F. Does the method work? Is it a silly method?

$$Z(T,V,N) = \sum_{\text{all } N\text{-particle states } i} e^{-E_i/kT} = \sum_{\text{all energies } E_i} \underbrace{W_s(E_i,V,N)}\, e^{-E_i/kT}$$

If we know $W_s(E_i,V,N)$ to construct $Z(T,V,N)$, why don't we simply use $W_s(E_i,V,N)$ to get $S(E_i,V,N)$ and then we are done!

Microcanonical

- Sort out states of specified energy E_i
- Every state (microstate) carries equal weight $\left(\frac{1}{W_s}\right)$, i.e. equally probable

Canonical

- List out all states and their energies†
- Weight a state of energy E_i by $\dfrac{e^{-E_i/kT}}{Z}$

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† It may be more convenient (easier) to list all states than sorting out states of fixed energy!

Go to Examples of Applications

- To illustrate the method and the Math skills
- More important, bring out the physics in physical systems with a lot of stuff and how kT affects the behavior

Go To : Application A on "two-level" distinguishable N particles (Paramagnetic materials)

Go to Examples of Applications

- To illustrate the method and the Math skills
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Go To : Application B on Heat Capacity of Solids and the Debye Model

G. Fluctuations in Energy

- System has probability P_i to be in a state of energy E_i

$$\Rightarrow \langle E \rangle = \sum_i E_i P_i = -\frac{\partial}{\partial \beta} \ln Z$$

all N-particle states i

- What is the standard deviation? (Spread?)

$$\sigma_E^2 = \langle (\Delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle$$

Variance in energy (SD squared)

definition $\langle (\text{deviation from mean})^2 \rangle$

average using P_i

$$\boxed{\text{Here, } \langle \cdots \rangle = \sum_i (\cdots) P_i = \sum_i (\cdots) \frac{e^{-\beta E_i}}{Z}}$$

$$\sigma_E^2 = \langle (\Delta E)^2 \rangle = \langle E^2 \rangle - 2\langle E \rangle^2 + \langle E \rangle^2 = \underbrace{\langle E^2 \rangle}_{\text{"new"}} - \underbrace{\langle E \rangle^2}_{\text{already did}}$$

$$\langle E^2 \rangle = \frac{1}{Z}\sum_i E_i^2 e^{-\beta E_i} = \frac{1}{Z}\left[\frac{\partial^2}{\partial\beta^2}\underbrace{\left(\sum_i e^{-\beta E_i}\right)}_{Z}\right]$$

conditions are left out for simplicity

$$= \frac{1}{Z}\left(\frac{\partial^2 Z}{\partial\beta^2}\right)$$

$$\sigma_E^2 = (\Delta E)^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 = \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right) = -\frac{\partial\langle E\rangle}{\partial\beta} = kT^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{V,N}$$

$\therefore\ \sigma_E^2 = kT^2 C_V$ where C_V is the Heat Capacity of the System

OR standard deviation $\sigma_E = \sqrt{kT^2 C_V}$

Physics Here!

$\langle E\rangle$ is U in thermodynamics, it is extensive (think 10^{24}) $\sim N$

σ_E^2 (variance) $= kT^2 C_V$, it is extensive (think 10^{24}) $\sim N$

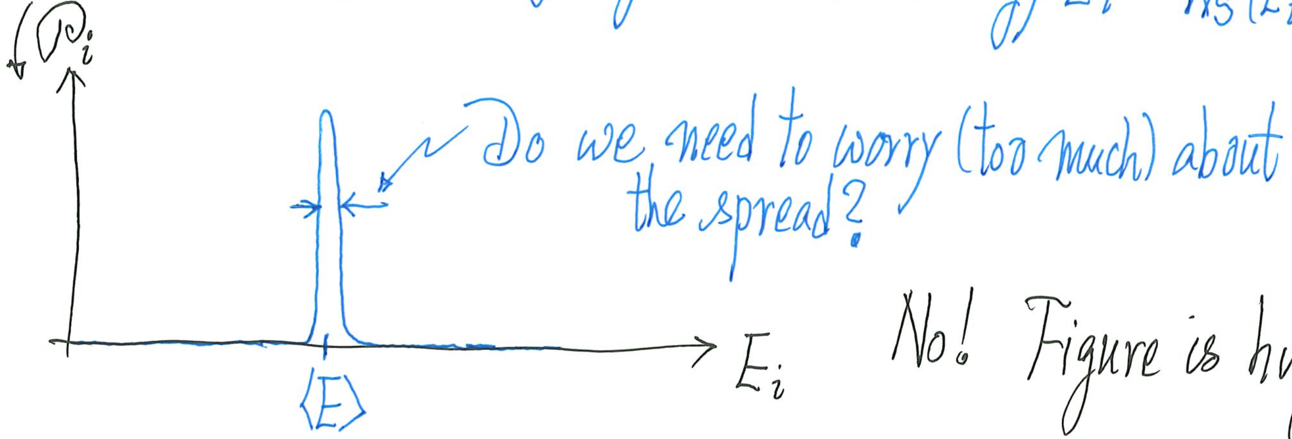
σ_E (standard deviation)(spread) $= \sqrt{kT^2 C_V}$, it is $\sqrt{\text{extensive}}$ (think 10^{12}) $\sim \sqrt{N}$

