Quantum Statistics of Identical Particles

• *Introduction:* We have already seen the important consequences that the indistinguishability of identical particles has for the entropy of a system. In quantum theory, however, Boltzmann's procedure of simply including an $N!$ factor in the counting of states needs to be changed, because (i) It does not lead to correct results when particle states are discrete, and (ii) There are two different types of particles, as regards their statistics. We now set up the formalism needed to discuss this point, and its effect on thermodynamics.

Quantum States for Identical Particles

• *Particle permutations:* One way to write down an N-particle state is to specify a complete set of variables for each particle, for example $\psi(\mathbf{r}_1, ..., \mathbf{r}_N)$. If we permute the labels of the particles, $\{1, ..., N\} \mapsto P\{1, ..., N\} = \{P1, ..., PN\}$, the state must be physically indistinguishable, so $|\psi(\mathbf{r}_{P1}, ..., \mathbf{r}_{PN})| = |\psi(\mathbf{r}_1, ..., \mathbf{r}_N)|$. If the permutation consists in exchanging just two particles we get only two possibilities, $\psi(..., \mathbf{r}_{Pi}, ..., \mathbf{r}_{Pj}, ...) = \pm\,\psi(..., \mathbf{r}_i, ..., \mathbf{r}_j, ...)$, which implies that more generally, if $[P]$ is the parity of P,

$$\psi(\mathbf{r}_{P1}, ..., \mathbf{r}_{PN}) = (\pm 1)^{[P]}\,\psi(\mathbf{r}_1, ..., \mathbf{r}_N)\ .$$

• *Fermions and Bosons:* It is experimentally seen, and can be shown, that particles whose spin is an integer multiple of $\hbar$ satisfy this equation with the upper (+) sign. They are said to satisfy Bose-Einstein statistics and called bosons; examples are photons, gluons, the W and Z mesons, the Higgs boson, and all integer-spin composite particles. Particles whose spin is a half-integer multiple of $\hbar$ satisfy the equation with the lower (−) sign. They are said to satisfy Fermi-Dirac statistics and called fermions; examples are the electron, muon, neutrino, all quarks, the proton and neutron, etc. One immediate consequence of the antisymmetry of ψ for fermions is that no two of them can occupy the same state; for example, $\psi(..., \mathbf{r}, ..., \mathbf{r}, ...) = 0$ for any $\mathbf{r}$.

• *N-particle basis:* Given a choice of 1-particle basis of states $\phi_\alpha(\mathbf{r}) = \langle \mathbf{r}|\alpha\rangle$, we can define a complete set of states for N identical bosons or fermions, respectively. Each N-particle state corresponds to an unordered set of labels $\{\alpha\} = \{\alpha_1, ..., \alpha_N\}$ and, to ensure that it satisfies the appropriate property under permutations, it is obtained as a sum over all $P \in \mathcal{P}_N$, the set of permutations of the first N integers, If all α_i are different,

$$\phi_{\{\alpha\}}(\mathbf{r}_1, ..., \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_{P\in\mathcal{P}_N} (\pm 1)^{[P]}\,\phi_{\alpha_1}(\mathbf{r}_{P1}) \cdots \phi_{\alpha_N}(\mathbf{r}_{PN})\ .$$

• *Plane-wave basis:* Let us assume for now that the particles are structureless, so the state label α is just the particle's wave number $\mathbf{k}$. Then, for a particle of mass m in a rectangular box of volume $V = L_1L_2L_3$, a convenient basis is often the one in which single-particle states are plane waves $\phi_\mathbf{k}(\mathbf{r}) = \langle \mathbf{r}|\mathbf{k}\rangle = V^{-1/2}\,\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$. If we choose periodic boundary conditions at the walls (easier to handle than other ones, and physically reasonable for $L \gg \lambda$), then the allowed values of $\mathbf{k}$ are given by $k_i = (2\pi/L_i)\,n_i$, for $n_i \in \mathbf{Z}$, and

$$\phi_{\{\mathbf{k}\}}(\mathbf{r}_1, ..., \mathbf{r}_N) = \frac{1}{\sqrt{N!\,V^N}} \sum_{P\in\mathcal{P}_N} (\pm 1)^{[P]}\,\mathrm{e}^{\mathrm{i}\mathbf{k}_1\cdot\mathbf{r}_{P1}} \cdots \mathrm{e}^{\mathrm{i}\mathbf{k}_N\cdot\mathbf{r}_{PN}}\ .$$

Quantum Canonical State

• *One particle:* For a free particle of mass m the Hamiltonian is $\hat{H} = \hat{p}^2/2m$, where $\mathbf{p} = \hbar\,\mathbf{k}$ and $\mathbf{k}$ labels the single-particle states $\phi_\mathbf{k}(\mathbf{r})$. The partition function for an equilibrium state at temperature T is

$$Z_1 = \mathrm{tr}\,\mathrm{e}^{-\beta\hat{H}} = \sum_\mathbf{k} \langle \mathbf{k}|\mathrm{e}^{-\beta\hat{H}}|\mathbf{k}\rangle = \prod_{i=1}^{3} \sum_{n_i=-\infty}^{+\infty} \exp\{-(\beta h^2/2mL_i^2)\,n_i^2\}\ .$$

If the exponential varies slowly with n_i (e.g., for $T \to \infty$) the sum over n_i can be replaced by an integral.

• *More particles:* For $N > 1$ particles, we could formally write $Z_N = \mathrm{tr}\,\mathrm{e}^{-\beta\hat{H}} = \sum_{\{\mathbf{k}\}} \langle\{\mathbf{k}\}|\mathrm{e}^{-\beta\hat{H}}|\{\mathbf{k}\}\rangle$, but the sum over discrete values of $\{\mathbf{k}\}$ is made difficult to handle by the fact that we have to keep track of how many of the $\mathbf{k}$s are different in each term, and we need to come up with a more convenient approach.

