Last time, we got an introduction to the partition function $Z$

(1.1) $$Z = \sum_{s} e^{-\varepsilon_s/\tau}$$

energy of microstate labelled by $\{s\}$

MICRO states

Then

(1.2) $$P_s = \frac{e^{-\varepsilon_s/\tau}}{Z}$$

Today, we'll learn about more ways in which $Z$ can be very, VERY useful.

---

- Consider the $\boxed{\text{average energy}}$ of our system $\mathcal{S}$ in thermal contact with reservoir $\mathcal{R}$ at temperature $\tau$.

  exchange of energy only (not particles which make up our system $\mathcal{S}$ of interest)

We know the abstract formula for the thermal average of any $X$:

(1.3) $$\langle X \rangle = \sum_{s} X_s \cdot \left( \frac{e^{-\varepsilon_s/\tau}}{Z} \right)$$

So for energy we have

(1.4) $$\langle \varepsilon \rangle = \sum_{s} \varepsilon_s \frac{e^{-\varepsilon_s/\tau}}{Z}$$

$\langle \varepsilon \rangle$ is traditionally called $U$. ← "big U"

(1.5) $$\rightarrow \quad U = \sum_{s} \varepsilon_s \frac{e^{-\varepsilon_s/\tau}}{Z}$$

Now let's do some mathematical manipulations, with the physics goal of finding the average energy.

We know $U = \sum_s \varepsilon_s \left( \frac{e^{-\varepsilon_s/\tau}}{Z} \right)$

$= \frac{1}{Z} \sum_s \varepsilon_s e^{-\varepsilon_s/\tau}$ ($\because$ $Z$ independent of $s$)

Now what ?!

Well, the goal is to use $Z$ to find $U$.
What operations do we know how to do to $Z$?

▷ We can take derivative(s), for one example...
But we should take the derivative w.r.t a macroscopic variable
So try $\tau$ : $Z$ depends on this explicitly.

(2.1) $$\frac{\partial Z}{\partial \tau} = \frac{\partial}{\partial \tau} \sum_s e^{-\varepsilon_s/\tau}$$

$$= \sum_s \frac{\partial}{\partial \tau} e^{-\varepsilon_s/\tau}$$

(2.2) $$= \sum_s \left( + \frac{\varepsilon_s}{\tau^2} \right) e^{-\varepsilon_s/\tau}$$

(2.3) $$= \frac{1}{\tau^2} \underbrace{\sum_s \varepsilon_s e^{-\varepsilon_s/\tau}}_{\text{aha!}}$$

☺

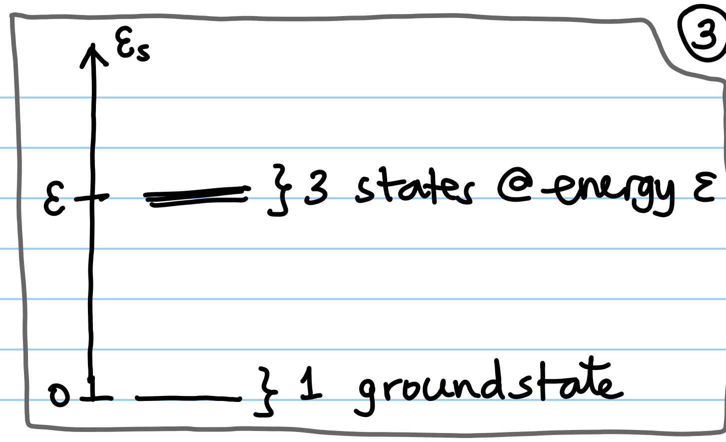
So... we've discovered that

(2.4) $$\frac{\partial Z}{\partial \tau} = \frac{1}{\tau^2} (UZ)$$

(2.5) i.e. $$\boxed{U = \frac{\tau^2}{Z} \frac{\partial Z}{\partial \tau}}$$

This works for completely general system $\mathcal{S}$ in thermal contact with $\mathcal{R}$ @ temperature $\tau$ ☺

## Example




As we found last time,

(3.1) $$Z = 1 + 3e^{-\varepsilon/\tau}$$

So $$\frac{\partial Z}{\partial \tau} = 3e^{-\varepsilon/\tau}\cdot\left(\frac{+\varepsilon}{\tau^2}\right)$$

