

Physics 127a: Class Notes

Lecture 13: Ideal Quantum Gases

Quantum States

Consider an ideal gas in a box of sides L with periodic boundary conditions

$$\psi(x + L, y, z) = \psi(x, y, z) \quad \text{etc.} \quad (1)$$

For a single particle the wavefunction of the energy eigenstate satisfies

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = \varepsilon \psi \quad (2)$$

and the eigenstates are plane waves

$$\phi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{x}} \quad (3)$$

with $V = L^3$. The eigenstates are labelled by a wave vector \mathbf{k} which to satisfy the periodic boundary conditions must be of the form

$$\mathbf{k} = \frac{2\pi}{L}(l, m, n) \quad l, m, n \text{ integers (positive, negative or zero)}. \quad (4)$$

The energy eigenvalues are

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}. \quad (5)$$

For N particles we must construct the many particle wavefunction $\psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ satisfying

$$-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 \Psi = E \Psi, \quad (6)$$

the periodic boundary conditions, and in addition symmetry restrictions under the interchange of any two particles in the wavefunction

Bosons: (integer spin particles)

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_a, \dots, \mathbf{x}_b, \dots, \mathbf{x}_N) = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_b, \dots, \mathbf{x}_a, \dots, \mathbf{x}_N) \quad (7)$$

Fermions: (half integral spin particles)

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_a, \dots, \mathbf{x}_b, \dots, \mathbf{x}_N) = -\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_b, \dots, \mathbf{x}_a, \dots, \mathbf{x}_N). \quad (8)$$

Without the symmetry restriction the eigenstates would be the products of the single particle eigenstates

$$\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \phi_{\mathbf{k}_1}(\mathbf{x}_1) \phi_{\mathbf{k}_2}(\mathbf{x}_2) \dots \phi_{\mathbf{k}_N}(\mathbf{x}_N) \quad (9)$$

with \mathbf{k}_α any choice of the single particle wave vectors (not necessarily all different). The symmetry requirements are given by taken appropriate linear combinations of the product wavefunctions with the particles permuted amongst the different single particle states (these necessarily all are degenerate, so that the linear combination is also an eigenstate):

Bosons:

$$\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = C_B \sum_P P[\phi_{\mathbf{k}_1}(\mathbf{x}_1)\phi_{\mathbf{k}_2}(\mathbf{x}_2) \dots \phi_{\mathbf{k}_N}(\mathbf{x}_N)] \quad (10)$$

where P permutes the particle coordinates, the sum runs over all permutations and C_B is a normalization constant that we will not need to calculate. For example for two particles and single particle states \mathbf{k} and \mathbf{k}' with $\mathbf{k} \neq \mathbf{k}'$

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\phi_{\mathbf{k}}(\mathbf{x}_1)\phi_{\mathbf{k}'}(\mathbf{x}_2) + \phi_{\mathbf{k}}(\mathbf{x}_2)\phi_{\mathbf{k}'}(\mathbf{x}_1)]. \quad (11)$$

Fermions: It is easiest to use the *Slater determinant* notation

$$\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = C_F \begin{vmatrix} \phi_{\mathbf{k}_1}(\mathbf{x}_1) & \phi_{\mathbf{k}_1}(\mathbf{x}_2) & \dots & \phi_{\mathbf{k}_1}(\mathbf{x}_N) \\ \phi_{\mathbf{k}_2}(\mathbf{x}_1) & \phi_{\mathbf{k}_2}(\mathbf{x}_2) & \dots & \phi_{\mathbf{k}_2}(\mathbf{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{\mathbf{k}_N}(\mathbf{x}_1) & \phi_{\mathbf{k}_N}(\mathbf{x}_2) & \dots & \phi_{\mathbf{k}_N}(\mathbf{x}_N) \end{vmatrix} \quad (12)$$

with C_F another normalization constant. Note, for Fermions, all the $\phi_{\mathbf{k}_\alpha}$ must be different for a nonzero result—the *Pauli exclusion principle*.