Fock Space Representation

• *Idea:* Another way to write down an N-particle state, without having to deal with sums over permutations, is to specify the number N_{α_i} of particles in each single-particle state α_i, and use as basis the vectors

$$|N_{\alpha_1}, N_{\alpha_2}, ..., N_{\alpha_i}, ...\rangle \ ,$$

for all sets of non-negative integers $\{N_{\alpha_1}, N_{\alpha_2}, ..., N_{\alpha_i}, ...\}$; this is called a Fock basis for the Hilbert space.

• *Conditions on the states:* If the system has a total of N particles, and if it has a total energy E, then the set of numbers $\{N_\alpha\}$ has to satisfy the conditions

$$\textstyle\sum_\alpha N_\alpha = N \ , \qquad \sum_\alpha N_\alpha \epsilon_\alpha = E \ .$$

Quantum Grand Canonical State for Identical Particles

• *Idea:* One of the examples of systems we will see soon is that of a gas of photons, in which the temperature will be assumed known but the number of particles varies; this situation is well described by a grand canonical density matrix and it will be very convenient to use the Fock basis for the Hilbert space. But even for gases with a fixed number N of massive particles the calculation of Z becomes much simpler if we (i) use a Fock basis for the Hilbert space—which eliminates the need for summing over permutations—and (ii) allow the number of particles to range from 0 to ∞—which provides us with simple closed-form expressions for many sums over states. We therefore find it convenient to work with a grand canonical state and simply require that μ be adjusted so that the total mean number $\bar{N}$ of particles coincide with the known N.

• *Grand canonical partition function:* Using a Fock basis one can get that, for non-interacting particles,

$$Z_{\rm g} = {\rm tr}\, {\rm e}^{-\beta\hat{H}+\beta\mu\hat{N}} = \sum_{\{N_\alpha\}} {\rm e}^{\Sigma_\alpha N_\alpha(\mu-\epsilon_\alpha)\,\beta} = \prod_\alpha \begin{cases} [1-{\rm e}^{(\mu-\epsilon_\alpha)\beta}]^{-1} & \text{(bosons)} \\ 1+{\rm e}^{(\mu-\epsilon_\alpha)\beta} & \text{(fermions)}\ , \end{cases}$$

where we used $E = \sum_\alpha N_\alpha\epsilon_\alpha$ and $N = \sum_\alpha N_\alpha$, and the single-particle energies are given by $\epsilon_\alpha = \hbar^2k_\alpha^2/2m$ for massive particles (electrons, neutrinos, ...) and $\epsilon_\alpha = \hbar\omega_\alpha$ for massless particles (photons). For bosons, we must have ${\rm e}^{\beta\mu} > 0$. Notice that to use these results we need to be able to find the value of μ.

• *Number of particles:* Using the grand canonical partition function we can derive, for example, the mean total number of particles $\bar{N}$ and the mean occupation number $\bar{N}_\alpha$ for each state α. We start from the general expression for the grand potential $\Omega = \bar{E} - TS - \mu N$ in terms of the partition function,

$$\Omega = -k_{\rm B}T\, \ln Z_{\rm g} = \pm\, k_{\rm B}T \sum\nolimits_\alpha \ln[1 \mp {\rm e}^{(\mu-\epsilon_\alpha)\beta}] \ .$$

Then the mean total number of particles, from the general expression in terms of Ω, is

$$\bar{N} = -\frac{\partial\Omega}{\partial\mu}\Big|_{T,V} = \sum\nolimits_\alpha \frac{1}{{\rm e}^{(\epsilon_\alpha-\mu)\beta} \mp 1} = \sum\nolimits_\alpha \bar{N}_\alpha\ , \quad \text{where} \quad \bar{N}_\alpha = \frac{1}{{\rm e}^{(\epsilon_\alpha-\mu)\beta} \mp 1}\ .$$

In practice, we will often view this result as a relationship between $\bar{N}$ and μ, for a given β, and use it to find μ in terms of $\bar{N}$. For fermions this last expression, as a function of the energy, is called the Fermi function,

$$F(\epsilon) = \frac{1}{{\rm e}^{\beta(\epsilon-\mu)}+1}\ .$$

[Notice that from that expression we also get that for all α, $\ln(\bar{N}_\alpha \pm 1) - \ln\bar{N}_\alpha = \beta\,(\epsilon_\alpha - \mu)$.]

• *Other quantities:* We can now go on to derive thermodynamical quantities, such as the mean energy, entropy $S = -\partial\Omega/\partial T|_{V,\mu}$, heat capacity, etc, and the quantum corrections to the equation of state; we can also derive a fluctuation-response relation $(\Delta N_\alpha)^2 = k_{\rm B}T\,\partial\bar{N}_\alpha/\partial\mu|_{T,V}$. One hard part of these calculations will be evaluating the sums over modes α. However, if we can justify replacing sums by integrals over wave vectors $\mathbf{k}$ and the latter by ones over energies ϵ, and obtain an expression for the density of states $g(\epsilon)$, then those sums will be reduced to expressions of the type

$$\bar{N} = \int_0^\infty {\rm d}\epsilon\, \bar{N}(\epsilon)\, g(\epsilon)\ , \qquad \bar{E} = \int_0^\infty {\rm d}\epsilon\, \epsilon\, \bar{N}(\epsilon)\, g(\epsilon)\ .$$

Reading

• *Main textbooks:* Kennett, Chapter 7; Pathria & Beale, Chapters 5 and 6.
• *Other books:* Halley, Ch 5; Plischke & Bergersen, § 2.4; Reif, § 9.8; Schwabl, §§ 4.2–4.3.