(3.2) $$= \frac{3\varepsilon}{\tau^2}\, e^{-\varepsilon/\tau}$$

hence $$U = \frac{\tau^2}{Z}\frac{\partial Z}{\partial \tau}$$

$$= \frac{\tau^2}{(1+3e^{-\varepsilon/\tau})}\cdot\frac{3\varepsilon}{\tau^2}e^{-\varepsilon/\tau}$$

(3.3) i.e. $$U = \frac{3\varepsilon\, e^{-\varepsilon/\tau}}{(1+3e^{-\varepsilon/\tau})}$$

$$= \frac{e^{-0}\cdot 0}{(1+3e^{-\varepsilon/\tau})} + \frac{3e^{-\varepsilon/\tau}\cdot\varepsilon}{(1+3e^{-\varepsilon/\tau})}$$

$$= 0\,P_0 + 3\,P_\varepsilon \quad \checkmark$$

---

## $\boxed{\text{Heat Capacity}}$

(3.4) $$\boxed{C_V = \left(\frac{\partial U}{\partial \tau}\right)_V}$$ ← how much energy increase you get if you crank up $\tau$ ☺

↖ dimensionless

Here, for our example,

$$C_V = \frac{\partial}{\partial\tau}\left\{\frac{3\varepsilon\, e^{-\varepsilon/\tau}}{(1+3e^{-\varepsilon/\tau})}\right\}$$

$$\Rightarrow \frac{C_V}{3\varepsilon} = \frac{\left[(1+3e^{-\varepsilon/\tau})\cdot(\varepsilon/\tau^2)e^{-\varepsilon/\tau}\right] - \left[e^{-\varepsilon/\tau}\cdot 3\,(\varepsilon/\tau^2\, e^{-\varepsilon/\tau})\right]}{(1+3e^{-\varepsilon/\tau})^2}$$

$$= \frac{1}{(1+3e^{-\varepsilon/\tau})^2}\,\frac{\varepsilon}{\tau^2}e^{-\varepsilon/\tau}\left(\left[1+\cancel{3e^{-\varepsilon/\tau}}\right] - \left[\cancel{3e^{-\varepsilon/\tau}}\right]\right)$$

(3.5) $$C_V = \frac{3\,\varepsilon^2 e^{-\varepsilon/\tau}}{\tau^2(1+3e^{-\varepsilon/\tau})^2}$$

Notice that again, this is a function of $(\varepsilon/\tau)$ only.

④

Let's plot it.

- First, consider $\frac{\varepsilon}{\tau} \to 0$.

(4.1) Then $C_V \to 3\left(\frac{\varepsilon}{\tau}\right)^2 \cdot \frac{1}{(1+0)^2} = 3\left(\frac{\varepsilon}{\tau}\right)^2 \to 0$ (quadratically)

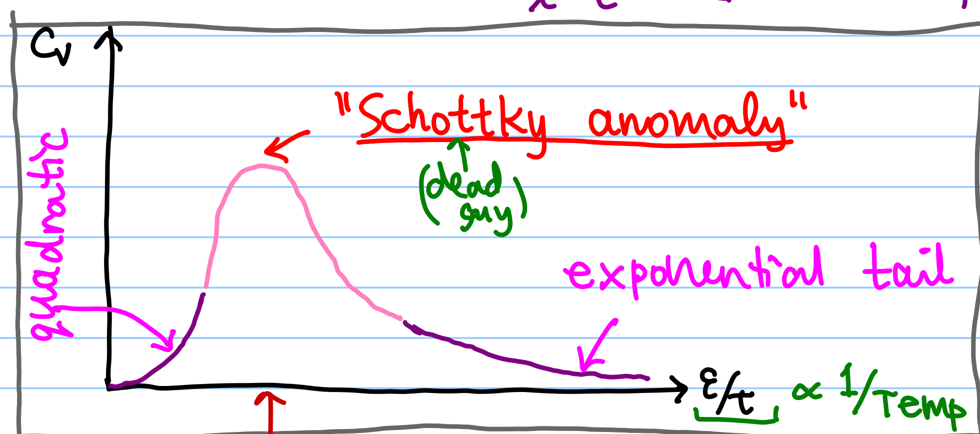
Second, consider $\frac{\varepsilon}{\tau} \to \infty$.

