{\alpha,\beta} \exp(-\beta E_\alpha)(\delta_{\alpha,\beta})^2}{Z} \qquad \text{by Eq. 10.21} && (11.5)\\ &= \frac{\sum_{\alpha} \exp(-\beta E_\alpha)}{Z} && (11.6)\end{aligned}$$

Note that $\mathrm{tr}\,\{\rho\} = 1$ by definition. Or, if you like, by Eq. 10.22, $\mathrm{tr}\,\{\rho\}$ is the ensemble average of the identity operator, and it must be 1. Therefore, we get

$$Z(T,V,N) = \sum_\alpha \exp(-\beta E_\alpha) \tag{11.7}$$

So, this *is why* we have this expression, which was already given in Eq. 10.30, and which is already familiar with any one familiar with statistical mechanics.

While this derivation is trivial, it does show the density matrix formalism at work. It also shows the density matrix is naturally a diagonal matrix in the energy basis. But, note that if we use other basis, say position basis, then it will no longer be diagonal.

11.1.2 Single oscillator properties

The computation of the partition function for one oscillator is simple.

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} \exp\left(-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right) && (11.8)\\ &= \frac{\exp\left(-\frac{\beta\hbar\omega}{2}\right)}{1-\exp\left(-\beta\hbar\omega\right)} && (11.9)\end{aligned}$$

From which

$$\begin{aligned} E &= -\frac{\partial \log Z}{\partial \beta} = \frac{\hbar\omega}{2} + \hbar\omega\, n_P(\omega) && (11.10)\\ n_P(\omega) &= \frac{1}{\exp(\beta\hbar\omega)-1} && (11.11)\end{aligned}$$

The interpretation of this expression is simple and is very important. The term $\hbar\omega/2$ is the zero point energy, or the quantum fluctuation energy, term. It arises due to the

Heisenberg uncertainty principle.[2] The function $n_P(\omega)$ is the occupation number of "oscillation quanta." This oscillation quantum is what we call a photon, a phonon, or a molecular vibration, in a suitable context. **Namely, each vibrational mode in quantum mechanics means a boson mode.** It is a boson, since many quanta can co-exist ($n > 1$ is perfectly OK). Note that the chemical potential for this type of boson can be considered zero, which is why it does not appear in Eq. 11.11. The reason is that the number of these bosons is not an independent variable. It cannot be specified independently of T and V. Rather, it is *determined* by the values of T and V. So, μ should not be defined at all, which is the same as saying that it is zero. Note that

$$n_P(\omega) = \overline{\langle n \rangle} \tag{11.12}$$

Taking the temperature derivative of E, we get

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \ldots = k_B \frac{(\beta\hbar\omega)^2}{4\sinh^2\frac{\beta\hbar\omega}{2}} \tag{11.13}$$

From this it follows that

$$C_V \to \begin{cases} k_B\,(\beta\hbar\omega)^2 \exp(-\beta\hbar\omega) & T \to 0,\ \text{Quantum regime, Activated behavior} \\ k_B & T \to \infty,\ \text{Du-Long Petit law, Equipartion} \end{cases} \tag{11.14}$$

So, at low T, C_V does go to zero! It is turned on when $T \sim \hbar\omega/k_B \equiv \theta_{vib}$ is the vibrational temperature scale (which can be as much as 1000 K, easily). This shows that quantum mechanics triumphantly explains the two puzzling behaviors – why C_V is reduced to zero at low T and why sometimes C_V is turned on to another plateau at high temperatures.[3]

While this theory has these strong merits, we will see in the next lecture that the success of the low T heat capacity is only qualitative when it is applied to solids. The heat capacity of solids at low T follows the universal Debye T^3 law, instead of showing the exponential behavior like the one shown here.

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[2] The zero point energy should not be considered just a constant, having no physical consequence. Its modification due to boundary conditions imposed by neutral matters in vacuum accounts for the (familiar) van der Waals force and the Casimir force.

[3] For this latter discussion, clearly one oscillator problem is not enough. One must have multiple oscillators, or kinetic energy plus oscillators.

11.2 Rotational mode

A quantum rigid body has the Hamiltonian

$$H_{rot} = \frac{\vec{L}^2}{2I} \tag{11.15}$$

where I is the rotational inertia, and $\vec{L}$ is the angular momentum.

The analysis of this problem with the quantized angular momentum proceeds much like in the previous section, as outlined in class, except that the partition function cannot be summed exactly. Nevertheless, the (constant volume) heat capacity shows the same qualitative behavior – it is exponentially suppressed at low T, while it goes to the classical value k_B at high T.

The characteristic temperature scale for the quantum rotation can be defined as

$$\theta_{rot} = \frac{\hbar^2}{2Ik_B} \tag{11.16}$$

Using $k_B = 25.85$ meV / 300 K, $\hbar c = 1973$ eV Å, and using typical values for Ic^2 (keeping in mind that $I = Ma^2$, where M is the atomic mass and a is the atomic dimension), one can estimate that $\theta_{rot} \sim 1$ K. So, the crossover from the quantum regime to the classical regime occurs at very low temperature in this case, quite different from the vibrational case.