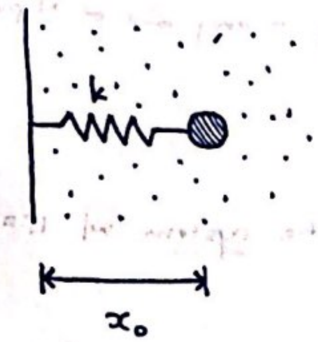
Boltzmann Distribution — Instructional

- consider a canonical problem in statistical mechanics: harmonic osc. in a viscous fluid:

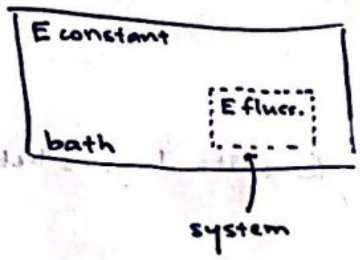


this is very difficult!

- one massive particle — easy
- $\sim 10^{23}$ molecular species all moving in a coupled manner

but really, not interested in the molec. species, only in the motion of the oscillator.

- standard solution: divide into a system and a bath:



Boltzmann distribution yields a prob. dist. for the system exclusively!

$\nu \equiv$ state of the system ($x = 0.05$, or $x = 0.25$...)

$\mathcal{H}_\nu \equiv$ energy of that state

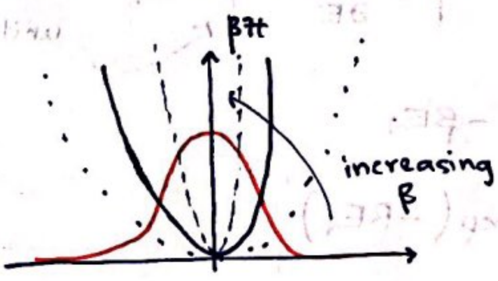
$\beta \equiv 1/k_BT$ = inverse temp. of the bath

$$\boxed{P(\nu) \propto \exp\{-\beta\mathcal{H}_\nu\}}$$

- practical use of the result:

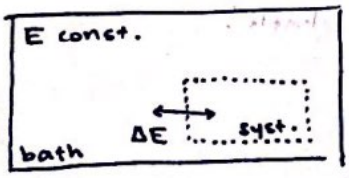
$$\mathcal{H}(x) = \frac{1}{2}kx^2$$

$$P(x) \propto \exp\left\{-\frac{\beta}{2}kx^2\right\}$$



observable, confirmed through experiments!

- how did we get here? Boltzmann distribution is an incredibly strong result!



[derivation 1]

do we know anything about the distribution of the bath?

most general assumption we can make is to say that every single state of the bath is exactly as likely!

$$P(\nu_{bath}) = 1/\Omega_{bath}$$

- how did we get here? (derivation 1).

$P(\nu_{bath}) = 1/\Omega_{bath}$ ← this must be dependent on the amount of energy the bath contains.

$$P(\nu_{bath}) = \frac{1}{\Omega_{bath}(E)}$$

- $E=0$: only one vacuum state.
- $E=1$: can put the energy in any one of N places
- $E=2$: $N \cdot N$, etc.
- ⋮ $E=K$: N^K

this is for the whole bath. what about for a state of the system w/ $E=E_\nu$?

$$
\begin{aligned}
P(\nu_{syst.}) &= P(\text{system has } E=E_\nu) \\
&= P(\text{bath has } E=E_{tot.}-E_\nu) \qquad \text{(conservation of energy)} \\
&= \Omega(E_{tot.}-E_\nu)/\Omega(E_{tot.})
\end{aligned}
$$

I want to Taylor expand, but $\Omega(\cdot)$ is a very ill-behaved fcn. its log. is better:

$$
\begin{aligned}
\log P(\nu_{syst.}) &= -\log\Omega(E_{tot}) + \log\Omega(E_{tot.}-E_\nu) \\
&\approx -\log\Omega(E_{tot.}) + \log\Omega(E_{tot.}) + \left.\frac{\partial\log\Omega(E)}{\partial E}\right|_{E=E_{tot.}} \cdot (-E_\nu) \\
&= -\left[\frac{\partial\log\Omega(E)}{\partial E}\right]\cdot E_\nu
\end{aligned}
$$

units: $\frac{1}{\text{energy}}$ ⇒ this defines inverse temp. β!

$$= -\beta E_\nu$$

$$\boxed{P(\nu_{syst.}) = \exp(-\beta E_\nu)}$$

takeaways:

1.) that was uncomfortably hand-wavey...
2) required assuming uniform dist. over the bath
3) ultimately, the system has lower prob. to be high E b/c there are so many more ways to distribute that energy to the bath!

