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
  Diffusion processes
  Maxwell-Boltzmann energy distributions
  Fluctuating (Langevin) dissipative forces

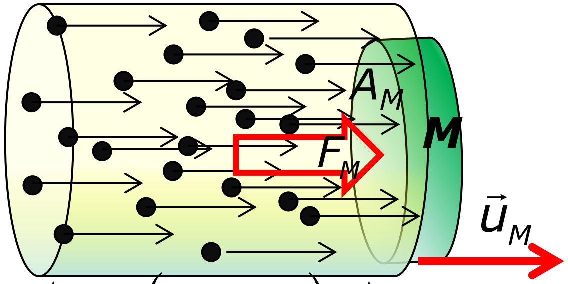
- Kinetics of dilute gases
  Work and heat transfer
    Flow of heat and radiation
    Laws of thermodynamics, thermodynamic ensembles, entropy
- Fundamental ideal gas laws, Equation of state (EoS)

Reading Assignments
Weeks 5 & 6
LN IV.1-4:

Kondepudi Ch. 1-3.
Additional Material

McQuarrie & Simon
Ch. 2, 5
Math Chapter B, C

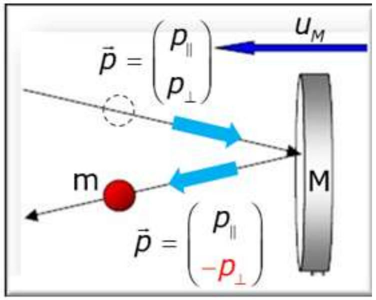
Macroscopic Effects of Dissipative Energy Transfer



$$\Delta x = (u - u_M)\cdot \Delta t$$

$$\Delta V = A_M \cdot \Delta x$$

$$F_M = -2\rho_m \cdot A_M \cdot (u - u_M)^2$$



Discussion Points

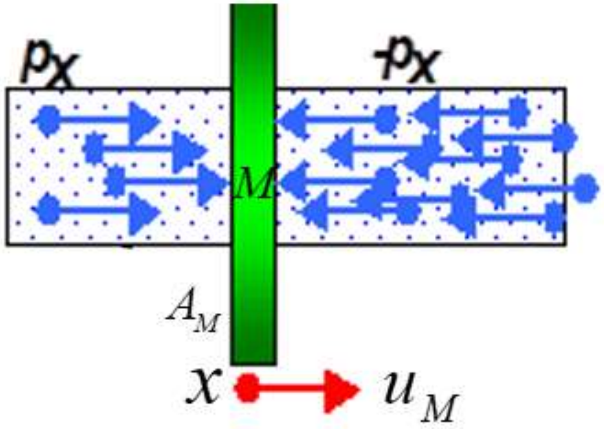
Collision layer, Effects of multiple collisions with Mm

Trends to push M → pV-work= conversion of random energy to directed flow/motion

Momentum mismatch with F/B ensembles, pos/neg p boost

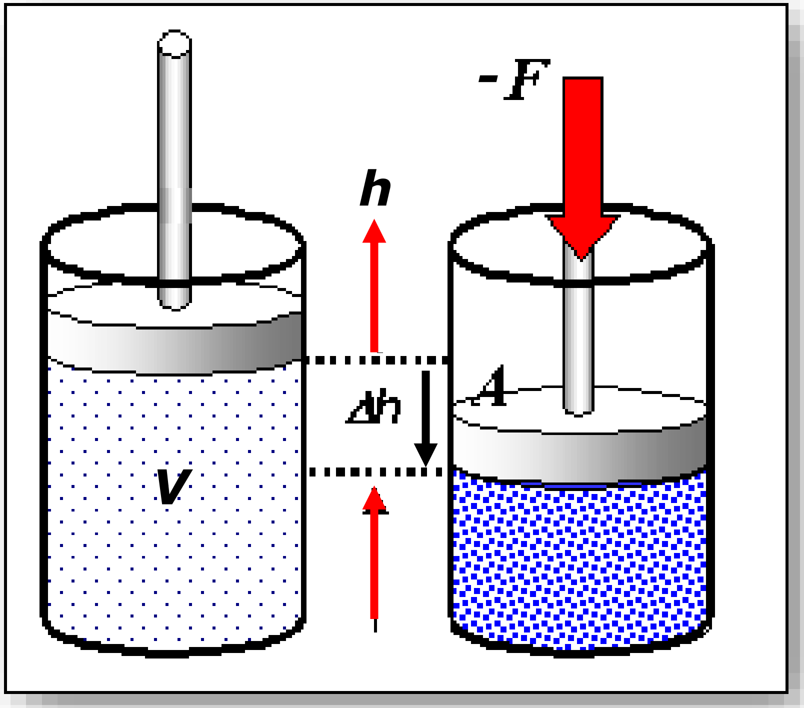
Exponents ^1 vs. ^2

Relation force-pressure @$\boldsymbol{u}_M$=0, ext vs. internal Expansion-cooling



$$\underline{\underline{\langle F_M \rangle}} = -[4A_M m\int d\vec{p}^{\,3}\, f(\vec{p})\cdot|\upsilon_x|]\cdot u_M \underline{\underline{= -\gamma \cdot u_M}} \quad \text{with} \quad \gamma > 0$$

