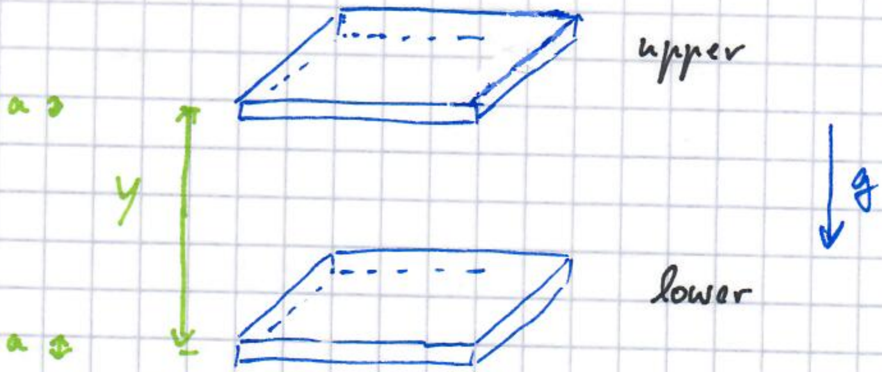
A bit more discussion of the chemical potential

→ to do this, we consider an example:



$y \gg a$

Each slab is an ideal gas

→ treat gas as distinguishable particles

Let the ~~energy~~ Hamiltonian of the i^{th} particle be $\frac{\vec{p}_i^{\,2}}{2m} + mgy_i$

kinetic energy — potential energy

For particles in the lower slab: $y_i = 0$

For particles in the higher slab: $y_i = y$

} we are assuming that the slabs are infinitely thin

Let's assume: $A_L = A_u$: equal area → Write as $V_L = V_u$

Why use V insted of A? We will be calculating the Helmholtz free energy A later on and I want to avoid confusion!!!

$T_L = T_u$: equal temperature

Goal: Calculate μ_L and μ_u, i.e., chemical potentials of the two isolated and separated slabs.

Approach: 1) Calculate Q_L and Q_u

→ note: We are working with fixed N_L, T_L, and V_L (as well as fixed N_u, T_u, and V_u); this implies that we want to work in the canonical ensemble.

2) Once we have $Q_L(N_L, T_L, V_L)$ and $Q_u(N_u, T_u, V_u)$, we can calculate $A_L(N_L, T_L, V_L) = -kT \log Q_L$ (same for A_u).

From A_L and A_u, we obtain

$$\mu_L = \left(\frac{\partial A_L}{\partial N_L}\right)_{T_L, V_L}$$

Start with 1):

Consider lower slab first. We have a Ni gas, i.e., we can calculate the partition function for a single particle and then ~~then~~ take the result to the power of N_L.

We do, of course, know the result.

$$Q_L(N_L, T_L, V_L) = \frac{1}{N_L!}\left(\frac{V_L}{\lambda_L^2}\right)^{N_L}$$

note: we have a power of 2 here since we are treating a slab and not a 3D system

$$\text{where } \lambda_L = \sqrt{\frac{(2\pi)^2\hbar^2}{mkT_L}}$$

de Broglie wave length

What about Q_u? The integration over the momenta gives the same result. In addition, the gravitational energy, which is discrete due to our setup, yields an additional factor of $\exp\left(-\frac{mgy}{kT_u}\right)$ for each particle.

Hence: $$Q_u(N_u, T_u, V_u) = \frac{1}{N_u!}\left(\frac{V_u}{\lambda_u^2}\right)^{N_u} e^{-\frac{mgyN_u}{kT_u}}$$

Let's rewrite the partition fcts using that $V_L = V_u$ and $T_L = T_u$.

$$Q_L(N_L, T, V) = \frac{1}{N_L!}\left(\frac{V}{\lambda^2}\right)^{N_L}$$

$$Q_u(N_u, T, V) = \frac{1}{N_u!}\left(\frac{V}{\lambda^2}\right)^{N_u}\exp\left(-\frac{mgyN_u}{kT}\right)$$

with $N = N_L + N_u$ (N: total # of particles)

Move on to 2):

$$A_L \overset{\text{def}}{=} -kT \log Q_L \overset{\text{result from previous page}}{=} -kT \log\left(\frac{1}{N_L!}\left(\frac{V}{\lambda^2}\right)^{N_L}\right)$$

$$= -kT\left[\log\left(\left(\frac{V}{\lambda^2}\right)^{N_L}\right) - \underbrace{\log(N_L!)}_{\approx N_L \log N_L - N_L}\right]$$

$$\mu_L = \left(\frac{\partial A_L}{\partial N_L}\right)_{T,V}$$

$$= -kT \log\left(\frac{V}{N_L \lambda^2}\right)$$

using $\frac{\partial \log N_L!}{\partial N_L} \approx \log N_L$

Similarly:

