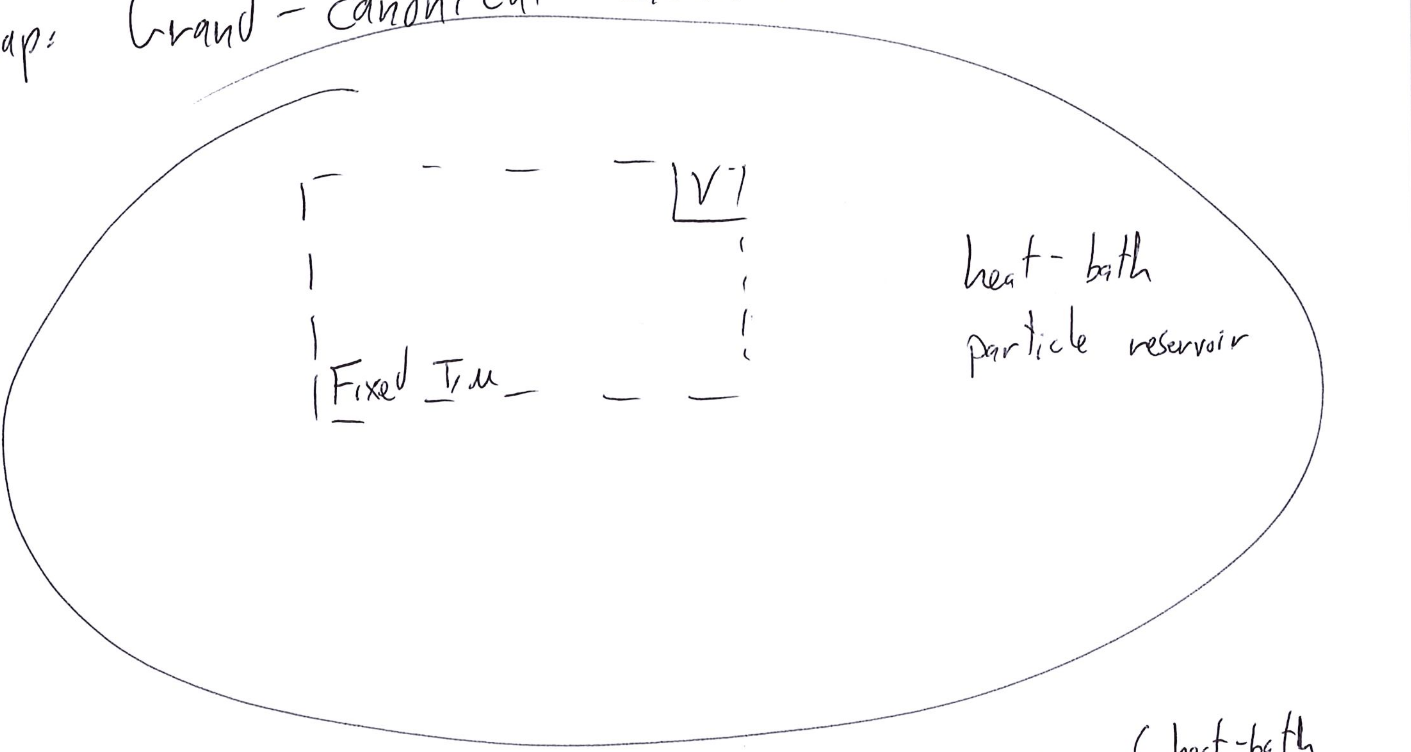
13 March

Recap: Grand-canonical ensemble



Working with fixed T & μ hide role of "big" $\begin{cases}\text{heat-bath}\\ \text{part. reservoir}\end{cases}$

Thermodynamical equilibrium:

Microstate probability $p_i = \frac{1}{Z_g}\exp(-\beta E_i + \beta\mu N_i)$

$Z_g = \sum_{i=1}^{M} \exp(-\beta E_i + \beta\mu N_i)$ grand-canonical partition function

$\beta = \frac{1}{T}$ $\mu = -\frac{T}{N}\frac{\partial S}{\partial N_p}\Big|_{E_{tot}} = \frac{\partial\langle E\rangle}{\partial N_p}\Big|_S$

Grand-canonical potential: $\Omega(T,\mu) = -T\ln Z_g(T,\mu)$

Internal energy & particle # fluctuate

As functions of T, μ

$$\langle N\rangle(T,\mu) = -\frac{\partial}{\partial\mu}\Omega(T,\mu)$$

$$\langle E\rangle(T,\mu) = -T^2\frac{\partial}{\partial T}\left(\frac{\Omega(T,\mu)}{T}\right) + \mu\langle N\rangle(T,\mu) = \Omega + T\cdot \overset{-\frac{\partial\Omega}{\partial T}}{S} + \mu\langle N\rangle$$