Boltzmann Distribution – Instructional

- let's try a more rigorous derivation with a more classical guiding principle: systems maximize entropy.

Gibbs defn. of entropy: $S = -k_B \sum_\nu P_\nu \log P_\nu$

we need to apply some constraints on the maximization.

1) distribution remains normalized: $\sum_\nu P_\nu = 1$

2) on average, the system has an avg. specified energy: $\langle E \rangle = \sum_\nu E_\nu P_\nu$

formally:
$$\max_{P_j} \; -k_B \sum_\nu P_\nu \log P_\nu$$
$$\text{s.t.} \quad 0 = 1 - \sum_\nu P_\nu$$
$$0 = \langle E \rangle - \sum_\nu E_\nu P_\nu$$

solve w/ Lagrange multipliers:

$$\mathcal{L} = S + \alpha \langle E \rangle + \gamma \cdot 1$$
$$\delta \mathcal{L} = \delta\left(S + \alpha \langle E \rangle + \gamma \cdot 1\right) = 0$$
$$= \sum_\nu -k_B \log P_\nu \cdot \delta P_\nu - \sum_\nu k_B \delta P_\nu + \sum_\nu \alpha E_\nu \delta P_\nu + \sum_\nu \gamma \delta P_\nu = 0$$
$$= \sum_\nu \left\{ -k_B \log P_\nu - k_B + \alpha E_\nu + \gamma \right\} \delta P_\nu = 0$$

must be true for <u>all</u> variations δP_ν:

$$\log P_\nu = \frac{\alpha E_\nu - k_B + \gamma}{k_B}$$

now we need to solve for the Lagrange multipliers α, γ:

$$\delta \langle E \rangle = \sum_\nu E_\nu \delta P_\nu$$
$$\delta S = \sum_\nu -k_B \cdot \delta P_\nu \cdot \log P_\nu = -\sum_\nu \delta P_\nu \left(\alpha E_\nu - k_B + \gamma\right)$$
$$\delta S = -\alpha \sum_\nu E_\nu \delta P_\nu$$

$$\frac{\delta S}{\delta E} = -\alpha$$

the inverse temperature!

the final result:

$$\log P_\nu = \frac{\alpha E_\nu - k_B + \gamma}{k_B} \Rightarrow \boxed{P_\nu \propto \exp\{-\beta E_\nu\}}$$

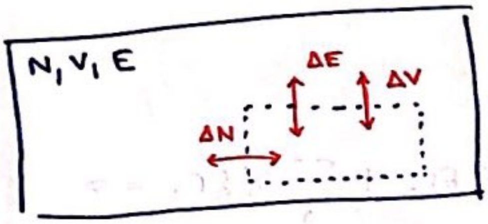
takeaways:

- more rigorous, the key point in introducing the exp() is the entropy
- avg. constraint introduces the Lagrange multiplier which becomes β.
- the key point is the same: system avoids high-E states b/c there are so many more ways to sequester that energy in the bath!

note on generalized ensembles:

- we considered systems that can exch. energy
- in the isoT iso-baric ensemble, can exch. <u>volume</u> and energy.
- in the GC ensemble, can exch. mass/particles and energy:

the picture is the exact same:



introduce new conj. variables:

$$\left.\frac{\partial \log \Omega(V,E)}{\partial V}\right|_E = \beta p$$

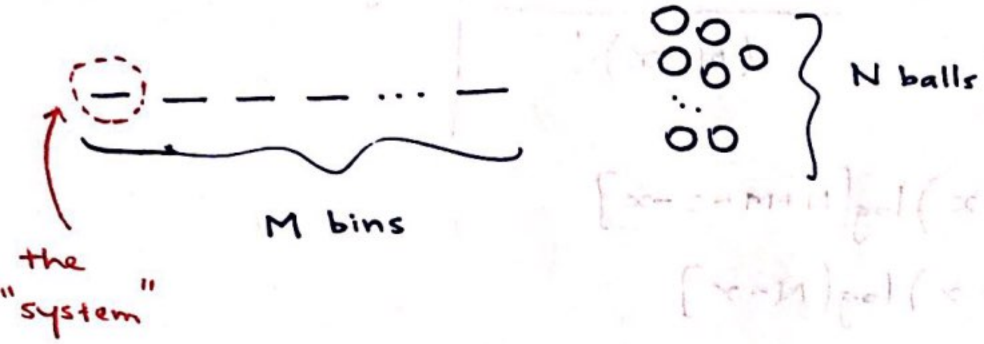
what is the statistical price for removing a packet of volume/particles from the bath and putting it in the system?

