

# Statistical Physics

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## 7 Quantum ideal gas

### 7.1 Particle interchange

The indistinguishability of particles implies that the multi-particle wavefunction must be the same, up to a complex phase, as the one corresponding to an interchange of particle position. If we swap two particles which are at positions  $\mathbf{x}_1$  and  $\mathbf{x}_2$ , also swapping any internal states  $\alpha_1, \alpha_2$  they might be in (like spin) then we must have

$$\Psi(\mathbf{x}_2, \alpha_2, \mathbf{x}_1, \alpha_1, \dots, \mathbf{x}_N, \alpha_N; t) = e^{i\theta} \Psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, \dots, \mathbf{x}_N, \alpha_N; t). \quad (7.1.1)$$

In nature, only 2 values for  $\theta$  are observed (leaving aside composite excitations in 2 dimensions, called anyons):

$$\Psi(\mathbf{x}_2, \alpha_2, \mathbf{x}_1, \alpha_1, \dots, \mathbf{x}_N, \alpha_N; t) = \begin{cases} +\Psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, \dots, \mathbf{x}_N, \alpha_N; t) & \text{bosons} \\ -\Psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, \dots, \mathbf{x}_N, \alpha_N; t) & \text{fermions} \end{cases} \quad (7.1.2)$$

The spin-statistics theorem of quantum field theory says that particles with integer spin are bosons, while those with half-integer spin are fermions.

If the particles are non-interacting (as in an ideal gas) then the wavefunction is separable

$$\Psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, \dots, \mathbf{x}_N, \alpha_N; t) = \psi_1(\mathbf{x}_1, \alpha_1; t) \psi_2(\mathbf{x}_2, \alpha_2; t) \cdots \psi_N(\mathbf{x}_N, \alpha_N; t) \quad (7.1.3)$$

For brevity, we will now stop explicitly writing wavefunctions as functions of time.

We can work with symmetrized (bosons) or anti-symmetrized (fermions) wavefunctions. For 2 particles, for example,

$$\Psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2) = \sqrt{\frac{1}{2}} \left( \psi_1(\mathbf{x}_1, \alpha_1) \psi_2(\mathbf{x}_2, \alpha_2) \pm \psi_1(\mathbf{x}_2, \alpha_2) \psi_2(\mathbf{x}_1, \alpha_1) \right) \quad (7.1.4)$$

The generalisation to  $N$  bosons is straightforward, we just sum over all permutations of positions in the  $N$  single particle wavefunctions. For  $N$  fermions the antisymmetry is realised through the **Slater determinant**:

$$\Psi = \sqrt{\frac{1}{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1, \alpha_1) & \psi_1(\mathbf{x}_2, \alpha_2) & \dots & \psi_1(\mathbf{x}_N, \alpha_N) \\ \psi_2(\mathbf{x}_1, \alpha_1) & \psi_2(\mathbf{x}_2, \alpha_2) & \dots & \psi_2(\mathbf{x}_N, \alpha_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{x}_1, \alpha_1) & \psi_N(\mathbf{x}_2, \alpha_2) & \dots & \psi_N(\mathbf{x}_N, \alpha_N) \end{vmatrix} \quad (7.1.5)$$

As required, the fermionic  $\Psi$  vanishes if  $\psi_i = \psi_j$ . This is a realisation of **Pauli's exclusion principle**, that no 2 fermions can be in the same single particle state.

We do not need these (anti)symmetrized wavefunctions for the following discussion, but we will use the Pauli exclusion principle.

### 7.2 Mean occupancy

Below we need an index  $r$  to label the single particle states in addition to a label  $i$  for the multi-particle states. In state  $|i\rangle$  there are  $n_r$  particles in the single particle

state  $|r\rangle$ . We might write, for example,  $|i\rangle = |r\rangle \otimes |s\rangle \otimes \dots \otimes |q\rangle$ , where  $s$  and  $q$  are other single particle states, and where  $r$  might appear again in the ellipsis. The total number of particles in  $|i\rangle$  is  $N_i$  and the energy of  $|i\rangle$  is  $E_i$ , so

$$N_i = \sum_r n_r^{(i)}, \quad E_i = \sum_r n_r^{(i)} \varepsilon_r \quad (7.2.1)$$

The superscript  $(i)$  is used on the right-hand sides since different multi-particle states correspond to different products of single particle states.