Application of grand-canonical ensemble: Quantum gases

Setup: N_i indistinguishable particles in microstate i

$S_p \quad p = 1, \dots, N_i$

Each particle has energy E_p, $\quad E_i = \sum_{p=1}^{N_i} E_p$

Quantum ~~m~~ input:

Only countable (possibly infinite) number of energy levels are discrete (~~q~~"quantized") $\quad E_1, E_2, \cdots E_L$

Classical assumption:

Sum of micro-states given ~~as~~ by sum over all energies each particle can have

Classical ideal gas: Each particle has $E_\ell = \frac{\vec{p}_\ell^{\,2}}{2m}$

$$Z_1 = \frac{V}{(2\pi\hbar)^3} \int d^3p \, \exp\left(\frac{-p^2}{2mT}\right) = V\left(\frac{\sqrt{2\pi m T}}{2\pi\hbar}\right)^3 = \frac{V}{\lambda^3}$$

single-particle partition function

(pages 67-68 Eqs. 45-46)

N distinguishable particles: $Z_{dist} = Z_1^N$

N indistinguishable particles: $Z_{indis} = \frac{1}{N!} Z_1^N$

Quantum correction:

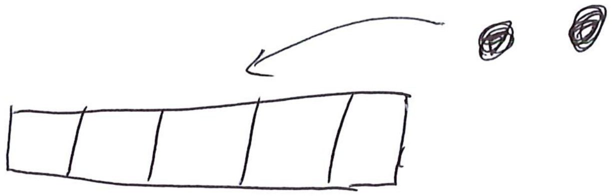
Sum over microstates given by sum over occupation number n_ℓ for each energy level E_ℓ

Bosons: $n_\ell = 0, 1, 2, \cdots$ $\qquad$ Fermions: $n_\ell = 0, 1$

Worked example

Place 2 balls in 5 boxes

particles — energy levels



How many microstates?

- If distinguishable

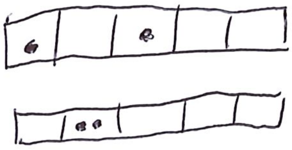
$M_{dist} = 5 \times 5 = 5^2 = 25$

- Classical indistinguishable

$M_{indis} = \frac{1}{2!} 5^2 = 12.5$ Oops!

Quantum: Count occupation #s (indistinguishable)

Label



= 10100

= 02000

11000
10100
10010
10001
01100
01010
01001
00110
00101
00011

Doubled if distinguishable

20000
02000
00200
00020
00002

not fermions

$M_{bose} = 15$

$M_{Fermi} = 10$

If each particle had been in unique energy level, then classical counting would have worked

→ Expect quantum gases to be approximately classical when many more energy levels than particles

Warm-up: System w/ only one energy level E_i

energy microstate = occ. #

$$Z_{bose} = \underline{\sum_{n_i=0}^{\infty} \exp(-\beta E_i n_i + \beta \mu n_i)}$$

$$= \exp(-\beta E_i \cdot 0 + \beta\mu 0) + \exp(-\beta E_i + \beta\mu) + \exp(-2\beta E_i + 2\beta\mu) + \dots$$

$$= 1 + x + x^2 + \dots = \frac{1}{1-x} = \frac{1}{1-\exp\left(-\frac{E_i-\mu}{T}\right)}$$

$$\boxed{\begin{aligned} Z_{bose} &= \sum_{n_1=0}^{\infty} \cdots \sum_{n_M=0}^{\infty} \exp(-\beta E_1 n_1 + \beta\mu n_1 - \beta E_2 n_2 + \beta\mu n_2 + \dots) \\ &= \sum_{n_1} \cdots \sum_{n_M} \exp(-\beta E_1 n_1 + \beta\mu n_1) \times \exp(-\beta E_2 n_2 + \beta\mu n_2) \times \dots \\ &= \left(\sum_{n_1=0}^{\infty} \underline{\exp(-\beta E_1 + \beta\mu)}^{n_1}\right)\left(\sum_{n_2=0}^{\infty} \exp(-\beta E_2 + \beta\mu)^{n_2}\right) \times \dots \\ &= \left(\frac{1}{1-\exp(-\beta E_1 + \beta\mu)}\right)\left(\frac{1}{1-\exp(-\beta E_2 + \beta\mu)}\right) \times \dots \\ &= \prod_{i=1}^{M} \frac{1}{1-\exp\left(-\frac{E_i-\mu}{T}\right)} \end{aligned}} \longleftarrow$$

We finally obtain the sometimes called *Bose Statistics*;

$$-\frac{\Omega}{T} = \ln Z_{bose} = -\sum_{i=1}^{M} \ln\left[1 - \exp\left(-\frac{E_i - \mu}{T}\right)\right] . \tag{79}$$

As in the classical physics case, we arrive at a sum over all energy levels, but now with different terms (compare with (78)).

