Lecture 36:
Monday, April 20, 2020

In the last lecture, we worked out that

$$N(\mu) = \int \mathrm{d}\epsilon \, \frac{D(\epsilon)}{e^{\beta(\epsilon-\mu)} \pm 1}$$

for Fermions and Bosons. This equation is often used to find μ as a function of N. This is useful if we with to re-express things as a function of N, since we lost this control when we moved to the grand canonical ensemble.

What is the average energy? To do this, note that

$$\begin{aligned}
\frac{\partial}{\partial \beta} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) &= \frac{\pm e^{-\beta(\epsilon-\mu)}}{1 \pm e^{-\beta(\epsilon-\mu)}}(-(\epsilon-\mu)) \\
&= \mp f_{\pm}(\epsilon-\mu)(\epsilon-\mu) \\
&\implies \epsilon f_{\pm}(\epsilon-\mu) = \mp \frac{\partial}{\partial \beta} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) + \mu f_{\pm}(\epsilon-\mu)
\end{aligned}$$

$$\begin{aligned}
E = \langle H \rangle &= \sum_{\alpha} \epsilon_{\alpha} \langle n_{\alpha} \rangle \\
&= \int \mathrm{d}\epsilon \, D(\epsilon) \epsilon f_{\pm}(\epsilon-\mu) \\
&= \int \mathrm{d}\epsilon \, D(\epsilon) \left[\mp \frac{\partial}{\partial \beta} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) + \mu f_{\pm}(\epsilon-\mu)\right] \\
&= \underbrace{\frac{\partial \beta \Omega}{\partial \beta}}_{E-\mu N} - \mu \underbrace{\frac{\partial \Omega}{\partial \mu}}_{-N}
\end{aligned}$$

0.1 Density of States for Free Particles in a Cubic Box

In general, we can do this for a box with volume $V = L^d$ for any dimension d. We know that the energy levels should be

$$\frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\vec{\mathbf{n}}\right)^2 \qquad \vec{\mathbf{n}} \in \mathbb{N}_0^d - \{\vec{\mathbf{0}}\}$$

Therefore,

$$\begin{aligned}
D(\epsilon) &= \int_{\mathbb{R}_+^d} \mathrm{d}^d n \, \delta\left(\epsilon - \frac{\hbar^2 \pi^2}{2mL^2} \vec{\mathbf{n}}^2\right) \\
&= \frac{1}{2^d} \int_{\mathbb{R}^d} \delta\left(\epsilon - \frac{\hbar^2 \pi^2}{2mL^2} \vec{\mathbf{n}}^2\right) \\
y^2 = \frac{\hbar^2 \pi^2}{2mL^2} n^2 & \qquad \mathrm{d}y = \frac{\pi \hbar}{\sqrt{2mL^2}} \mathrm{d}n \\
D(\epsilon) &= \frac{1}{2^d} \int \mathrm{d}^d y \left(\frac{\sqrt{2m}L}{\pi \hbar}\right)^d \delta(\epsilon - y^2) \\
&= \frac{1}{2^d} \left(\frac{\sqrt{2m}}{\pi \hbar}\right)^d V \int_0^{\infty} \mathrm{d}y \, A_d y^{d-1} \delta(\epsilon - y^2) \\
x = y^2 & \qquad \mathrm{d}y = \frac{1}{2\sqrt{x}} \mathrm{d}x
\end{aligned}$$

$$
\begin{aligned}
D(\epsilon) &= \frac{1}{2^d}\left(\frac{\sqrt{2m}}{\pi\hbar}\right)^d V\int_0^\infty \frac{\mathrm{d}x}{2\sqrt{x}} A_d x^{\frac{d-1}{2}}\delta(\epsilon - x) \\
&= \frac{1}{2}\frac{(2m)^{d/2}}{h^d} V A_d \epsilon^{d/2-1}
\end{aligned}
$$

Recall that the surface area of a d-sphere is

$$
A_d = \frac{2\pi^{d/2}}{\Gamma\left(\frac{d}{2}\right)}
$$

so

$$
D(\epsilon) = \left(\frac{\sqrt{2\pi m}}{h}\right)^d \frac{V}{\Gamma\left(\frac{d}{2}\right)}\epsilon^{\frac{d}{2}-1}
$$

This expression does not include any mention of spin, which may be important later.

0.1.1 The Equation of Clapeyron

Recall that $D(\epsilon) = c_d \epsilon^{d/2-1}$. Because of this, we can write

$$
D(\epsilon) = \frac{2}{d}\left[\frac{\mathrm{d}}{\mathrm{d}\epsilon}(\epsilon D(\epsilon))\right]
$$

$$
PV = -\Omega = \pm k_B T \int_0^\infty \mathrm{d}\epsilon\, D(\epsilon) \ln\Big(1 \pm e^{-\beta(\epsilon-\mu)}\Big)
$$

Now we ware going to insert this weird rewriting of $D(\epsilon)$:

$$
\begin{aligned}
PV &= \pm k_B T \frac{2}{d}\int_0^\infty \mathrm{d}\epsilon\, \frac{\mathrm{d}}{\mathrm{d}\epsilon}(\epsilon D(\epsilon)) \ln\Big(1 \pm e^{-\beta(\epsilon-\mu)}\Big) \\
&= \mp k_B T \frac{2}{d}\int_0^\infty \mathrm{d}\epsilon\, \epsilon D(\epsilon) \frac{\mp\beta e^{-\beta(\epsilon-\mu)}}{1 \pm e^{-\beta(\epsilon-\mu)}} \\
&= \frac{2}{d}\int \mathrm{d}\epsilon\, \epsilon D(\epsilon) f_{\pm}(\epsilon - \mu) \\
&= \frac{2}{d}E
\end{aligned}
$$

so

$$
E = \frac{d}{2}PV
$$

This is incredible, since this is exactly the classical result, but we derived it using quantum statistics.

0.1.2 Grand Potential of a Free Ideal Quantum Gas

$$
\Omega(T, V, \mu) = \mp k_B T \int_0^\infty \mathrm{d}\epsilon\, D(\epsilon) \ln\Big(1 \pm e^{-\beta(\epsilon-\mu)}\Big)
$$

Define

$$
z \equiv e^{\beta\mu}
$$

as the “fugacity” and

$$
D(\epsilon) = (2s+1)\left(\frac{\sqrt{2\pi m}}{h}\right)^d \frac{V}{\Gamma\left(\frac{d}{2}\right)}\epsilon^{d/2-1}
$$

including the spin degeneracy.

$$\Omega = \mp k_B T(2s+1)\left(\frac{\sqrt{2\pi m}}{h}\right)^d \frac{V}{\Gamma\left(\frac{d}{2}\right)} \int \mathrm{d}\epsilon\, \epsilon^{\frac{d}{2}-1} \ln\bigl(1 \pm z e^{-\beta\epsilon}\bigr)$$
$$(t = \beta\epsilon \qquad \mathrm{d}t = \beta\, \mathrm{d}\epsilon)$$
$$\Omega = \mp k_B T(2s+1)\left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^d V \underbrace{\frac{1}{\Gamma\left(\frac{d}{2}\right)} \int_0^\infty \mathrm{d}t\, t^{\frac{d}{2}-1} \ln\bigl(1 \pm z e^{-t}\bigr)}_{-L_{\frac{d}{2}-1}(\mp z)}$$

where $L_\nu(z)$ is a polylogarithm.

$$\Omega(T,V,\mu) = \pm k_B T(2s+1)\frac{V}{\lambda_{\mathrm{th}}^d} L_{\frac{d}{2}+1}(\mp Z)$$

Now we can use some of the properties of the polylog:

$$\frac{PV}{k_B T} = -\beta\Omega = \mp(2s+1)\frac{V}{\lambda_{\mathrm{th}}^d} L_{\frac{d}{2}+1}(\mp z)$$

and

$$N = -\frac{\partial\Omega}{\partial\mu} = z\frac{\partial}{\partial z}(-\beta\Omega) = \mp(2s+1)\frac{V}{\lambda_{\mathrm{th}}^d} L_{\frac{d}{2}}(\mp z)$$

These two equations can be seen as a parametric representation of the thermal equation of state (with z being the parameter). If we take the ratio of these equations, we find that

$$\frac{PV}{N k_B T} = \frac{L_{\frac{d}{2}+1}(\mp z)}{L_{\frac{d}{2}}(\mp z)} = \begin{cases} \geq 1 & \text{Fermions} \\ = 1 & \text{Boltzmann (Classical)} \\ \leq 1 & \text{Bosons} \end{cases}$$

In the case of Fermi/Bose statistics, we find an additional repulsions/attraction between particles which is not present in the classical case.