5 Quantum Statistics : Summary

• *Second-quantized Hamiltonians*: A noninteracting quantum system is described by a Hamiltonian $\hat{H} = \sum_\alpha \varepsilon_\alpha \, \hat{n}_\alpha$, where ε_α is the energy eigenvalue for the single particle state ψ_α (possibly degenerate), and $\hat{n}_\alpha$ is the number operator. Many-body eigenstates $|\vec{n}\rangle$ are labeled by the set of occupancies $\vec{n} = \{n_\alpha\}$, with $\hat{n}_\alpha \, |\vec{n}\rangle = n_\alpha |\vec{n}\rangle$. Thus, $\hat{H} \, |\vec{n}\rangle = E_{\vec{n}} \, |\vec{n}\rangle$, where $E_{\vec{n}} = \sum_\alpha n_\alpha \, \varepsilon_\alpha$.

• *Bosons and fermions*: The allowed values for n_α are $n_\alpha \in \{0, 1, 2, \ldots, \infty\}$ for bosons and $n_\alpha \in \{0, 1\}$ for fermions.

• *Grand canonical ensemble*: Because of the constraint $\sum_\alpha n_\alpha = N$, the ordinary canonical ensemble is inconvenient. Rather, we use the grand canonical ensemble, in which case

$$\Omega(T, V, \mu) = \pm k_B T \sum_\alpha \ln\Big(1 \mp e^{-(\varepsilon_\alpha - \mu)/k_B T}\Big) \quad ,$$

where the upper sign corresponds to bosons and the lower sign to fermions. The average number of particles occupying the single particle state ψ_α is then

$$\langle \hat{n}_\alpha \rangle = \frac{\partial \Omega}{\partial \varepsilon_\alpha} = \frac{1}{e^{(\varepsilon_\alpha - \mu)/k_B T} \mp 1} \quad .$$

In the Maxwell-Boltzmann limit, $\mu \ll -k_B T$ and $\langle n_\alpha \rangle = z \, e^{-\varepsilon_\alpha / k_B T}$, where $z = e^{\mu / k_B T}$ is the fugacity. Note that this low-density limit is common to both bosons and fermions.

• *Single particle density of states*: The single particle density of states per unit volume is defined to be

$$g(\varepsilon) = \frac{1}{V} \, \mathsf{Tr} \; \delta(\varepsilon - \hat{h}) = \frac{1}{V} \sum_\alpha \delta(\varepsilon - \varepsilon_\alpha) \quad ,$$

where $\hat{h}$ is the one-body Hamiltonian. If $\hat{h}$ is isotropic, then $\varepsilon = \varepsilon(k)$, where $k = |\boldsymbol{k}|$ is the magnitude of the wavevector, and

$$g(\varepsilon) = \frac{\mathsf{g} \, \Omega_d}{(2\pi)^d} \, \frac{k^{d-1}}{d\varepsilon / dk} \quad ,$$

where g is the degeneracy of each single particle energy state (due to spin, for example).

• *Quantum virial expansion*: From $\Omega = -pV$, we have

$$n(T, z) = \int\limits_{-\infty}^{\infty} \! d\varepsilon \, \frac{g(\varepsilon)}{z^{-1} \, e^{\varepsilon / k_B T} \mp 1} = \sum_{j=1}^{\infty} (\pm 1)^{j-1} \, z^j \, C_j(T)$$

$$\frac{p(T, z)}{k_B T} = \mp \int\limits_{-\infty}^{\infty} \! d\varepsilon \; g(\varepsilon) \; \ln\big(1 \mp z \, e^{-\varepsilon / k_B T}\big) = \sum_{j=1}^{\infty} (\pm 1)^{j-1} \, \frac{z^j}{j} \, C_j(T) \quad ,$$

where

$$C_j(T) = \int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon)\, e^{-j\varepsilon/k_B T} \quad .$$

One now inverts $n = n(T,z)$ to obtain $z = z(T,n)$, then substitutes this into $p = p(T,z)$ to obtain a series expansion for the equation of state,

$$p(T,n) = nk_B T\Big(1 + B_2(T)\, n + B_3(T)\, n^2 + \ldots\Big) \quad .$$

The coefficients $B_j(T)$ are the *virial coefficients*. One finds

$$B_2 = \mp\frac{C_2}{2C_1^2} \quad , \quad B_3 = \frac{C_2^2}{C_1^4} - \frac{2\,C_3}{2\,C_1^3} \quad .$$

• *Photon statistics*: Photons are bosonic excitations whose number is not conserved, hence $\mu = 0$. The number distribution for photon statistics is then $n(\varepsilon) = 1/(e^{\beta\varepsilon} - 1)$. Examples of particles obeying photon statistics include phonons (lattice vibrations), magnons (spin waves), and of course photons themselves, for which $\varepsilon(k) = \hbar ck$ with $\mathsf{g} = 2$. The pressure and number density for the photon gas obey $p(T) = A_d\, T^{d+1}$ and $n(T) = A'_d\, T^d$, where d is the dimension of space and A_d and A'_d are constants.

