Agenda: Kinetics and Transport in Multiparticle Systems

Dynamics of interacting multi-particle systems

- Interaction energies
  Dissipation via multiple scattering

- Probabilistic evolution
  Random walk and binomial distribution, limits
  Master Equation & Diffusion/Fokker-Planck processes
  Maxwell-Boltzmann equilibrium energy distributions
  Fluctuating (Langevin) dissipative forces

- Kinetics of dilute gases
  Fundamental ideal gas laws, Equation of state (EoS)
  Work and heat transfer
    Flow of heat and radiation
    Laws of thermodynamics, thermodynamic ensembles

Reading Assignments
Weeks 3 &4
LN II.6, III.1:

Kondepudi Ch. 9.6
Additional Material

McQuarrie & Simon
Ch. 3.1 -3.4

Math Chapters
MC B, C, D,

ME @Dissipative Transport

Cell populations after some time has elapsed? Dependence on transition probabilities $\boldsymbol{w}_{n\rightarrow m}$ and $\boldsymbol{w}_{m\rightarrow n}$? → Simplified model : $\boldsymbol{w}_{n\rightarrow m} = \boldsymbol{w}_{m\rightarrow n}$ (time reversal invariance, quantum requirement)

Dimension =1

$$\frac{\partial}{\partial t} f_n(t) = \sum_m w_{m,n} \left\{ f_m(t) - f_n(t) \right\} = \begin{cases} >0 & f_m > f_n \\ <0 & f_m < f_n \end{cases}$$

→ *Expand to 2 D*

$\boldsymbol{f_n}(t)$ and $\boldsymbol{f_m}(t)$ are the actual, instantaneous populations of cells *n, m* at time *t*.

Cell *n* receives population from all cells *m* with higher population and loses to cells with lower pops. Rate $\partial f_n(t)/\partial t$ depends on population difference

→ Mean rate slows when all $\langle f_m \rangle \approx \langle f_n \rangle$ But instantaneous rate doesn't vanish!

Asymptotic Stationary state

$$\lim_{t\to\infty} \langle f_n(t) \rangle = \langle (f_n) \rangle_{equ} \approx const.\ (\text{"equilibrium"})$$

Average

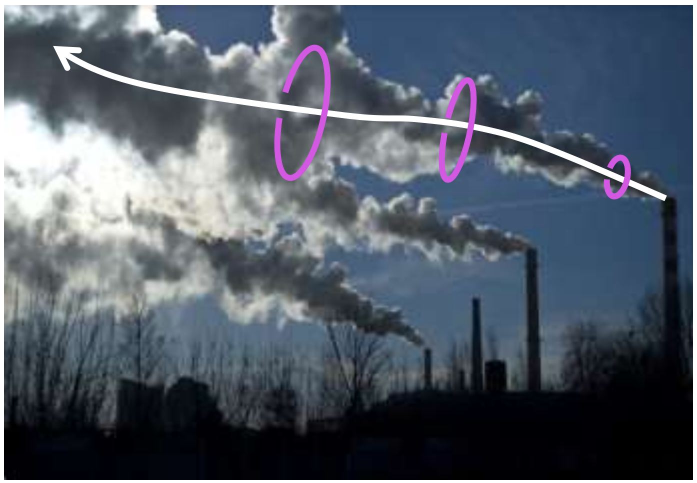
Animation: *N*=200 particle cluster f_{00}=1(200), f_{xy}=0, w_{nm}=w_{mn},=const

Fokker-Planck Transport Equation

2nd order Taylor Expansion

$$\frac{\partial}{\partial t} f_n(t) \approx -\frac{\partial}{\partial n}\left[\left(w_+(n) - w_-(n)\right) f_n\right] + \frac{1}{2}\frac{\partial^2}{\partial n^2}\left[\left(w_+(n) + w_-(n)\right) f_n\right]$$

$$\frac{\partial}{\partial t} f_n(t) \approx -\frac{\partial}{\partial n}\left[v_n \cdot f_n\right] + \frac{\partial^2}{\partial n^2}\left[D_{nn} \cdot f_n\right]$$



$$v_n = w_+(n) - w_-(n) \quad \textit{Drift Coefficient}$$

$$D_n = \frac{1}{2}\left(w_+(n) + w_-(n)\right) \quad \textit{Diffusion Coefficient}$$

$v_n \leftrightarrow$ *anisotropy of probability flow*

$D_n \leftrightarrow$ *average probability out flow*

Mass (density ρ_M*)* $\rightarrow$ *mass flux* $\vec{j}_M \sim \rho_M \cdot \vec{v}_n$

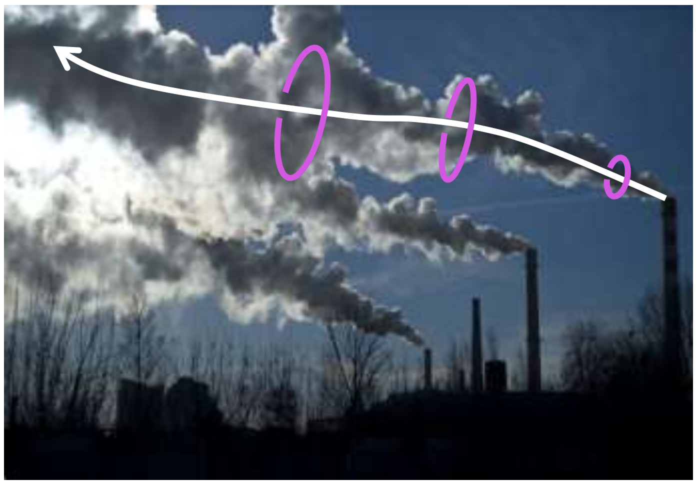
General trends in the evolution of cell *n* population:

1. overall stream of population away (or towards) cell = **drift**, $w_+(n) \neq w_-(n)$
2. diffuse broadening of stream envelope = **diffusion**, $\bar{w}(n) = \left(w_+(n) + w_-(n)\right)/2$

Solutions to Fokker-Planck Equation

For constant Drift & Diffusion coefficients

$$\frac{\partial}{\partial t} f_n(t) \approx -\frac{\partial}{\partial n}\left[v_n \cdot f_n\right] + \frac{\partial^2}{\partial n^2}\left[D_n \cdot f_n\right] \Rightarrow \frac{\partial}{\partial t} f_n(t) \approx -v_n \cdot \frac{\partial f_n}{\partial n} + D_n \cdot \frac{\partial^2 f_n}{\partial n^2}$$