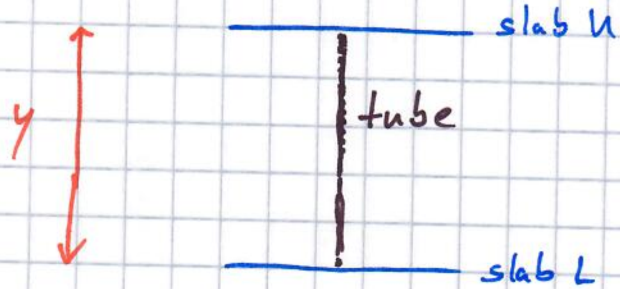
$$A_u = -kT \log Q_u = -kT \log\left[\frac{1}{N_u!}\left(\frac{V}{\lambda^2}\right)^{N_u} \exp\left(-\frac{mgy N_u}{kT}\right)\right]$$

$$= -kT \log\left[\frac{1}{N_u!}\left(\frac{V}{\lambda^2}\right)^{N_u}\right] + kT\left(\frac{mgy N_u}{kT}\right)$$

$$\mu_u = -kT \log\left(\frac{V}{N_u \lambda^2}\right) + mgy$$

Let's assume now that the upper and lower slabs contain the same number of particles: $N_L = N_u$.

Let's further assume that the two slabs get connected by a tube of negligible volume so that particles can move from one slab to another:



(I'm drawing a front view)

We now have a composite system with fixed number of particles N — N_L and N_u can vary now but V and T are fixed.

Question: Starting with $N_u = N_L$, how will the particle numbers change when the connection (via the tube) is established?

Note: We will not be able to determine what happens as a fct. of time! We will only be able to determine what the new equilibrium configuration is when the lower and upper systems are connected.

Approach: 1) Calculate partition function of composite system.

2) Calculate Helmholtz free energy of composite system.

3) Minimize A of composite system to obtain N_L (and then N_u through $N = N_L + N_u$).

only one of these two variables is independent

Let's do it!

1) We have no interactions between the particles in the lower and upper slabs.
Moreover, the volume of the tube can be neglected.

$$\Rightarrow Q(N,T,V) = Q_L(N_L,T,V)\, Q_u(N_u,T,V)$$

2) $$A(N,T,V) = -kT \log\left(Q(N,T,V)\right)$$

$$= -kT\left[\log\left(Q_L(N_L,T,V)\right) + \log\left(Q_u(N_u,T,V)\right)\right]$$

3) $$\left(\frac{\partial A}{\partial N_L}\right)_{T,V} = \left\{\frac{\partial}{\partial N_L}\left[-kT\log\left(Q_L(N_L,T,V)\right)\right] + \frac{\partial}{\partial N_L}\left[-kT\log\left(Q_u(N_u,T,V)\right)\right]\right\}_{T,V}$$

now: N_u is not independent of N_L

$\rightarrow N_u = N - N_L$

$N_L = N - N_u$

$$\frac{\partial}{\partial N_L} = \frac{\partial}{\partial(N-N_u)} = -\frac{\partial}{\partial N_u}$$

$$= \mu_L - \mu_u$$

Now, we are looking for a minimum of the Helmholtz free energy of the composite system

$$\Rightarrow \left(\frac{\partial A}{\partial N_L}\right)_{T,V} = 0 \quad \text{or} \quad \mu_L = \mu_u$$

So: minimizing the Helmholtz free energy is identical to enforcing $\mu_L = \mu_u$!!!

What does this mean for the particle numbers in the two slabs?

Write out $\mu_L = \mu_u$:

$$-kT \log\left(\frac{V}{N_L \lambda^2}\right) = -kT \log\left(\frac{V}{N_u \lambda^2}\right) + mgy$$

Rearrange:

$$+kT \log N_L = kT \log N_u + mgy$$

$$kT \log \frac{N_L}{N_u} = mgy$$

$$\Rightarrow \quad \log\left(\frac{N_L}{N_u}\right) = \frac{mgy}{kT}$$

$$N_L = N_u \, e^{mgy/kT}$$

Finally:

$$N_u = N_L \, e^{-mgy/kT}$$

<1 for $y > 0$ (assuming T positive)

Thus: at equilibrium, we have $N_u < N_L$.
Particles flow from the slab with higher potential to the slab with lower potential energy.