Lecture 9

Canonical ensemble

Average values, equipartition, speed distribution, free energy

Recap+ plan

Statistical mechanics

Models	Counting states @constant (NVU)	Counting states @constant (NVT)	Counting states @constant (μVT)
• Two-state:	$\Omega(N,n) = \frac{N!}{(N-n)!n!}$	Partition function $Z = \sum_i e^{-\beta\varepsilon_i}$	Gibbs sum $Z_G = \sum_i e^{-\beta(\varepsilon_i - \mu N_i)}$
• Einstein crystal	$\Omega(N,q) = \frac{(N-1+q)!}{(N-1)!q!}$		
• Ideal gas	$\Omega(U,V) = f(N)V^N U^{3N/2}$		
• MD	measure & average	Maxwell-Boltzmann speed distribution	
Interacting systems -------------------------> Equilibrium	irreversible $\Omega \longrightarrow \max\Omega$		
$S = k\ln\Omega$		$F = -kT\ln Z$	$U - TS = -kT\ln Z_G$
	$\Delta S_{tot} \geq 0$ $\quad T_1 = T_2$, $P_1 = P_2$, $\mu_1 = \mu_2$	$\Delta F \leq 0$	$\Delta G \leq 0$
		$F \equiv U - TS$ $dF = -PdV - SdT$	$G \equiv F + PV$ $dG = VdP - SdT$

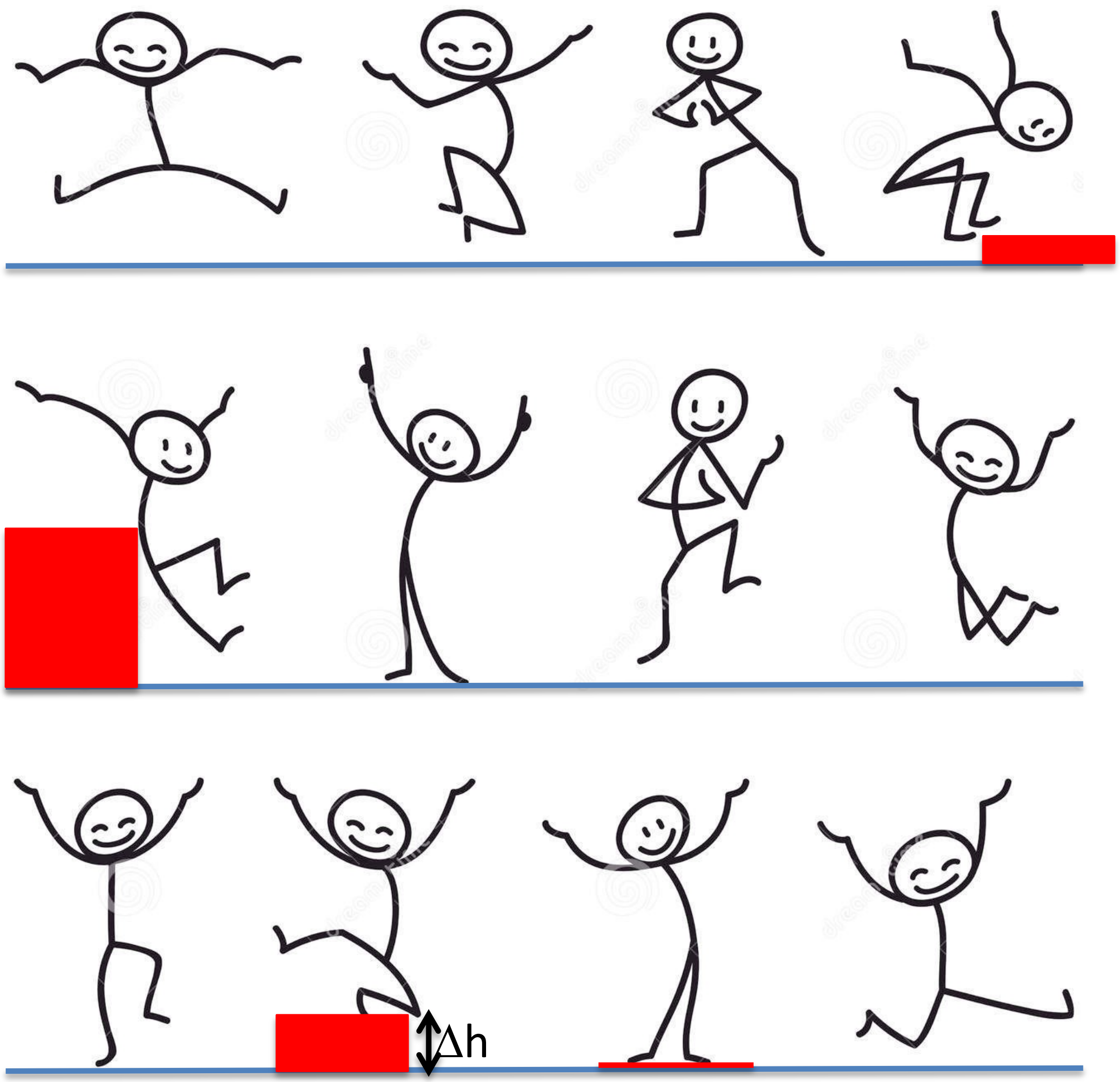
Thermodynamics

Implications:

- Thermodynamic identity $dU = TdS - PdV$
- 1st law $dU = Q + W$
- Ideal gas: $PV = NkT$, equipartition, heat capacity, entropy of mixing, heat, work, state variables, path independence

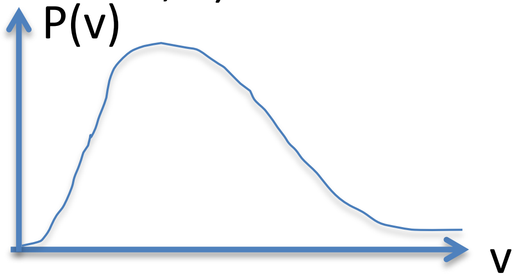
Experiments: measure and model

Probability of jumping people



To states: 1) On the floor, 2) on red box

MB velocity distr.



Mean kinetic energy

$$m\langle v^2\rangle/2 = kT$$

Mean potential energy

$$mg\langle h\rangle = m\langle v^2\rangle/2$$

Relative probability

$$
\begin{aligned}
P(2)/P(1) &= \exp(-E_2/kT)/\exp(-E_1/kT) \\
&= \exp(-(E_2-E_1)/kT) \\
&= \exp(-\Delta E/kT) \\
&= \exp(-mg\Delta h/kT)
\end{aligned}
$$

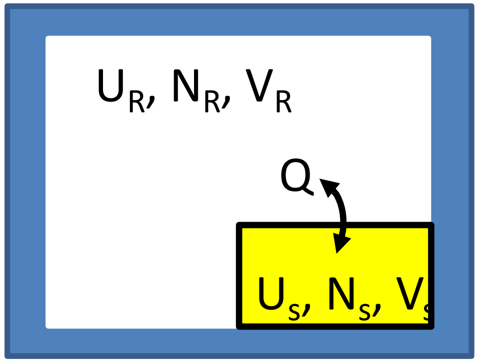
Microcanonical & canonical ensemble

Microcanonical, (NVU) kept constant

Number of microstates in a macrostate: Multiplicity Ω

Probability of a macrostate: $\mathrm{P} = \Omega / \sum \Omega$

Entropy: $\mathrm{S} = \mathrm{k}\ \ln\Omega$



Canonical, (NVT) kept constant

Exchanges Q with (NVU) reservoir to keep T constant

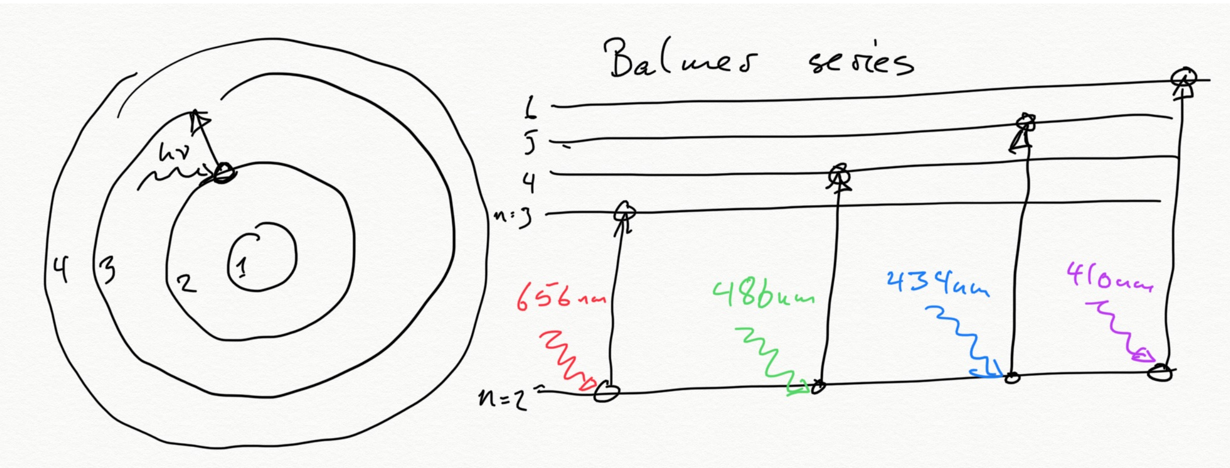
Boltzmann factor: $e^{-\beta\varepsilon_i}$, $\beta = \frac{1}{kT}$