Mass flux $\vec{j}_M \sim \rho_M \cdot \vec{v}_M$

Time evolution of cell *n* population:
Probability distribution $\boldsymbol{f}_{\mathrm{n}}$ has *t-dependent* bell-shape, maximum around the mean, falling off sideways → Gaussian normal distribution

Population Probability cell *n*

$$f_n(t) = \frac{1}{\sqrt{2\pi\sigma_n^2(t)}} \exp\left\{-\frac{\left(n - \bar{n}(t)\right)^2}{2\sigma_n^2(t)}\right\}$$

Mean $\bar{n}(t) = \bar{n}(0) + v_n \cdot t$

Variance $\sigma_n^2(t) = \sigma_n^2(0) + 2D_n \cdot t$

$$\Rightarrow \frac{\Delta\bar{n}(t)}{\sigma_n^2(t)} = \frac{\bar{n}(t) - \bar{n}(0)}{\sigma_n^2(t) - \sigma_n^2(0)} = \frac{v_n}{2D_{nn}} = const.$$

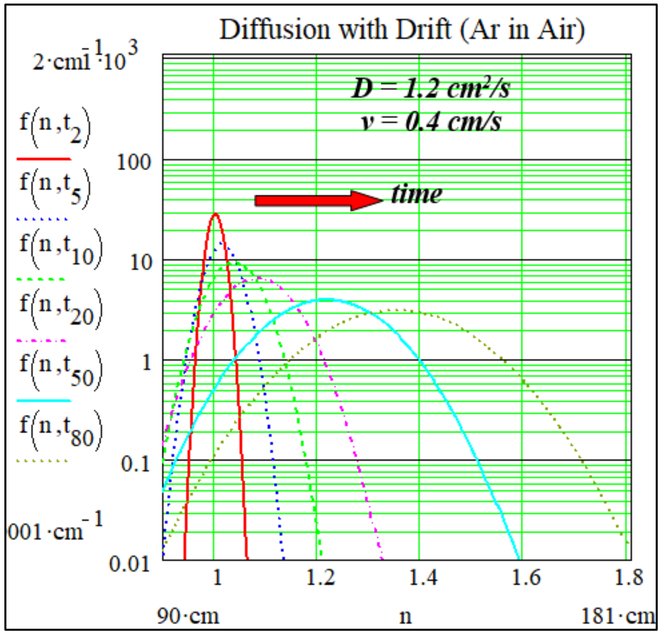
$Typical\ gas\ in\ gas\ (@T \approx 288K): D \sim 10^{-5}\, m^2/s$

Strong T dependence

Solutions to Fokker-Planck Equation

For constant Drift & Diffusion coefficients

$$\frac{\partial}{\partial t} f_n(t) \approx -\frac{\partial}{\partial n}\left[v_n \cdot f_n\right] + \frac{\partial^2}{\partial n^2}\left[D_n \cdot f_n\right] \Rightarrow \frac{\partial}{\partial t} f_n(t) \approx -v_n \cdot \frac{\partial f_n}{\partial n} + D_n \cdot \frac{\partial^2 f_n}{\partial n^2}$$



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Diffusive Transport: Diffusion Equation

No advection→ zero drift *(isotropic→ v_n=0)* & constant diffusion *(D_n>0)* coeff's

$$\frac{\partial}{\partial t} f_n(t) \approx -v_n \cdot \frac{\partial f_n}{\partial n} + D_n \cdot \frac{\partial^2 f_n}{\partial n^2}$$

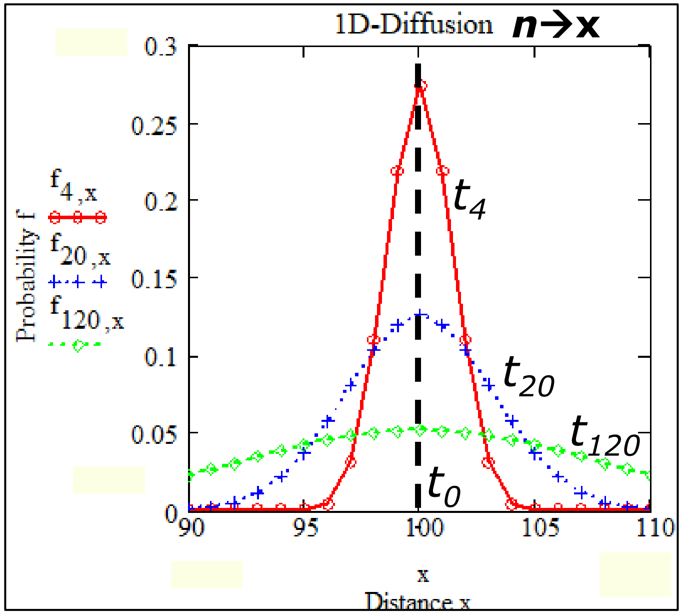
$$\frac{\partial}{\partial t} f_n(t) = D_n \cdot \frac{\partial^2 f_n}{\partial n^2}$$

Diffusion Equation

Time evolution of cell population:
Distribution ***f***$_n$ on average stationary but broadens → model with Gaussian normal distribution

Population cell *n*

$$f_n(t) = \frac{1}{\sqrt{2\pi\sigma_n^2(t)}} \exp\left\{-\frac{(n-\bar{n}(0))^2}{2\sigma_n^2(t)}\right\}$$



$$\langle x(t)\rangle_{rms} = \sqrt{\left\langle (x-\langle x\rangle)^2 \right\rangle} = \sqrt{2D_x t}$$

Variable transformation → Gaussian (x,t)

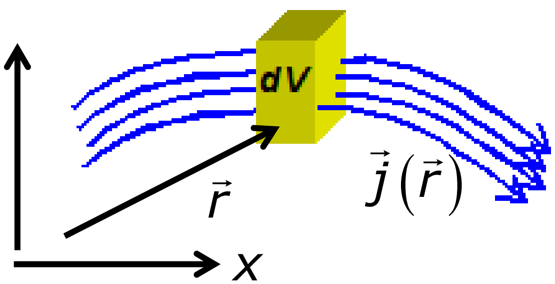
$$f_n(t) \to f(x,t) \sim \exp\left\{-\left(\frac{x}{\sqrt{4D\cdot t}}\right)^2\right\}$$

Fick's Diffusion Laws

Diffusion limit of Fokker-Planck process

$$\frac{\partial}{\partial t} c(\vec{r},t) = D_n \cdot \Delta c(\vec{r},t)$$

Change depends on non-linearity of environment



Fluid dynamics for stream of ***N=const.*** particles➔ temporal rate of change in *specific* population ***f*(x,y,z)**=*concentration* ***c*** *of* volume element ***dV*** → total time derivative of population.