(4.2) Then $C_V \to 3\left(\frac{\varepsilon}{\tau}\right)^2 \frac{e^{-\varepsilon/\tau}}{(1+0)^2} = 3\left(\frac{\varepsilon}{\tau}\right)^2 e^{-\varepsilon/\tau} \to 0$ (exponential always beats power-law!)

"$x^2 e^{-x}$"

$\Rightarrow$

(4.3)



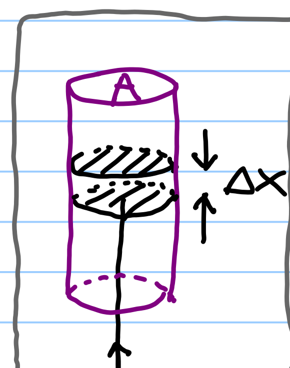

---

## Work and Pressure

← We all know a bit about these, eh? ☺

Suppose we had a piston.

Let it have cross-sectional area $A$, and suppose it moves a distance $\Delta x$.




(4.4) We know $dW = \vec{F} \cdot d\vec{x}$

$$\Rightarrow \Delta W = p \cdot A \cdot \Delta x$$

(4.5) $$= p\,\Delta V$$

This formula generalizes to 3-d expansions too

(5.1) Generally, $\Delta U = \Delta Q - \Delta W$

so $\Delta U = 0 - p\,\Delta V$ if $\sigma =$ constant

(5.2) $\Rightarrow$ $\boxed{p = -\left(\frac{\partial U}{\partial V}\right)_\sigma}$

If $U$ & $V$ were the two independent variables for our thermodynamic system, $\sigma = \sigma(U, V)$.

(Generally, keeping $\sigma =$ const. is experimentally tricky!)

(5.3) $d\sigma = 0$

says $\left(\frac{\partial \sigma}{\partial U}\right)_V dU + \left(\frac{\partial \sigma}{\partial V}\right)_U dV = 0$

So * at constant $\sigma$ only * can "divide by $dV$"

$\Rightarrow \left(\frac{\partial \sigma}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_\sigma + \left(\frac{\partial \sigma}{\partial V}\right)_U = 0$

i.e. $\frac{1}{\tau} \cdot -p + \left(\frac{\partial \sigma}{\partial V}\right)_U = 0$

(5.4) Hence $\boxed{p = \tau \left(\frac{\partial \sigma}{\partial V}\right)_U}$ ← These are equivalent

In general, $d\sigma = \left(\frac{\partial \sigma}{\partial U}\right)_V dU + \left(\frac{\partial \sigma}{\partial V}\right)_U dV = \frac{1}{\tau} dU + \frac{p}{\tau} dV$

(5.5) i.e. $\boxed{dU = \tau\, d\sigma - p\, dV}$ First Law

---

## Free Energy

Suppose magician destroyed rabbit(!)

(5.6) 


What happens to energy?

← [Thanks to Dan Schroeder for pic.]

We expect that it won't be possible to capture the whole energy and put it to work — we will lose some heat to the surroundings (which effectively constitute a thermal reservoir).

$\Delta$(energy) $\rightarrow$ (work done) + (heat lost)

Traditionally, $\begin{cases} U = \text{energy of system} \\ Q = \text{heat added } \underline{\text{to}} \text{ system} \\ W = \text{work done } \underline{\text{by}} \text{ system} \end{cases}$

(6.1) $\therefore \quad \Delta U = \Delta Q - \Delta W$

(6.2) or $\boxed{dU = đQ - đW}$

▷ What is heat? It is macroscopic, a form of energy.

(6.3) $\boxed{đQ = \tau\, d\sigma} = T\,dS$ ← "tedious" (pron.) (ha ha!)

so, for our rabbit-destruction process,

$\Delta Q = \tau \Delta \sigma$ since $\mathcal{R}$ keeps $\tau =$ const.

