Notes for Lecture 12

Quantum ideal gas

In the last lecture, we already introduced one kind of quantum particles. Those may seem rather peculiar ones: bosons whose numbers are dependent on other thermodynamic variables. For those particles, the particle number is not an independent thermodynamic variable, as it is subordinate to other conditions such as the temperature and the volume. For such particles, the chemical potential is zero by definition, as has been discussed at length in page 3 of LN 9.

Here in this lecture, we give some formal presentation of quantum ideal gas, i.e. non-interacting quantum particles, whether or not their chemical potential is zero.

While zero chemical potential bosons such as phonons or photons seem peculiar, they are not, from a fundamental point of view. One must keep in mind that the particle conservation is eventually related to the energy conservation. Notice that some of the particles that we addressed in the last class (photons and Debye phonons) have zero masses. Then, using Einstein's mass and energy equivalence, one may see that, in the last lecture, we dealt with the cases where the temperature (k_BT) is on the order of the rest mass (m_0c^2) or greater. Namely, if the rest mass is much greater than the temperature, when both are converted to energy, then physical mechanisms for the actual creation or destruction of particles must be taken into account – at such a high temperature, the particle will appear or disappear as the temperature is varied.

12.1 Grand canonical ensemble

The grand canonical ensemble is the most convenient ensemble to use, when one is dealing with the quantum ideal gas.

$$Q = \sum_{\mathrm{μ}} \exp(\beta\mu\mathcal{N})\exp(-\beta\mathcal{E}_{\mathrm{μ}}) \qquad = \sum_{\mathcal{N}} e^{\beta\mu\mathcal{N}} Z(T,V,\mathcal{N}) \tag{12.1}$$

where the microstate μ is any energy eigenstate with a fixed, but arbitrary, number $\mathcal{N}$ of particles.

Now, since the particles do not interact, we can set

$$\mathcal{E}_{\mathrm{μ}} = E_0 + \sum_i \varepsilon_i n_i \tag{12.2}$$

where E_0 is the zero point energy (i.e. the energy of the vacuum) and i is the one particle energy level index. Note that i is in general a collective index, $i \equiv (\vec{k}, \sigma_z)$ for example for an electron gas, where $\sigma_z = \pm 1$ and S_z (the spin quantum number) $= \sigma_z \hbar/2$. In other words, i is the collection of all unique single particle quantum numbers. Here, n_i is the number of particles that occupy the level i. So, for fermions, $n_i = 0$ or 1. For bosons, n_i can be any non-negative integer. For any microstate μ, we must have $\sum_i n_i = \mathcal{N}$, where $\mathcal{N}$ is the number of particles for the microstate μ.

For simplicity, we will drop E_0, the energy corresponding to no particles, from now on. However, it is very easy to put it back in later on, if necessary (like in the case of photons and phonons). For E, we can simply add E_0. For P, we can use the fact that E_0 cannot depend on T or N, and so $P_0 = -\frac{dE_0}{dV}$ need to be added. The number of particles N or the entropy S does not depend on E_0.

Combining the above two expressions, we get

$$Q = \sum_{\{n_i\}} \exp\left[-\beta \sum_i (\varepsilon_i n_i - \mu n_i)\right] \tag{12.3}$$

where we simply replaced μ with $\{n_i\}$, which completely specifies a microstate when there is no interaction.

We may define

$$Q_i = \sum_{n_i} \exp\left[-\beta(\varepsilon_i n_i - \mu n_i)\right] \tag{12.4}$$

where the sum over n_i is an unrestricted sum over all allowed values of n_i. Then, the full grand partition function simply becomes

$$Q = \prod_i Q_i \tag{12.5}$$

$$\Phi = \sum_i \Phi_i \qquad \Phi_i \equiv -k_B T \log Q_i,\ \Phi \equiv -k_B T \log Q \text{ (Eq. 7.12)} \tag{12.6}$$

So, we can simply do the one level statistical mechanics on level i, and then trivially add/multiply answers to get the final answer.

This situation is analogous to the semi-classical case (Secs. 8.1, 8.3, 8.4) where we saw, the easy factorization such as this one (with a multiplicative factor to compensate for double counting, in some cases) occurs for the partition function or the Gibbs partition function, not the grand partition function.