In general *D(x,y,z) is anisotropic 3x3 tensor.*

Particle Flux (flow density) $\vec{j}(\vec{r}) = -\bar{w} \cdot \vec{\nabla} c(\vec{r}) = -D \cdot \vec{\nabla} c(\vec{r})$ Fick's 1^{st} Law

Check for consistency

Continuity Equation
total ***t***-derivative

$$\frac{dc}{dt} = \frac{\partial c}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0$$

$$\frac{\partial c}{\partial t} = -\vec{\nabla} \cdot \vec{j} = +\vec{\nabla} \cdot \left[D \cdot \vec{\nabla} c(\vec{r}) \right] \approx D \cdot \Delta c(\vec{r})$$

➔

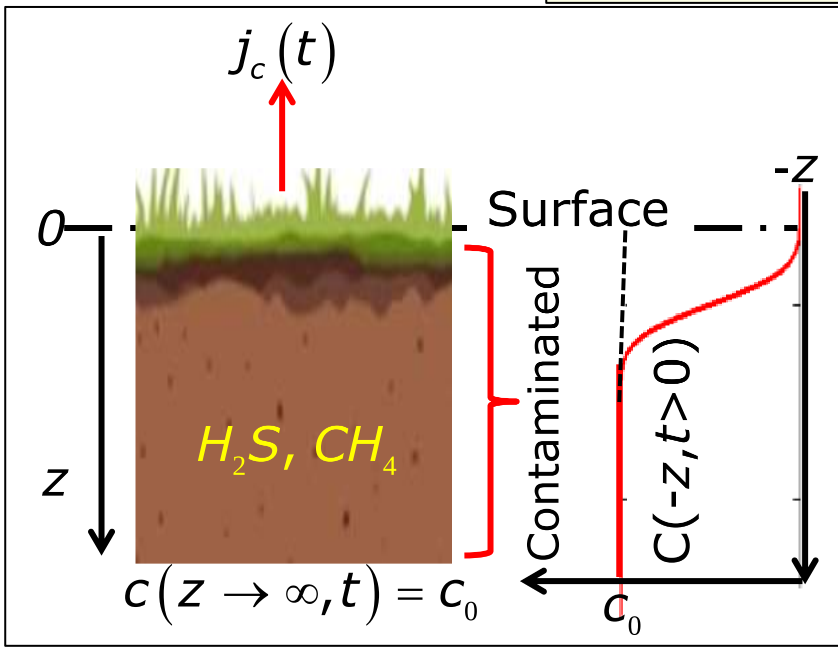
$$\frac{\partial c(\vec{r})}{\partial t} \approx D \cdot \Delta c(\vec{r})$$

Fick's 2^{nd} Law

Example: Cumulative Diffusion Flow

Warming tundra soil releases sequestered greenhouse gases.

Equation of "motion" $\frac{\partial}{\partial t} c(z,t) = D \cdot \frac{\partial^2 c}{\partial z^2}$



Initial Conditions

$c(z, t=0) = c_0$

$c(z=0, t>0) = 0$

$c(z \to -\infty, t) = c_0$

Cumulative effect (over all z<0)

$$C(z,t) \propto \frac{1}{\sqrt{\pi}} \int_{-\infty}^{z} c(x,t)dx$$

$$c(z,t) = c_0 \cdot erf\left\{\frac{z}{\sqrt{4D \cdot t}}\right\}$$

Error Function $erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-x^2} \cdot dx$

