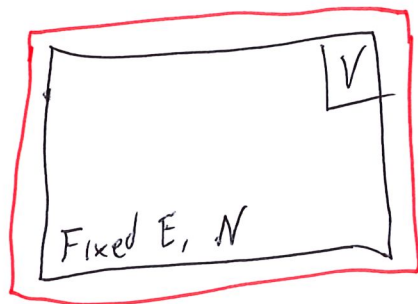


Recap 10 March

Big picture: Statistical ensembles

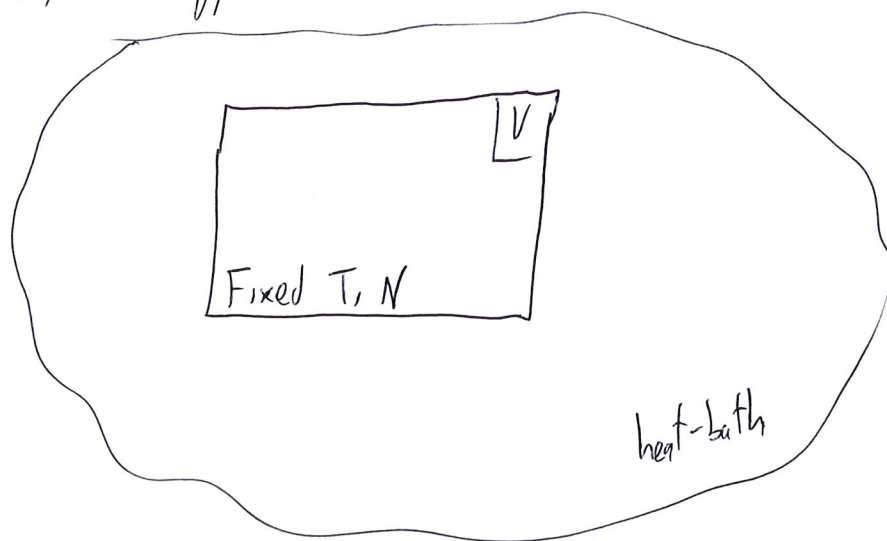
Output space of prob. process
Physics-based system to model } Ensemble

Microcanonical ensemble
Energy & particle # both conserved
↳ First Law of Thermodynamics



Derived $T(E)$

Fix temperature, energy fluctuate $E(T)$



Hide heat-bath, work in terms of T, N of "small" system

Applications of canonical ensemble

Ideal gas: Equation of state $p \cdot V = N \cdot T$

1) Microstates: Complete description of \wedge particles
all, up to distinguishability

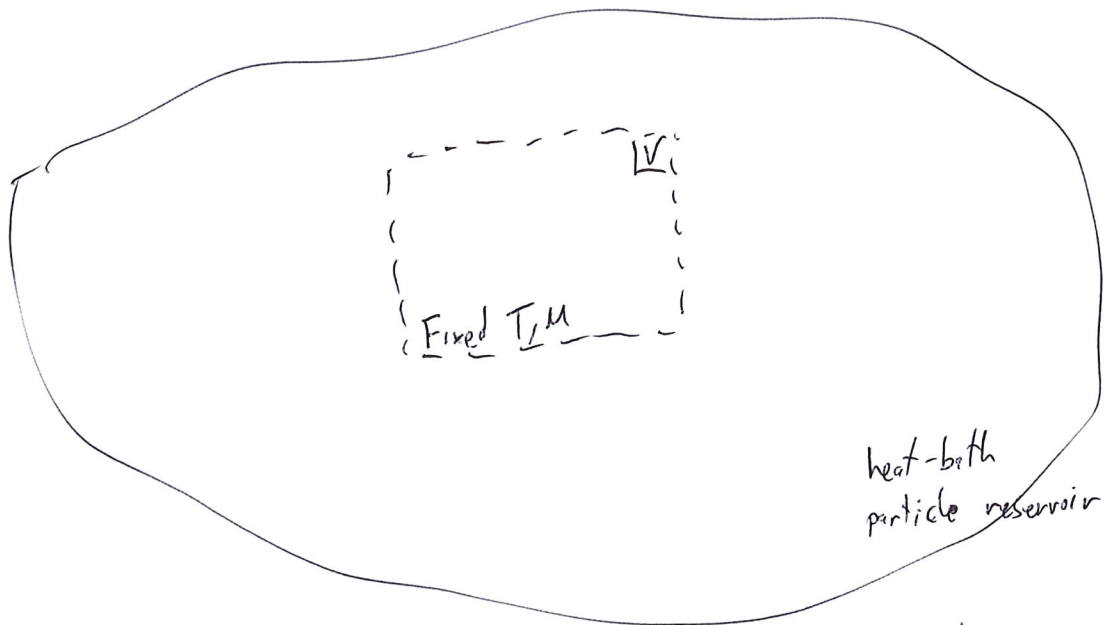
2) (Macro-)state: Overall characteristics — pressure, volume, temperature.