The grand partition function

$$\begin{aligned} \mathcal{Z} &= \sum_i \exp(-\beta(E_i - \mu N_i)) \\ &= \sum_i \exp\left[-\beta\left(\sum_r n_r^{(i)} \varepsilon_r - \mu \sum_r n_r^{(i)}\right)\right] \end{aligned} \quad (7.2.2)$$

$$= \sum_i \prod_r \exp[-\beta n_r^{(i)} (\varepsilon_r - \mu)] \quad (7.2.3)$$

This form of the partition function is useful for deriving the **mean occupancy** of a specific single particle state. Let us differentiate  $\mathcal{Z}$  with respect to the single particle energy  $\varepsilon_s$ , keeping everything else constant

$$\left. \frac{\partial \mathcal{Z}}{\partial \varepsilon_s} \right|_{\beta, \mu, \varepsilon_r \neq s} = \sum_i (-\beta n_s^{(i)}) \prod_r e^{-\beta n_r^{(i)} (\varepsilon_r - \mu)}. \quad (7.2.4)$$

So we can see now that the mean number of particles occupying state  $s$  is given by

$$\bar{n}_s \equiv \langle n_s \rangle = \frac{1}{\mathcal{Z}} \sum_i n_s^{(i)} \prod_r e^{-\beta n_r^{(i)} (\varepsilon_r - \mu)}$$

or

$$\boxed{\bar{n}_s = -\frac{1}{\beta} \left( \frac{\partial}{\partial \varepsilon_s} \log \mathcal{Z} \right)_{\beta, \mu, \varepsilon_r \neq s}}. \quad (7.2.5)$$

It will also be useful below to trade the sum over microstates for a sum over all allowed values of  $n_r$ . We can replace

$$\sum_i \rightarrow \sum_{n_1} \sum_{n_2} \dots \quad (7.2.6)$$

Generalising the identity

$$\begin{aligned} \sum_{j,k,\ell} X_j Y_k Z_\ell &= (X_1 + X_2 + \dots)(Y_1 + Y_2 + \dots)(Z_1 + Z_2 + \dots) \\ &= \left[ \sum_j X_j \right] \left[ \sum_k Y_k \right] \left[ \sum_\ell Z_\ell \right] \end{aligned} \quad (7.2.7)$$

we arrive at the following for **the ideal gas grand partition function**

$$\mathcal{Z} = \left[ \sum_{n_1} \exp[-\beta n_1 (\varepsilon_1 - \mu)] \right] \left[ \sum_{n_2} \exp[-\beta n_2 (\varepsilon_2 - \mu)] \right] \dots$$

which yields

$$\mathcal{Z} = \prod_r \sum_{n_r} \exp(-\beta n_r (\varepsilon_r - \mu)). \quad (7.2.8)$$

This form of the partition function takes on simple forms depending on specific allowed values for  $n_r$ . We will see this next.

### Bosons

For bosons, the sums in (7.2.8) are straightforward to evaluate. In this case  $0 \leq n_r < \infty$  and the series is geometric;  $\sum_{n=0}^{\infty} x^n = 1/(1-x)$ , if  $|x| < 1$ . Therefore,

$$\mathcal{Z} = \prod_r \frac{1}{1 - e^{-\beta(\varepsilon_r - \mu)}}. \quad (7.2.9)$$

Convergence requires that  $\mu$  must be less than the lowest energy state. The mean particle number is

$$N = \frac{1}{\beta} \left( \frac{\partial}{\partial \mu} \log \mathcal{Z} \right)_{\beta, V} = \sum_r \frac{1}{e^{\beta(\varepsilon_r - \mu)} - 1}. \quad (7.2.10)$$

We can find the mean number of particles in the single particle state  $s$  using (7.2.4)

$$\bar{n}_s = -\frac{1}{\beta} \left( \frac{\partial}{\partial \varepsilon_s} \log \mathcal{Z} \right)_{\beta, \mu, \varepsilon_{r \neq s}} = \frac{1}{e^{\beta(\varepsilon_s - \mu)} - 1}. \quad (7.2.11)$$

Eqn. (7.2.11) is called the **Bose-Einstein distribution**. Instead of working with a probability distribution which is a function of the multiparticle state  $|i\rangle$ , we work with a distribution of occupation numbers referring to single particle states labelled by  $r$ .

### Fermions

For fermions  $n_r = 0$  or  $1$  only, due to Pauli's exclusion principle. Thus the sums over  $n_r$  in (7.2.8) are easy

$$\mathcal{Z} = \prod_r (1 + e^{-\beta(\varepsilon_r - \mu)}) \quad (7.2.12)$$

and

$$N = \frac{1}{\beta} \left( \frac{\partial}{\partial \mu} \log \mathcal{Z} \right)_{\beta, V} = \sum_r \frac{1}{e^{\beta(\varepsilon_r - \mu)} + 1}. \quad (7.2.13)$$

The mean occupancy is then

$$\bar{n}_s = -\frac{1}{\beta} \left( \frac{\partial}{\partial \varepsilon_s} \log \mathcal{Z} \right)_{\beta, \mu, \varepsilon_{r \neq s}} = \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1}. \quad (7.2.14)$$

Eqn. (7.2.14) is called the **Fermi-Dirac distribution**.

