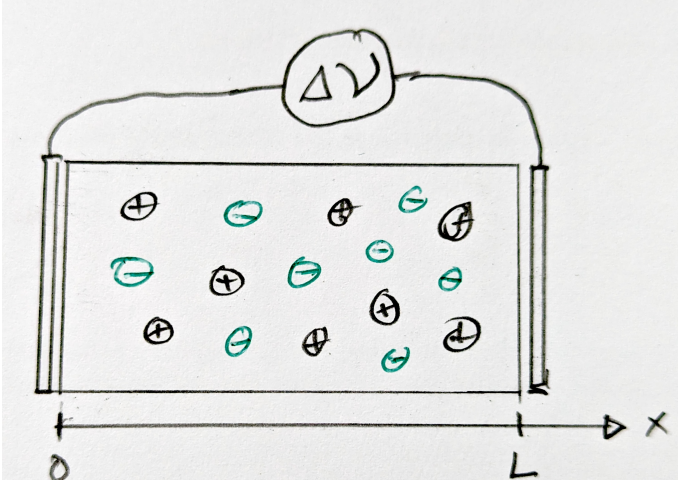
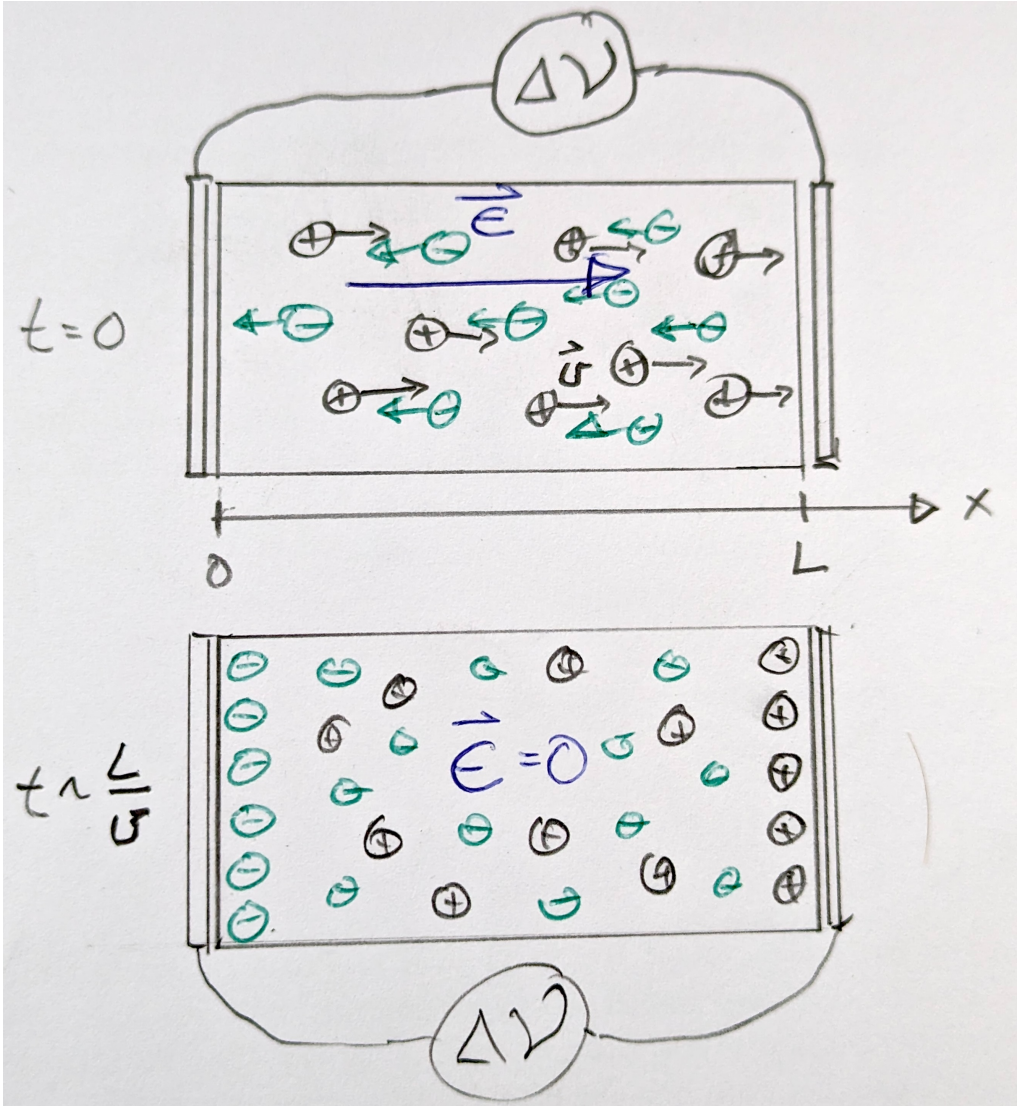
Electrolytes in electric field