12.1.1 Fermions

For fermions, $n_i = 0, 1$, and so

$$Q_i = 1 + e^{-\beta(\varepsilon_i - \mu)} \tag{12.7}$$

The ensemble average of the level i is given by

$$\overline{\langle n_i \rangle} = \frac{1}{\beta}\frac{\partial \log Q_i}{\partial \mu} \qquad \text{Eq. 7.13} \tag{12.8}$$

$$= \frac{e^{-\beta(\varepsilon_i-\mu)}}{1 + e^{-\beta(\varepsilon_i-\mu)}} \tag{12.9}$$

$$= \frac{1}{e^{\beta(\varepsilon_i-\mu)} + 1} \qquad \equiv f_{FD}(\varepsilon_i) \tag{12.10}$$

where f_{FD} is the so-called the Fermi-Dirac function, and its meaning is, as we just calculated it, the thermal occupancy of the energy level i by a fermion.

The grand potential is given by (from Eq. 12.6)

$$\Phi = -k_B T \sum_i \log\left(1 + e^{-\beta(\varepsilon_i-\mu)}\right) \tag{12.11}$$

$$= -PV \qquad \text{for an extensive system} \tag{12.12}$$

The total energy (from Eq. 12.2) and the total number of particles are given by

$$E = \sum_i \varepsilon_i f_{FD}(\varepsilon_i) \tag{12.13}$$

$$N = \sum_i f_{FD}(\varepsilon_i) \tag{12.14}$$

12.1.2 Bosons

For bosons, $n_i = 0, 1, 2, 3, ...$, and so

$$Q_i = \left(1 - e^{-\beta(\varepsilon_i - \mu)}\right)^{-1} \tag{12.15}$$

The ensemble average of the level i is given by

$$\begin{aligned}
\overline{\langle n_i \rangle} &= \frac{1}{\beta}\frac{\partial \log Q_i}{\partial \mu} && \text{Eq. 7.13} && (12.16)\\
&= \frac{e^{-\beta(\varepsilon_i-\mu)}}{1 - e^{-\beta(\varepsilon_i-\mu)}} && && (12.17)\\
&= \frac{1}{e^{\beta(\varepsilon_i-\mu)} - 1} && \equiv f_{BE}(\varepsilon_i) && (12.18)
\end{aligned}$$

where f_{BE} is the so-called the Bose-Einstein function, the thermal occupancy of the level i by a boson.

The grand potential is given by (from Eq. 12.6)

$$\begin{aligned}
\Phi &= k_B T \sum_i \log\left(1 - e^{-\beta(\varepsilon_i-\mu)}\right) && && (12.19)\\
&= -PV && \text{for an extensive system} && (12.20)
\end{aligned}$$

The total energy (from Eq. 12.2) and the total number of particles are given by

$$\begin{aligned}
E &= \sum_i \varepsilon_i f_{BE}(\varepsilon_i) && (12.21)\\
N &= \sum_i f_{BE}(\varepsilon_i) && (12.22)
\end{aligned}$$

12.1.3 Notation

The common notation for $f_{FD}(\varepsilon)$ is $f(\varepsilon)$, and the common notation for $f_{BE}(\varepsilon)$ is $n(\varepsilon)$. Also, note that often the energy and the frequency are considered equivalent (because $\varepsilon = \hbar\omega$), so do not be surprised if you see expressions like $f(\omega)$ or $n(\omega)$ for $f(\varepsilon)$ or $n(\varepsilon)$ respectively. In this note, we will freely go back and forth between all these notations, while the notations $f(\varepsilon)$ and $n(\varepsilon)$, or their frequency versions, will be given more weight.

Note that n is the symbol used for N/V, also. So, if n is used without any argument, then it means the number density N/V, not the Bose-Einstein function.

12.2 Fugacity

Let us define this convenient parameter.

$$z \equiv \exp(\beta\mu) \tag{12.23}$$

Note that, in either definition, the fugacity is proportional to[1] the number density of the gas *if* the gas were a classical ideal gas at the given temperature and the given chemical potential.