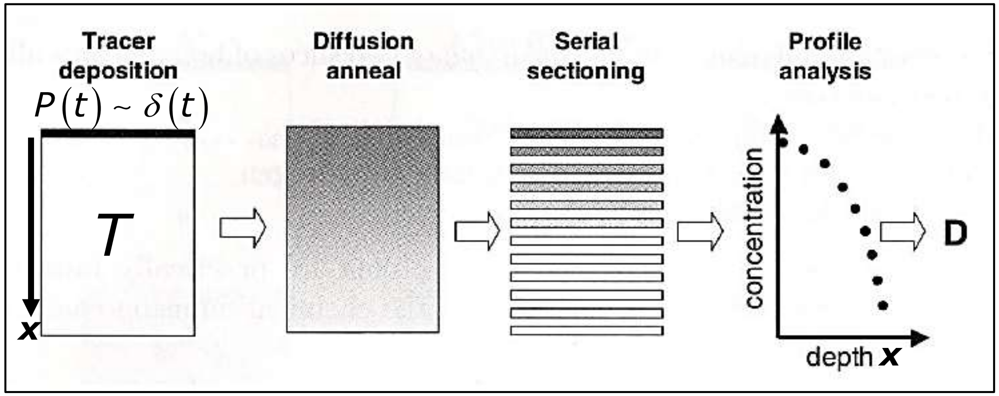
$erf(z) = -erf(z)$; $erf(\infty) = 1$

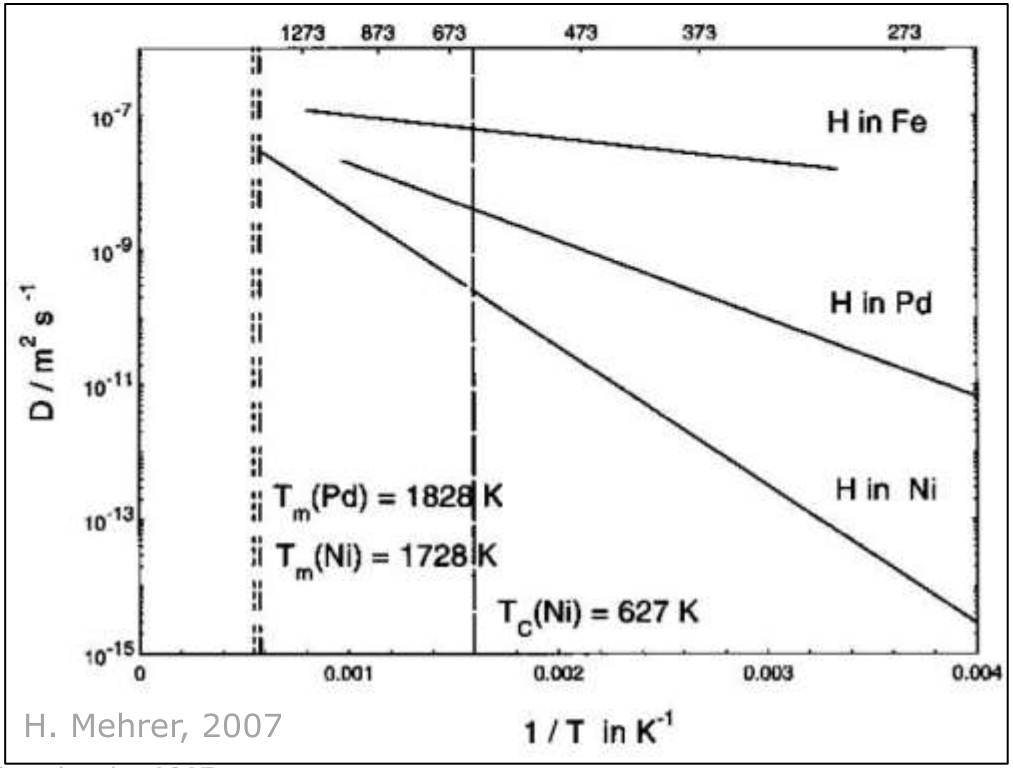
Complementary error function

$erfc(z) = 1 - erf(z)$

Surface flow $j_c(t) = c_0 \cdot \sqrt{\frac{D}{\pi \cdot t}}$

Example: *D* for Hydrogen Diffusion in Metals





Tracer= radioactive species (hydrogen isotope tritium ^{3}H).

Apply thin tracer activity ***A*** on clean surface of ***Fe*** sample at *x=0* @ *t*=0, sample @ temperature ***T*** → *pulse @t=0*

Wait for Δt several hours, then section sample in x direction → measure *T* concentration as

$$c(x,\Delta t) = \frac{A}{\sqrt{\pi D \cdot \Delta t}} err\left(\frac{x}{\sqrt{4D \cdot \Delta t}}\right)$$

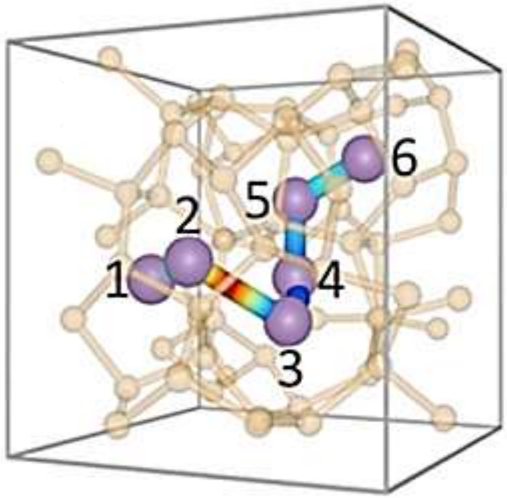
Found ***T*** dependent diffusion coefficients of ^{3}H in Fe, Pd, Ni

$$D^i(T) = D_0^i e^{-Q_i/k_B T} \sim \left(10^{-15} - 10^{-7}\right)\frac{m^2}{s}$$

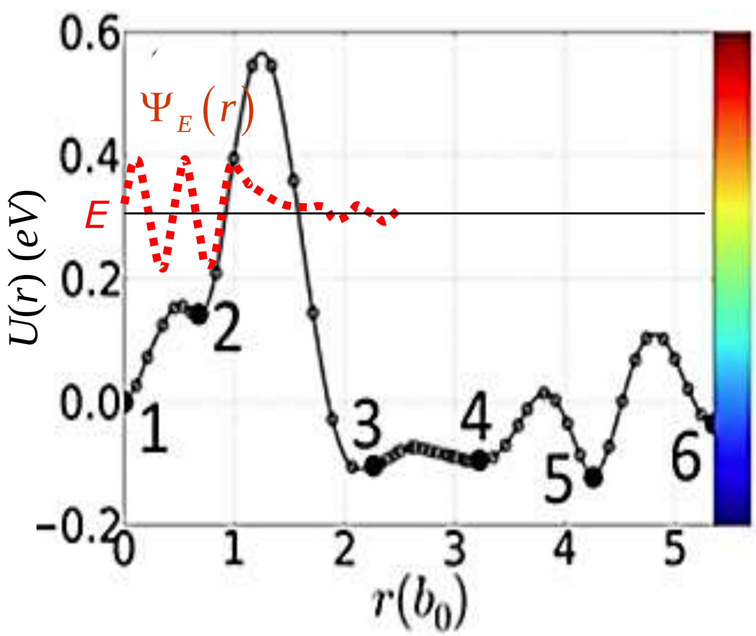
Rxn energy Q_i; $i = Fe, Pd, Ni$

Boltzmann $k_B = 1.38 \cdot 10^{-23}\ J/K$

Lithium Diffusion In Silicon



Example of a pathway for the diffusion of a lithium atom (violet) in bulk amorphous silicon. The numbers label the (interstitial) equilibrium sites between which lithium hops. Crystal bond length b_0 = 2.37 Å.



Quantum mechanical Tunnel Effect

Transmission through barrier @ particle E

$$T(E_p) \approx \exp\left\{-2d\sqrt{2m(U-E_p)/\hbar^2}\right\}$$

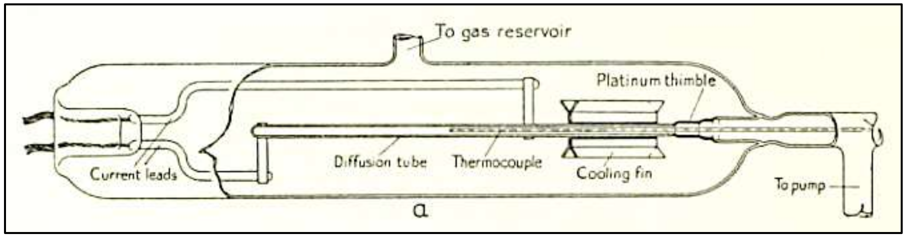
$$E_p \geq U \rightarrow T \sim 1$$

Effective diffusion coefficient

$$D(U, E_p) = D_0 \cdot \begin{cases} \ll 1 \ for\ E_p < U \\ \sim 1 \ for\ E_p \geq U \end{cases}$$

Depends on particle energy spectrum

Gas Diffusion/Permeation through Metals



Effect of Temperature on Rate of Diffusion/Permeation
Table I—Hydrogen-Molybdenum