Thermodynamical cycles: Two reservoirs, hot T_H & cold T_L
Heat $dQ = T dS$ From hot \rightarrow cold produces work

Grand-canonical ensemble

Energy & particle # fluctuate

Governed by fixed temperature T & chemical potential μ



Picturing surroundings as $(N-1)$ replicas of "small" system

Total energy of system + surroundings $E_{tot} = N \langle E \rangle$ conserved

Total particle # " $N_{tot} = N N_p = N \langle N \rangle$

$$\langle E \rangle = \sum_{i=1}^M P_i E_i$$

$$\langle N \rangle = N_p = \sum_{i=1}^M P_i N_i$$

Determine p_i by considering entropy

$$S = - \sum_{i=1}^n p_i \ln p_i = S(E_{\text{tot}}, N_{\text{tot}})$$

Equilibrium: Maximize $S \rightarrow p_i = \frac{1}{Z_g} \exp[-\beta E_i + \beta \mu N_i]$

Constraint $\sum_{i=1}^n p_i = 1 \rightarrow Z_g = \sum_{i=1}^n \exp[-\beta E_i + \beta \mu N_i]$

Grand-canonical partition function

$$\frac{1}{T(E_{\text{tot}}, N_{\text{tot}})} = \left. \frac{\partial S(E_{\text{tot}}, N_{\text{tot}})}{\partial E_{\text{tot}}} \right|_{N_{\text{tot}}} = \beta(E_{\text{tot}}, N_{\text{tot}})$$

$$N_p = \langle N \rangle$$

$$\left(\cdot \right) = \frac{\partial}{\partial N_p} \left(\cdot \right)$$

$$S = \beta N \langle E \rangle - \beta \mu N N_p + N \ln Z_g$$

$$Z_g = \sum_{i=1}^n \exp(-\beta E_i + \beta \mu N_i)$$

$$\begin{aligned} \left. \frac{\partial S}{\partial N_p} \right|_E &= \cancel{\beta N \langle E \rangle} - \beta \mu N - \cancel{(\beta \mu) N N_p} \\ &+ N \underbrace{\frac{\partial \ln Z_g}{\partial \beta}}_{-\langle E \rangle} \dot{\beta} + N \underbrace{\frac{\partial \ln Z_g}{\partial (\beta \mu)}}_{N_p} (\dot{\beta \mu}) \\ &= -\beta \mu N = -\frac{N}{T} \mu \end{aligned}$$

Key Definition: The derived quantity

$$\mu = -T \frac{1}{N} \left. \frac{\partial S}{\partial N_p} \right|_E \quad (71)$$

is called *chemical potential*. It is related to the change of the entropy of a statistical system by adding a particle to the system while keeping its energy constant.

This is a definition that hinges on the “big” system, which is specified by the overall energy E and the total number of particles N_p . It also contains a reference to the number of boxes N . It would be convenient to have an expression for the chemical potential μ that only depends on “small” box properties. This can be indeed achieved.