Physical Changes: Compression of (Ideal) Gases



Compression of a gas ***"System"*** volume *V* with a constant force *F* (e.g., weight) on a constant area *A*:

→ Pressure *p* = Force *F*/Area *A*,

at $p = p_{ext}$ =const.(external, not internal)

$$\boxed{p = \frac{F}{A} = p_{ext} \rightarrow \underbrace{\Delta V}_{<0} = A \cdot \Delta h < 0}$$

Compression work done on system

$$w = -F \cdot \Delta h = -(p \cdot A) \cdot \Delta h = -p \cdot \underbrace{\Delta V}_{<0} > 0$$

$$\boxed{\textit{Internal energy gain of gas}: \Delta U = -p \cdot \underbrace{\Delta V}_{<0} > 0 \rightarrow \Delta T > 0}$$

Sign Convention work: Compressional work on a gas volume (=system) increases the internal energy ***E*** of the gas .

→ Work done on gas is counted as positive *w > 0*().

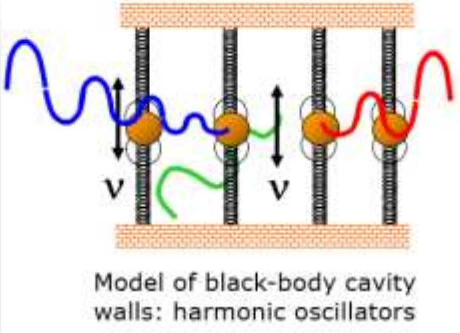
Planck's Thermal (Blackbody) Radiation


Max Planck (1900)

Experimental electromagnetic energy spectrum emitted by a mass ("black" body) @ *T*. Radiation (photon) energy

→ Electromagnetic Energy Quantum

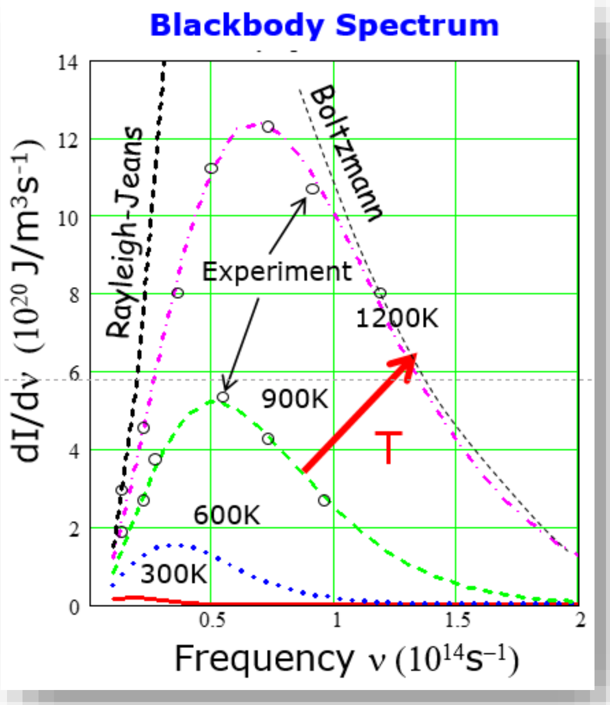
$$\boxed{\begin{array}{l} E_\nu = h\cdot\nu = h\cdot c/\lambda \\ light\ vel.\ c = \lambda\cdot\nu \end{array}}$$



Model of black-body cavity walls: harmonic oscillators

Planck's constant, from fit

$h = 6.62618\cdot 10^{-34}\,J\cdot s$


Blackbody Spectrum

Power (energy/time) density@universal shape

$$\boxed{\frac{dI}{d\nu dV}(\nu,T) = \langle E_\nu\rangle\,\rho_\nu = \frac{8\pi}{c^3}\,\frac{h\nu^3}{e^{h\nu/k_BT}-1}}$$

Stefan-Boltzmann Law:
Total radiated thermal power

$$\boxed{F = \int_0^\infty \frac{dI}{d\lambda\cdot dV}\,d\lambda = \sigma_{SB}\cdot T^4\,\left(W/m^2\right)}$$

$$SB\ Constant\ \sigma_{SB} = 5.67\cdot 10^{-8}\,\frac{W}{m^2K^4}$$

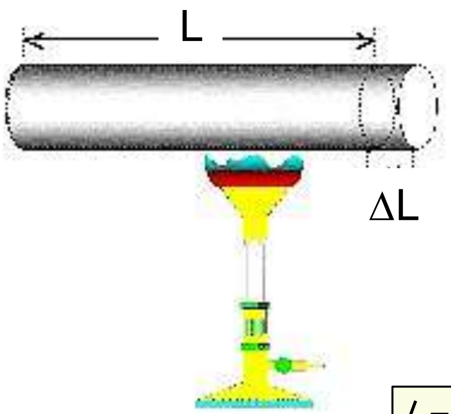
$$Def.\ "Watt"\ W = J/s$$

Conversion of Heat to Macroscopic Potential Energy

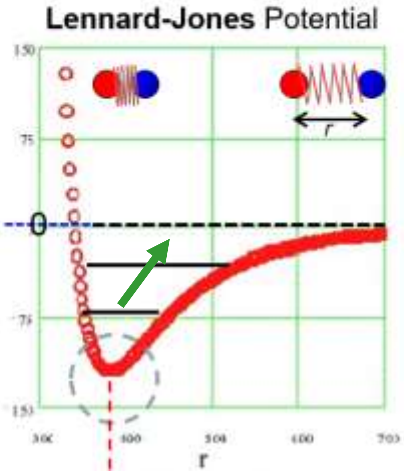
Heating a metal bar transfers energy to solid crystal lattice → bar expands in 3D. Reason: shape of the interaction potential between atoms/ions

(Lennard-Jones-type or harmonic oscillator potential).

