

8.044 Lecture Notes

Chapter 8: Chemical Potential

Lecturer: McGreevy

Reading: Baierlein, Chapter 7.

So far, the number of particles N has always been fixed. We suppose now that it can vary, and we want to learn how to determine its value in equilibrium.

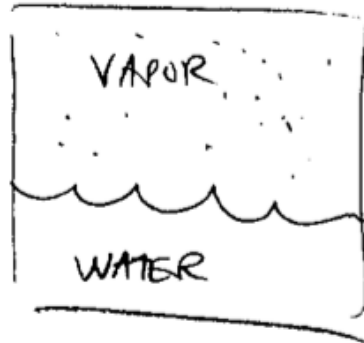
The concept we'll need to introduce to answer this question is *chemical potential*. This is the last core concept in thermodynamics; it arises via a simple extension of the logic which led to the canonical ensemble. The fact that we delayed its introduction until now is not because it's very fancy, just because we didn't need it yet. We'll need it in Chapter 9.

Motivating examples

Some situations where the number of particles of a given type is not fixed, and needs to be determined:

- **Phase equilibrium**

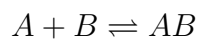
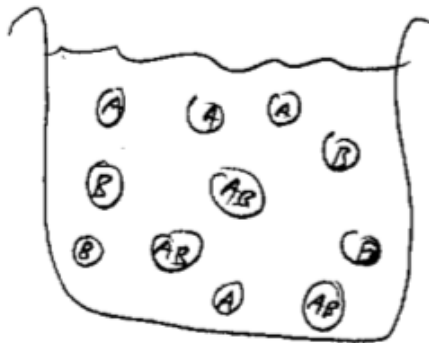
Vessel of water at 100° C:



Atoms in the gas can join the liquid, and vice versa. N_{gas} not fixed. N_{liquid} not fixed.
 $N = N_{\text{gas}} + N_{\text{liquid}}$ is fixed.

- **Chemical equilibrium**

Beaker with solution:



N_A, N_B, N_{AB} not fixed

$N_A + N_{AB}$ and $N_B + N_{AB}$ fixed.

For more on these examples, see Baierlein Chapters 11 and 12, or 8.08, or a chemistry class.
We'll introduce chemical potential in a simpler example.

• Diffusion of a monatomic ideal gas against gravity

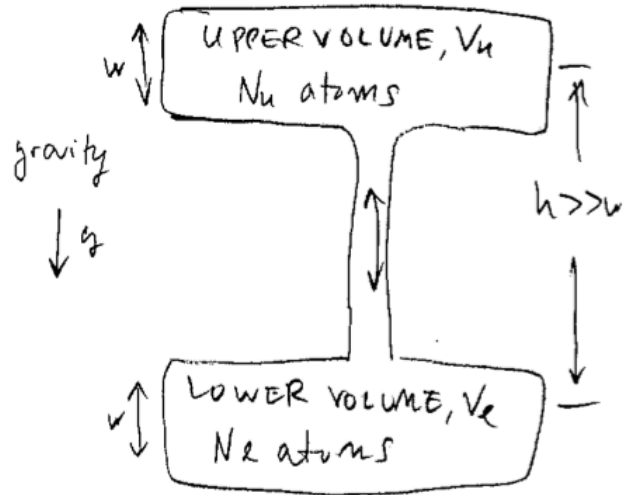
Put the whole system at temperature T . There is a fixed number of particles in the container:

$$N_{\text{total}} \equiv N_l + N_u \quad \text{is fixed.}$$

Q: what's the most probable N_l, N_u ?

What happens? Two wrong answers:

- 8.01: a big pile on the floor.
- 8.044, so far: ignore gravity. Density and pressure the same everywhere.



$$\begin{aligned}
 p(N_l, N_u) &\equiv \text{Prob} \left(\begin{array}{l} N_l \text{ atoms in lower volume,} \\ N_u \text{ atoms in upper volume} \end{array} \right) \\
 &= \underbrace{\frac{1}{Z}}_{\text{sum over all states with any } N_l, N_u, N_{\text{tot}} \text{ fixed}} \cdot \sum_{\text{states with } N_l(N_u) \text{ in lower (upper) volume}} e^{-\beta E_{\text{state}}} \\
 &= \frac{Z(N_l, N_u)}{Z}
 \end{aligned}$$

[More explicitly: $Z = \sum_{N_l=0}^{N_{\text{tot}}} Z(N_l, N_u = N_{\text{tot}} - N_l)$.]