### Degeneracies

If there are multiple states with energy  $\varepsilon_r$ , say  $g(\varepsilon_r)$ , then

$$\bar{n}(\varepsilon_r) = \frac{g(\varepsilon_r)}{e^{\beta(\varepsilon_r - \mu)} \mp 1} \quad (7.2.15)$$

where the upper sign is for bosons and the lower sign for fermions.

In the thermodynamic limit, we can drop the label  $r$  on the energies  $\varepsilon$ , since the whole continuum of energies are allowed.

$$n(\varepsilon) d\varepsilon = \frac{g(\varepsilon) d\varepsilon}{e^{\beta(\varepsilon - \mu)} \mp 1} \quad (7.2.16)$$

Then

$$\log \mathcal{Z} = \mp \int_0^\infty d\varepsilon g(\varepsilon) \log(1 \mp e^{-\beta(\varepsilon - \mu)}) \quad (7.2.17)$$

(upper/lower signs for bosons/fermions). This implies

$$N = \int_0^\infty \frac{g(\varepsilon) d\varepsilon}{e^{\beta(\varepsilon - \mu)} \mp 1} \quad (7.2.18)$$

$$E = \int_0^\infty \frac{\varepsilon g(\varepsilon) d\varepsilon}{e^{\beta(\varepsilon - \mu)} \mp 1}. \quad (7.2.19)$$

The density of states for nonrelativistic particles in 3 dimensions in the thermodynamic limit was calculated in (4.1.12). Then we find

$$\log \mathcal{Z} = \mp \frac{g_s V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon \sqrt{\varepsilon} \log(1 \mp e^{-\beta(\varepsilon - \mu)}) \quad (7.2.20)$$

Integrating by parts yields

$$\begin{aligned} \log \mathcal{Z} &= \frac{g_s V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{3} \beta \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon - \mu)} \mp 1} \\ &= \frac{2}{3} \beta \int_0^\infty \frac{\varepsilon g(\varepsilon) d\varepsilon}{e^{\beta(\varepsilon - \mu)} \mp 1} \\ &= \frac{2}{3} \beta E \end{aligned} \quad (7.2.21)$$

The grand potential,  $\Omega = -PV = -kT \log \mathcal{Z}$ , so

$$PV = \frac{2}{3} E. \quad (7.2.22)$$

This form of the ideal gas equation of state agrees with our derivation using the canonical ensemble (3.1.9). While the canonical ensemble is completely valid for quantum systems, our treatment of ideal gases in Chapter 4 was valid only in the classical limit, where the interparticle spacing  $(V/N)^{1/3}$  was much larger than the thermal wavelength  $\lambda = \sqrt{2\pi\hbar^2/(mkT)}$ . If this is not the case, then the particle wavefunctions in some sense overlap, and interference effects spoil the independence which allowed us to write  $Z \propto z^N$ . In the grand canonical ensemble, we have treated the full quantum regime properly. Below we see that, for example, the equipartition of energy (4.2.10) holds only in the classical limit.

### 7.3 Classical limit

For convenience, let us abbreviate the collection of constants

$$\frac{g_s}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \equiv K \quad (7.3.1)$$

so that the nonrelativistic density of states in 3 dimensions is  $g(\varepsilon) = KV\sqrt{\varepsilon}$ . Let us also introduce notation for a set of integrals

$$I_n(y) = \int_0^\infty \frac{x^n dx}{e^{x+y} \mp 1} \quad (7.3.2)$$

where we will identify  $y = -\beta\mu$  and  $x = \beta\varepsilon$ . The expressions (7.2.18) and (7.2.19) then become

$$N = \frac{KV}{\beta^{3/2}} I_{\frac{1}{2}}(-\beta\mu) \quad (7.3.3)$$

$$E = \frac{KV}{\beta^{5/2}} I_{\frac{3}{2}}(-\beta\mu). \quad (7.3.4)$$

If  $e^{-\beta\mu} \gg 1$  (i.e. if  $e^y \gg 1$ ) then denominator of the integrand in (7.3.2) can be expanded

$$\frac{1}{e^{x+y} \mp 1} = e^{-(x+y)} (1 \pm e^{-(x+y)} + e^{-2(x+y)} \pm \dots), \quad (7.3.5)$$

using the Taylor expansion for  $(1 \mp w)^{-n}$ , where  $w = e^{-(x+y)}$  is much smaller than 1. We will keep only the first 2 terms. For the particle number, we have

$$N = \frac{KV}{\beta^{3/2}} e^{\beta\mu} \left[ \int_0^\infty dx \sqrt{x} e^{-x} \pm e^{\beta\mu} \int_0^\infty dx \sqrt{x} e^{-2x} + \dots \right]. \quad (7.3.6)$$