Macroscopic application: Avoid expansion effects by gaps between segments of bridges, highway concrete surface plates exposed to solar radiation



Effect of particle interaction potential V(distance=r). Increased internal lattice energy weakens attractive forces → Increased atomic distance = macroscopic expansion.



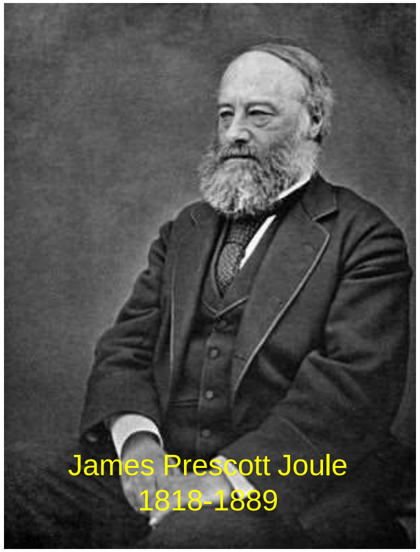
$$\boxed{\langle L(T)\rangle = \langle L(T_0)\rangle\left[1+\alpha\left(T-T_0\right)\right] > \langle L(T_0)\rangle}$$

Linear expansion coefficient $\alpha > 0$

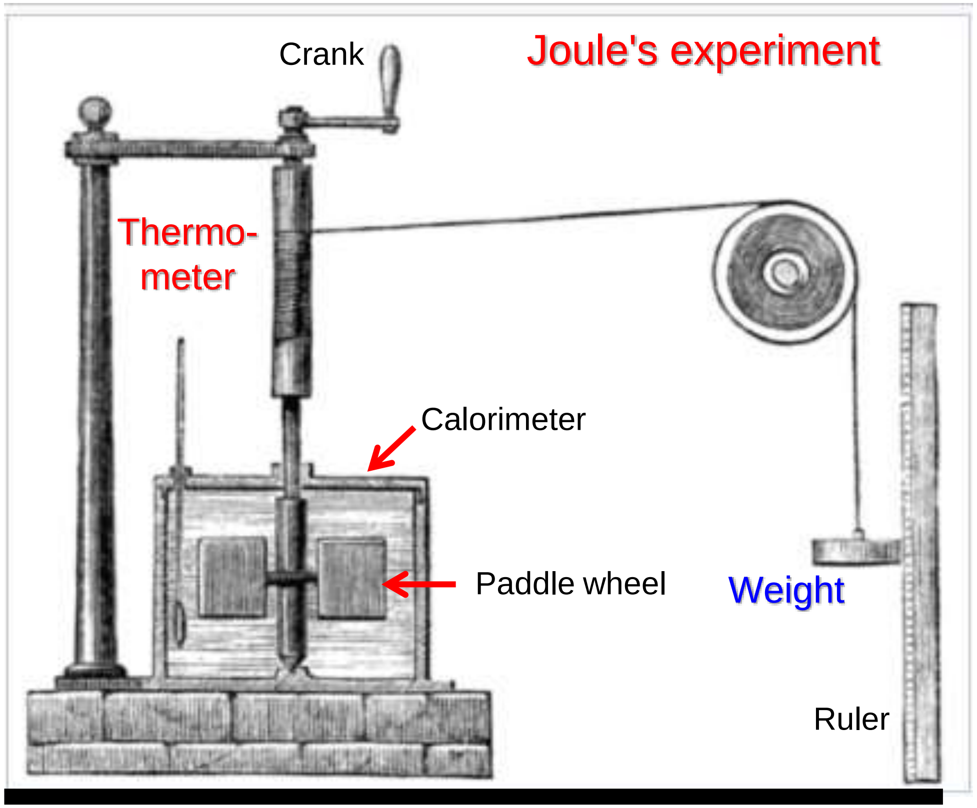
Can be anisotropic in 3D (lattice structure)

Equivalence of heat and mechanical etc. work ?

Mechanical Equivalent of Heat


James Prescott Joule
1818-1889

"An Experimental Enquiry Concerning the Source of the Heat which is Excited by Friction", (1798), Phil. Transactions of the Royal Society p. 102