12.3 General expressions for E, P, N

Notice that Q_i for both fermion and boson can be written in one equation

$$Q_{i,\eta} = \left(1 - \eta z e^{-\beta\varepsilon_i}\right)^{-\eta} \tag{12.24}$$

if we introduce a sign variable, $\eta = 1$ for boson and -1 for fermion. Also, note that

$$\overline{\langle n_i \rangle}_\eta = \frac{1}{z^{-1}\, e^{\beta\varepsilon_i} - \eta} \tag{12.25}$$

Therefore, the key thermodynamic quantities can be written as

$$\begin{aligned} PV\beta &= -\sum_i \eta \log\left(1 - \eta z e^{-\beta\varepsilon_i}\right) & (12.26)\\ N &= \sum_i \frac{1}{z^{-1}\, e^{\beta\varepsilon_i} - \eta} & (12.27)\\ E &= \sum_i \frac{\varepsilon_i}{z^{-1}\, e^{\beta\varepsilon_i} - \eta} & (12.28) \end{aligned}$$

Using the density of states, $D(\varepsilon)$, we can convert the sum into an integral, and can write

$$\begin{aligned} PV\beta &= -\eta \int d\varepsilon\, D(\varepsilon) \log\left(1 - \eta z e^{-\beta\varepsilon}\right) & (12.29)\\ N &= \int d\varepsilon\, D(\varepsilon) \frac{1}{z^{-1}\, e^{\beta\varepsilon} - \eta} & (12.30)\\ E &= \int d\varepsilon\, D(\varepsilon) \frac{\varepsilon}{z^{-1}\, e^{\beta\varepsilon} - \eta} & (12.31) \end{aligned}$$

Note that, while the expressions for both PV and E are written here for completeness, the following is quite worth noting.

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[1] Since $\exp(\beta\mu) = n\lambda^3$ for the classical ideal gas (Eq. 8.8).

For a simple power law dispersion relation, $\varepsilon(\vec{k}) \propto k^\alpha$,

$$PV = \frac{\alpha}{d} E \qquad d \text{ is the spatial dimension} \qquad (12.32)$$

The proof is an immediate generalization of the derivation given for Eq. 11.19, if one notes that $k \propto V^{-1/d}$, and is left for your exercise, which you must absolutely do! So, it is unnecessary to calculate both E and P if the dispersion has a nice standard form, since one immediately leads to another, by the above relation.

Note that the expressions given in this section are completely general. They are applicable to relativistic particles, as well. They apply whether N is an independent variable representing a conserved quantity or not.

12.4 Classical limit

Recall that the validity of the semi-classical statistical mechanics hinges on the thermal Debye wavelength scale $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ being much smaller than the average distance between particles, i.e. $n\lambda^3 \ll 1$, since, otherwise, it is not possible to consider the Newtonian mechanics at all.

This means that in the classical limit, the fugacity must be very small:

$$z = \exp(\beta\mu) = n\lambda^3 \ll 1 \qquad \text{Eq. 8.8} \qquad (12.33)$$

It follows that the classical limit is either a high temperature limit or a low density limit. And, in this limit, $\beta\mu \to -\infty$, which means that

$$\mu < 0 \quad \text{and} \quad |\mu| \gg k_B T \qquad \text{classical limit} \qquad (12.34)$$

In other words, in the classical limit, the chemical potential is a very large negative number.

Now, we wish to examine the equation of state in the classical limit. Note that in the previous section, we obtained general expressions for both P and N. In the classical limit, it makes sense to consider an expansion in z.

It is quite clear what to do, starting from Eqs. 12.29, 12.30. Using the expansions

$$\log\left(1+z'e^{-\beta\varepsilon}\right) = -\sum_{j=1}^{\infty}\frac{(-z'e^{-\beta\varepsilon})^j}{j} \tag{12.35}$$

$$\frac{1}{z'^{-1}\,e^{\beta\varepsilon}+1} = z'e^{-\beta\varepsilon}\sum_{j=0}^{\infty}(-z'e^{-\beta\varepsilon})^j = -\sum_{j=1}^{\infty}(-z'e^{-\beta\varepsilon})^j \tag{12.36}$$

where $z' \equiv -z\eta$, we get

$$P\beta = \sum_{j=1}^{\infty}\frac{\eta^{j+1}a_j}{j}\,z^j \tag{12.37}$$

$$n = \frac{N}{V} = \sum_{j=1}^{\infty}\eta^{j+1}a_j\,z^j \tag{12.38}$$

$$a_j \equiv \frac{1}{V}\int d\varepsilon D(\varepsilon)e^{-j\beta\varepsilon} \tag{12.39}$$

Note that a_j, defined here, is an intensive quantity that must have the dimension of the density. It is well-defined by the exponentially decreasing function, as long as ε is bounded from below. And, it is a strictly positive number.

To find the equation of state, we seek to express $P\beta$ as a function of n, not z. To express P in powers of n, all we need to do is to invert the equation for n to express z in terms of n, and then plug that result into the above expression for P. The resulting expansion of $P\beta$ in terms of n is called the **virial expansion**.