$$\left.\frac{\partial \log \Omega(N,E)}{\partial N}\right|_E = \beta \mu$$

Boltzmann Distribution – Research

the takeaway in both cases was essentially combinatorial. there are just more ways to put E into the bath than in the system.

take a stripped-down toy model:



if all configurations are equally likely, find probability that bin 1 has x balls:

$$\Pr(n_1 = x)$$

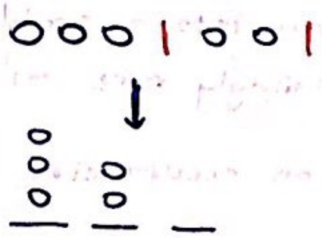
let ν denote "configuration" (assignment of balls to bins).

$$\Pr(\nu) = 1/\Omega(M,N)$$ [uniform distribution]

we need to know how to actually compute $\Omega(M,N)$. pretty standard counting problem ("stars and bars")

— | — | — | — | — | — M bins $\equiv$ M−1 bin dividers

arranging N balls + M−1 dividers yields a uniquely-mappable assignment of balls to bins!



hence, $\Omega(M,N) = \binom{N+M-1}{N} = \binom{N+M-1}{M-1}$

okay. now,

$$\Pr(n_1 = x) = \left[\text{ways to put } N-x \text{ balls into } M-1 \text{ bins}\right] \Big/ \left[\text{ways to put } N \text{ balls into } M \text{ bins}\right] = \frac{\binom{N+M-2-x}{N-x}}{\binom{N+M-1}{N}}$$

only this part is dependent on x!

from before:

$$\Pr(n_1 = x) \propto \binom{N+M-2-x}{N-x}$$

recall:

$$\binom{N}{k} = \frac{N!}{k!\,(N-k)!}$$

$$\propto \frac{(N+M-2-x)!}{(N-x)!\,(M-2)!} \propto \frac{(N+M-2-x)!}{(N-x)!}$$

Stirling's approx:

$$\log N! = N\log N - N$$

$$\log \Pr(n_1 = x) = (N+M-2-x)\log[N+M-2-x] - (N-x)\log(N-x]$$

$$\log \Pr(n_1 = x) = (N-x)\log\left[1 + \frac{M-2}{N-x}\right] + (M-2)\log(M+N-x-2)$$

logarithm is linear to leading order: $\log \Pr(n_1 = x) \tilde{\propto} \exp(-\beta x)$.

this is like β, but now dep. on x.

subleading dependence on x here, not as important.

how do we know if any of this is even close to correct?. try numerical sampling!

- immediately run into a problem: configs. w/ lots of balls in one bin are exceedingly rare $\rightarrow$ it's difficult to sample them!

- a histogram on occupancies can be written as follows:

$$H_n = \sum_{\substack{\text{configs} \\ \nu}} \delta_{\nu_1, n} \cdot \frac{1}{\Omega(N,M)}$$

- we can try to "stack the deck" by sampling configurations that start with k balls already.

$$\underbrace{\circ\circ\cdots\circ}_{k}\ \underbrace{\circ|\circ\circ|\cdots}_{\substack{N-k \text{ balls} \\ M-1 \text{ bins}}}$$

but obviously we need to correct for the fact that we are drawing from a <u>new</u> sampling distribution?.

Boltzmann Distribution – Research

importance sampling:

in general, to compute an average of a function $f(x)$ under a dist. $p(x)$,

$$\langle f \rangle_p = \int dx\, f(x)\, p(x) = \sum_{\substack{\nu \text{ drawn} \\ \text{from } p(x)}} f(\nu)$$

$$\langle f \rangle_p = \int dx\, \frac{f(x)\, p(x)}{q(x)}\, q(x) = \sum_{\substack{\nu \text{ drawn} \\ \text{from } q(x)}} f(\nu) \cdot \frac{p(\nu)}{q(\nu)}$$

here, $p(\nu) = \dfrac{1}{\Omega(N, M)}$

$q(\nu) = \dfrac{1}{\Omega(N-k, M-1)}$