Let us consider the case of high temperatures $T \gg E_i$, for which we can assume

$$\begin{matrix} T \to \infty \\ \mu \to -\infty \end{matrix} \quad \text{so that } \exp\left(-\frac{E_i - \mu}{T}\right) \ll 1 . \qquad -\mu \gg T \gg E_i$$

We then can use the leading order of the expansion:

$$-\ln(1-x) = x + \mathcal{O}(x^2) ,$$

and find:

$$-\frac{\Omega_{bose}}{T} = \ln Z_{bose} = \sum_{i=1}^{M} \exp\left(-\frac{E_i - \mu}{T}\right) \overset{?}{=} \ln Z_{\text{classical}} .$$

We make the important observation that we recover the classical physics result at high temperatures. It depends, of course, on the energy spectrum

$$Z_{bose} = \sum_{n_1} \cdots \sum_{n_M} \exp\left(-\beta \sum_{l=1}^{M} E_l n_l + \beta\mu \sum_{l=1}^{M} n_l\right)$$

$$\to \prod_{l=1}^{M} \frac{1}{1-\exp\left(-\frac{E_l-\mu}{T}\right)}$$

Used geometric series $\frac{1}{1-x} = 1 + x + x^2 + \ldots$ $x = \exp\left(-\frac{(E_l-\mu)}{T}\right)$

Need $|x|<1$ for convergence

$0 < \exp\left(-\frac{E_l-\mu}{T}\right) < 1$ $-\frac{E_l-\mu}{T} < 0$

Physics input $T>0 \longrightarrow -E_l+\mu < 0$, $\mu < E_l$

Typically ground-state energy $E_1 = 0 \to \mu < 0$ For Bose gas

$\mu < 0$ meaning

$\mu = \frac{-T}{N} \left.\frac{\partial S}{\partial N_p}\right|_{E_{tot}} \to \left.\frac{\partial S}{\partial N_p}\right|_{E_{tot}} > 0$ Increasing entropy when dividing fixed energy among more particles

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$\mu = \left.\frac{\partial \langle E \rangle}{\partial N_p}\right|_{S} < 0$ Must decrease internal energy in order to add more particles with fixed entropy

Addendum: The high-temperature limit of the Bose gas

The high-temperature limit of the Bose gas is a bit subtle. To reveal this, let's compute the average particle number from the corresponding grand-canonical potential

$$\Omega_{\text{bose}} = -T \ln Z_{\text{bose}} = T \sum_{\ell=1}^{L} \ln\left[1 - \exp\left(-\beta E_\ell + \beta\mu\right)\right],$$

labelling the energy levels E_ℓ with $\ell = 1, \cdots, L$ to reduce possible confusion with the micro-states $i = 1, \cdots, M$. We have

$$\boxed{\begin{aligned} \langle N \rangle = -\frac{\partial \Omega}{\partial \mu} &= -T \sum_{\ell=1}^{L} \frac{\partial}{\partial \mu} \ln\left[1 - \exp\left(-\beta E_\ell + \beta\mu\right)\right] \\ &= \cancel{-}T \, \frac{\cancel{-}\beta \exp\left(-\beta E_\ell + \beta\mu\right)}{1 - \exp\left(-\beta E_\ell + \beta\mu\right)} \\ &= \sum_{\ell=1}^{L} \frac{1}{\exp\left(\beta E_\ell - \beta\mu\right) - 1} = \sum_{\ell=1}^{L} \langle n_\ell \rangle \end{aligned}}$$

We can organize this as $\langle N \rangle = \sum_{\ell=1}^{L} \langle n_\ell \rangle$, defining the average occupation number for each energy level as

$$\langle n_\ell \rangle = \frac{1}{\exp\left(\beta E_\ell - \beta\mu\right) - 1}$$

When considering the high-temperature limit $\beta \to 0$ (so that $T \to \infty$), we need to keep in mind the grand-canonical constraint on the total number of particles in the system and its surroundings, from Eq. (65):

$$N_{\text{tot}} = N_r \langle N \rangle = N_r N_p \qquad \text{is conserved,}$$

where $\langle N \rangle = N_p$ is the average number of particles in the "small" system, and the surroundings are made up of a fixed number $(N_r - 1)$ of replicas of that small system.