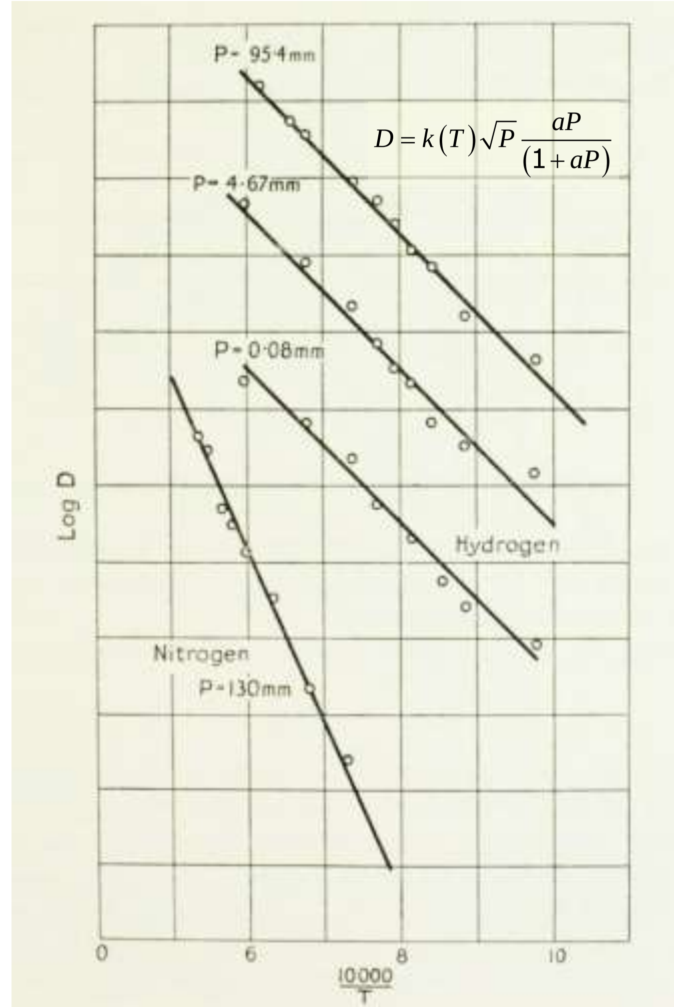
Pressure mm	Temp °K	Rate D
95·4	823	$0{\cdot}7 \times 10^{-6}$
	1023	5·1
	1133	9·0
	1188	17·3
	1228	21·6
	1263	30·0
4·67	823	$0{\cdot}12 \times 10^{-6}$
	1023	1·02
	1123	1·70
	1188	2·54
	1228	3·77
0·08	1023	$0{\cdot}12 \times 10^{-6}$
	1133	0·21
	1173	0·29
	1228	0·51

Diffusion Tube
External diameter___ 1.0 mm (approx.)
Wall thickness .... 0.075 mm
Heated length .... 38.0 mm

D given as gas volume cm³ @ N.T.P. diffusing per second through 1 cm² surface @1 mm thick. Richardson Equ, for D(P,T)

$$D = \frac{k}{d} \cdot \sqrt{P \cdot T} \cdot e^{-b/T}$$

Molybdenum Gas Diffusion Constant



$$D = k(T)\sqrt{P}\,\frac{aP}{(1+aP)}$$

C. J. Smithells and C.E. Ransley (Proc. Royal Society, 1935)
https://royalsocietypublishing.org/

Experimental Magnitudes of Transport Coefficients

Gas in Gas	D_g ($m^2\ s^{-1}$)
O_2 in O_2	1.89×10^{-5}
N_2 in N_2	1.98×10^{-5}
CO_2 in CO_2	1.04×10^{-5}
O_2 in Air	1.78×10^{-5}
CO_2 in Air	1.38×10^{-5}
H_2O in Air	2.36×10^{-5}

Table IV-1: Experimental Diffusion Coefficients

System	D/cm^2s^{-1}	T/K	System	$D/10^{-5}cm^2s^{-1}$	T/K
He-He	2.38	275	Au in Ag	2.46	1253
He-H_2	0.25	90	In in Ag	3.81	1253
He-N_2	0.09	77	Sb in Ag	4.11	1253
He-SF_6	16.36	2900	Ag in Ag	$1.27\ 10^{-9}$	723
Ne-H_2	0.15	90	Co in Co	$0.95\ 10^{-9}$	1043

Gas	M_{mol} (10^{-3} kg mol^{-1})	ρ_g at SP, $T = 288$ K (kg m^{-3})
Nitrogen	28	1.19
Oxygen	32	1.36
Air	28.9	1.22
Hydrogen	2	0.08
Methane	10	0.42
Water Vapour	18	0.76
Carbon Dioxide	38	1.61
Radon	222	9.40

Typical for gas in gas

$$D \sim 10^{-5}\, m^2/s$$

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Math Chapters
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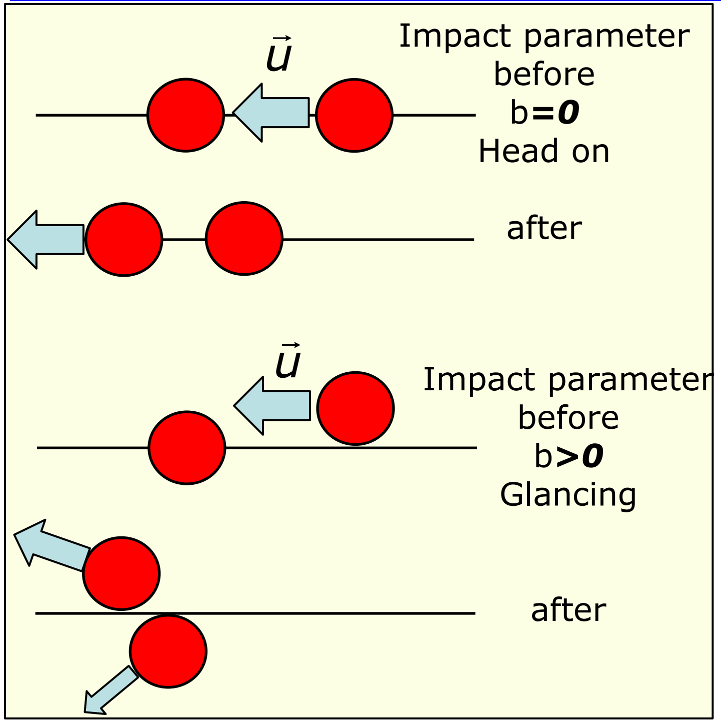
Random Velocity Distribution



Particle velocities change differently through different collisions
→ random speeds, random 3D directions
→ for all possible $\vec{u}$; $0 \le |\vec{u}| \le \infty$