Mechanical work equivalent of heat energy

$$w \propto Q \rightarrow w = C \cdot Q$$

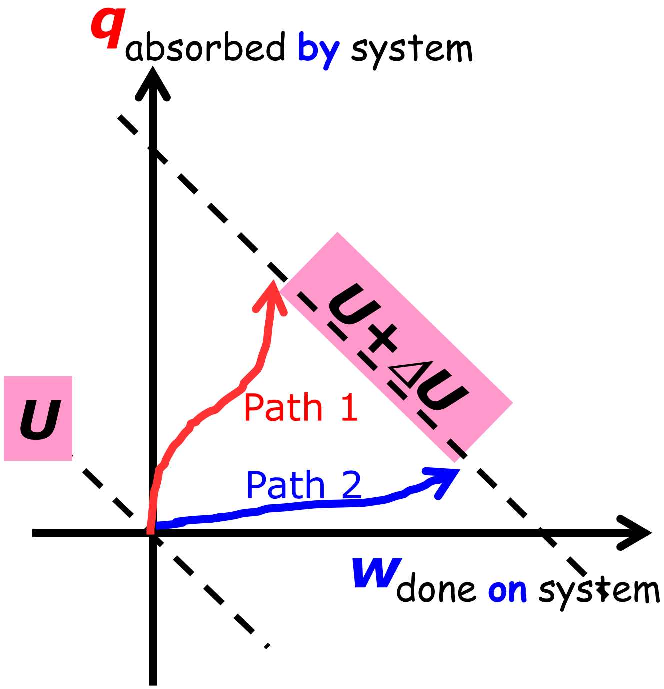
$$C = 4.186\ kJ/kcal$$

Specific heat C →
Energy (ΔT): $q = C \cdot \Delta T$

Heat energy ***q*** required for heating of H_2O: $C_V(\ldots) \approx (4.17\text{-}\ 4.22)\ J/(g\cdot{}^\circ C)$
1g material by $\Delta T = 1^0C$

Equivalence of Work and Heat Energy

Conservation of total Energy (First Law of Thermodynamics): Energy ***U*** of an isolated system is conserved. → ***U*** *is a state function* (characterizes state)



If system can exchange energy with environment, it can do that by

1) doing or receiving work ***w*** or by
2) absorbing or emitting heat ***q***.

$$\boxed{\Delta U = w + q}$$

→ ***W and q are path dependent, and*** *NOT state functions.*

Both are counted positive, if they increase ***U***

Example: Internal energy loss suffered $\Delta U<0$ = sum of work done by ($w < 0$) and heat emitted by ($q < 0$) by the system.

In asymptotic (long times) state, most likely, system equilibrium state, ***U fluctuates in time*** and distributes randomly over all degrees of freedom.
→ No historic memory about production pathway.

Stationary state of m.p. system, interactions w. environment?

Energy Transfer between *m.p.* Systems & Surroundings

- Energy transferred to and from ***N***-particle systems (e.g., a gas or liquid volume) by mechanical, radiation, or other work is dissipated by multiple interactions of system constituents (particles in a gas or solid lattice).

- Energy dissipation process may take some "relaxation time," after which all ***N*** system particles move randomly (populate all states) & share total energy on average equally over all degrees of freedom **(Equipartition Law):**

$$\boxed{\left\langle \varepsilon_{kin} + \varepsilon_{pot} \right\rangle_N \propto T}$$

- *Apparently stationary macroscopic state* = "**Thermal Equilibrium**" is a dynamic process, with multi-particle configurations fluctuating over entire range with equal probabilities → historic memory is lost (Markov Process).

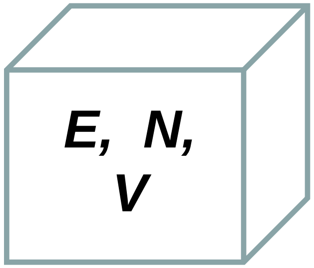
- (Total) Energy ***U(N)*** is an *extensive* state variable ("state function"), characteristic of the (macroscopic) state of the system, *scales with size*.

$$\boxed{\langle U \rangle = N \cdot \langle \varepsilon \rangle \propto T} \quad (factor = heat\ capacity\ \ \Delta\langle U \rangle = C_V \cdot \Delta T$$

Idealized Classification: Random Statistical Ensembles

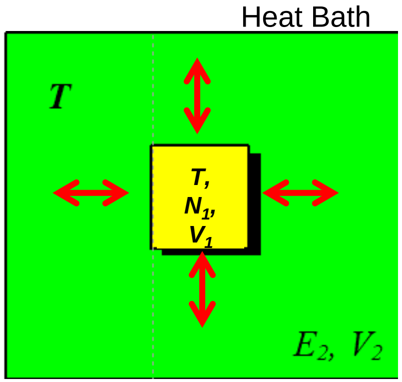
E (or U): total energy, ***V*** : containment volume, ***N*** $\gg 1$ ($\sim 10^{20}$) constituents

Ensemble: many ($\gg 1$) identically prepared N-particle systems



Micro-canonical ensemble

Isolated systems: Total energy E, linear and angular momentum well defined and conserved. Particle number *N* and system volume *V* well defined and conserved. *Macro-& microstates:* ***E, N,V*** *constant*



Canonical ensemble

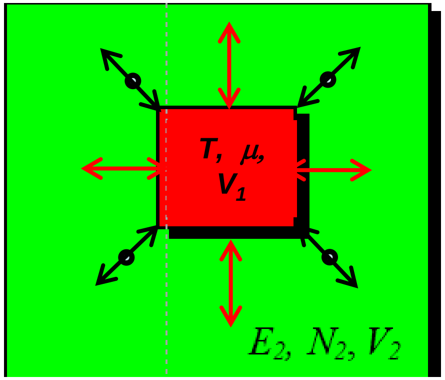
Closed systems: Particle number *N* and system volume *V* well defined and conserved.
Exchange of energy (lin & angular momentum) occurs with surrounding "Heat Bath"→ fluctuate
*Stationary macro-&micro states:****T,N,V*** constant

→ (System plus reservoirs) = isolated system

Idealized Classification: Random Statistical Ensembles

E ***(or U)***: total energy, ***V*** : containment volume, ***N*** $\gg 1$ ($\sim 10^{20}$) constituents

Ensemble: many ($\gg$***1***) identically prepared *N*-particle systems



Grand-canonical ensemble

Open systems: Exchange of energy and particles occur with surrounding particle reservoirs and ”Heat Bath.”