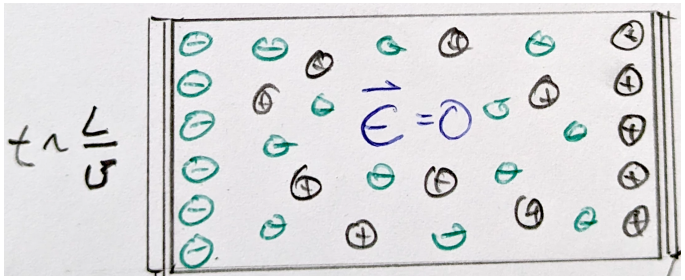


- Electrical field $\vec{\epsilon} = -\nabla\mathcal{V} = -\frac{d\mathcal{V}}{dx} = -\frac{\Delta\mathcal{V}}{L}$
- Force on charge $\vec{f} = q\vec{\epsilon}$
- **Turn on $\Delta\mathcal{V}$, what will happen?**

Electrolytes in electric field



Electrolyte in cell in electric field

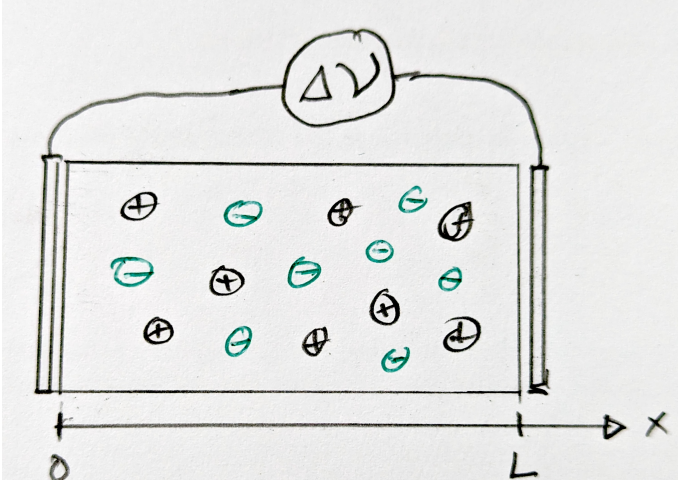


- **How fast is screening $\nu = \frac{v}{\Delta x}$? Compared to power line and mobile telephone frequencies?**
- Power line $\approx 10^5$V 10 m over ground $\Rightarrow \epsilon = 10^4$ V/m
- Drag force: $F_d = \xi v$, Einstein relation: $\xi D = kT$
- $D \approx 10^{-9}$ m^2/s, $e = 1.6 \cdot 10^{-19}$C, assume $\Delta x \approx 10^{-7}$ m
- $v = \frac{F_d}{\xi} = \frac{q\epsilon}{kT/D}$
- $\nu = \frac{q\epsilon D}{\Delta x kT}$
- $\nu = \frac{1.6 \cdot 10^{-19} 10^4 10^{-9}}{10^{-7} 1.4 \cdot 10^{-23} 3 \cdot 10^2}$
- $\nu \approx 3$ kHz.

Electrolyte in cell: shift Δx

- Homogeneous charge density $\rho = e \cdot c_{phys}$. $e = 1.6 \cdot 10^{-19}$C, $c_{phys} = 0.15$M.
- Homogeneous field in x-direction from a volume $V = A\Delta x$ of charge density ρ:
- $\vec{\epsilon} = \frac{\rho V}{\varepsilon A} = \frac{\rho \Delta x}{\varepsilon}$,
- permittivity $\varepsilon = \varepsilon_r \varepsilon_0 = 80 \cdot 8.8 \cdot 10^{-12}$F/m.
- $\Delta x = \frac{\vec{\epsilon}\varepsilon}{\rho} = \frac{\vec{\epsilon}\varepsilon}{e \cdot c_{phys}}$
- $\Delta x = \frac{10^4 \cdot 7 \cdot 10^{-10}}{1.6 \cdot 10^{-19} \cdot 1.5 \cdot 10^{-4} 6 \cdot 10^{23}}$
- $\Delta x = 5 \cdot 10^{-7}$m
- In fact $\nu = \frac{Dce^2}{\varepsilon kT}$ is independent of $\vec{\epsilon}$