$N \cdot N_p$

Assume that we have calculated the entropy, which is consequently a function of E and N_p :

$$S = S(E, N_p). \quad (72)$$

If we solve this equation for E , i.e.,

$$E = E(S, N_p),$$

we can use the latter to replace E as variable in all sort of equations. Hence, S and N_p are becoming our new *independent* variables. The constraint (68)

$$\sum_{i=1}^M p_i E_i = \langle E \rangle = \frac{E(S, N_p)}{N}$$

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

then becomes:

$$\langle E \rangle = \frac{1}{Z_g} \sum_{i=1}^M E_i \exp\{-\beta E_i + \beta \mu N_i\} = \frac{1}{N} E(S, N_p).$$

We then find:

$$\left. \frac{\partial \langle E \rangle}{\partial N_p} \right|_S = \frac{1}{N} \left. \frac{dE(S, N_p)}{dN_p} \right|_S \quad S: \text{constant.} \quad (73)$$

We then differentiate (72) by N_p and keep in mind that S is constant:

$$S(E, N_p) \quad 0 = \left(\frac{\partial S}{\partial E} \right)_{N_p} \frac{dE}{dN_p} + \left(\frac{\partial S}{\partial N_p} \right)_E = \frac{dS}{dN_p}$$

Using the definition of temperature and chemical potential, this becomes:

$$0 = \frac{1}{T} \frac{dE}{dN_p} - N \frac{\mu}{T}$$

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{N_p}$$

Using this in (73), we finally obtain:

$$\left. \frac{\partial \langle E \rangle}{\partial N_p} \right|_S = \mu. \quad (74)$$

$$\frac{-N}{T} \mu = \left. \frac{\partial S}{\partial N_p} \right|_E$$

$$E = N \cdot \langle E \rangle$$

Interpretations:

- The chemical potential is the change in internal energy when we adiabatically (without changing its entropy) add a particle to the system.
- Above, we still have S and N_p as independent variables. We can, however, now use some constraint equations and express S and N_p as a function of μ and T . In this case, μ and T are becoming the two independent variables.

$$Z_g(T, \mu)$$

Supplement: The grand-canonical potential

We now have the grand-canonical partition function $Z_g(T, \mu)$ defined with no explicit reference to the heat-bath or particle reservoir. Their role is simply to set the temperature T and chemical potential μ that characterize the “small” system in the grand-canonical ensemble. Similarly to the Helmholtz free energy considered for the canonical ensemble in Section 3.2, it is convenient to define a quantity related to the logarithm of the grand-canonical partition function.¹⁰

Key definition: With $Z_g(T, \mu)$ the grand-canonical partition function, the grand-canonical potential is

$$\Omega(T, \mu) \equiv -T \ln Z_g(T, \mu). \quad (74-S1)$$

Analogously to the Helmholtz free energy, derivatives of the grand-canonical potential are related to the internal energy $\langle E \rangle$, the average particle number $\langle N \rangle$ and the entropy S . Let's first consider the derivative with respect to the chemical potential:

$$\begin{aligned} \frac{\partial \Omega}{\partial \mu} &= -T \frac{1}{Z_g} \frac{\partial}{\partial \mu} \sum_{i=1}^M \exp \left(-\frac{E_i - \mu N_i}{T} \right) \\ &= -T \frac{1}{Z_g} \sum_{i=1}^M N_i \exp \left(-\frac{E_i - \mu N_i}{T} \right) = -\langle N \rangle \end{aligned}$$

We find

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

¹⁰The grand-canonical potential is sometimes called the “Landau free energy” to highlight its similarity with the Helmholtz free energy.

$$\Omega = -T \ln Z_g$$

The derivative with respect to the temperature is a little more complicated:

$$\begin{aligned} \frac{\partial \Omega}{\partial T} &= -\ln Z_g - \frac{T}{Z_g} \frac{\partial}{\partial T} \sum_{i=1}^M \exp\left(-\frac{E_i - \mu N_i}{T}\right) \\ &= -\ln Z_g - \frac{T}{Z_g} \frac{1}{T^2} \sum_i (E_i - \mu N_i) \exp\left(-\frac{E_i - \mu N_i}{T}\right) \\ &= -\ln Z_g - \frac{1}{T} \langle E \rangle + \frac{\mu}{T} \langle N \rangle \end{aligned}$$