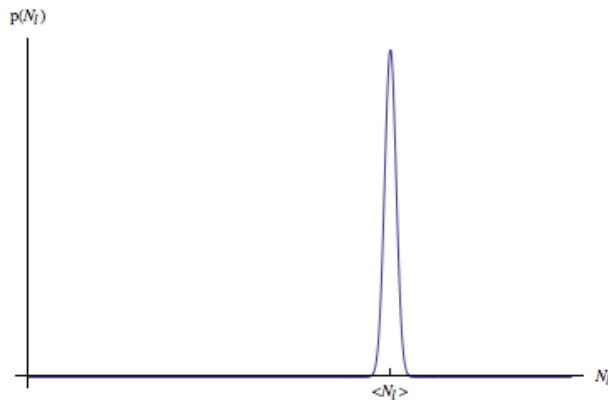
$$E_{\text{state}} = \underbrace{\epsilon_1 + \epsilon_2 + \dots + \epsilon_{N_l}}_{\text{single-particle energies for ideal gas in } V_l} + \underbrace{\epsilon_1^u + \epsilon_2^u + \dots + \epsilon_{N_u}^u}_{\text{single-particle energies for ideal gas in } V_u - \text{includes an extra } mgh \text{ term}}$$

This extra potential energy for particles in the upper chamber means that the partition function for one u particle is: $Z_u(1) = \int_{V_u} d^3x \int d^3p e^{-\beta(p^2 + mgh)}$. Note that it's still an ideal gas in that the energy doesn't depend on the *separations* between the u particles. This constant potential energy matters because we are comparing it to that of the particles in the lower chamber – it's the difference in potential energy between upper and lower which matters.

$$\begin{aligned}
 Z(N_u, N_l) &= \underbrace{\left(V_l \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \right)^{N_l}}_{\equiv Z_l(N_l)} \cdot \underbrace{\left(V_u \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} e^{-\beta mgh} \right)^{N_u}}_{\equiv Z_u(N_u)} \\
 p(N_l, N_u) &= \frac{Z_l(N_l) Z_u(N_u)}{Z}
 \end{aligned}$$

[End of Lecture 20.]

For a macroscopic system, we expect that this probability distribution will be well-peaked around the average value. Plotting the function, we see that this is the case: (Exercise: compute the variance as a function of N .)



To find $\langle N_l \rangle$, we need the maximum of $\ln p(N_l, N_u = N_{\text{tot}} - N_l)$:

$$0 = \frac{\partial \ln p(N_l, N_u)}{\partial N_l} = \frac{\partial \ln Z_l(N_l)}{\partial N_l} + \frac{\partial \ln Z_u(N_u)}{\partial N_l}$$

$$\frac{\partial \ln Z_l(N_l)}{\partial N_l} = -\frac{dN_u}{dN_l} \frac{\partial \ln Z_u(N_u)}{\partial N_u}$$

$$(N_u = N_{\text{tot}} - N_l \implies \frac{dN_u}{dN_l} = -1).$$

Therefore the maximum probability occurs when

$$\boxed{\frac{\partial \ln Z_l(N_l)}{\partial N_l} = \frac{\partial \ln Z_u(N_u)}{\partial N_u}}. \quad (1)$$

The LHS only depends on the lower system, the RHS depends only on the upper system; we've shown that when they are in equilibrium, their $\partial_N \ln Z$ s are the same. Notice the similarity of the logic here to our derivation of the zeroth law – when two systems are in equilibrium, their temperatures are equal. This quantity $\partial_N \ln Z$ (which will acquire a name in a moment) plays the role for N that T plays for E .