• *Blackbody radiation*: The energy density per unit frequency of a three-dimensional blackbody is givenP by

$$\varepsilon(\nu,T) = \frac{8\pi h}{c^3} \cdot \frac{\nu^3}{e^{h\nu/k_B T} - 1} \quad .$$

The total power emitted per unit area of a blackbody is $\frac{dP}{dA} = \sigma T^4$, where $\sigma = \pi^2 k_B^4/60\hbar^3 c^2 = 5.67 \times 10^{-8}\ \mathrm{W/m^2\,K^4}$ is Stefan's constant.

• *Ideal Bose gas*: For Bose systems, we must have $\varepsilon_\alpha > \mu$ for all single particle states. The number density is

$$n(T,\mu) = \int_{-\infty}^{\infty} d\varepsilon \, \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)} - 1} \quad .$$

This is an increasing function of μ and an increasing function of T. For fixed T, the largest value $n(T,\mu)$ can attain is $n(T,\varepsilon_0)$, where ε_0 is the lowest possible single particle energy, for which $g(\varepsilon) = 0$ for $\varepsilon < \varepsilon_0$. If $n_c(T) \equiv n(T,\varepsilon_0) < \infty$, this establishes a *critical density* above which there is *Bose condensation* into the energy ε_0 state. Conversely, for a given density n there is a *critical temperature* $T_c(n)$ such that n_0 is finite for $T < T_c$. For $T < T_c$, $n = n_0 + n_c(T)$, with $\mu = \varepsilon_0$. For $T > T_c$, $n(T,\mu)$ is given by the integral formula above, with $n_0 = 0$. For a ballistic dispersion $\varepsilon(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m$, one finds $n\lambda^d_{T_c} = \mathsf{g}\,\zeta(d/2)$, *i.e.* $k_B T_c = \frac{2\pi\hbar^2}{m}\big(n/\mathsf{g}\,\zeta(d/2)\big)^{2/d}$. For $T < T_c(n)$, one has $n_0 = n - \mathsf{g}\,\zeta(\frac{1}{2}d)\,\lambda_T^{-d} = n\big(1 - (T/T_c)^{d/2}\big)$ and $p = \mathsf{g}\,\zeta(1 + \frac{1}{2}d)\,k_B T\,\lambda_T^{-d}$. For $T > T_c(n)$, one has $n = \mathsf{g}\,\mathrm{Li}_{\frac{d}{2}}(z)\,\lambda_T^{-d}$ and $p = \mathsf{g}\,\mathrm{Li}_{\frac{d}{2}+1}(z)\,k_B T\,\lambda_T^{-d}$, where

$$\mathrm{Li}_q(z) \equiv \sum_{n=1}^{\infty} \frac{z^n}{n^q}.$$

• *Ideal Fermi gas*: The Fermi distribution is $n(\varepsilon) = f(\varepsilon - \mu) = 1\big/\big(e^{(\varepsilon-\mu)/k_{\rm B}T} + 1\big)$. At $T = 0$, this is a step function: $n(\varepsilon) = \Theta(\mu - \varepsilon)$, and $n = \int\limits_{-\infty}^{\mu} d\varepsilon\, g(\varepsilon)$. The chemical potential at $T = 0$ is called the *Fermi energy*: $\mu(T = 0, n) = \varepsilon_{\rm F}(n)$. If the dispersion is $\varepsilon(\boldsymbol{k})$, the locus of $\boldsymbol{k}$ values satisfying $\varepsilon(\boldsymbol{k}) = \varepsilon_{\rm F}$ is called the *Fermi surface*. For an isotropic and monotonic dispersion $\varepsilon(k)$, the Fermi surface is a sphere of radius $k_{\rm F}$, the *Fermi wavevector*. For isotropic three-dimensional systems, $k_{\rm F} = (6\pi^2 n/{\rm g})^{1/3}$.

• *Sommerfeld expansion*: Let $\phi(\varepsilon) = \frac{d\Phi}{d\varepsilon}$. Then

$$\begin{aligned}\int\limits_{-\infty}^{\infty} d\varepsilon\, f(\varepsilon - \mu)\,\phi(\varepsilon) &= \pi D \csc(\pi D)\,\Phi(\mu)\\ &= \left\{1 + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\,\frac{d^2}{d\mu^2} + \frac{7\pi^4}{360}\,(k_{\rm B}T)^4\,\frac{d^4}{d\mu^4} + \ldots\right\}\Phi(\mu) \quad ,\end{aligned}$$

where $D = k_{\rm B}T\,\frac{d}{d\mu}$. One then finds, for example, $C_V = \gamma V T$ with $\gamma = \frac{1}{3}\pi^2 k_{\rm B}^2\, g(\varepsilon_{\rm F})$.