To first order in n, we get

$$z \approx \frac{n}{a_1} \qquad \text{up to 1st order} \tag{12.40}$$

$$P\beta \approx n \qquad \text{up to 1st order} \tag{12.41}$$

which are, of course, the equations for the classical ideal gas, as expected. Note that $a_1 z = n_{semi-classical}(\mu)$, i.e. the density of the classical gas that has the same chemical potential as the quantum system that we are dealing with here. To get the leading order quantum correction, we proceed as

$$z = \frac{n}{a_1} - \frac{1}{a_1}\sum_{j=2}^{\infty}\eta^{j+1}a_j\,z^j \qquad \text{just a re-write of Eq. 12.38} \tag{12.42}$$

$$z \approx \frac{n}{a_1}\left(1-\eta\,\frac{a_2}{a_1^2}\,n\right) \qquad \text{up to 2nd order} \tag{12.43}$$

$$P\beta \approx a_1 z^{(2)} + \frac{\eta}{2}a_2\left(z^{(1)}\right)^2 = n - \frac{\eta}{2}\,\frac{a_2}{a_1^2}\,n^2 \qquad \text{up to 2nd order} \tag{12.44}$$

Note that the expansion above can be generalized to any order. Also, the expression given here is valid for *any* density of states.

The last result shows that the pressure increases by the factor $\frac{1}{2}\frac{a_2}{a_1^2}n^2$ for fermions ($\eta = -1$) and decreases by the same factor for bosons ($\eta = 1$). So, this is the leading order quantum mechanical result: the quantum statistics acts as an effective repulsive interaction for fermions and an effective attractive interaction for bosons.

To calculate the values of a_j's we need to specify the dispersion relation. As an example, let us take the case when $\varepsilon(\vec{k}) = \hbar^2 k^2/(2m)$ and the spatial dimension is 3. This is the case of non-relativistic particles in three dimensions. In this case, the total number of states up to energy ε is given by $N_s = \frac{4\pi k^3}{3}/\frac{8\pi^3}{V} = V\frac{4\pi(2m\varepsilon)^{3/2}}{3h^3}$. By taking the ε-derivative, and taking into consideration of any spin degeneracy g, we get

$$D(\varepsilon) = Vg\frac{2\pi(2m)^{3/2}}{h^3}\varepsilon^{1/2} \tag{12.45}$$

$$a_j = \frac{1}{V}\int d\varepsilon D(\varepsilon)e^{-j\beta\varepsilon} = \left(\frac{k_BT}{j}\right)^{3/2} g\frac{2\pi(2m)^{3/2}}{h^3}\int_0^\infty dx\, x^{1/2}e^{-x} \tag{12.46}$$

Using $\int_0^\infty dx\, x^{1/2}e^{-x} = \left(\frac{1}{2}\right)! = \frac{\sqrt{\pi}}{2}$, we get

$$a_j = \left(\frac{k_BT}{j}\right)^{3/2} g\frac{(2m\pi)^{3/2}}{h^3} = \frac{g}{j^{3/2}\lambda^3} \tag{12.47}$$

So, the second virial coefficient from quantum statistics is given by

$$-\frac{\eta}{2}\frac{a_2}{a_1^2} = -\frac{\eta}{4\sqrt{2}}\frac{\lambda^3}{g} \tag{12.48}$$

Thus, in this particular case, we get

$$P\beta \approx n\left(1 - \frac{\eta}{2^{5/2}}\frac{n\lambda^3}{g}\right) \tag{12.49}$$

which agrees with Eq. 10.55 (if one uses $g = 1$, which was the assumption for Eq. 10.55), as it must, since the grand canonical ensemble considered here and the canonical ensemble considered for Eq. 10.55 must give the same result in the thermodynamic limit.

One mathematical point is worth noting here. By re-examining the above calculation of a_j, one can write down the following general expression, which will prove handy later on.

$$\frac{1}{V}\int_0^\infty d\varepsilon D(\varepsilon)F(\varepsilon) = \frac{g}{\lambda^3\left(\frac{1}{2}\right)!}\int_0^\infty dx x^{1/2}\mathcal{F}(x) \tag{12.50}$$

where $\mathcal{F}(x) = F(\varepsilon = x/\beta)$ is the mere consequence of substituting the variable $x = \beta\varepsilon$ on function $F(\varepsilon)$. This identity is a mathematical identity valid in quantum regime as well as in classical regime.