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Quantum gases in the grand-canonical ensemble

↳ Quantum statistics → Define micro-states

From energy level occupation #s

Bosons vs. Fermions, w/different occupation numbers

↳ $n_\ell = 0, 1, 2, \ldots$ → $n_\ell = 0, 1$

Classical & quantum coincide at high temperatures statistics. This is actually a question we have already considered, back in Section 3.4 (and the first homework assignment). There we used the canonical ensemble to analyze classical spin systems with discrete energy levels, finding that at low temperatures the systems are dominated by their lowest-energy micro-states, with only exponentially suppressed corrections coming from any higher-energy micro-states. In the present context, this corresponds to a classical prediction of exponentially small probabilities for particles to occupy any energy levels with $E_\ell > E_0$ — effectively guaranteeing that the lowest energy level $\mathcal{E}_0$ will be occupied by multiple particles and classical statistics will break down.

In short, the low-temperature regime is where quantum and classical statistics disagree, while **high temperatures correspond to the classical limit** of quantum statistics. If you are not convinced by the argument leading to this conclusion, you can find a more detailed derivation based on the equation of state and thermal de Broglie wavelength in Section 3.5 of David Tong's *Lectures on Statistical Physics* (the first item in the list of further reading on page 5).

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For now, we want to consider the grand-canonical ensemble at high temperatures, to see whether the quantum and classical statistics we derived in the previous sections become equivalent in this regime. However, it can be subtle to work with the grand-canonical ensemble at high temperatures, due to the dependence of the average number of particles on the temperature. To demonstrate this subtlety, let's compute the average particle number $\langle N\rangle(T,\mu)$ starting from the grand-canonical partition function, for both classical and quantum statistics.

For convenience, let's collect our earlier results for the grand-canonical partition functions corresponding to classical Maxwell–Boltzmann statistics (Eq. 87), the quantum Bose–Einstein statistics of bosons (Eq. 86) and the quantum Fermi–Dirac statistics of fermions (Eq. 88):

$$Z_g^{\text{MB}} = \prod_{\ell=0}^{L} \exp\left[e^{-\beta(E_\ell-\mu)}\right]$$

$$Z_g^{\text{BE}} = \prod_{\ell=0}^{L} \frac{1}{1-e^{-\beta(E_\ell-\mu)}} \qquad\qquad Z_g^{\text{FD}} = \prod_{\ell=0}^{L} \left[1+e^{-\beta(E_\ell-\mu)}\right].$$

Recalling $\log\left[\prod_i x_i\right] = \sum_i \log x_i$, the corresponding grand-canonical potentials $\Phi = -T\log Z_g$ for these three cases are

$$\Phi_{\text{MB}} = -T\sum_{\ell=0}^{L} e^{-\beta(E_\ell-\mu)}$$

$$\Phi_{\text{BE}} = T\sum_{\ell=0}^{L} \log\left[1-e^{-\beta(E_\ell-\mu)}\right] \qquad\qquad \Phi_{\text{FD}} = -T\sum_{\ell=0}^{L} \log\left[1+e^{-\beta(E_\ell-\mu)}\right].$$

We are now ready to compute the average particle numbers. Using the result we derived in Section 6.3,

$$\langle N \rangle = -\frac{\partial \Phi}{\partial \mu},$$

what are the average particle numbers resulting from the three grand-canonical potentials above?

$$x_\ell = \beta(E_\ell - \mu)$$

$$\langle N \rangle_{\mathsf{MB}} = T \sum_{\ell=0}^{L} \frac{\partial}{\partial \mu} e^{-\beta(E_\ell - \mu)} = T \sum_\ell \beta e^{-\beta(E_\ell - \mu)}$$

$$= \sum_\ell e^{-x_\ell} = \sum_\ell \frac{1}{e^{x_\ell}} = \sum_\ell \langle n_\ell \rangle_{MB}$$

$$\langle N \rangle_{\mathsf{BE}} = -T \sum_{\ell=0}^{L} \frac{\partial}{\partial \mu} \log\left[1 - e^{-\beta(E_\ell - \mu)}\right] = -T \sum_\ell \frac{-\beta e^{-x_\ell}}{1 - e^{-x_\ell}}$$