Stationary macro-& micro states: ***T***, μ constant.

μ : chemical potential energy per particle.

→ (System plus reservoirs) = isolated system

Heterogenous ***system phases*** (*solid, liquid, gas*) are homogenous subparts, separating surfaces are ***phase boundaries***.

Extensive (additive) state variables ***scale*** in proportion to system size (mass, number of particles). Examples: volume, total energy, entropy.

Intensive state variables ***do not scale*** with the size of the system. Examples: pressure, temperature, refractive index

Basic Laws of Statistical Thermodynamics

Statistical Thermodynamics: Physics of equilibration & equilibrium

0) Systems in contact equalize mean internal (kinetic ++) energies,
→ "temperatures" equalize. Equipartition of thermal energy
"Canonical & grand canonical" ensembles (of many identical systems).

1) Energy (of system plus surroundings) is conserved.

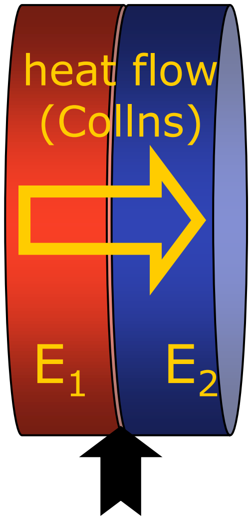
2) Complex m.p. systems evolve spontaneously **toward state of maximum randomness** (complexity)→ Measure = Entropy $\Delta S = S_{fin} - S_{in} > 0$

3) There exists an absolute "zero point" of energy for any system:
energy and complexity are at a minimum (@ **absolute *T=0 K***).

0. LTD and consequences

Energy Equilibration By Heat Exchange

Composite System
CS=Sys$_1$ Sys$_2$



Thermal Contact

Constant energy $E = E_1 + E_2$ → initially in exc. hot $\Omega_1(E_1 = E)$

→ Most likely final energy partition E_1/E_2?

Spontaneous exchange $\Delta q_1 = -\Delta E_1 = +\Delta E_2$ to increase average excited population probability P_{CS} of states in CS

maximize Ω = # populated states

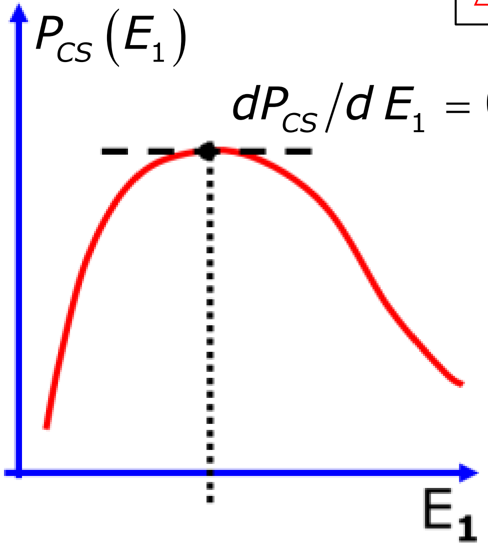
$$\boxed{\Delta P_{CS}(E,E_1) \propto \Delta\Omega_{CS}} = \Delta[\Omega_1(E_1)\cdot\Omega_2(E_2)]$$

$$= [\Delta\Omega_1(E_1)]\cdot\Omega_2(E_2) + \Omega_1(E_1)\cdot[\Delta\Omega_2(E_2)]$$

$$\boxed{\frac{\Delta P_{CS}}{\Delta E_1} \propto \frac{\Delta\Omega_1(E_1)}{\Delta E_1}\Omega_2(E_2) - \Omega_1(E_1)\frac{\Delta\Omega_2(E_2)}{\Delta E_2}}$$

CS Exc. probability change

with $\Delta E_1 = -\Delta E_2 < 0$



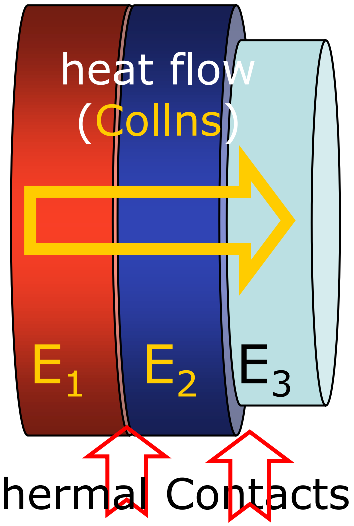
Maximize P_{CS}

$$\frac{dP_{CS}}{dE_1} = 0 \rightarrow \boxed{\underbrace{\frac{1}{\Omega_1}\frac{d\Omega_1(E_1)}{dE_1}}_{\text{Depends only on Sys1}} \overset{!}{=} \underbrace{\frac{1}{\Omega_2}\frac{d\Omega_2(E_2)}{dE_2}}_{\text{Depends only on Sys2}}}$$

dimension
$[\;\;] = 1/Energy$

Energy Equilibration By Heat Exchange

Composite System
CS=Sys_1 Sys_2 Sys_3



Constant energy $\boldsymbol{E}=E_1+E_2+E_3$ → Search for the most likely final energy partition $E_1/E_2/E_3$. For each **spontaneous exchange** of heat $\boldsymbol{-\Delta q_1}=\Delta E_2+\Delta E_3$ → increase excited P_{CS}