To interpret this, let us recall the fundamental definition of the entropy (now also a function of T and μ):

$$S(T, \mu) = - \sum_{i=1}^M p_i \ln p_i \quad p_i = \frac{1}{Z_g} \exp\left\{-\frac{E_i - \mu N_i}{T}\right\}$$

$$\begin{aligned} S &= - \sum_{i=1}^M \frac{1}{Z_g} \exp\left(-\frac{E_i - \mu N_i}{T}\right) \left(-\ln Z_g - \frac{E_i}{T} + \frac{\mu}{T} N_i\right) \\ &= \ln Z_g + \frac{1}{T} \langle E \rangle - \frac{\mu}{T} \langle N \rangle = - \frac{\partial \Omega}{\partial T} \\ &= - \frac{\Omega}{T} + \frac{\langle E \rangle}{T} - \mu \frac{\langle N \rangle}{T} \end{aligned}$$

$\sum_{i=1}^M \exp\left(-\frac{E_i - \mu N_i}{T}\right) = Z_g$

This tells us two things:

$$\begin{aligned} S(T, \mu) &= - \frac{\partial \Omega(T, \mu)}{\partial T} \\ \Omega(T, \mu) &= -T \cdot S(T, \mu) + \langle E \rangle(T, \mu) - \mu \langle N \rangle(T, \mu). \end{aligned}$$

Finally, to extract the internal energy $\langle E \rangle(T, \mu)$, we need to consider

$$\begin{aligned}
 -\frac{\partial \ln Z_g(T, \mu)}{\partial T} &= \frac{\partial}{\partial T} \left[\frac{\Omega(T, \mu)}{T} \right] = -\frac{\Omega}{T^2} + \frac{1}{T} \frac{\partial \Omega}{\partial T} = -\frac{\Omega}{T^2} + \frac{-S}{T} \\
 &= -\frac{\Omega}{T^2} + \frac{\Omega}{T^2} - \frac{\langle E \rangle}{T^2} + \mu \frac{\langle N \rangle}{T^2} \\
 \langle E \rangle &= -T^2 \frac{\partial}{\partial T} \left[\frac{\Omega}{T} \right] + \mu \langle N \rangle
 \end{aligned}$$

In summary, we find the following:

Key observations: With $\Omega(T, \mu)$ the grand-canonical potential,

$$\langle N \rangle(T, \mu) = -\frac{\partial \Omega(T, \mu)}{\partial \mu} \quad (74-S2)$$

$$S(T, \mu) = -\frac{\partial \Omega(T, \mu)}{\partial T} \quad (74-S3)$$

$$\langle E \rangle(T, \mu) = -T^2 \frac{\partial}{\partial T} \left[\frac{\Omega(T, \mu)}{T} \right] + \mu \langle N \rangle \quad (74-S4)$$

$$\Omega(T, \mu) = -T \cdot S(T, \mu) + \langle E \rangle(T, \mu) - \mu \langle N \rangle(T, \mu) \quad (74-S5)$$

$n = 0, 1, \dots, \infty$

Single-particle energies $E_n = \frac{1}{2m} p_n^2 = \frac{1}{2m} \left(\frac{h\pi}{L} n \right)^2$

$$Z_1 = \sum_{n=1}^{\infty} \exp(-\beta E_n) = \sum_{n=1}^{\infty} \exp\left(-\frac{h^2 \pi^2}{2mT L^2} n^2\right)$$

8 Application: quantum gases

We already said in section 5.1 the sum over all states is not the same as the sum over all particles. In classical Newtonian mechanics (see the "ideal gas"), the only characteristic was the energy: the sum over all micro-states then became a sum over all energies.