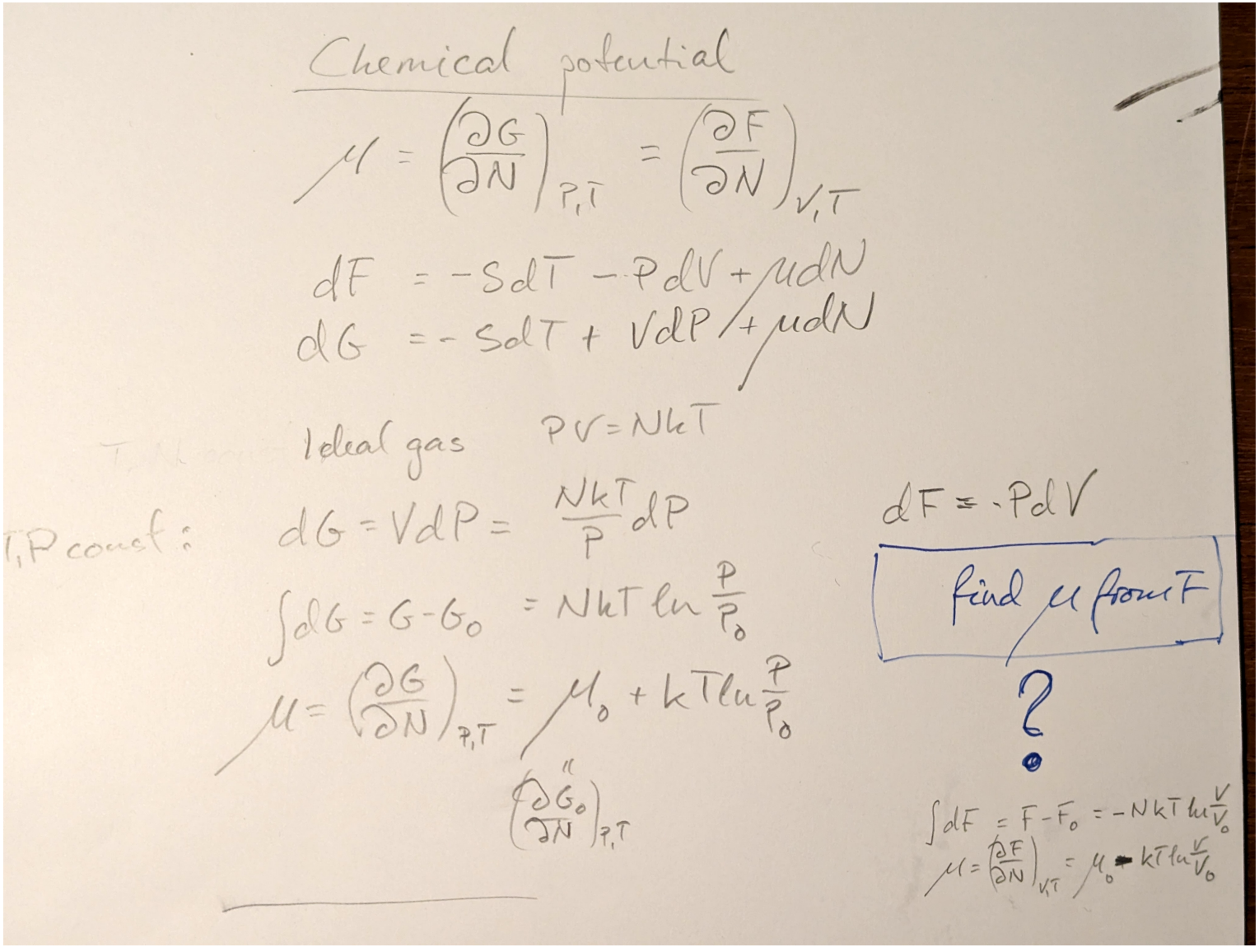
Electrolytes in electric field



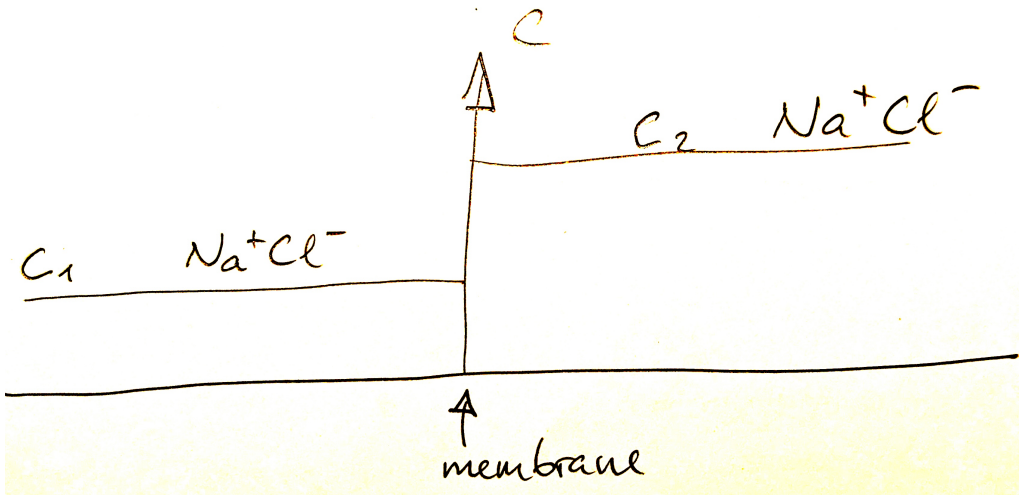
- Electrical field $\vec{\epsilon} = -\nabla\mathcal{V} = -\frac{d\mathcal{V}}{dx} = -\frac{\Delta\mathcal{V}}{L}$
- Force on charge $\vec{f} = q\vec{\epsilon}$
- **Turn on $\Delta\mathcal{V}$, what is the potential energy of a charge q in the electrical field?**
- Force due to potential energy: $f = -\frac{dU}{dx} = q\vec{\epsilon} = -q\frac{d\mathcal{V}}{dx}$
- $\Rightarrow U(x) = q\mathcal{V}(x)$