Now, recall that $F = -k_B T \ln Z$. We can rewrite (1) as

$$\boxed{\left(\frac{\partial F_l}{\partial N_l} \right)_{T, V_l} = \left(\frac{\partial F_u}{\partial N_u} \right)_{T, V_u}}$$

Since N is a discrete variable, what we mean by $\frac{\partial F}{\partial N}$ here is

$$\begin{aligned} \frac{\partial F}{\partial N} &= \frac{\Delta F}{\Delta N} \text{ with } \Delta N = 1 \\ &= F(T, V, N) - F(T, V, N - 1) \end{aligned} \quad (2)$$

We define the *chemical potential* as

$$\boxed{\mu(T, V, N) \equiv \left(\frac{\partial F}{\partial N} \right)_{T, V} = F(T, V, N) - F(T, V, N - 1)}.$$

We have shown that in equilibrium,

$$\mu_l = \mu_u.$$

That is, μ is uniform throughout the system.

Comments about μ

- μ is the free energy cost for adding one more particle (at constant T, V).
- Recall: at constant T, V , equilibration proceeds by minimizing F .

Suppose $\mu_l < \mu_u$. Then we can lower the total free energy by removing a particle from u and adding it to l .

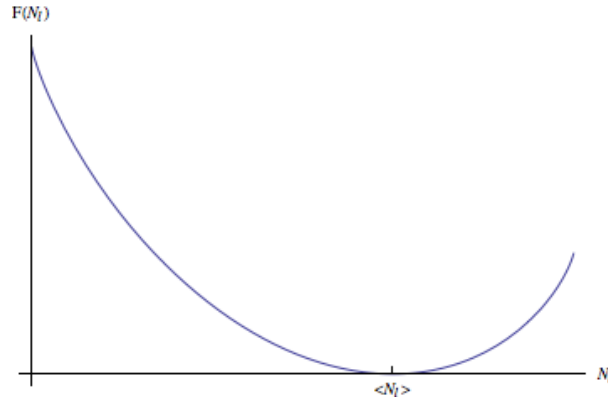
Therefore, $\mu_l \neq \mu_u$ means we are not in equilibrium. The particles will diffuse between u and l until $\mu_l = \mu_u$.

Recall: T told us the direction of heat flow when we put two systems of different temperatures in contact. Similarly, μ tells us the direction of particle flow.

- In the phase equilibrium example, $\mu_{\text{liquid}} = \mu_{\text{gas}}$ in equilibrium. Also: $T_{\text{liquid}} = T_{\text{gas}}$ and $P_{\text{liquid}} = P_{\text{gas}}$.
- Note:

$$F = F_l + F_u = -k_B T \ln \underbrace{(Z_l Z_u)}_{\propto p(N_l, N_u)}$$

Therefore: equilibrium \Leftrightarrow max probability \Leftrightarrow min F .



Back to the gravity example:

You can recognize that these concepts transcend this example with an ideal gas in a constant gravitational field.

But let's return to this example and work out the consequences of imposing equilibrium:

$$\begin{aligned}\mu_l &= \frac{\partial F_l}{\partial N_l} = -k_B T \frac{\partial}{\partial N_l} \ln \left(\frac{Z_1^{N_l}}{N_l!} \right) \\ &= -k_B T \frac{\partial}{\partial N_l} (N_l \ln(Z_1) - N_l \ln N_l + N_l) \\ &= -k_B T \ln \left(\frac{Z_1}{N_l} \right) = -k_B T \ln \left(\frac{V_l}{N_l} \lambda_{\text{th}}^{-3} \right)\end{aligned}$$

[This manipulation happens frequently and is worth recording: we just showed that

$$\boxed{\text{If } Z = \frac{Z_1^N}{N!} \text{ then } \frac{\partial}{\partial N} \ln Z = \ln \left(\frac{Z_1}{N} \right)} \quad .]$$

So:

$$\begin{aligned}\mu_u &= \left(\frac{\partial F_u}{\partial N_u} \right) = -k_B T \ln \left(\frac{V_u}{N_u} \lambda_{\text{th}}^{-3} e^{-\beta mgh} \right) \\ &= mgh - k_B T \ln \left(\frac{V_u}{N_u} \lambda_{\text{th}}^{-3} \right)\end{aligned}$$