The substitution  $u = \sqrt{x}$  makes clear these are Gaussian-type integrals, the first equal to  $\sqrt{\pi/4}$  and the second  $\sqrt{\pi/8}$ .

$$\begin{aligned} N &= \frac{KV}{\beta^{3/2}} e^{\beta\mu} \frac{\sqrt{\pi}}{2} \left( 1 \pm \frac{e^{\beta\mu}}{2\sqrt{2}} + \dots \right) \\ &= \frac{g_s V}{\lambda^3} e^{\beta\mu} \left( 1 \pm \frac{e^{\beta\mu}}{2\sqrt{2}} + \dots \right). \end{aligned} \quad (7.3.7)$$

We can solve (7.3.7) for the following assortment of terms (in the process inverting the Taylor expansion) to find

$$g_s \frac{V}{N\lambda^3} = e^{-\beta\mu} \left( 1 \mp \frac{e^{\beta\mu}}{2\sqrt{2}} + \dots \right). \quad (7.3.8)$$

It is clear from this expression that the large  $e^{-\beta\mu} \gg 1$  limit is the same as the limit  $V/N \gg \lambda^3$ . Recalling the definition of the thermal wavelength (4.2.6), we see the classical limit is where

$$\boxed{\frac{V}{N} \gg \left( \frac{2\pi\hbar^2}{mkT} \right)^{3/2}}. \quad (7.3.9)$$

Note we have an explicit  $\hbar$  on the right-hand side, highlighting that Planck's constant sets the scale for quantum physics. We can only see deviations from classical physics when the right-hand side becomes comparable to the volume per particle, which occurs at very low temperatures, for very small masses, or in very dense systems.

Similar manipulations for the energy lead to the following steps

$$\begin{aligned}
 E &= \frac{KV}{\beta^{5/2}} e^{\beta\mu} \left[ \int_0^\infty dx x^{3/2} e^{-x} \pm e^{\beta\mu} \int_0^\infty dx x^{3/2} e^{-2x} \pm \dots \right] \\
 &= \frac{KV}{\beta^{5/2}} e^{\beta\mu} \left( \frac{3\sqrt{\pi}}{4} \pm \frac{3}{16} \sqrt{\frac{\pi}{2}} e^{\beta\mu} + \dots \right) \\
 &= \frac{g_s V}{\lambda^3} e^{\beta\mu} \frac{3}{2\beta} \left( 1 \pm \frac{e^{\beta\mu}}{4\sqrt{2}} + \dots \right). \tag{7.3.10}
 \end{aligned}$$

Solving (7.3.7) for  $g_s V e^{\beta\mu} / \lambda^3$  and inserting above we find

$$\begin{aligned}
 E &= \frac{N}{\beta} \left( 1 \mp \frac{e^{\beta\mu}}{2\sqrt{2}} + \dots \right) \frac{3}{2} \left( 1 \pm \frac{e^{\beta\mu}}{4\sqrt{2}} + \dots \right) \\
 &= \frac{3}{2} NkT \left( 1 \mp \frac{e^{\beta\mu}}{4\sqrt{2}} + \dots \right). \tag{7.3.11}
 \end{aligned}$$

We recover both the classical result (4.2.10) plus the leading quantum correction. Using  $PV = \frac{2}{3}E$  we see the correction to the classical equation of state (4.2.11)

$$PV = NkT \mp \frac{NP}{(kT)^{3/2}} \frac{1}{K\sqrt{8\pi}}. \tag{7.3.12}$$

Note that  $K^{-1} \propto \hbar^3$ , so this correction would indeed vanish if we were to take  $\hbar \rightarrow 0$ .

## Further reading

1. F Reif, *Fundamentals of Thermal and Statistical Physics*, (McGraw-Hill, 1965), §§9.2-3.
2. L D Landau and E M Lifshitz, *Statistical Physics*, (Pergamon Press, 1980), §§53-54.
3. R K Pathria, *Statistical Mechanics*, (Pergamon Press, 1991), §§6.2-3.