$\therefore \quad 0 - Q = \tau(\sigma - 0)$ i.e. $\Delta Q = -\tau\sigma$

$\Rightarrow \quad 0 - U = -\tau\sigma - \Delta W$

or $\Delta W_{rabbit} = U - \tau\sigma$

This is the energy available, or "free", for doing work. Cool! This is what we wanted. ☺

(6.4) <u>Helmholtz free energy</u> $\boxed{F = U - \tau\sigma}$

An equivalent* definition, which I strongly prefer, is

$\boxed{F = -\tau \log Z}$ ⊛

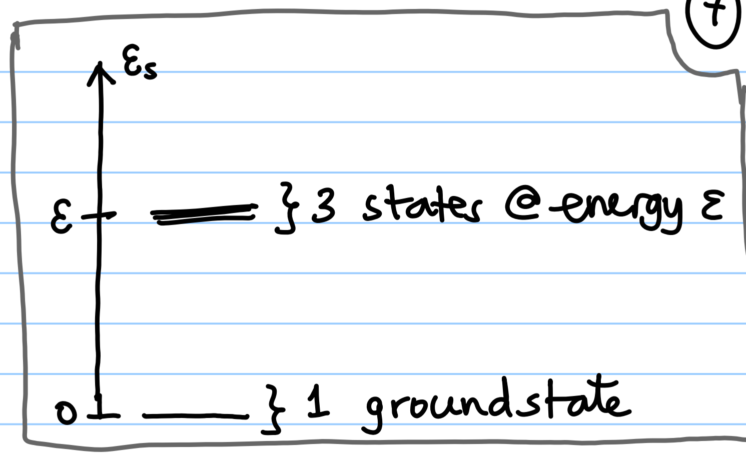
• Since $dF = dU - \tau d\sigma - \sigma d\tau$ $\quad (F = U - \tau\sigma)$

$= -p\,dV - \sigma\,d\tau$ $\quad (dU = \tau d\sigma - p\,dV)$

$\Rightarrow \quad \boxed{p = -\left(\frac{\partial F}{\partial V}\right)_\tau}$ ⊛ $\quad \boxed{\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V}$ ⊛ mega-useful!

* see KK!

## Example?




For our system with we had

$$Z = 1 + 3e^{-\varepsilon/\tau}.$$

So

- $F = -\tau \log Z$

i.e. $F = -\tau \log\left(1 + 3e^{-\varepsilon/\tau}\right)$

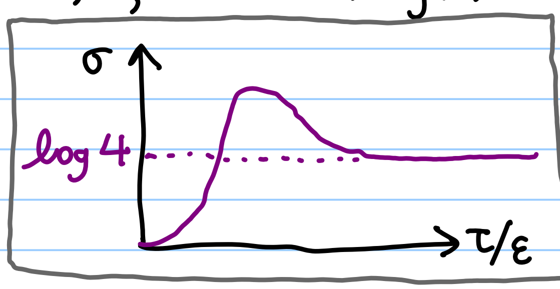
- $$\left(\frac{\partial F}{\partial \tau}\right)_V = -\log\left(1+3e^{-\varepsilon/\tau}\right) - \frac{\tau}{\left(1+3e^{-\varepsilon/\tau}\right)} \cdot + \frac{3\varepsilon}{\tau^2} e^{-\varepsilon/\tau}$$

$$\therefore \quad \sigma = \log\left(1+3e^{-\varepsilon/\tau}\right) + \frac{3(\varepsilon/\tau)\, e^{-\varepsilon/\tau}}{\left(1+3e^{-\varepsilon/\tau}\right)}$$

As $\underbrace{\varepsilon/\tau}_{:=x} \to \infty$ $(\tau \to 0)$, $\sigma \to 0 + \mathcal{O}(e^{-x})$

As $\varepsilon/\tau \to 0$ $(\tau \to \infty)$, $\sigma \to \log(4) + \mathcal{O}(x)$

$\Rightarrow$




- $\left(\frac{\partial F}{\partial V}\right)_\tau = ?$ Well, $Z = Z(\varepsilon/\tau) = Z(\varepsilon)$ @ $\tau = \text{const.}$

$\Rightarrow$ to find pressure, we need to know how $\varepsilon$ depends on V.

$\rightarrow$ We'll start that problem in the second half of next lecture ☺ i.e. finding $\left(\frac{\partial \varepsilon}{\partial V}\right)_\tau$ – for ideal gas.