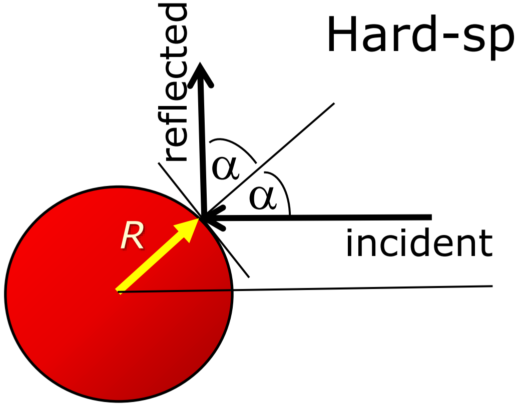
Probability distribution $d^3P(\vec{u})/d^3\vec{u}$

Cartesian coordinates

$$d^3P(\vec{u}) = f(\vec{u})\cdot d^3\vec{u} = f(u_x,u_y,u_z)\cdot \underbrace{du_x\cdot du_y\cdot du_z}_{d^3\vec{u}}$$

$$f(+\vec{u}) = f(-\vec{u}) \rightarrow f(\vec{u}) = f(\vec{u}^2) = f(u_x^2+u_y^2+u_z^2)$$

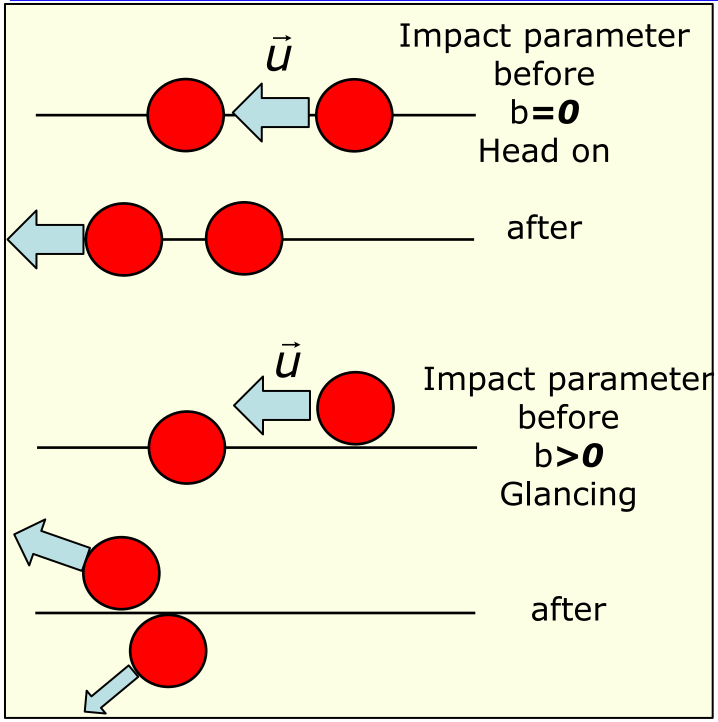
Hard-sphere scattering has isotropic angular distribution



Independent components u_x, u_y, u_z

$$\rightarrow d^3P(\vec{u}) = \left[f(u_x)du_x\right]\left[f(u_y)du_y\right]\left[f(u_z)du_z\right]$$

Random Velocity Distribution



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$$f(u^2) = f(u_x^2 + u_y^2 + u_z^2) = f(u_x^2)\cdot f(u_y^2)\cdot f(u_z^2)$$

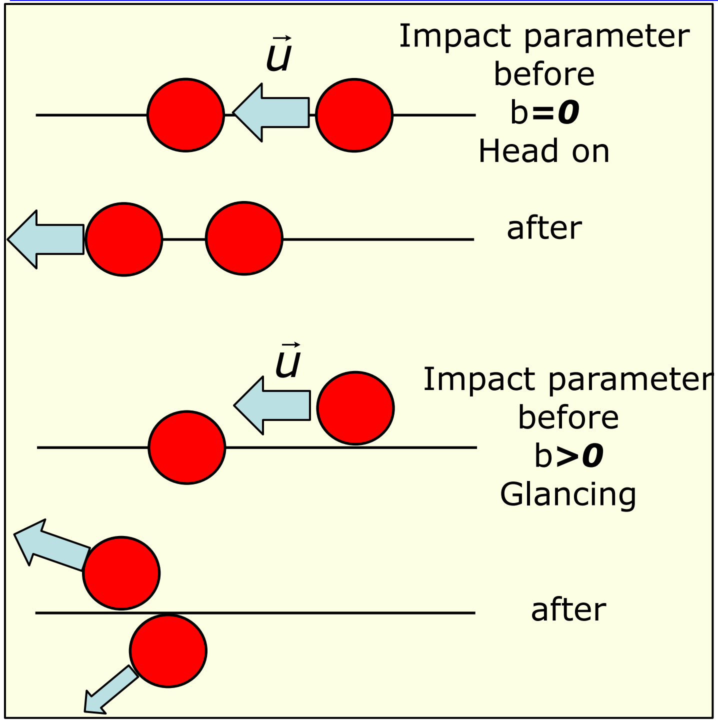
Only suitable function

$$f(u^2) = C\cdot e^{-au^2}$$

$$Differential\ probabilities\ f(u_x) = \frac{dP(u_x)}{du_x};\ \cdots$$

Need to determine exponent constant ***a***

Maxwell-Boltzmann Velocity Distribution



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→ for all possible $\vec{u};\ 0 \le |\vec{u}| \le \infty$

⇒ *Probability distribution* $d^3P(\vec{u})/d^3\vec{u}$

Cartesian coordinates

$$d^3P(\vec{u}) = f(\vec{u})\cdot d^3\vec{u} = f(u_x,u_y,u_z)\cdot d^3\vec{u}$$

$$\langle \varepsilon_{kin}\rangle = \frac{m}{2}\langle u_x^2\rangle \ \text{with}\ \langle u_x^2\rangle = \int_{-\infty}^{+\infty} du_x\, u_x^2 \cdot f\left(u_x^2\right) \rightarrow$$