Chemical potential

Chemical potential

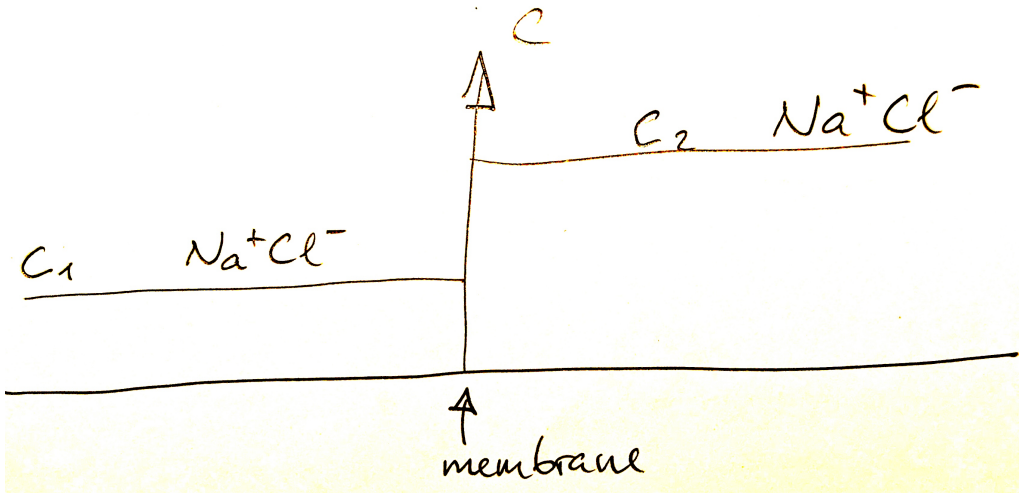


Semipermeable membranes



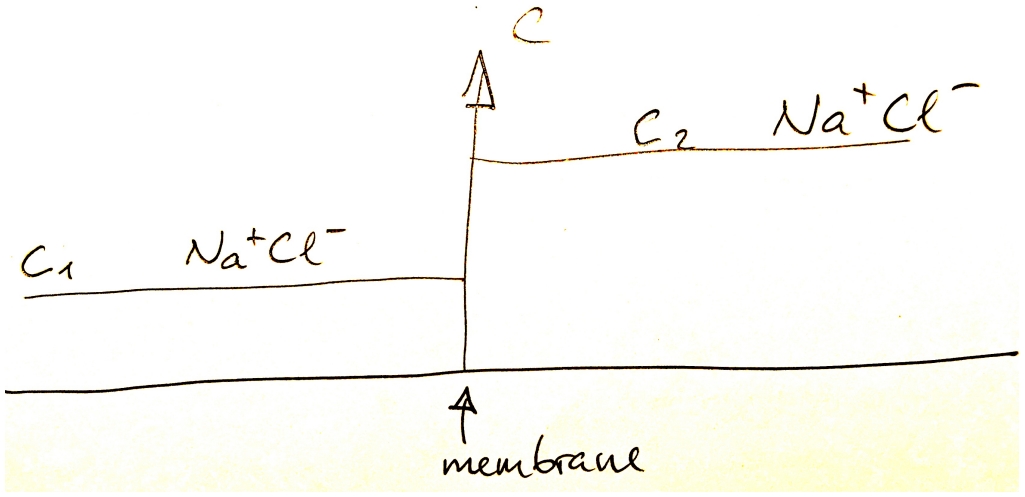
- **What happens when**
  - no ions permeate?
  - both species permeate?
  - membrane permeable to Na^+ only?
- **What is the equilibrium condition?**

Semipermeable membranes



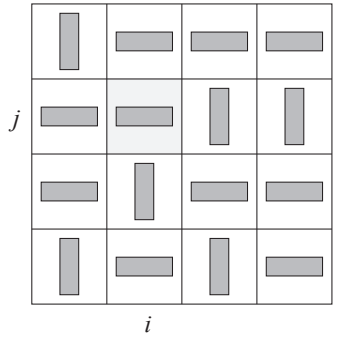
- **What is the chemical potential of Na^+?**
  - $\mu = \mu_{int} + \mu_{ext}$
  - $\mu_{int} = \mu_0(c_0) + kT \ln \frac{c}{c_0}$
  - μ_{ext} = energy per particle in external potential = **?**
  - $\mu_{ext} = \Delta U_{Na^+} = -e\Delta\mathcal{V}$

Semipermeable membranes



- **What is the electrical potential difference that balances the concentration difference $\Delta c = c_2 - c_1$?**