We then noticed (see section 5.1) that the sum over all micro-states is actually badly defined for continuous degrees of freedom: the energy of a gas in a box of volume V can be any real number, the sum would involve to count all real numbers, which is mathematical impossible. At this point, we encounter quantum physics: a particle in a box still has an infinite amount of states, but those *can* be counted.

COMMENTS:

- Although quantum mechanics came to the rescue, the sum over all energies is still considered classical physics. It makes the assumption that micro-states are labelled by the energy, and quantum statistical physics is more subtle than this.
- We have developed the mathematical apparatus of Statistical Physics in the sections 3, 4, and 6. The only new element here will be the definition of micro-states for the quantum case.

In the following, we will study the quantum statistics of non-interacting particles. Particles could be traditional matter particles such as electrons or photons - the particles of light.

Our starting point is an energy spectrum consisting of discrete (countable) energies E_i ; some of the energies can be the same: we say that this energy level is degenerate, but we still account for them here with different labels i .

In classical physics, micro-states are characterised by these energies and, e.g., the grand-canonical partition function is given by

$$Z_{\text{classical}} = \sum_{i=1}^M \exp\{-\beta \sum_r E_i + \beta \mu N\}. \quad (78)$$

$$Z_{\text{classical}} = \sum_{i=1}^M \exp\{-\beta E_i + \beta \mu N_i\}$$

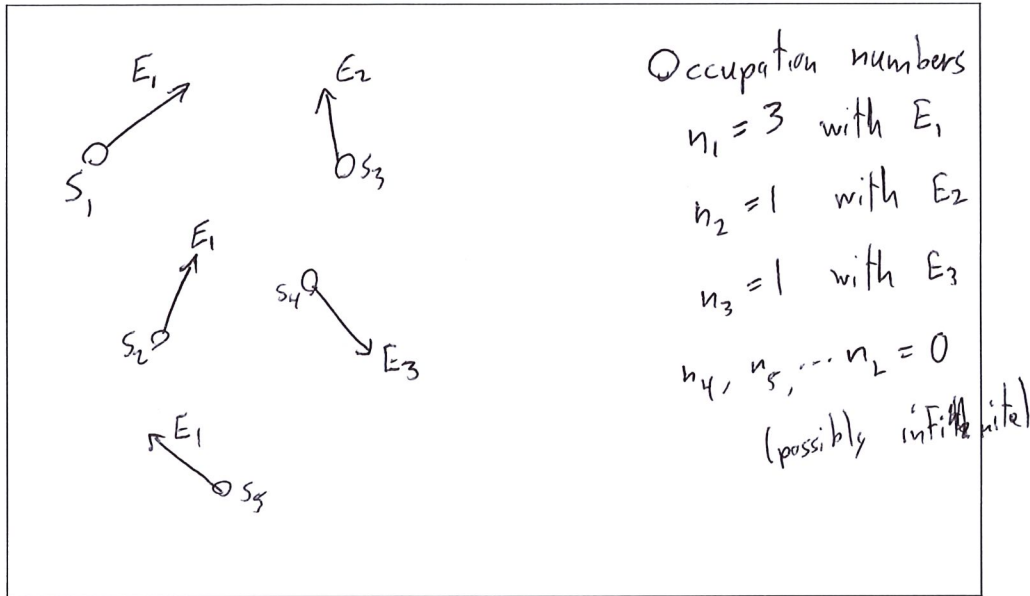
$$E_i = \sum_{p=1}^{N_i} E(s_p) \quad \text{non-interacting}$$

Energy "states"

degenerate

classical Z_g

While classical physics can be an extremely good approximation (as we will find below), the underlying definition of micro-states in nature is different. Here, we map, say N , particles, to the energies:



Physics background: If particles are indistinguishable, they can be exchanged without changing physics observables. We say that 'swapping' two particles is a symmetry. The quantum physics framework implies that particles can then be labeled by 'quantum numbers', rising from the representations from the corresponding symmetry group. The case of the "swapping symmetry" leads to a binary characterisation of particles: we say particles are either *fermions* or *bosons*. Well known examples are electrons, which are fermions, and photons (particles of light), which are bosons. Another particle, which recently came to fame, is the Higgs boson, who is the only 'matter' particle (so far) that is a boson.