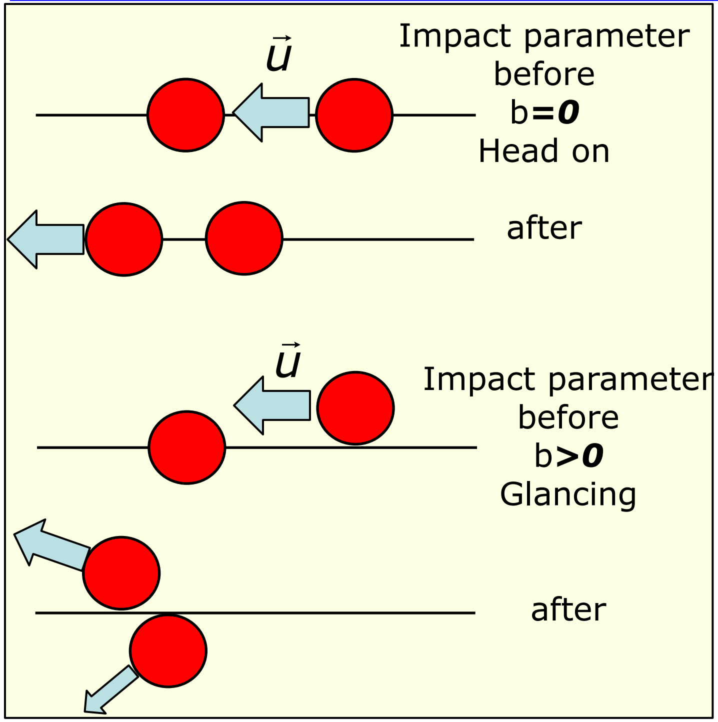
$$\langle u_x^2\rangle = \sqrt{\frac{a}{\pi}}\int_{-\infty}^{+\infty} du_x\, u_x^2\, e^{-au_x^2} = 2\sqrt{\frac{a}{\pi}}\int_{0}^{+\infty} du_x\, u_x^2\, e^{-au_x^2} = \frac{1}{2a}$$

⇒ We call $\langle \varepsilon_{kin}\rangle = \dfrac{m}{4a}$

random "Heat" or thermal energy
→ "*Temperature*" *T*

T is measure of *mean* particle kinetic energy → ε_{kin} has also fluctuations (is a spectrum). → *N*-particle ensemble constitutes a *heat reservoir* = "heat bath"

Maxwell-Boltzmann Velocity Distribution



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$$\langle u_x^2 \rangle = \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} du_x\, u_x^2\, e^{-a u_x^2} = 2\sqrt{\frac{a}{\pi}} \int_{0}^{+\infty} du_x\, u_x^2\, e^{-a u_x^2} = \frac{1}{2a}$$

$$Thermal\;\; energy \rightarrow "Temperature"\;\; T$$

$$\langle \varepsilon_{kin} \rangle = \frac{m}{4a} \propto T \rightarrow a = \frac{m}{2\langle 2\varepsilon_{kin} \rangle} = \frac{m}{2\left(k_B T\right)}$$

MB-velocity spectrum

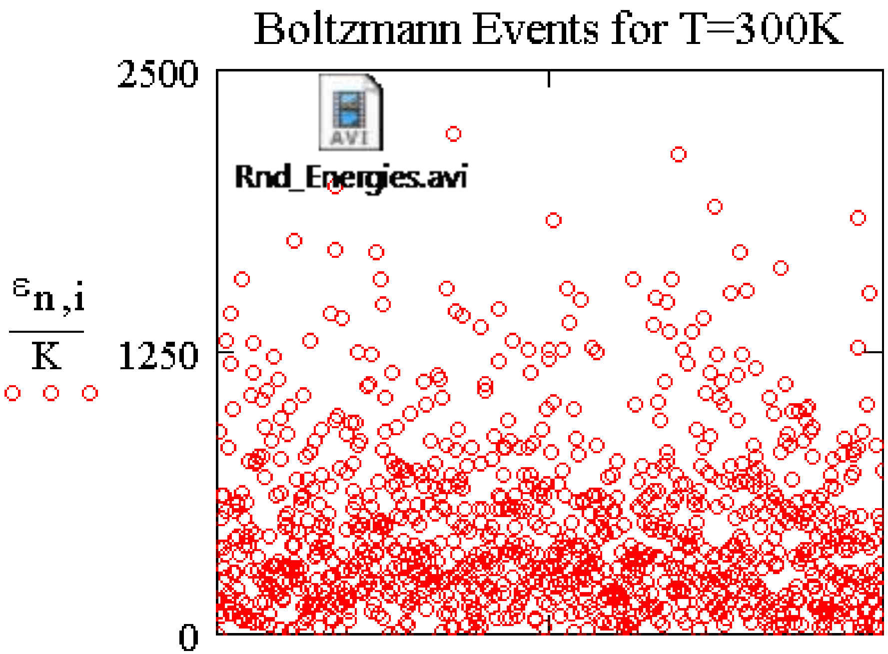
$$f(u^2) \rightarrow \quad \frac{dP(u)}{du} = C \cdot e^{-\left(\frac{m \cdot u^2}{2}\right) / k_B T}$$

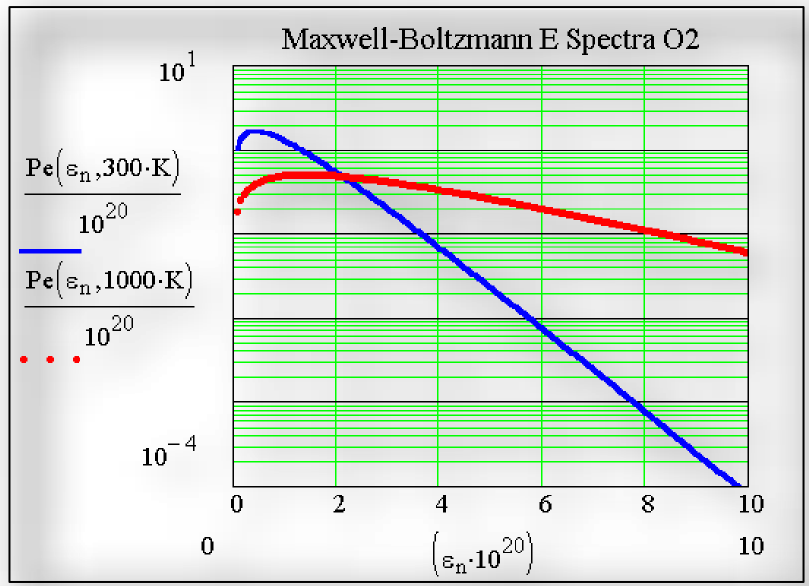
Boltzmann Factor

=Shape of ANY randomly distributed energy distribution

Here, T is the mean particle kinetic energy → ε_{kin} has fluctuations (a spectrum)
→ *N*-particle ensemble constitutes a *heat reservoir* = “heat bath”

The Final State: Randomized Thermal Energy





$$P(\varepsilon,T)=\frac{dN}{d\varepsilon}\propto\sqrt{\varepsilon}\cdot e^{-\frac{\varepsilon}{k_BT}}$$