- $\Delta\mu = 0 = kT \ln \frac{c_2}{c_1} - e\Delta\mathcal{V}$
- $\Delta\mathcal{V} = \frac{kT}{e} \ln \frac{c_2}{c_1}$

Liquid Crystals: A Simple Model



- Liquid crystals: State of matter between liquid and solid
- Exhibit order in orientation of molecules
- Applications: Displays, sensors, etc.
- Our Model:
  - 2D grid of N particles, constant T
  - Two orientations: vertical or horizontal
  - Energy depends on neighboring orientations

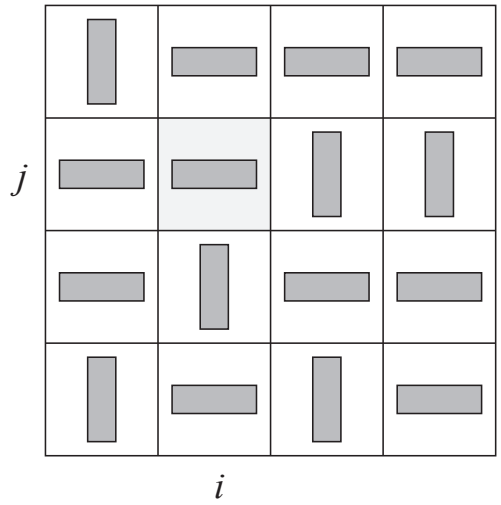
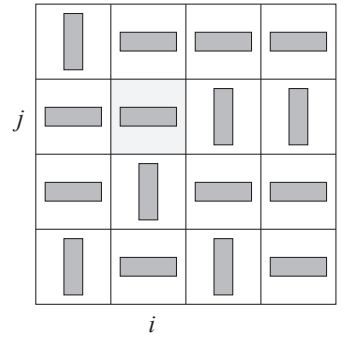


Figure: Illustration of a liquid crystal. Each particle in the crystal may have one of two possible orientations: vertical or horizontal. Particle (i, j) is shown. It is horizontally oriented.