$$= \sum_\ell \frac{1}{e^{x_\ell} - 1} = \sum_\ell \langle n_\ell \rangle_{BE}$$

$$\langle N \rangle_{\mathsf{FD}} = T \sum_{\ell=0}^{L} \frac{\partial}{\partial \mu} \log\left[1 + e^{-\beta(E_\ell - \mu)}\right] = T \sum_\ell \frac{\beta e^{-x_\ell}}{1 + e^{-x_\ell}}$$

$$= \sum_\ell \frac{1}{e^{x_\ell} + 1} = \sum_\ell \langle n_\ell \rangle_{FD}$$

You should find that the average particle number in all three cases can be expressed as a sum over the average occupation numbers,

$$\langle N \rangle = \sum_{\ell=0}^{L} \langle n_\ell \rangle,$$

where the average occupation numbers for Maxwell–Boltzmann statistics, Bose–Einstein statistics and Fermi–Dirac statistics are

$$\langle n_\ell \rangle_{\text{MB}} = \frac{1}{e^{\beta(E_\ell - \mu)}}$$

$$\langle n_\ell \rangle_{\text{BE}} = \frac{1}{e^{\beta(E_\ell - \mu)} - 1} \qquad\qquad \langle n_\ell \rangle_{\text{FD}} = \frac{1}{e^{\beta(E_\ell - \mu)} + 1}.$$

Note that $0 \leq \langle n_\ell \rangle_{\text{FD}} \leq 1$, as required for fermions. From these results it is easy to see that the classical limit $\langle n_\ell \rangle_{\text{BE}} \approx \langle n_\ell \rangle_{\text{FD}} \approx \langle n_\ell \rangle_{\text{MB}}$ corresponds to

$$e^{\beta(E_\ell - \mu)} \pm 1 \approx e^{\beta(E_\ell - \mu)} \qquad \Longrightarrow \qquad e^{\beta(E_\ell - \mu)} \gg 1.$$

We can also confirm that this limit corresponds to $\langle n_\ell \rangle \ll 1$ for all energy levels $\mathcal{E}_\ell$ and all three types of statistics, connecting to our starting point of very small probabilities for multiple particles to occupy the same energy level.

Now we can appreciate the subtlety promised above, because

$$\beta(E_\ell - \mu) = \frac{E_\ell - \mu}{T} \gg 1. \tag{89}$$

does not look like a high-temperature limit! Indeed, if we consider the naive high-temperature limit $\beta = 1/T \to 0$ with fixed $(E_\ell - \mu)$, we would find large average occupation numbers,

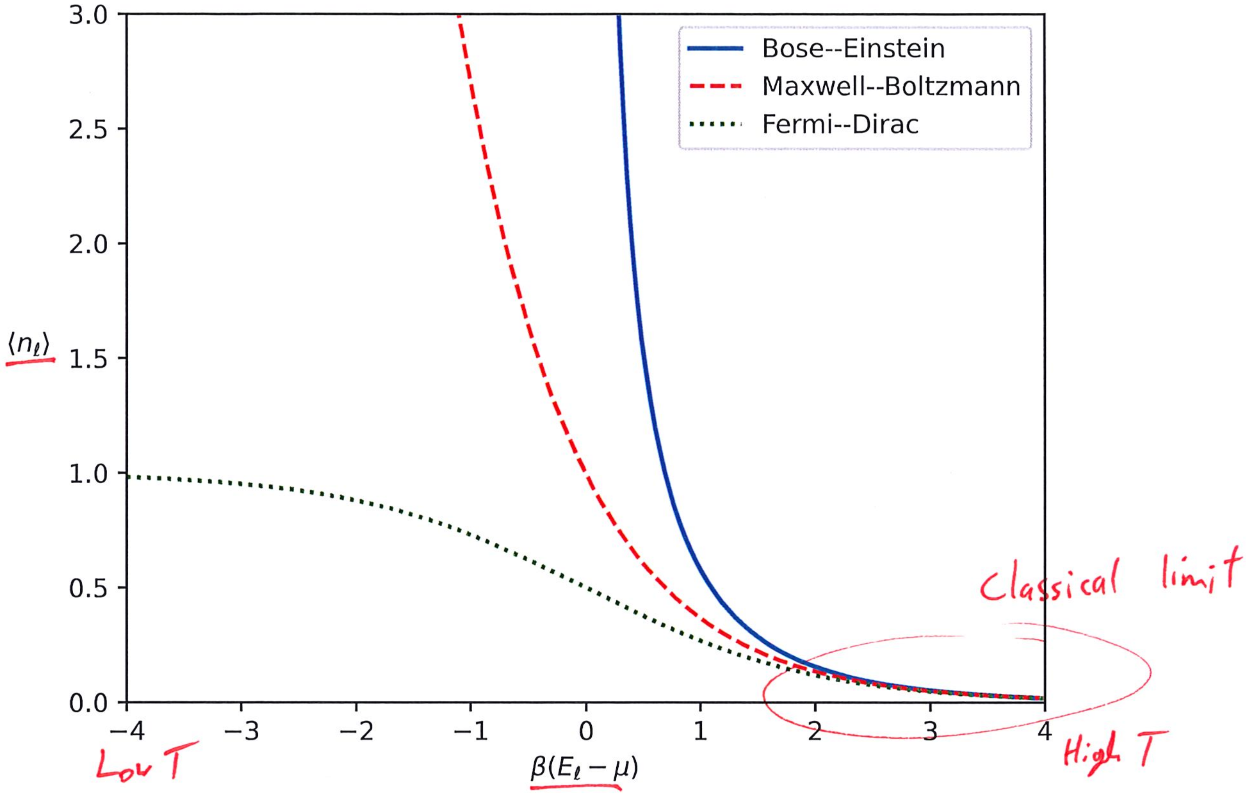
$$\langle n_\ell \rangle_{\text{MB}} \approx 1 \qquad\qquad \langle n_\ell \rangle_{\text{BE}} \to \infty \qquad\qquad \langle n_\ell \rangle_{\text{FD}} \approx \frac{1}{2}.$$