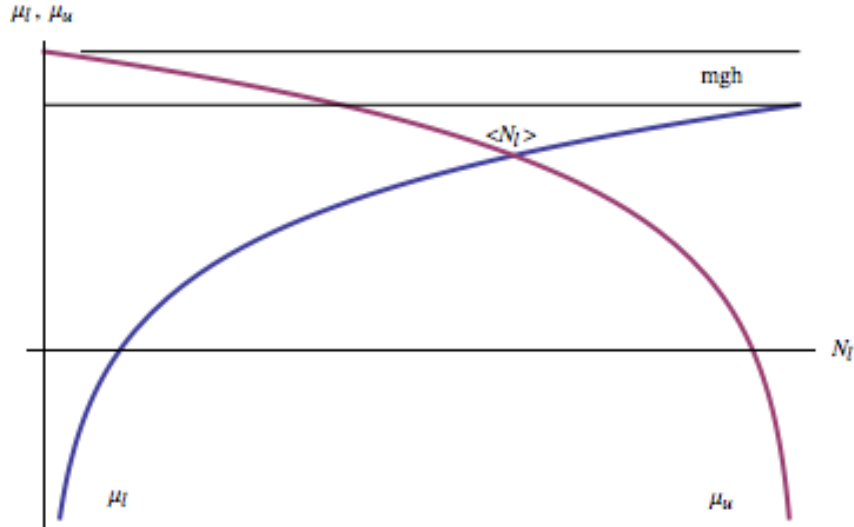
Therefore

$$\begin{aligned}\mu_l = \mu_u &\Leftrightarrow \frac{V_l}{N_l} = \frac{V_u}{N_u} e^{-\beta mgh} \\ &\Leftrightarrow \frac{N_u}{V_u} = \frac{N_l}{V_l} e^{-mgh/k_B T}\end{aligned}$$

Lower density higher up! $\rho_u < \rho_l$. Another good check: turning off gravity $g \rightarrow 0$ restores $\rho_u = \rho_l$.

This is the 'Law of Isothermal Atmospheres'. Problem Set 10 gives a more realistic accounting of the density of air as a function of height in the atmosphere.

For simplicity, set $V_u = V_l$.



Note that if $mgh = 0$, $\langle N_l \rangle = N/2$. If $mgh > 0$, $N_l > N/2 > N_u$.

If $\mu_u > \mu_l$, $N_l < N_l^{\text{eqbm}}$, atoms diffuse from u to l .

If $\mu_u < \mu_l$, $N_l > N_l^{\text{eqbm}}$, atoms diffuse from l to u .

Just as energy diffuses in response to a temperature gradient, particles diffuse in response to a gradient of chemical potential.

e.g. If we start with equal densities at u and l , then $\mu_u > \mu_l$ by mgh and the atoms with diffuse downward until this difference is equalized.

Chemical potential measures the tendency to diffuse.

Increasing density, N/V increases μ .

Increasing the energy difference mgh increases μ .

\implies particles diffuse away from large density N/V , and from large mgh .

Note that once N is allowed to vary

$$dF = -SdT - PdV + \underbrace{\mu}_{= \left(\frac{\partial F}{\partial N} \right)_{T,V}} dN$$

$$dE = TdS - PdV + \mu dN \implies \mu = \left(\frac{\partial E}{\partial N} \right)_{V,S}$$

Note that $\mu < 0$ for classical ideal gas:

$$\mu = -k_B T \ln \left(\frac{V}{N \lambda_{\text{th}}^3} \right)$$

¹ Why is this? μ is the energy to add a particle, keeping the entropy constant. Examining the formula for the entropy shows that keeping the entropy constant while increasing N forces you to lower the temperature. The system over-compensates for the extra kinetic energy.

The differentials of all four thermodynamic potentials (E, F, G, H) acquire a $+\mu dN$ term. We could now define four more th. potentials by Legendre transforming by subtracting μN , to change $+\mu dN$ to $-Nd\mu$.

¹As we will in Chapter 9, if the argument of the logarithm here is not much bigger than 1 (meaning that the logarithm is positive: $\ln(x > 1) > 0$), it's not a *classical* ideal gas.