Physics input: (non-degenerate) energy states can be populated by any number of bosons, but only by at most one fermion.

Swap labels
Boson: state $(s_1, s_2) = \text{state}(s_2, s_1)$
 particle s_1 has energy E_1 , s_2 has E_2
 particle s_2 has energy E_1 , s_1 has E_2

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Fermion: state $(s_1, s_2) = -\text{state}(s_2, s_1) = -\text{state}(s_1, s_2) \rightarrow \text{Vanishes!}$

IF indistinguishable $s_1 \neq s_2$ have same energy level/state

"Pauli exclusion principle"

Definition of the quantum statistical ensemble:

- The quantum statistical ensemble of non-interacting particles is defined by an energy spectrum $E_i, i = 1 \dots M$ (M can go to infinity) and by occupation numbers n_i for each energy.
- $n_i \in \mathbb{N}_0$ for bosons and $n_i = \{0, 1\}$ for fermions.
- The total energy E of the (non-interacting) system is given by:

$$E = \sum_i E_i n_i .$$

/ microstate \ energy state or energy level

Energy states

$N = 0, 1, 2, \dots$

BOSE GAS

Let us consider now a gas of bosons in a volume V . We consider the situation that this volume is immersed in a bigger system and that we allow energy exchange (heatbath characterised with temperature T) and particle exchange (particle reservoir characterised by the chemical potential μ). We have studied the mathematics of the so-called grand-canonical ensemble in detail in section 6. The partition function is given, as usual, by the sum over all micro-states, which is now a sum over all mappings of particles to energies:

grand-canonical
 $Z_g(T, \mu)$

Energy level $E_1 : n_1$
 Energy level $E_2 : n_2$
 ...
 Energy level E_M

$$Z_{bose} = \left(\sum_{n_1=0}^{\infty} \right) \dots \sum_{n_M=0}^{\infty} \exp \left\{ -\beta, \sum_{i=1}^M E_i n_i + \beta \mu \left(\sum_{i=1}^M n_i \right) \right\} .$$

We can carry out one sum after the other:

$$Z_g = \sum_{i=1}^M \exp \left(- \frac{E_i - \mu n_i}{T} \right) \quad \text{sum over microstates}$$

$$N(\text{microstate}) = \sum_{i=1}^M n_i \quad \text{sum over energy levels}$$

Warm-up: System w/ only one energy level E_i (Energy microstate = occ. #)

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

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

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

$$Z_{\text{bose}} = \sum_{n_1=0}^{\infty} \dots \sum_{n_M=0}^{\infty} \exp(-\beta E_1 n_1 + \beta \mu n_1 - \beta E_2 n_2 + \beta \mu n_2 + \dots)$$

$$= \sum_{n_1} \dots \sum_{n_M} \exp(-\beta E_1 n_1 + \beta \mu n_1) \times \exp(-\beta E_2 n_2 + \beta \mu n_2) \times \dots$$

$$= \left(\sum_{n_1=0}^{\infty} \exp(-\beta E_1 + \beta \mu)^{n_1} \right) \left(\sum_{n_2=0}^{\infty} \exp(-\beta E_2 + \beta \mu)^{n_2} \right) \times \dots$$

$$= \left(\frac{1}{1 - \exp(-\beta E_1 + \beta \mu)} \right) \left(\frac{1}{1 - \exp(-\beta E_2 + \beta \mu)} \right) \times \dots$$

$$= \prod_{i=1}^M \frac{1}{1 - \exp\left(-\frac{E_i - \mu}{T}\right)}$$

We finally obtain the sometimes called *Bose Statistics*;

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

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

$$\exp\left(-\frac{E_i - \mu}{T}\right) \ll 1.$$

We then can use the leading order of the expansion:

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

and find:

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

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