In addition to implying non-negligible classical probabilities for multiple particles to occupy the same energy level, this result indicates that higher temperatures in the grand-canonical ensemble lead to larger particle numbers in total — at least when $(E_\ell - \mu)$ is fixed.

In order to balance this effect, we need to adjust the other parameter offered by the grand-canonical ensemble: the chemical potential μ. Specifically, in order to satisfy Eq. 89 in the high-temperature limit, we need $E_\ell - \mu \gg T$, requiring that $\mu \to -\infty$ as $T \to \infty$. Making the chemical potential more negative reduces the probability of having large numbers of particles in the system, at the same time as the smaller β increases the number of energy levels that these particles can occupy with non-negligible probability. Taken together, these two effects guarantee that there are many more accessible energy levels than there are particles, allowing us to conclude that the true high-temperature limit in which quantum statistics becomes classical is

$$-\mu \gg T \gg E_\ell \qquad \Longrightarrow \qquad \frac{E_\ell - \mu}{T} \gg 1. \tag{90}$$

This corresponds to the right edge of the plot on the next page, where we can confirm excellent agreement between all three predictions for the average occupation number $\langle n_\ell \rangle$.



In the low-temperature regime $\frac{E_\ell-\mu}{T} \ll 1$ corresponding to the left portion of the plot, we see dramatically different behaviour for the three cases. The classical Maxwell–Boltzmann prediction for the average occupation number grows exponentially, while the quantum Bose–Einstein prediction diverges as $E_\ell \to \mu$ and the Fermi–Dirac prediction slowly approaches its maximum possible value $\langle n_\ell \rangle_{\text{FD}} \to 1$. In the next unit we will study in more detail the quantum gases of bosons and fermions that correspond to these results.

Unit 8: Quantum gases

8.1 The photon gas

8.1.1 Massive bosons in a box

In Section 7.3 we derived the grand-canonical partition function (Eq. 86) that defines quantum Bose–Einstein statistics for systems of non-interacting bosons,

$$Z_g^{\mathsf{BE}}(\beta,\mu) = \prod_{\ell=0}^{\mathcal{L}} \frac{1}{1-e^{-\beta(E_\ell-\mu)}}.$$

Following the quantum approach, we obtained this result by considering in turn each energy level $\mathcal{E}_\ell$ with energy E_ℓ, and summing over all possible occupation numbers that it could have. For bosons, $n_\ell \in \mathbb{N}_0$ produces sums that only converge if $\mu < E_\ell$ for all ℓ. The corresponding grand-canonical potential is

$$\Phi_{\mathsf{BE}} = -T\log Z_g = T\sum_{\ell=0}^{\mathcal{L}} \log\left[1-e^{-\beta(E_\ell-\mu)}\right],$$

from which we can determine the large-scale properties of the system, including its average internal energy $\langle E\rangle$, average particle number $\langle N\rangle$, entropy S, and pressure P.