Spontaneous energy transfer maximizes

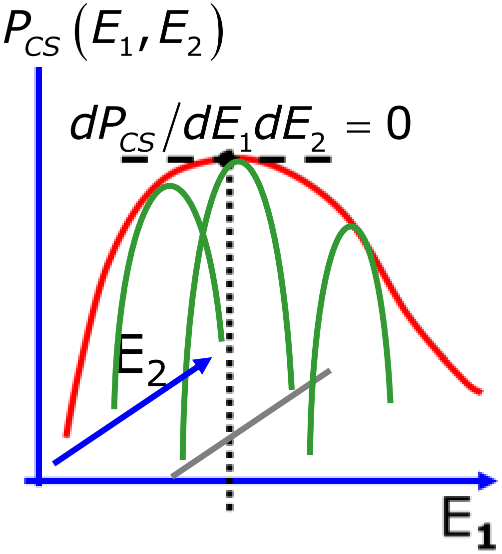
excited $P_{CS} \sim \Omega_{CS} = \Omega_1 \cdot \Omega_2 \cdot \Omega_3$

Check 2^{nd} *derivatives* (*Saddles*)

$$\boxed{\frac{dP_{CS}}{dE_1 dE_2}=0}$$

$$\boxed{\frac{1}{\Omega_1}\frac{d\Omega_1(E_1)}{dE_1}=\frac{1}{\Omega_2}\frac{d\Omega_2(E_2)}{dE_2}=\frac{1}{\Omega_3}\frac{d\Omega_3(E_3)}{dE_3}=\cdots}$$

$$\boxed{\textit{Universal function dimension } [\;] = 1/\textit{Energy}}$$

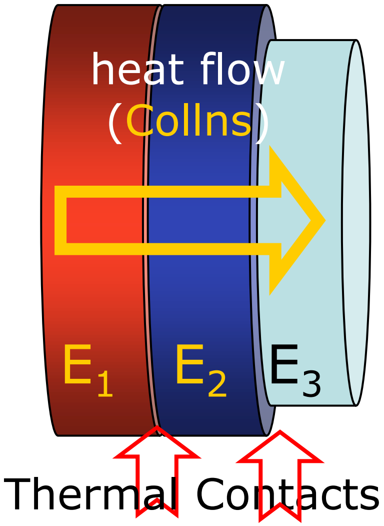


Independent of index → independent of material properties 1,2,…; → common mean energy/particle (***T***)

But common temperature ***T*** depends on total energy ***E*** in all systems/total mass → $\boxed{\langle E\rangle_N = E/N \sim T}$

Energy Equilibration By Heat Exchange

Composite System
CS=Sys_1 Sys_2 Sys_3



Constant energy $\boldsymbol{E}=E_1+E_2+E_3$ → Search for the most likely **final** energy partition $E_1/E_2/E_3$. For each **spontaneous exchange** of heat $-\Delta \boldsymbol{q_1}=\Delta E_2+\Delta E_3$ → increase exc. P_{CS}

Equilibrium partition $\{E_1,\dots,E_n\}$ *maximizes excited* Ω_{CS}

$$\boxed{\frac{1}{\Omega_n}\frac{d\Omega_n(E_n)}{dE_n} = const.\ function\ (E=\sum_n E_n)}$$

$\boxed{dimension\ [\ ] = 1/Energy}$

Plausible Ansatz:

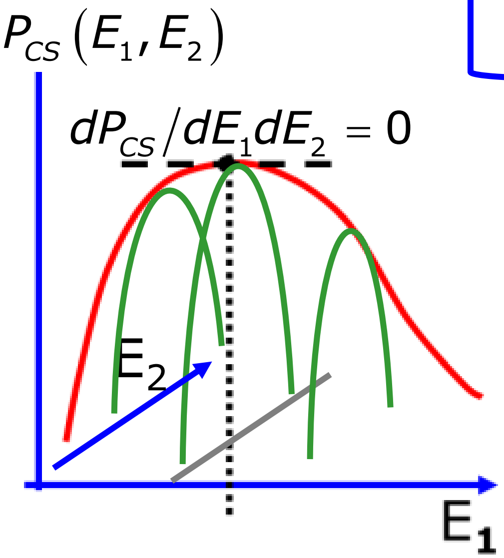
$$\frac{d}{dE}\underbrace{Ln\,\Omega_{CS}(E)} = const.(\langle E\rangle) \propto \frac{1}{k\cdot T}$$