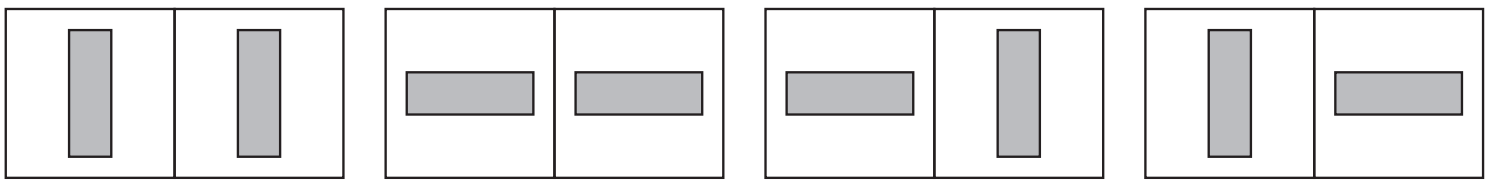


Single particle:

- 2 states: vertical or horizontal orientation
- energy independent of orientation
- **Find the partition function for the system.**
- **Find the probability for the particle to be vertically oriented.**
- $$Z = \sum_i e^{-\epsilon_i/kT} = 1 + 1 = 2 \, .$$
- $$P(1) = \frac{1}{Z} e^{-\epsilon_i/kT} = \frac{1}{2} 1 = \frac{1}{2} \, .$$

Two particles:

- single particle energy $= 0$
- adjacent particles:
  - same orientation: $\epsilon = 0$
  - different orientation: $\epsilon > 0$
- **Sketch the possible states. Write the energy of each state**
- **Show that the partition function for this system is $Z = 2\left(1 + e^{-\epsilon/kT}\right)$.**
  Compare with the result above and comment.



-
-

$$Z = \sum_i e^{-\epsilon_i/kT} = e^0 + e^0 + e^{-\epsilon/kT} + e^{-\epsilon/kT} \ .$$

When $\epsilon = 0$ $Z = 4 = 2^2$ for non-interacting particles.

Two particles:

- single particle energy $= 0$
- adjacent particles:
  - same orientation: $\epsilon = 0$
  - different orientation: $\epsilon > 0$
- **Find the internal energy, E, of the two-particle system.**
-
  - differentiate Z
  - or find F, then S and $E = F + TS$.

$$
\begin{aligned}
E &= kT^2 \frac{\partial \ln Z}{\partial T} = kT^2 \frac{1}{1 + e^{-\epsilon/kT}} e^{-\epsilon/kT} (-1) \left(\frac{-\epsilon}{kT^2} \right) \\
&= \epsilon \frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}}
\end{aligned}
$$

N particles, simulation:

- 2D system, $N = 10\ 000$ particles
- function energy(m) that returns the energy of a state m
- function m = rndstate() that returns a random state m
- **Sketch a program to find an approximate value for the partition function Z and the average of the energy of the system E for 10 000 random states at temperature T.**
- ```
  Z = 0.0;
  E = 0.0;
  kT = ...;
  for i = 1:10000
    m = rndstate();
    en = energy(m);
    ee = exp(-en/kT);
    Z = Z + ee;
    E = E + en*ee;
  end
  E = E/Z
  ```
  ```

N particles, simplified:

- N particles, of which $N_v = f\,N$ are vertically oriented
- **Show that the entropy of the system is approximately:**

$$S = -Nk\,(f \ln f + (1-f)\ln(1-f))$$

- Choose N_v from N: $\Omega = N!/(N_v!(N-N_v)!) \Rightarrow$ Entropy is:

$$S = k \ln \Omega = k\,(\ln N! - \ln N_v! - \ln(N-N_v)!)\ .$$

Stirlings approximation

$$S/k = N \ln N - N - N_v \ln N_v + N_v - (N-N_v)\ln(N-N_v) + (N-N_v)\ ,$$

use $N_v = fN$ and $N - N_v = (1-f)N\ldots$

N particles, simplified:

- Choose N_v from N: $\Omega = N!/(N_v!(N-N_v)!) \Rightarrow$ Entropy is:

$$S = k \ln \Omega = k \left(\ln N! - \ln N_v! - \ln(N-N_v)! \right) \ .$$

Stirlings approximation

$$S/k = N \ln N - N - N_v \ln N_v + N_v - (N-N_v) \ln(N-N_v) + (N-N_v) \ ,$$

use $N_v = fN$ and $N - N_v = (1-f)N$:

$$\begin{aligned} S/k &= N \ln N - Nf \ln Nf - (1-f) \ln N(1-f) \\ &= N \ln N - (Nf + (1-f)N) \ln N - Nf \ln f \\ &\quad -N(1-f) \ln(1-f) \ , \end{aligned}$$

which yields:

$$S/k = -N \left(f \ln f + (1-f) \ln(1-f) \right) .$$