An important consequence of the (anti)symmetrization is that the quantum state is completely specified by how many times each $\phi_{\mathbf{k}}$ appears in the wave function. We call this the *occupation number* of the state $\phi_{\mathbf{k}}$ and denote it by $n_{\mathbf{k}}$. We do not have to say which particle is associated with each single particle state as we would for distinguishable particles. The set $\{n_{\mathbf{k}}\}$ completely defines the quantum state

$$|\Phi\rangle \Leftrightarrow \{n_{\mathbf{k}}\} \quad (13)$$

and to count the states we only need to count the number of different $\{n_{\mathbf{k}}\} = \{n_k\}$. For example, for 3 Bosons in 2 single particle states we would have just *four* states $|3, 0\rangle, |2, 1\rangle, |1, 2\rangle, |0, 3\rangle$ (where $|n_1, n_2\rangle$ is the state with single particle state 1 occurring n_1 times and single particle state 2 occurring n_2 times).

Distribution of particles amongst degenerate levels

To illustrate the different counting of states for particles of different statistics we consider the problem of a set of single particle energy levels ε_i with degeneracy g_i —there are g_i single particle eigenstates at the energy ε_i . We want to calculate the number of many-particle states of N such particles, where N_i particles are in each single particle level ε_i (so that the energy of the state is $\sum_i N_i \varepsilon_i$). We call this the statistical weight $W\{N_i\}$. You can probably see where this would come up in calculating the canonical partition function for example, although in practice, it is often best to do the counting for each case needed by hand, rather than using the formulas derived below.

Bosons Each single particle state may contain 0, 1, ... N_i particles, and we have g_i “boxes” to place a total of N_i particles. The counting is easily done by representing a particular state $|n_1, n_2 \dots n_{g_i}\rangle$ by the schematic form $\bullet\bullet \mid \mid \bullet \mid \bullet\bullet \mid \dots$, where each \mid denotes the wall to a new box and each \bullet denotes a particle (so this state would be $|2, 0, 1, 2 \dots\rangle$) The number of different states is then given by the number of ways we can arrange $N_i + g_i - 1$ particles and walls along the line, so that

$$W\{N_i\} = \prod_i \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}. \quad (14)$$

Fermions Each single particle state may only contain 0 or 1 particles, so we just have to pick N_i out of the g_i states which will contain a particle

$$W\{N_i\} = \prod_i \frac{g_i!}{N_i!(g_i - N_i)!}. \quad (15)$$

Obviously $g_i \geq N_i$ for all i for the state to exist.

Boltzmann Statistics It is interesting to consider a fictitious system of distinguishable identical particles, and then reduce the statistical weight by the Gibbs factor $N!$. For distinguishable particles we first have to pick out which particles to put into each set of degenerate levels ($N! / \prod_i N_i!$ ways of choosing). Then for each particle in the i th set of levels we need to pick out which level to put it in ($g_i^{N_i}$ ways of choosing). Reducing the product by $N!$ gives

$$W\{N_i\} = \prod_i \frac{g_i^{N_i}}{N_i!}. \quad (16)$$

Note that this expression is the *large degeneracy* limit $g_i \gg N_i$, 1 of either the Boson or Fermions expressions.

Partition functions

Bose and Fermi gases Consider first the canonical partition function for an ideal Bose or Fermi gas. Since the occupation numbers $\{n_{\mathbf{p}}\}$ uniquely defines the quantum state

$$Q_N = \sum'_{\{n_{\mathbf{p}}\}} e^{-\beta \sum_{\mathbf{p}} \varepsilon_{\mathbf{p}} n_{\mathbf{p}}} \quad (17)$$

where the sum is constrained (denoted by the prime) so that $\sum_{\mathbf{p}} n_{\mathbf{p}} = N$ and for Fermions each $n_{\mathbf{p}}$ can only be 0 or 1. (For particles with spin, the label \mathbf{p} really stands for \mathbf{p}, σ with σ the spin state.) The first constraint is hard to calculate with. Instead we look at the grand canonical partition function

$$Q(T, \mu, V) = \sum_{N=0}^{\infty} \sum'_{\{n_{\mathbf{p}}\}} e^{-\beta \sum_{\mathbf{p}} (\varepsilon_{\mathbf{p}} - \mu) n_{\mathbf{p}}}. \quad (18)$$

