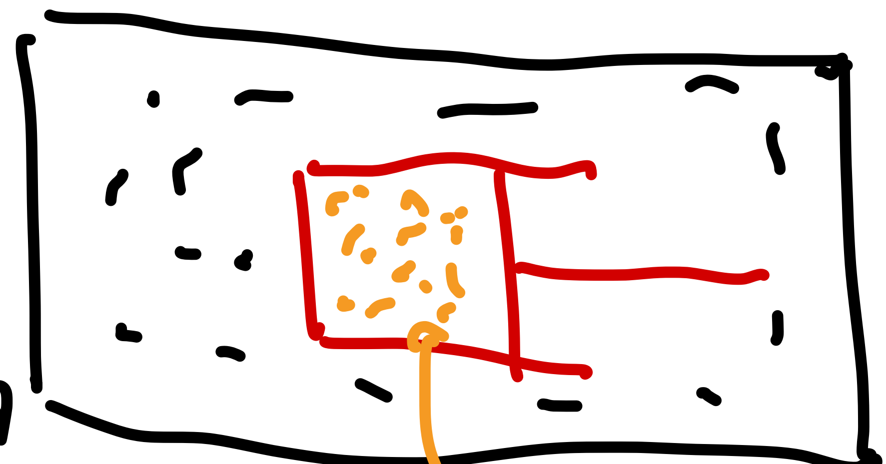
Lecture 4 - Thermo review

Last time:

- Discussed microcanonical partition function $\Omega(N,V,E)$
- Asserted that $S = k_B \log \Omega$ is a good definition of entropy
- To go farther, good time to review key parts of thermo

① First law: conservation of energy. Energy not created or destroyed however, when we study a system definition of system matters

Important situation:



system, const N

V can change, energy can flow

const N, V, E

for system, change in internal energy = heat in − work done

$$\boxed{dE = \text{đ}q - \text{đ}w}$$

Reminder: infinitessibles show the response of a function to a very tiny change in an argument

$$f(x+\Delta x) \approx f(x) + \Delta x \left[\frac{df}{dx}\right] + \ldots$$

so $\Delta f = f(x+\Delta x) - f(x) \approx \Delta x \left[\frac{df}{dx}\right]$

or $df = \frac{df}{dx} \cdot dx$

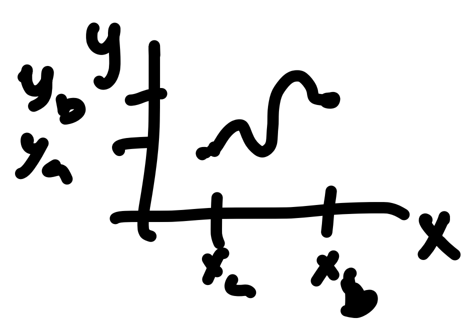
for multidimensions, $dx\,dy \approx 0$ so

$$df = f(x+\Delta x, y+\Delta y, \ldots) - f(x,y,\ldots)$$
$$\approx \left(\frac{\partial f}{\partial x}\right)_{y,\ldots} dx + \left(\frac{\partial f}{dy}\right)_{x,\ldots} dy + \ldots$$

Same idea as chain rule

$$\frac{df}{dz} = \left(\frac{\partial f}{\partial x}\right)\left(\frac{\partial x}{\partial z}\right) + \left(\frac{\partial f}{\partial y}\right)\left(\frac{\partial y}{\partial z}\right) + \ldots$$

total change in f from path



$$\Delta f = \int_{path} df$$

put $đ$, δ because depends on path taken. However, change in $\mathcal{E}$ does not

$$\Delta \mathcal{E} = \int_a^b (đq - đw)$$

$a = N_1, V_1, \mathcal{E}_1$
$b = N_1, V_2, \mathcal{E}_2$

for change in volume
$đw = P\,dV$ @ const P
$= -\mu\,dN$ @ const μ

different kinds of work
eg
mechanical, chemical

$\mathcal{E}$ is a <u>state function</u> -
depends only on macro variables

differentials

$$\mathcal{E}(A,B,C) \Rightarrow d\mathcal{E} = \left(\frac{\partial \mathcal{E}}{\partial A}\right) dA + \dots = \sum_i \left(\frac{\partial \mathcal{E}}{\partial \lambda_i}\right) d\lambda_i = -đw$$

② 2nd law. Heat is not a state function, but exists a quantity

$$dS = đQ/T,$$ which is

$$S(b) - S(a) = \int_a^b đQ/T$$ for any path from $a \to b$

S is called entropy

Rearrange first law

$$dE = đQ - đW$$

$$dS = \frac{1}{T} dE - \frac{1}{T} đW$$

$$= \frac{1}{T} dE - \frac{1}{T}\left(\sum_i \frac{\partial E}{\partial \lambda_i} d\lambda_i\right)$$

$$- PdV/T + \frac{\mu dN}{T}$$

Can do same differential for S

$S(N, V, \varepsilon)$:

$$dS = \underbrace{\left(\frac{\partial S}{\partial N}\right)_{V,\varepsilon}}_{-\mu/T} dN + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{N,\varepsilon}}_{= \frac{P}{T}} dV + \underbrace{\left(\frac{\partial S}{\partial \varepsilon}\right)_{N,V}}_{= \frac{1}{T}} d\varepsilon$$

Reminder: this follows from 1st law and definition of work

$\Delta S \geq 0$ for any process in an isolated system, with $\Delta S = 0$ only for reversible transformations

The universe as a whole is an isolated system so any process we do likely increases total entropy

Why do we need to know this?

for microcanonical ensemble,

S is a thermodynamic potential

It is maximized under any process

If we know $S(N,V,E)$, we can compute any thermodynamic quantity of interest

Recall, for N, V, E

$$S = k_B \ln \Omega(N,V,E)$$

And we see

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E} \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{V,E}$$

We will have analogous results for canonical ensemble (N,V,T)