Relative energy fluctuation $\dfrac{\sigma_E}{\langle E \rangle} = \dfrac{\sqrt{kT^2 C_V}}{\langle E \rangle} \sim \dfrac{1}{\sqrt{N}}$ ← this is the Key Point

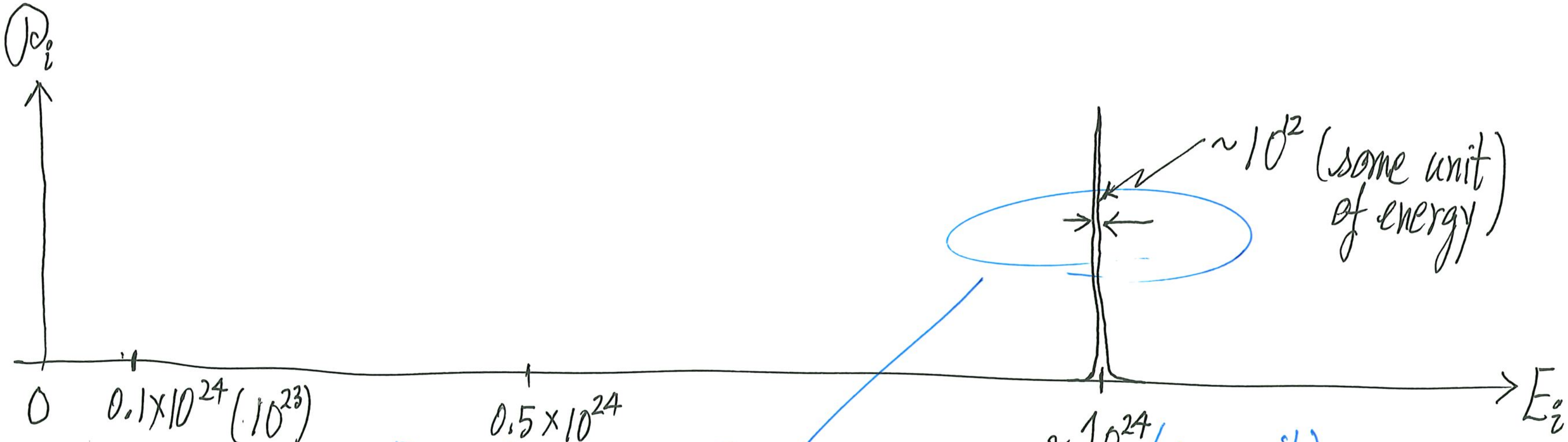
What does it mean?

- Don't worry about the fluctuations, $\langle E \rangle$ is sharply defined!

Recall: $\mathcal{P}_i$ = Prob. of finding system with energy $E_i = W_S(E_i, V, N) \cdot \dfrac{e^{-E_i/kT}}{Z(T,V,N)}$



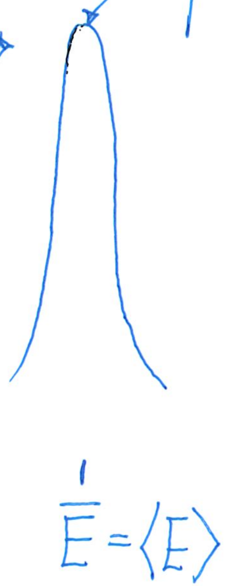
No! Figure is hugely exaggerated



if this is $\sim10^{24}$, how could you draw 10^{12} on this scale? (Can't draw it in!)