The sum over all N effectively removes the constraint, so that

$$Q = \sum_{\{n_{\mathbf{p}}\}} e^{-\beta \sum_{\mathbf{p}} (\varepsilon_{\mathbf{p}} - \mu) n_{\mathbf{p}}} \quad (19)$$

with now the sum constrained only by statistics. The sum can now be written as a product over all momentum states

$$Q = \prod_{\mathbf{p}} Q_{\mathbf{p}} \quad (20)$$

with $Q_{\mathbf{p}}$ the grand canonical potential for the single particle state \mathbf{p}

$$Q_{\mathbf{p}} = \sum_{n_{\mathbf{p}}} e^{-\beta (\varepsilon_{\mathbf{p}} - \mu) n_{\mathbf{p}}}. \quad (21)$$

For the grand potential $\Omega = -kT \ln Q$ this gives

$$\Omega = \sum_{\mathbf{p}} \Omega_{\mathbf{p}} \quad \text{with} \quad \Omega_{\mathbf{p}} = -kT \ln Q_{\mathbf{p}}. \quad (22)$$

For Fermions the sum over $n_{\mathbf{p}}$ is just two terms, and for Bosons the sum is a geometric series. The results are

$$\Omega = \mp kT \sum_{\mathbf{p}} \ln (1 \pm e^{-\beta(\varepsilon_{\mathbf{p}} - \mu)}) \quad (23)$$

with the top sign for Fermions and the bottom sign for Bosons.

Usually we are dealing with a large system, and know the number of particles rather than the chemical potential. We can evaluate $\mu(N, T, V)$ from $\mu = -(\partial\Omega/\partial N)_{T,V}$. This gives $N = \sum_{\mathbf{p}} \langle n_{\mathbf{p}} \rangle$ with the average occupation number of the state \mathbf{p} given by

$$\langle n_{\mathbf{p}} \rangle = \frac{1}{e^{\beta(\varepsilon_{\mathbf{p}} - \mu)} \pm 1} \quad (24)$$

(with the same sign convention).

“Boltzmann statistics” For the fictitious particles where we count the states as if the particles are distinguishable, and then divide by the Gibbs $N!$ factor the statistical weight of the set of occupation numbers $\{n_{\mathbf{p}}\}$ is $\prod_{\mathbf{p}} (n_{\mathbf{p}}!)^{-1}$ (the number of ways of choosing which $n_{\mathbf{p}}$ particles to put into each single particle state \mathbf{p} , and then divide by $N!$). So

$$\mathcal{Q}(T, \mu, V) = \sum_{N=0}^{\infty} \sum'_{\{n_{\mathbf{p}}\}} \prod_{\mathbf{p}} \left(\frac{1}{n_{\mathbf{p}}!} e^{-\beta(\varepsilon_{\mathbf{p}} - \mu)n_{\mathbf{p}}} \right). \quad (25)$$

Using the same tricks as in the Bose and Fermi cases this can be rewritten as

$$\mathcal{Q} = \prod_{\mathbf{p}} \left(\sum_{n_{\mathbf{p}}} \frac{1}{n_{\mathbf{p}}!} e^{-\beta(\varepsilon_{\mathbf{p}} - \mu)n_{\mathbf{p}}} \right) \quad (26)$$

$$= \prod_{\mathbf{p}} \left(\sum_{n_{\mathbf{p}}} \frac{1}{n_{\mathbf{p}}!} (e^{-\beta(\varepsilon_{\mathbf{p}} - \mu)})^{n_{\mathbf{p}}} \right) \quad (27)$$

$$\prod_{\mathbf{p}} \exp(e^{-\beta(\varepsilon_{\mathbf{p}} - \mu)}). \quad (28)$$