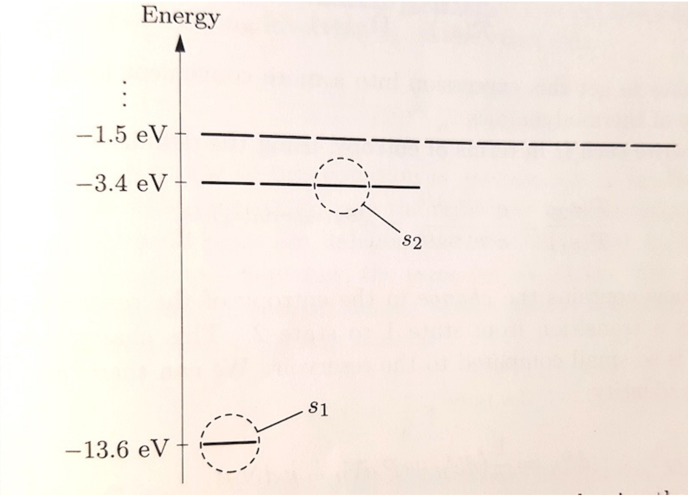
Partition function: sum over all possible microstates: $Z = \sum_i e^{-\beta\varepsilon_i}$

Probability of a microstate: $P_i = \frac{e^{-\beta\varepsilon_i}}{Z}$

Relative probability: $\frac{P_2}{P_1} = e^{-\beta(\varepsilon_2 - \varepsilon_1)}$

Example: Hydrogen in the stars



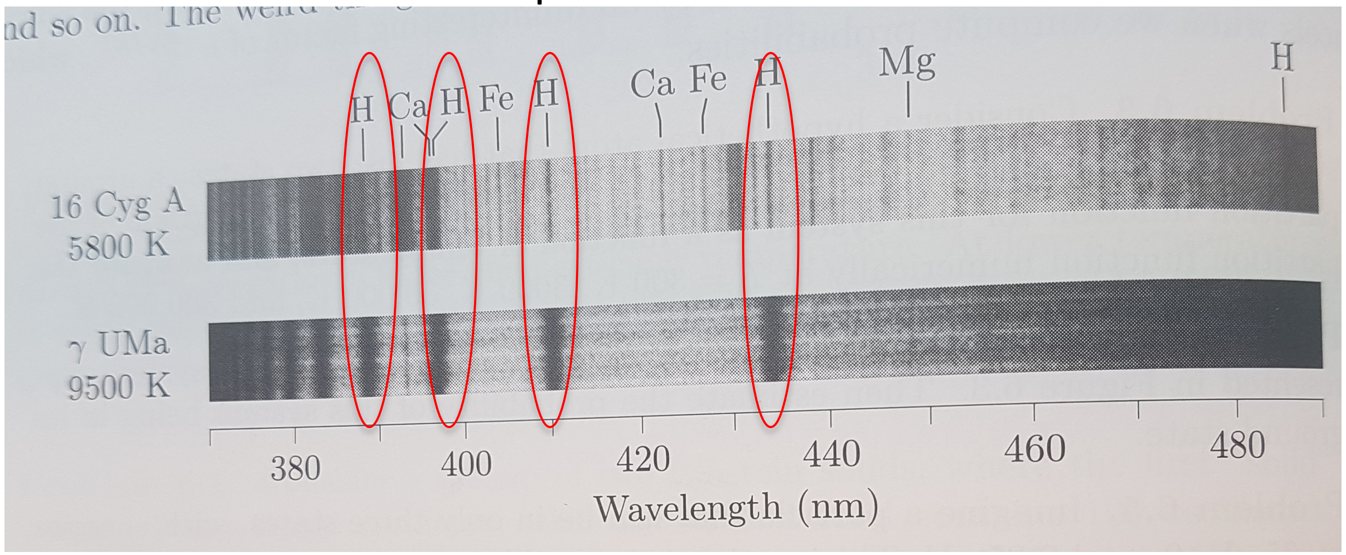


Probability of excited vs. ground state: $\frac{P(s_2)}{P(s_1)} = e^{-\beta(E_2-E_1)}$on sun ($T = 5800$K)

$\frac{(E_2-E_1)}{kT} = \frac{13.6-3.4}{8.6\cdot10^{-5}\cdot5800} = 20.4 \Rightarrow \frac{P(s_2)}{P(s_1)} = 1.4 \cdot 10^{-9}$

Excited atoms absorbs visible photons when $n = 2 \rightarrow i, \quad i > 2$

Absorption lines



5800 K, $P(s_2)/P(s_1) = 10^{-9}$

9500 K, $P(s_2)/P(s_1) = 10^{-6}$

Average values, Energy

Probability of a microstate: $\mathrm{P}(s) = \frac{e^{-\beta E(s)}}{Z}$

Partition function $Z = \sum_s e^{-\beta E(s)}$

The average value of a fluctuating quantity is the first moment of its distribution:

$$\bar{X} = < X > = \sum_s X(s)P(s)$$

For the Boltzmann distribution

$$\bar{X} = \frac{1}{Z(T)} \sum_s X(s)e^{-\beta E(s)}$$

Average energy $\mathrm{U} = \bar{E} = \frac{1}{Z(T)} \sum_s E(s)e^{-\beta E(s)}$

$$\frac{\partial Z}{\partial \beta} = \sum_s \frac{\partial}{\partial \beta} e^{-\beta E(s)} = \sum_s -E(s)e^{-\beta E(s)}$$

=> $\mathrm{U} = \bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$

Thermodynamics:Helmholtz free energy

Internal energy

- $dU = TdS - PdV + \mu dN$

Helmholtz free energy

- $F \equiv U - TS$
- $dF = dU - TdS - SdT$
- Thermodynamic identity for F: $dF = -PdV - SdT + \mu dN$
- $dF = \left(\frac{\partial F}{\partial V}\right)_{N,T} dV + \left(\frac{\partial F}{\partial T}\right)_{N,V} dT + \left(\frac{\partial F}{\partial N}\right)_{V,T} dN$
- $P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$, $S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$, $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

Natural variables: N, V, T, like the Canonical ensemble!