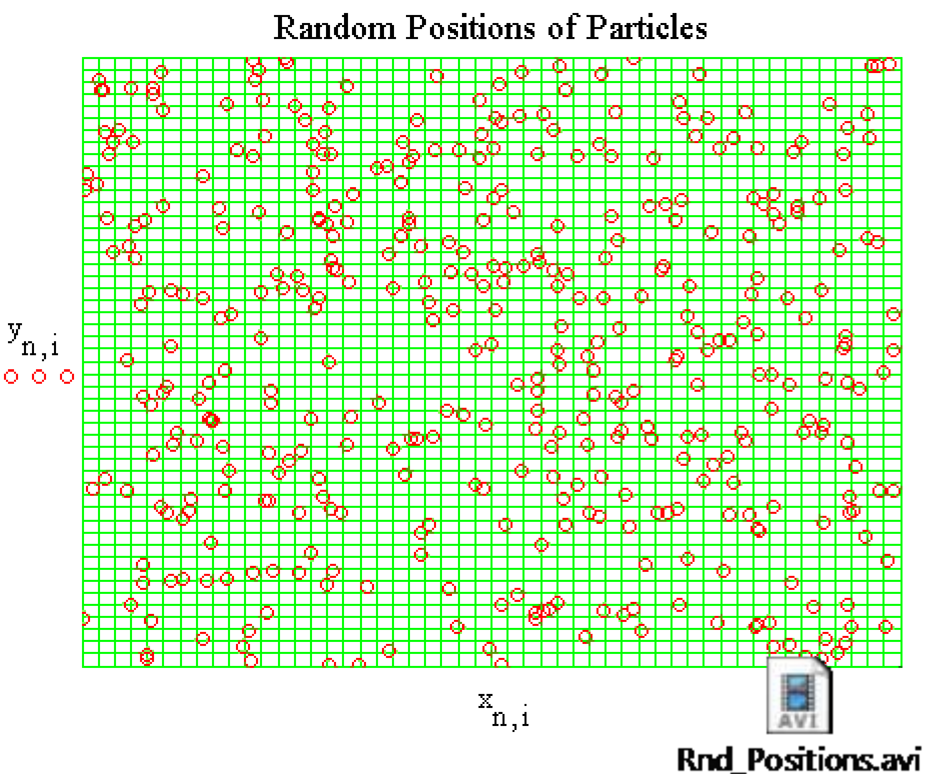
Particles in gas volume collide continuously. Transfer of momentum and energy occur depending centrality of collisions (head on,……., grazing) like ≙ **hard spheres**.

→ randomly fluctuating ("thermal") "Maxwell-Boltzmann" kinetic-energy spectrum.

$$Mean\ kinetic\ energy\ per\ particle\ \langle\varepsilon\rangle\propto T\ ("temperature")$$

(Ideal gas: internal U= ε (kinetic energy), no potential energy ≙ no interactions)

Random (Thermal) Motion in Space



Example: Motion in two dimensions of 300 non-interacting (ideal-gas) particles.

All particles move in random directions because of multiple collisions, which actually do occur but are not explicitly treated here.

Every particle visits every one of the energetically equivalent cells.

Contrast: Collective motion.

Particles in a gas move in different directions and at different speeds, colliding with one another often. Eventually, their positions at any given time are random.

→ All available (accessible) space is visited by all particles (in due time).

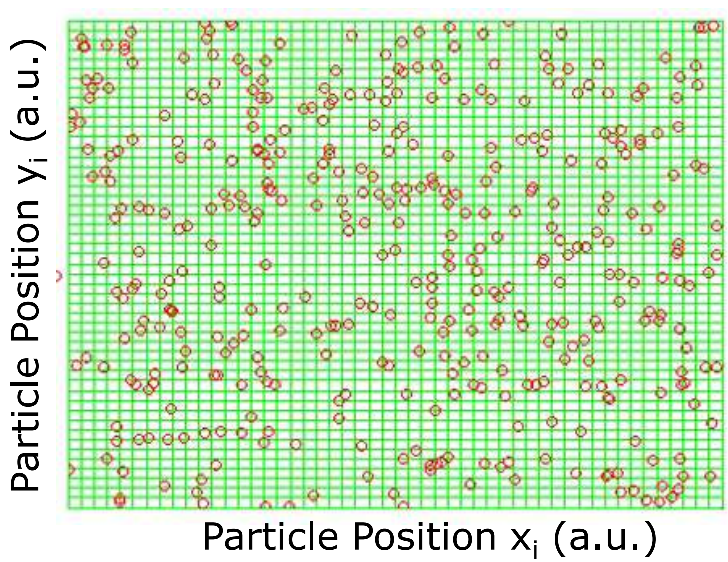
→ → Ergodic Theorem

Microscopic Particle Phase Space

Energy transfer to gas of independent particles in containment.
By scattering or by incoherent (short wavelength) radiation → chaotic motion of particles in space → transferred energy is dissipated → not totally reversible

$$\left\langle E_{kin} \right\rangle_{all\ particles} \triangleq Temperature\ T$$

Snapshot (*time*) = **microscopic state of multi-particle system**



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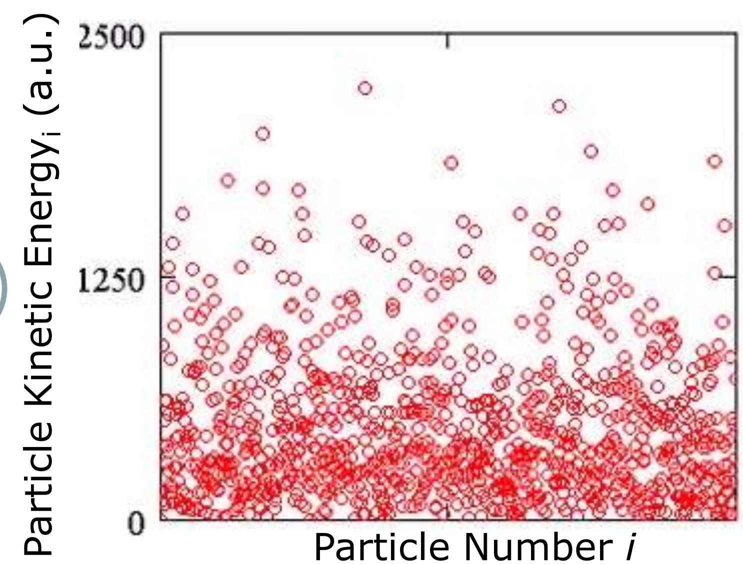

Chaotic motion in configuration space. Characteristic velocity and energy spectrum (Maxwell-Boltzmann).
Massive (m_i) particles: $positions\ \vec{q}_i,\ momenta\ \vec{p}_i \rightarrow$ $Phase\ space\ \{\vec{q}_i,\ \vec{p}_i\}$