Zooming in the peak

peak value of $\mathcal{P}_i$ occurs at $\bar{E}$



$$\mathcal{P}_i(E\approx\bar{E})=\underbrace{\mathcal{P}(\bar{E})}_{\text{Peak Value}}\cdot\underbrace{e^{-\frac{(E-\bar{E})^2}{2kT^2C_V}}}_{\substack{\text{Gaussian distribution}\\ \text{centered at } \bar{E}\\ \text{and with variance}\\ \sigma_E^2=kT^2C_V}}$$

Functional form of $\mathcal{P}_i$ nears its sharp peak at $E=\bar{E}$

A useful numerical by-product

$$\sigma_E^2 \equiv \underbrace{\langle E^2 \rangle}_{\substack{\text{can also} \\ \text{be calculated numerically}}} - \underbrace{\langle E \rangle}_{\substack{\text{can be calculated numerically (e.g. Monte Carlo simulation} \\ \text{of a given system (Hamiltonian))}}}^2 = kT^2 C_V$$

$\Rightarrow$ a way to calculate C_V numerically (than to take a derivative)

H. Canonical Ensemble

- System in contact with bath
  - energy in/out of system, system visits microstates of different energies, the prob. of system in energy E_i is P_i $\underbrace{\left(W_s(E_i, V, N) \cdot \frac{e^{-E_i/kT}}{Z} \right)}_{\text{sharply peaked at } E = \langle E \rangle}$

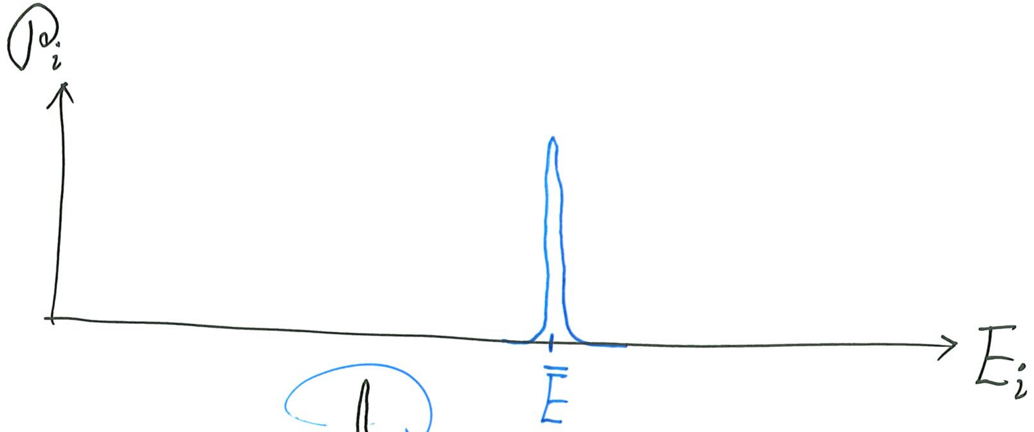
Recall: Microcanonical Ensemble

$\underbrace{W_s(E, V, N)}$ (E is U in thermodynamics)

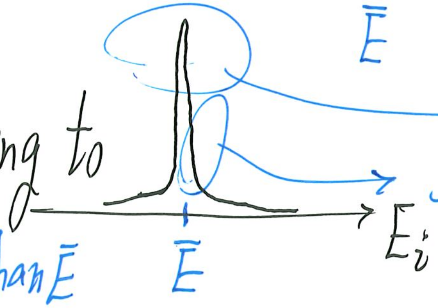
pick evenly no bias these microstates to form an ensemble

→ then ensemble average replaces time average

Canonical Ensemble



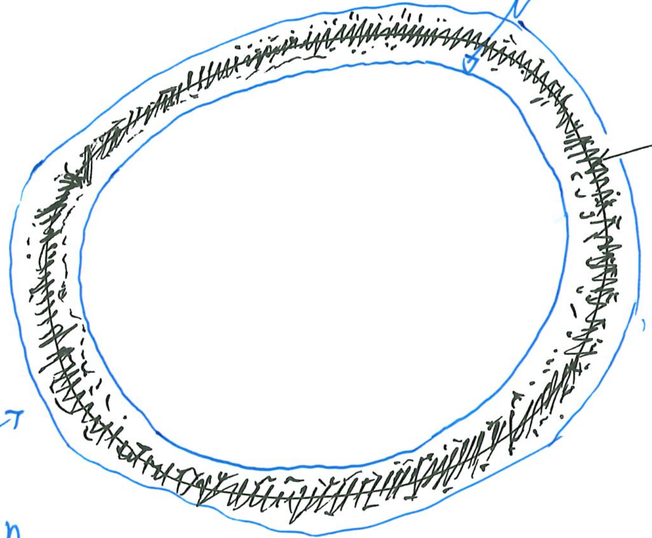
Should select members according to



many members here

some members here (importance sampling†)

lower than $\bar{E}$



$\bar{E}$ constant-energy surface

higher energy than $\bar{E}$

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† The most important application is in Monte Carlo simulations, see N. Metropolis, "Equation of state calculations by fast computing machines", J. Chem. Phys. 21, 1087 (1953).