Average values: Helmholtz free energy

Microcanonical ensemble (NVU):

Fundamental variables: Ω, S

Micro to macro: $S = k \ln \Omega$

Second law: $\Delta S \geq 0$

Derived definitions: $T^{-1} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V}, P \equiv T\left(\frac{\partial S}{\partial V}\right)_{N,U}, \; \mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$

Canonical ensemble (NVT):

Fundamental variables: $Z, \; F = U - TS$

Second law: $\Delta F \leq 0$

Derived definitions: $P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}, S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}, \; \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

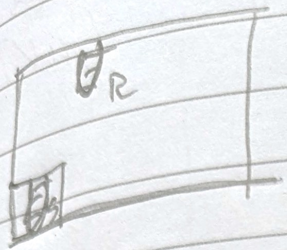
Micro to macro: $F = U + T\left(\frac{\partial F}{\partial T}\right)_{N,V}$

$F = -kT \ln Z$

$$\frac{\partial lnZ}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial lnZ}{\partial \beta} = \frac{-1}{kT^2}\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{U}{kT^2}$$

$$\Rightarrow \frac{\partial F}{\partial T} = -\ln Z \frac{\partial kT}{\partial T} - kT\frac{\partial lnZ}{\partial T} = \frac{F}{T} - \frac{U}{T}$$

F is minimum in equilibrium



Total energy $U = U_R + U_s$

" entropy $S = S_R + S_s$

$$S = S_R(U - U_s) + S_s(U_s)$$

$$\approx S_R(U) - U_s \underbrace{\left(\frac{\partial S_R}{\partial U_R}\right)_{V,N}}_{\frac{1}{T}} + S_s(U_s)$$

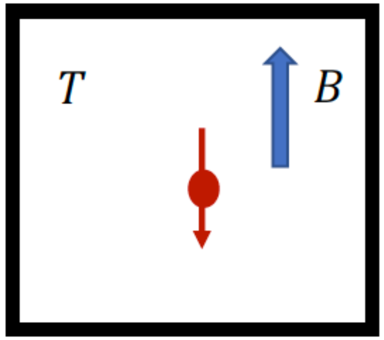
$$\Rightarrow S \approx S_R(U) - \frac{U_s}{T} + S_s(U_s)$$

$$TS = TS_R(U) \underbrace{- U_s + TS_s(U_s)}_{-F_s}$$

Equilibrium U is constant $\Rightarrow S_R(U)$ is constant

S is max $\Longleftrightarrow$ F is minimum.

Paramagnetism



One fluctuating spin

- magnet. moment: μ
- spin: $s = \pm\frac{1}{2}$
- energy: $\epsilon_s = -2s\mu B$

Probability up: $P_\uparrow = \frac{1}{Z} e^{-\beta\epsilon_s} = \frac{1}{Z} e^{\beta\mu B}$

Probability down: $P_\downarrow = \frac{1}{Z} e^{-\beta\epsilon_s} = \frac{1}{Z} e^{-\beta\mu B}$

Partition function: $Z = e^{-\beta\mu B} + e^{\beta\mu B} = 2\cosh(\beta\mu B)$

Average energy: $\bar{\epsilon} = -\frac{1}{Z} \frac{\partial Z}{\partial\beta} = -\frac{2\mu B \sinh \beta\mu B}{2\cosh(\beta\mu B)} = -\mu B \tanh(\beta\mu B)$

Average mag. mom.: $\bar{\mu} = (+\mu)P_\uparrow + (-\mu)P_\downarrow = \frac{\mu}{Z}(e^{\beta\mu B} - e^{-\beta\mu B})$

$= \mu \tanh(\beta\mu B)$

N spins, magnetization: $M = N\bar{\mu}$, energy: $U = -N\mu B \tanh(\beta\mu B)$

Equipartition theorem

Systems with quadratic degrees of freedom

$$E(q) = cq^2$$

Partition function $\quad Z = \sum_q e^{-\beta c q^2} = \frac{1}{\Delta q}\sum_q \Delta q e^{-\beta c q^2}$

$\Delta q \ll kT,$ $\quad = \frac{1}{\Delta q}\int_{-\infty}^{\infty} dq e^{-\beta c q^2} = \frac{1}{\Delta q}\sqrt{\frac{\pi}{\beta c}} = C\beta^{-\frac{1}{2}}$

Mean energy $\quad \bar{E} = U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\beta^{\frac{1}{2}}}{C}\left(-\frac{1}{2}C\beta^{-\frac{3}{2}}\right) = \frac{1}{2}kT$