⇨ $\boxed{dS(E)/k \propto \frac{dE}{k\cdot T}}$

Def. =***S/k*** → **Entropy** =*deg. disorganization*

$\boxed{dE = T\cdot dS}$

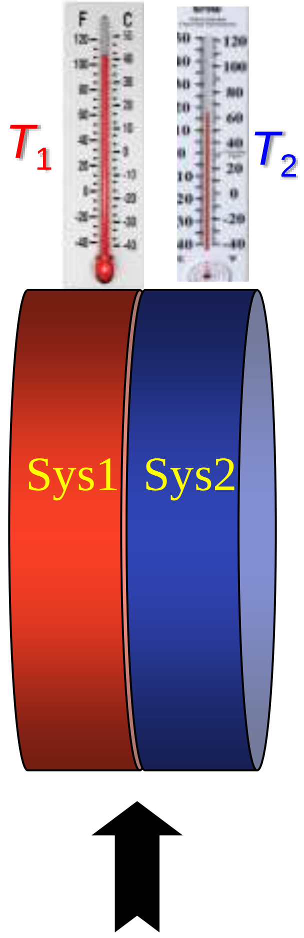
$$\boxed{dS = \frac{dq}{T} = \frac{Spont.\ Heat\ Transfer}{Temperature}}$$



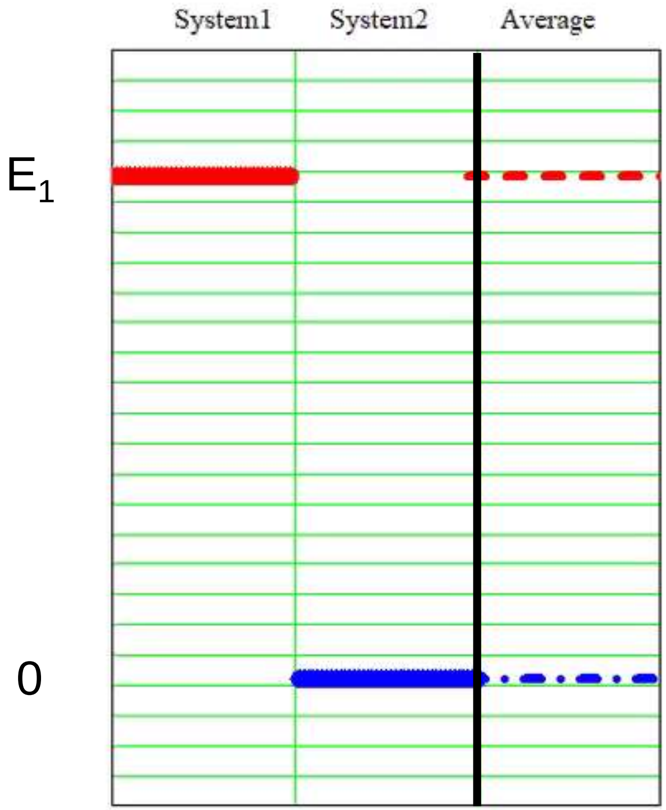
Spontaneous energy redistribution requires entropy increase ΔS>0 (opposite is not true!)

Simulation: Energy Equilibration

Observation: ***t***-dependent equilibration of temperatures



Thermal Contact



Discrete energy states of 2 similar interacting systems

Initial conditions

$\langle \boldsymbol{E_1} \rangle \approx E \qquad \langle \boldsymbol{E_2} \rangle \approx 0$

Initial mean energies

$\boldsymbol{e}_1 = E_1/A_1 > \boldsymbol{e}_2 = E_2/A_2$

Random ± energy and ± momentum exchange

Final mean energies *thermalization* achieved

$\boldsymbol{e}_i \rightarrow E_i/A_i \sim T_i = T$

Equil. energy fluctuations

$$\boxed{\sigma_{e_i}^2 = k_B T^2 C_V}$$

Entropy and Energy at Equilibrium

Independent of material, size, shape, amount → **Intensive function Const(E,N)**

$$\boxed{\frac{d}{dE}Ln\Omega(E,N)=\frac{dS(E,N)}{dE}=\underline{\underline{Const}}(E)}$$

depends on total energy E supplied to one of the sub-systems as heat and the total number of particles. Dimension [Const(E)]= 1/energy.

Obvious *intensive energy* variables: Energy per particle ~ temperature ***T***

→System energy content of an ideal gas (*N* particles): $\boxed{\langle E\rangle_N=\frac{E}{N}\propto\frac{P\cdot V}{N}=k_B\cdot T}$

$$\boxed{\textit{Adopt intensive function S with } \frac{dS}{dE}=\frac{1}{\Omega}\frac{d\Omega(E)}{dE}=\frac{d}{dE}k_B\cdot Ln\Omega(E)\propto\frac{1}{T}}$$