To do so, we have to specify the energy levels of the particles that compose the system of interest, taking care to note potentially degenerate energy levels $\{\mathcal{E}_m, \mathcal{E}_n\}$ with the same energy $E_m = E_n$ for $m \neq n$. One example of this that we have already considered is the analysis of non-relativistic ideal gas particles in Section 4.1. For a single particle with mass m in a volume $V = L^3$, we adopted an ansatz for the quantized energies, $E = \frac{p^2}{2m}$

$$E(k_x,k_y,k_z) = \frac{\hbar^2\pi^2}{2mL^2}\left(k_x^2+k_y^2+k_z^2\right) = \varepsilon\left(k_x^2+k_y^2+k_z^2\right) \qquad \varepsilon \equiv \frac{\hbar^2\pi^2}{2mL^2}, \tag{91}$$

where the integers $k_{x,y,z}$ specify the possible momenta of the particle,

$$\vec{p} = (p_x,p_y,p_z) = \hbar\frac{\pi}{L}(k_x,k_y,k_z) \qquad\qquad k_{x,y,z} = 1,2,\cdots.$$

Compared to Eq. 47, here we have adjusted our ansatz to require strictly positive $k_{x,y,z}$. This adjustment is required by another feature of quantum mechanics, which this paragraph will imprecisely describe for the curious. This description can be skipped without any problem, with the adjusted ansatz simply taken as input. The feature at play here is known as Heisenberg's uncertainty principle (named after Werner Heisenberg), which relates the precision with which the position and momentum of each particle can simultaneously be *defined*:

$$(\Delta x)\,(\Delta p_x) \gtrsim \hbar$$

and similarly for y and z. The '$\gtrsim$' sign here hints that we're ignoring irrelevant factors of 2 and π, while 'Δ' refers to the precision (or uncertainty) with which

x and p_x are defined. Since the particle is within a volume $V = L^3$, we know $\Delta x \lesssim L$. Therefore the uncertainty principle requires $\Delta p_x \gtrsim \hbar/L$, which is only possible if p_x is non-zero, corresponding to $k_x \geq 1$. Note that smaller lengths L imply larger momenta and therefore larger energies.

With this adjusted ansatz, $k_{x,y,z} \geq 1$, we can adapt an exercise from Section 4.1 and ask: What are the lowest energies and the degeneracies of the corresponding energy levels?

Ground state: $E_0 = 3\varepsilon$ $\vec{k} = (1,1,1)$ #: 1

$E = 6\varepsilon$ #: 3

$E = 9\varepsilon$ #: 3

$E = 11\varepsilon$ #: 3 $(3,1,1)$ $E = 12\varepsilon$ #: 1 $(2,2,2)$

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8.1.2 Massless photons

Now we will build on our experience with massive bosons to consider a gas of *photons*, massless bosonic quantum particles of light. For our purposes, with no prior knowledge of particle physics, we can define photons simply by specifying their energy levels. Clearly $E \propto 1/m$ from Eq. 91 is problematic for massless particles with $m = 0$. Instead, a photon's energy is proportional to the magnitude of its momentum,

$$E_{\text{ph}}(p) = c\sqrt{p_x^2 + p_y^2 + p_z^2} \equiv cp.$$

Here the speed of light c is really just a unit conversion factor (like the Boltzmann constant) that we could set to $c = 1$ by working in appropriate units.

This relation is connected to the non-relativistic energy $E = \frac{p^2}{2m}$ that we considered in Section 4.1 through the general expression

$$E^2 = \left(mc^2\right)^2 + (pc)^2,$$

which is sometimes called Einstein's triangle. When $m = 0$, or $m \ll p/c$ more generally, this reproduces the *ultra-relativistic* relation above. For stationary particles with $p = 0$ it reduces to the famous 'mass-energy' $E = mc^2$, while the non-relativistic kinetic energy is recovered for $m \gg p/c$: