Physics 305, Fall 2008
Fermi-Dirac and Bose-Einstein Distributions

Studying for the graduate preliminary examination here at Princeton many years ago, it seemed to me that all of statistical physics from an undergraduate problem set solving point of view could be boiled down to the following equation

$$\langle O \rangle = \int_0^\infty \mathcal{D}(\epsilon) f(\epsilon) O(\epsilon) d\epsilon \; . \tag{1}$$

This equation computes the average value of some observable O for a statistical ensemble of physical systems. The quantity $\mathcal{D}(\epsilon)$ is the density of states as a function of energy. Thus $\mathcal{D}(\epsilon)d\epsilon$ is the number of available states between ϵ and $\epsilon + d\epsilon$. The distribution $f(\epsilon)$ gives the average number of particles in those states. By integrating $O(\epsilon)$ with respect to this measure $\mathcal{D}(\epsilon)f(\epsilon)d\epsilon$, we are computing an average value for the ensemble of systems. For example, if we take $O(\epsilon) = 1$, we are computing the average number of particles in the system. Or if we take $O(\epsilon) = \epsilon$, we are computing an average energy. Clearly, there is more to statistical physics than Eq. (1). To pick an obvious inadequacy, if we were interested in computing momentum dependent quantities, it would be a good idea to take a step backward and convert the integral into an integral over the allowed momenta of the system. Nonetheless, I have found Eq. (1) to be a useful starting point for focusing my thoughts, and it has the advantage of being logical and fairly easy to remember.

The point of these notes was to discuss the distribution functions $f(\epsilon)$, presenting an alternate derivation to the one in Griffiths 5.4. There are two extremely important cases in statistical physics, the Fermi-Dirac and Bose-Einstein distributions,

$$f_{\mathrm{FD}}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/T} + 1} \; , \tag{2}$$

$$f_{\mathrm{BE}}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/T} - 1} \; . \tag{3}$$

The Fermi-Dirac distribution describes the average number of fermions in a quantum state of energy ϵ; note $0 \leq f_{\mathrm{FD}} \leq 1$. The Bose-Einstein distribution describes the average number of bosons in a quantum state of energy ϵ; note $f_{\mathrm{BE}} \geq 0$ provided $\mu < \epsilon$ and occasionally f_{BE} is much greater than one.

To derive, f_{FD} and f_{BE}, my first step will be to derive the Boltzmann factor in the grand canonical ensemble. The Boltzmann factor is the probability that a state with energy ϵ and N particles is occupied at a given temperature T and chemical potential μ:

$$P \sim e^{-\epsilon/T + N\mu/T} \; .$$

(I work in units where the Boltzmann factor $k_B = 1$ and thus find that temperature is measured in units of energy.) I have just used a lot of words without defining them. Most of you have an intuitive sense of what T is. The chemical potential and the grand canonical ensemble are more elusive notions which we will presently make more precise. We will also provide a precise if unintuitive notion of temperature.

I want to consider a large reservoir with energy ϵ_r and N_r particles. By exchanging energy and particles, this reservoir is allowed to come into equilibrium with a small system of energy ϵ_s and N_s particles. By large and small, I mean more precisely that $\epsilon_r \gg \epsilon_s$ and $N_r \gg N_s$. The ensemble of systems produced in this way is usually referred to as the grand canonical ensemble. If one insists that only energy and no particles can be exchanged between the system and reservoir, the ensemble of systems is called instead the canonical ensemble.

Consider $P(\epsilon_r, N_r, \epsilon_s, N_s)$, the total number of states with energies ϵ_r and ϵ_s and N_r and N_s particles. Clearly

$$P(\epsilon_r, N_r, \epsilon_s, N_s) = P_r(\epsilon_r, N_r)P_s(\epsilon_s, N_s)$$

where P_r and P_s are the numbers of states in the reservoir and system respectively. We expect the total energy and particle number are conserved. Hence $N = N_r + N_s$ and $\epsilon = \epsilon_r + \epsilon_s$. If we could count up all the different possible P with a fixed ϵ and N, then dividing this particular P by the total number of states would yield a probability.

By equilibrium, we mean we expect the reservoir to occupy the most probable set of states. The condition for equilibrium is thus the requirement that P be at a maximum subject to the constraints on total energy and particle number. Because the logarithm is a monotonic function, the condition P be a maximum is the same as the condition $\ln P$ be a maximum. Let's define the entropy of the system to be $S \equiv \ln P$ and maximize S instead. We will use the method of Lagrange multipliers. Define

$$Q \equiv S_r(\epsilon_r, N_r) + S_s(\epsilon_s, N_s) + (N - N_r - N_s)\alpha + (\epsilon - \epsilon_r - \epsilon_s)\beta .$$

The conditions for a critical point are

$$\frac{\partial Q}{\partial \epsilon_r} = \frac{\partial Q}{\partial \epsilon_s} = 0 \qquad \text{and} \qquad \frac{\partial Q}{\partial N_r} = \frac{\partial Q}{\partial N_s} = 0 .$$

Thus we find that

$$\frac{\partial S_r}{\partial \epsilon_r} = \beta = \frac{\partial S_s}{\partial \epsilon_s} \tag{4}$$

and

$$\frac{\partial S_r}{\partial N_r} = \alpha = \frac{\partial S_s}{\partial N_s} . \tag{5}$$

Now we are ready to give formal definitions of temperature and chemical potential. The temperature is related to the Lagrange multiplier that enforces energy conservation:

$$T \equiv \frac{1}{\beta} .$$

The chemical potential is related to the Lagrange multiplier that enforces particle number conservation:

$$\mu \equiv -\alpha T .$$

Physically, Eq. (4) is the requirement that at equilibrium, the system and reservoir be at the same temperature while Eq. (5) is the requirement that at equilibrium, the system and reservoir be at the same chemical potential.

Given these requirements for a maximum, we can now derive the Boltzmann factor:

$$
\begin{aligned}
P &= P_r(\epsilon - \epsilon_s, N - N_s)P_s(\epsilon_s, N_s) \\
&= \exp\left(S_r(\epsilon - \epsilon_s, N - N_s) + S_s(\epsilon_s, N_s)\right) \\
&\approx \exp\left(S_r(\epsilon, N) + S_s(\epsilon_s, N_s) - \epsilon_s \frac{\partial S_r}{\partial \epsilon} - N_s \frac{\partial S_r}{\partial N}\right) \\
&= \exp\left(S_r(\epsilon, N) + S_s(\epsilon_s, N_s)\right)\exp\left(-\epsilon_s/T + N_s\mu/T\right) .
\end{aligned}
$$

The factor e^{S_r} is a constant given that energy and particle number are fixed. The factor of $e^{S_s(\epsilon_s, N_s)}$ is essentially the density of states factor $\mathcal{D}(\epsilon)d\epsilon$ in Eq. (1). We are free to look at a system with a single state, in which case $e^{S_s} = 1$, and the main variation in the probability comes from the Boltzmann factor $P \sim e^{(-\epsilon_s + N_s\mu)/T}$. We emphasize again this expression for P is not properly normalized; we have to add up the P's for all the different ϵ_s and N_s and divide by this number to get a probability.

With the Boltzmann factor, we can derive the distributions f_{FD} and f_{BE}. Consider first the Fermi-Dirac distribution. We take our system to be a single quantum state of energy ϵ, dropping the subscript s. From the Pauli exclusion principle, the state can contain either one fermion or zero fermions. Thus, the average number of particles in the state is

$$
f_{\mathrm{FD}} = \langle N \rangle = \frac{e^{-\epsilon/T + \mu/T}}{1 + e^{-\epsilon/T + \mu/T}} = \frac{1}{e^{(\epsilon - \mu)/T} + 1} .
$$

For the Bose-Einstein distribution, the calculation is only slightly more complicated. Take again our system to be a single quantum state of energy ϵ. Now this state can have an arbitrary number n of bosons in it. The average number of particles is

$$
f_{\mathrm{BE}} = \langle N \rangle = \frac{\sum_{n=0}^{\infty} n e^{-\epsilon n/T + \mu n/T}}{\sum_{n=0}^{\infty} e^{-\epsilon n/T + \mu n/T}} .
$$

To evaluate these sums, note first the familiar result for geometric series

$$
\sum_{n=0}^{\infty} e^{-n\alpha} = \frac{1}{1 - e^{-\alpha}} .
$$

Now the series in the numerator of our expression for f_{BE} can be identified as a derivative of the series in the denominator:

$$
\sum_{n=0}^{\infty} n e^{-n\alpha} = -\frac{\partial}{\partial \alpha} \sum_{n=0}^{\infty} e^{-n\alpha} = \frac{\partial}{\partial \alpha}\left(\frac{1}{e^{-\alpha} - 1}\right) = \frac{e^{-\alpha}}{(e^{-\alpha} - 1)^2} .
$$

Thus we obtain our final result for the Bose-Einstein distribution:

$$
f_{\mathrm{BE}} = \frac{1}{e^{(\epsilon - \mu)/T} - 1} .
$$

Conservation of energy and particle number in the above discussion played a crucial role. What makes particle number conserved in our non-relativistic treatment is the mass

of the particle. It is extremely unlikely, given the Boltzmann suppression, to pop a particle with rest energy mc^2 out of the vacuum provided $mc^2 \gg T$. At very high temperatures, where $T \gg mc^2$, particle number is no longer conserved. However there may be charges, for example electric charge, which are. Even at extremely high temperatures, a single electron cannot pop out of the vacuum. However, an electron-positron pair may since then the total electric charge remains unchanged.

A photon gas is an important example where particle number is not conserved at any temperature. Photons are massless and thus fundamentally relativistic. One cannot work in the grand canonical ensemble for a photon gas. The chemical potential is not well-defined. Thus one works in the canonical ensemble and sets $\mu = 0$ in the distribution f_{BE} above.