Simplest form compatible

S extensive

Set integration constant =0

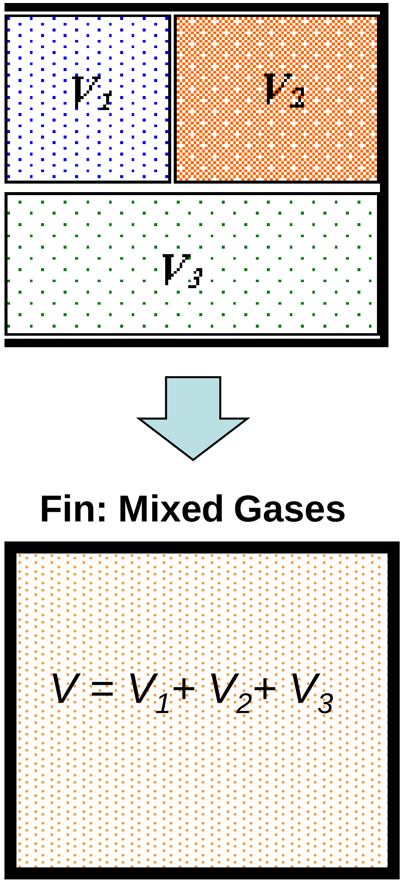
$$S(E)=k_B Ln\,\Omega=\cancel{S_0}+\frac{E}{T}\rightarrow \textit{Distributed heat energy}\ \boxed{E=T\cdot S}$$

$$\boxed{\textit{Heat absorption / emission by system @T}:\ \Delta\langle E\rangle=\Delta q\rightarrow\Delta S=\frac{\Delta q}{T}}$$

$$\boxed{\Delta S=S_{fin}-S_{in}=k_B\cdot Ln\left(\Omega_{fin}/\Omega_{in}\right)}$$

Example: Entropy Gain in Gas Mixing

In: Separated Gases



Fin: Mixed Gases

S - gain by individual gas components $\rightarrow \boxed{\Omega_i \propto V_i \text{ volume}}$

Entropy is extensive (*additive*). $\rightarrow$ *conponents add*

$\boxed{S_i = n_i \cdot R \cdot Ln(V_i) > 0}$ $\quad n_i =$ *number of moles i*

$$Total\ \#moles\ n = n = \sum_i n_i;\ total\ vol\ V = \sum_i V_i$$

$$Initial\ S_{in} = R \cdot \sum_i n_i \cdot Ln(V_i) \rightarrow S_{fin} = R \cdot \sum_i n_i \cdot Ln(V)$$

$$\boxed{\Delta S = -R \cdot \sum_i n_i \cdot Ln\left(\frac{V_i}{V}\right) > 0}$$

$S \nearrow$

$$total\ moles\ n = \sum_i n_i \rightarrow \Delta S = -n \cdot R \cdot \sum_i \left(\frac{n_i}{n}\right) \cdot Ln\left(\frac{V_i}{V}\right)$$

Relative abundance (probability for) particle type i

$$p_i = \frac{n_i}{n} = \frac{V_i}{V} < 1$$

$\boxed{\Delta S = -n \cdot R \cdot \sum_i p_i \cdot Ln\, p_i}$ *n moles*

N particles $\boxed{\Delta S = -N \cdot k_B \cdot \sum_i p_i \cdot Ln\, p_i}$

Can use other "State Functions" to calculate entropy, all related by EoS

Entropy of Mixing: Example

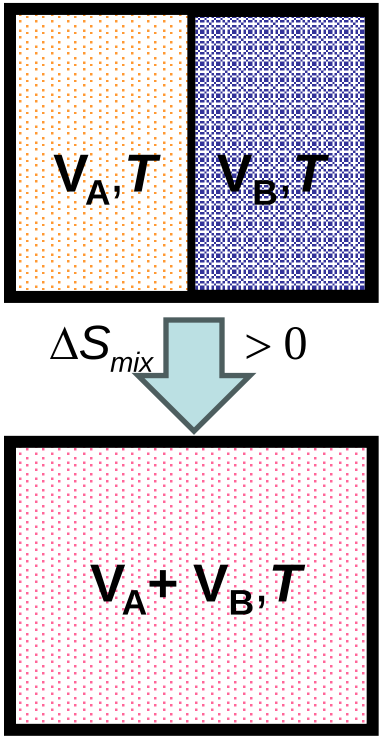
One mole each of two equivalent ideal gases, **$A=O_2$** and **$B=H_2$**, in their respective halves of a separated container at $P_A = P_B = 1atm$, $T_A = T_B = 298K$

s.p. spaces $\varpi_A \propto V_A$ and $\varpi_B \propto V_B$

When partition is removed, the gases will mix.

No change in energy

$\Delta q = 0$



Universal Gas Constant
R=8.31 $J/mol \cdot K$

Information on s.p. configuration space from EoS

Ideal gases $P \cdot V = n \cdot R \cdot T \rightarrow \varpi_{A,B} \propto V_{A,B} \propto n_{A,B}$

Total $n = 2$ *moles* ; Mole fractions: $n_A/n = n_B/n = 0.5$.

→ probabilities are $p_A = p_B = 0.5$ *also in state space*

→ "Entropy of Mixing"

$$\Delta S_{mix} = -nR\left\{\frac{n_A}{n} \cdot Ln\left(\frac{n_A}{n}\right) + \frac{n_B}{n} \cdot Ln\left(\frac{n_B}{n}\right)\right\} =$$

$$= -2R\left\{0.5 \cdot Ln(0.5) + 0.5 \cdot Ln(0.5)\right\} = 11.5 J/mol \cdot K > 0$$

Entropy is gained ←→ mixing occurs spontaneously.

$\Delta S \geq \frac{\Delta q}{T}$ *in spontaneous processes*

Mixed gases are difficult to unmix (costs energy)!

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