Kinetic energy $\quad \overline{E_k} = \frac{1}{2}m\overline{v^2} = \frac{1}{2}m\left(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\right) = \frac{3}{2}kT$

RMS speed $\quad v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$

Partition function of many particles

Getting the counting right

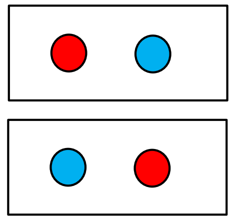
1 particle, N states $\quad Z_1 = \sum_s^N e^{-\beta \epsilon_s}$

Identical particles

Noninteracting / independent particles

no extra states are created due to having more particles

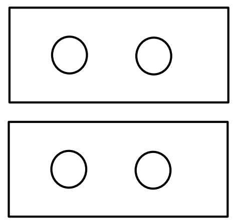
Distinguishable particles



2 particles, N states: total energy $\sum_i^2 \epsilon_{i,s} = \epsilon_{1,s} + \epsilon_{2,s}$

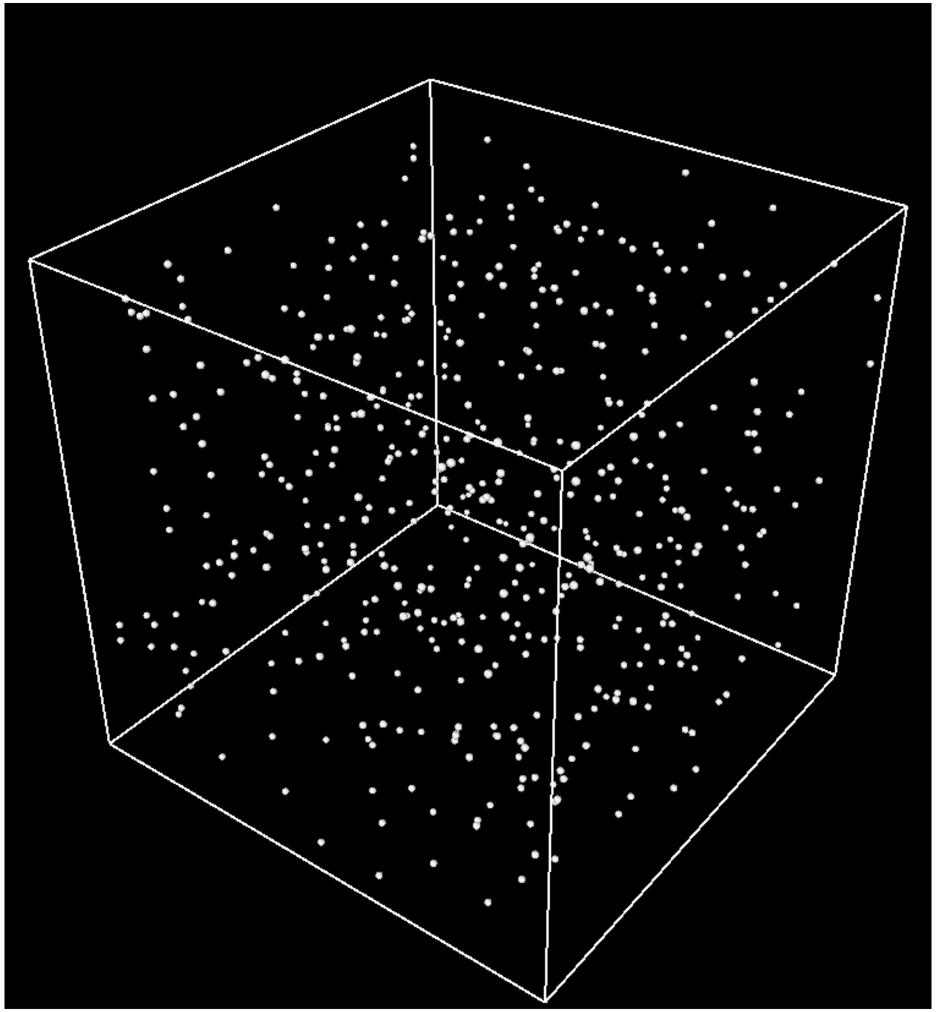
$$
\begin{aligned}
Z_2 &= \sum_s e^{-\beta(\epsilon_{1,s}+\epsilon_{2,s})} \\
&= \sum_s e^{-\beta\epsilon_{1,s}} e^{-\beta\epsilon_{2,s}}, \qquad s = (s_1, s_2) \\
&= \sum_{s_1} \sum_{s_2} e^{-\beta\epsilon_{1,s_1}}\, e^{-\beta\epsilon_{2,s_2}} \\
&= Z_1 Z_1 = Z_1^2 \\
Z_N &= Z_1^N
\end{aligned}
$$

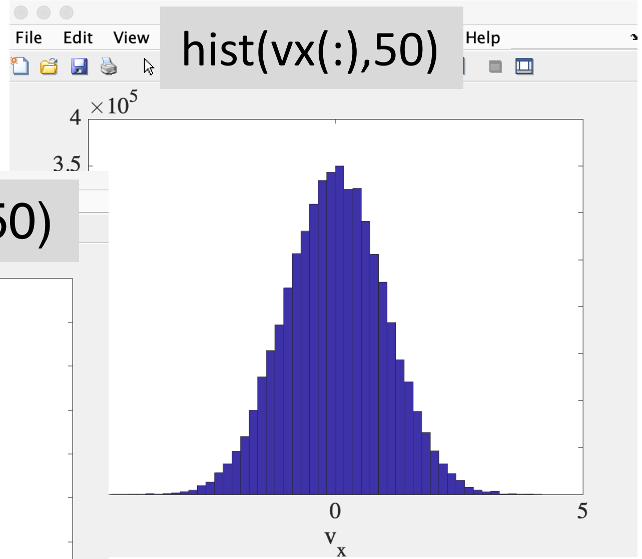
Indistinguishable particles

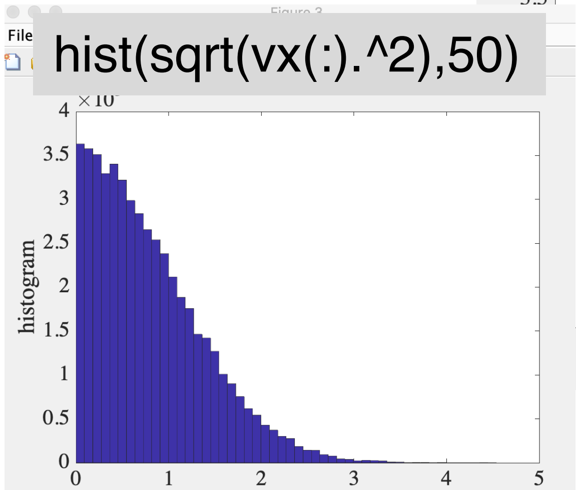


$$
\begin{aligned}
Z_2 &= \frac{1}{2} Z_1^2 \\
Z_N &= \frac{1}{N!} Z_1^N
\end{aligned}
$$

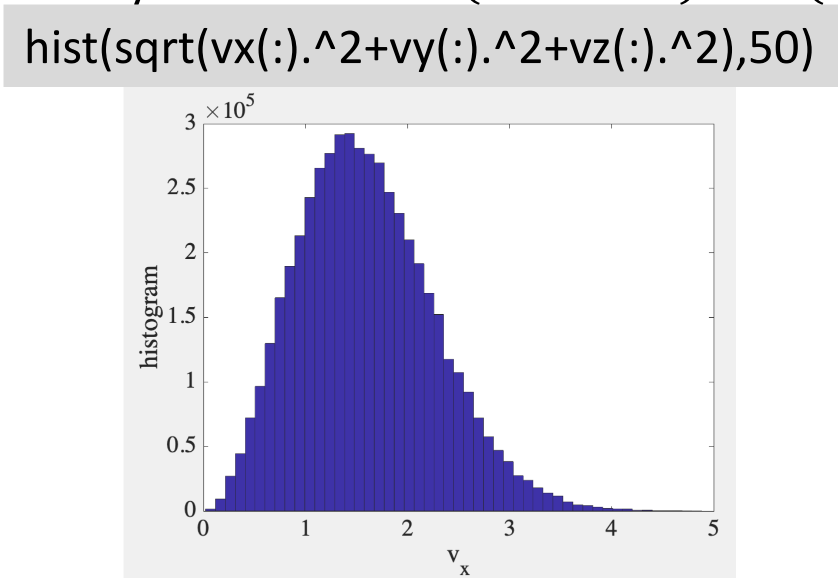
Maxwell-Boltzmann speed distribution







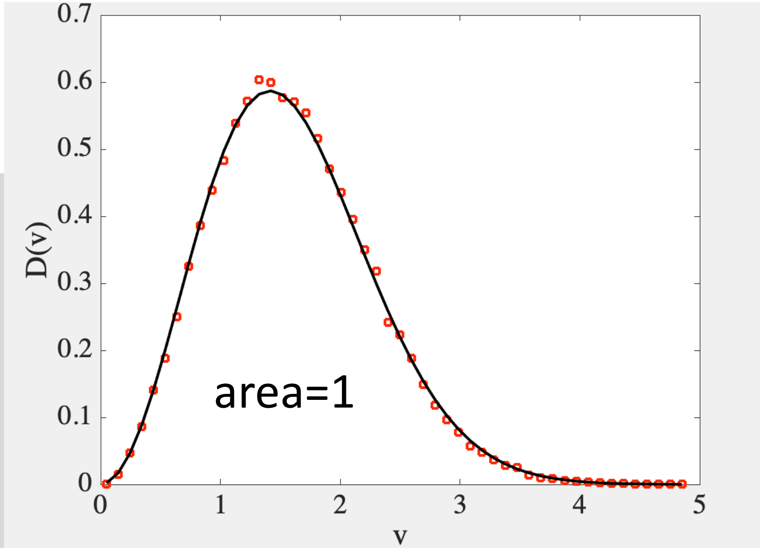
- Average velocity $\overline{v_x} = 0$
- Velocity is a vector, speed is a scalar
- Velocity is in 3D
- Probability of speed $v, P(v) = 0$
- Probability distribution: $P(v: v + dv) = D(v)dv$



```
# Define variables
# Length of sides of cubic box
variable L equal 5
# Temperature:
variable T equal 1
# Density:
variable rho equal 0.001
# Pressure:
variable P equal 0.01
# Set Pconst=1 for pressure constant, Pconst=(
variable Pconst equal 0

units lj
dimension 3
lattice fcc ${rho}
region simbox block 0 $L 0 $L 0 $L
create_box 1 simbox
create_atoms 1 box

mass 1 1.0
velocity all create $T 87287
pair_style lj/cut 2.5
pair_coeff 1 1 1.0 1.0 2.5

if "${Pconst} == 0" then &
"fix nvt all nvt temp $T $T 1" &
else &
"fix npt all npt temp $T $T 1 iso $P $P 1"
neigh_modify every 1 delay 0 check yes


#Thermalization run
run 1000

if "${Pconst} == 0" then &
"unfix nvt" &
"fix nve all nve" &
else &
"unfix npt" &
"fix nph all nph iso $P $P 1"

#Start heat addition and run to stabilize
variable eFlux equal 1
#fix heat all heat 1 ${eFlux} region simbox
run 1000

#Define new thermodynamic output and trajectory dump and start production run
thermo_style custom step temp epair etotal press
thermo 100
dump 1 all custom 100 dump.lammpstrj id x y z vx vy vz
run 1000000
```

-:--- **heatcapLJ.in**   All L51   (Fundamental)

$ lmp_serial < heatcapLJ.in




```
vsq=vx.^2+vy.^2+vz.^2;
speed=sqrt(vsq);
h = histogram(speed(:),50);
hv=h.Values;
s=sum(hv);
hbe=h.BinEdges;
dv=h.BinWidth;
hbc=hbe+dv/2;
v=hbc(1:end-1);
Dofv=hv/s/dv;
norm=sum(Dofv)*dv;
meanv=sum(v.*Dofv*dv)
vrms=sqrt(mean(vsq(:)))
```

v

$D(v)$

$\sum D(v)dv = 1$

$\bar{v} = \sum vD(v)dv = 1.5966$

$v_{rms} = \sqrt{< v_x^2 + v_y^2 + v_z^2 >}$

= 1.7287

```
plot(v,Dofv,'.',v,2*v.^2.*exp(-v.^2./2)./sqrt(2*pi),'-')
```

$kT = 1, m = 1 \;\Rightarrow$ $\quad \mathrm{D}(v) = \frac{2}{\sqrt{2\pi}} v^2 e^{-\frac{v^2}{2}}$

Distribution function: $[D(v)] = [v^{-1}]$

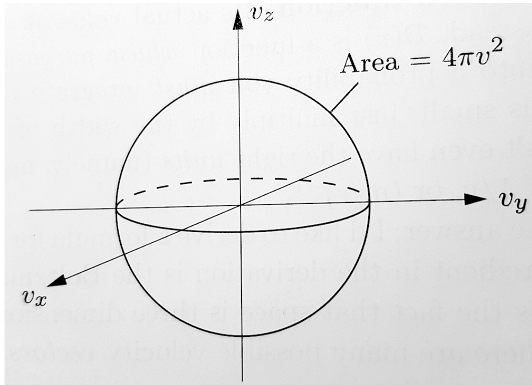
$$[P] = \left[\int D(v)dv\right] = 1$$

Maxwell-Boltzmann speed distribution

Probability distribution: $P(v : v + dv) = D(v)dv$

Boltzmann probability: $D(v)dv \propto e^{-\frac{E_k(v)}{kT}} dn = e^{-\frac{mv^2}{2kT}} dn$

Number of vectors of speed v: $dn \propto 4\pi v^2 dv$



Normalization $\int_0^\infty D(v)dv = 1$

$$C \int_0^\infty e^{-\frac{mv^2}{2kT}} 4\pi v^2 dv = 1 \implies C = \left(\frac{m}{2\pi kT}\right)^{3/2}$$

M-B speed distribution $D(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-\frac{mv^2}{2kT}}$