If we naively take $\beta \to 0$, we have

$$\exp\left(\beta E_\ell - \beta\mu\right) \to 1 \quad \text{and} \quad \langle n_\ell \rangle = \frac{1}{\exp\left(\underset{\downarrow\, 0}{\beta E_\ell} - \bigcirc\!\!\!\!\!\beta\mu\right) - 1} \to \infty$$

for all ℓ! The number of particles in every energy level $\langle n_\ell \rangle$ is diverging, and so therefore is the total $\underline{\langle N \rangle = \sum_{\ell=1}^{L} \langle n_\ell \rangle}$.

The cure **required** in order for the Bose gas to satisfy the grand-canonical constraint is to send $\mu \to -\infty$ as $T \to \infty$. While a constant ratio μ/T would suffice to keep each individual $\langle n_\ell \rangle$ from diverging at high temperatures, because the constraint is on the sum $\langle N \rangle$ it turns out that we really need $\underline{-\mu \gg T} \gg E_i$ to satisfy the constraint. (We will not prove this here.) In this limit, $\underline{(E_\ell - \mu)/T \gg 1}$ and

$$\exp\left(-\frac{E_\ell - \mu}{T}\right) \ll 1,$$

which gets us back to page 121.

Addendum: The classical grand-canonical $Z_{\text{classical}}$

In the corrected Eq. (78) on page 118, we had the generic grand-canonical partition function

$$Z_g = \sum_{i=1}^{M} \exp\left\{-\beta E_i + \beta\mu N_i\right\},$$

where the sum is over **micro-states** i with energy E_i and particle number N_i.

As we did for the quantum Bose gas, let's rearrange this expression in terms of the occupation numbers n_ℓ for the energy levels E_ℓ with $\ell = 1, \cdots, L$. With these definitions, $E_i = \sum_{\ell=1}^{L} E_\ell n_\ell$ and $N_i = \sum_{\ell=1}^{L} n_\ell$.

The expression for Z_g above implicitly makes the assumption that the particles are distinguishable. While we are interested in the case of indistinguishable particles, in classical physics it is possible to distinguish particles with different energies. Only the n_ℓ particles with the same energy level are indistinguishable among themselves, which brings in factors of $n_\ell!$ to produce

$$Z_{\text{classical}} = \sum_{n_1=0}^{\infty} \cdots \sum_{n_L=0}^{\infty} \frac{1}{n_1!} \cdots \frac{1}{n_L!} \exp\left\{-\beta \sum_{\ell=1}^{L} E_\ell n_\ell + \beta\mu \sum_{\ell=1}^{L} N_\ell\right\}.$$

We can evaluate this much like we did for the quantum Bose gas:

$$Z_{cl} = \left(\sum_{n_1=0}^{\infty} \frac{1}{n_1!} \exp(-\beta E_1 + \beta\mu)^{n_1}\right) \times \cdots \times \left(\sum_{n_L=0}^{\infty} \frac{1}{n_L!} \exp(-\beta E_L + \beta\mu)^{n_L}\right)$$

$$= \prod_{l=1}^{L} \frac{1}{n_l!} x^{n_l} \qquad x = \exp(-\beta E_l + \beta\mu)$$

$$= \prod_{l=1}^{L} \exp\left[\exp\left(-\frac{E_l - \mu}{T}\right)\right]$$

We obtain the result

$$-\frac{\Omega_{\text{classical}}}{T} = \ln Z_{\text{classical}} = \sum_{\ell=1}^{L} \exp\left(-\frac{E_\ell - \mu}{T}\right),$$

matching the high-temperature limit of the Bose gas on page 121.

We can again compute the average particle number

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

We again obtain $\langle N \rangle = \sum_{\ell=1}^{L} \langle n_\ell \rangle$, but now with the classical average occupation number

$$\left\langle n_\ell^{(\text{cl})} \right\rangle = \exp\left(-\beta E_\ell + \beta\mu\right).$$

Recalling the expression for the quantum Bose gas,

$$\left\langle n_\ell^{(\text{bose})} \right\rangle = \frac{1}{\exp\left(\beta E_\ell - \beta\mu\right) - 1},$$

we see that classical physics is recovered in the high-temperature limit where $\beta(E_\ell - \mu) \gg 1$ makes the exponential factor much greater than 1.