The grand potential is then

$$\Omega = -kT \sum_{\mathbf{p}} e^{-\beta(\varepsilon_{\mathbf{p}} - \mu)}. \quad (29)$$

Alternatively we can write Eq. (25) using the multinomial (cf. binomial) expansion

$$\mathcal{Q}(T, \mu, V) = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\sum_{\mathbf{p}} e^{\beta(\varepsilon_{\mathbf{p}} - \mu)} \right) \quad (30)$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} Q_N \quad \text{with} \quad Q_N = \frac{Q_1^N}{N!} \quad \text{and} \quad Q_1 = \sum_{\mathbf{p}} e^{-\beta\varepsilon_{\mathbf{p}}} \quad (31)$$

giving the expression in terms of the canonical partition function of the “classical gas” we found earlier.

Note that the results can all be combined into

$$\Omega = -kT \frac{1}{a} \sum_{\mathbf{p}} \ln (1 + a e^{-\beta(\varepsilon_{\mathbf{p}} - \mu)}) \quad (32)$$

$$N = \sum_{\mathbf{p}} \frac{1}{e^{\beta(\varepsilon_{\mathbf{p}} - \mu)} + a} \quad (33)$$

with $a = -1$ for Bosons, $a = +1$ for Fermions, and $a \rightarrow 0$ for Boltzmann statistics.

Momentum Sums

For a gas in 3d in a box of sides L the allowed momenta are $\mathbf{p} = \hbar \mathbf{k}$ with $\mathbf{k} = \frac{2\pi}{L}(l, m, n)$ and l, m, n are any integers. For large N, L we can *usually* replace the discrete sum over momenta \mathbf{p} by an integral

$$\sum_{\mathbf{p}} \rightarrow \frac{V}{(2\pi\hbar)^3} \sum_{\sigma} \int \int \int dp_x dp_y dp_z, \quad (34)$$

with the spin sum remaining. If we are summing an isotropic function, such as any function of the energy $f(\varepsilon_p)$ which is spin independent as in the expressions for Ω and N

$$\sum_{\mathbf{p}} f(\varepsilon_p) = \frac{V(2s+1)V}{(2\pi\hbar)^3} \int_0^{\infty} dp 4\pi p^2 f(\varepsilon_p) \quad (35)$$

with $2s+1$ coming from the spin degeneracy. Now we can transform the p integration to an integration over the energy $\varepsilon(p) = \varepsilon_p$ to give

$$\sum_{\mathbf{p}} f(\varepsilon_p) = \int_0^{\infty} d\varepsilon \rho(\varepsilon) f(\varepsilon) \quad (36)$$

with $\rho(\varepsilon)$ the density of states (such that $\rho(\varepsilon)d\varepsilon$ is the number of single particle states between energies ε and $\varepsilon + d\varepsilon$)

$$\rho(\varepsilon) = \frac{V(2s+1)p^2}{2\pi^2\hbar^3 d\varepsilon/dp}. \quad (37)$$

For the energy spectrum $\varepsilon_p = p^2/2m$ this becomes

$$\rho(\varepsilon) = (2s+1) \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}. \quad (38)$$

The thermodynamic potential is then

$$\Omega = -kT \frac{1}{a} \int_0^{\infty} d\varepsilon \rho(\varepsilon) \ln(1 + a e^{-\beta(\varepsilon-\mu)}) \quad (39)$$

and the number of particles is

$$N = \int_0^{\infty} d\varepsilon \rho(\varepsilon) n(\varepsilon) \quad \text{with} \quad n(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + a}. \quad (40)$$

For classical particles in 3 dimensions the latter expression can be written

$$\frac{N}{V} \lambda^3 = (2s+1) \frac{2}{\pi^{1/2}} \int_0^{\infty} dy y^{1/2} \frac{1}{e^{y-\beta\mu} + a} \quad (41)$$

introducing the integration variable $y = \beta\varepsilon$, and the thermal length $\lambda = (h^2/\pi mkT)^{1/2}$. Note the right hand side is a function of $\beta\mu$, and so this implicitly fixes $\mu(T, N/V)$.