Maxwell-Boltzmann speed distribution

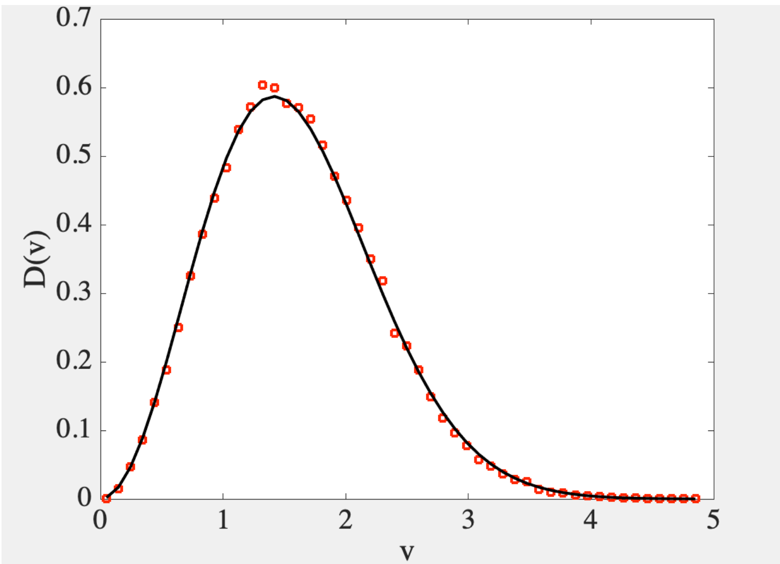
Average speed: $\bar{v} = \int_0^\infty vD(v)dv = \sqrt{\frac{8kT}{\pi m}}$ $(= 1.5958)$

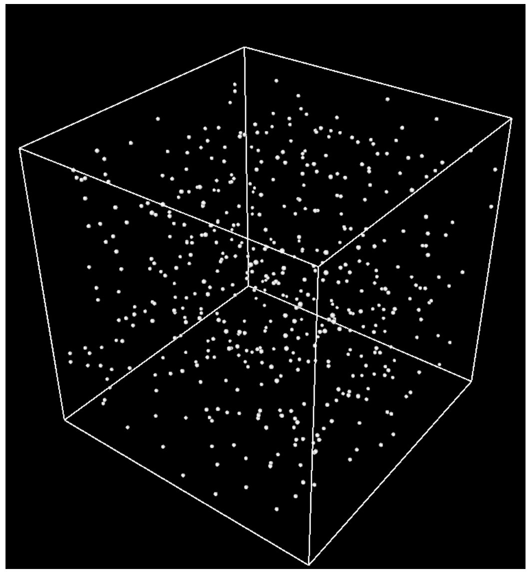
meanv=sum(v.*Dofv*dv)= 1.5966

RMS speed: $v_{rms} = \sqrt{\int_0^\infty v^2 D(v)dv} = \sqrt{\frac{3kT}{m}}$ $(= 1.7321)$

vrms=sqrt(mean(vsq(:)))=1.7287

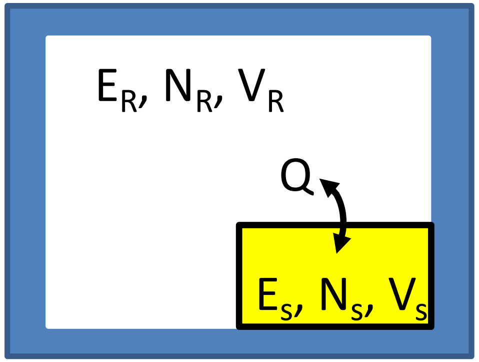
Most probable speed $\frac{\partial D(v)}{\partial v} = 0 \implies v_{mp} = \sqrt{\frac{2kT}{m}}$ $(= 1.4142)$



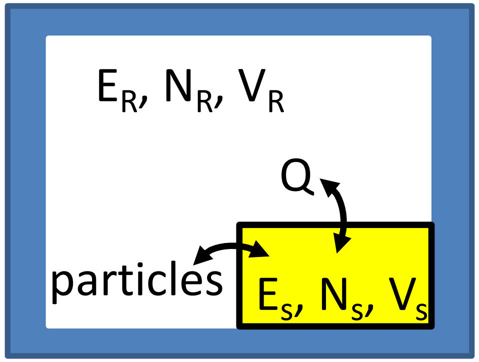


Ensembles, counting and probabilities

Microcanonical, (N, V, U) kept constant
Number of microstates, s, in a macrostate: Multiplicity Ω
Probability of macrostate: $P = {}^{\Omega}/_{\sum \Omega}$
Probability of a microstate for a given macrostate: $\mathrm{P(s)} = 1/\Omega$
Entropy: $\mathrm{S} = \mathrm{k}\ \ln\Omega$



Canonical, (N, V, T) kept constant
Exchanges Q with (N, V, U) reservoir to keep T constant
Boltzmann factor: $e^{-\beta\varepsilon_i}$
Partition function: sum over all possible microstates: $Z = \sum_i e^{-\beta\varepsilon_i}$
Probability of a microstate: $P_i = {}^{e^{-\beta\varepsilon_i}}/_{Z}$
Free energy: Helmholtz, $F = -kT \ln Z$



Grand canonical, (μ, V, U) kept constant
Exchanges Q & particles with (N, V, U) reservoir to keep T & μ constant
Gibbs factor: $e^{-\beta(\varepsilon_i - \mu N_i)}$
Gibbs sum: sum over all possible microstates: $Z_G = \sum_i e^{-\beta(\varepsilon_i - \mu N_i)}$
Probability of a microstate: $P_i = {}^{e^{-\beta(\varepsilon_i - \mu N_i)}}/_{Z_G}$
Free energy: Grand potential, $\Phi = -kT \ln Z_G = U - TS - \mu N$