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# Radiative transfer: thermodynamic equilibrium

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# Thermodynamic equilibrium

International Research Track

2023

## Outline

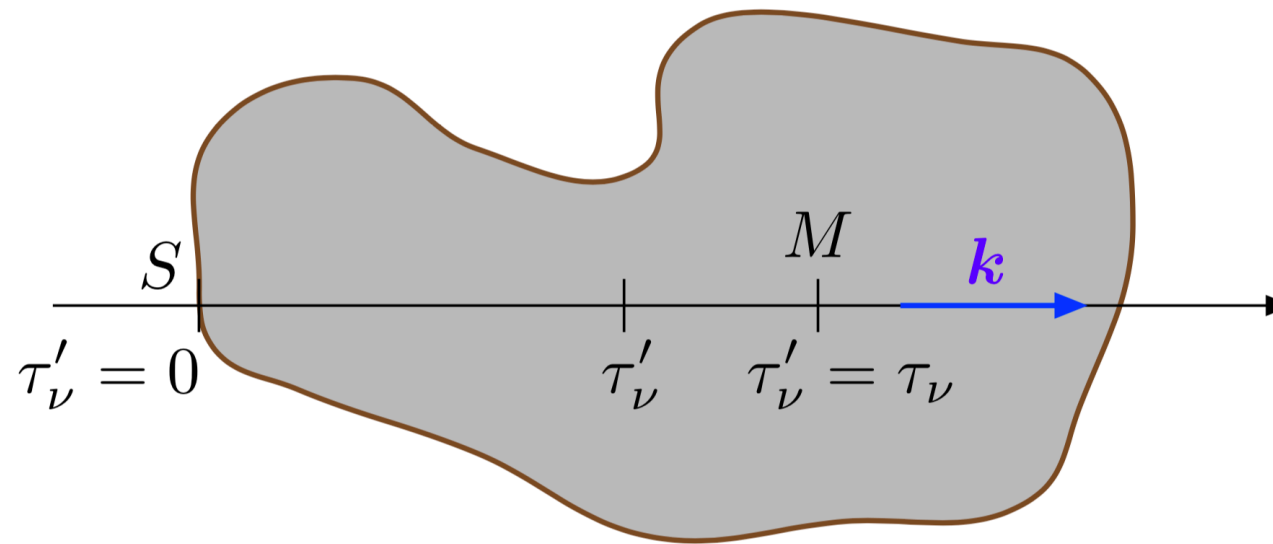
- introduction
- statistical mechanics
- Maxwell Boltzmann
- Saha's equation
- Planck's law black body
- Kirchhoff law
- collisions & chemistry
- conclusions

1. Introduction
2. Statistical mechanics
3. Maxwell-Boltzmann
4. Saha's law
5. Black-body emission
6. Kirchhoff law
7. Collision & Chemistry
8. Conclusions

# Radiative transfer complexity

## Outline

- introduction
- statistical mechanics
- Maxwell Boltzmann
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F. Levrier - radiative transfer lecture

$$\frac{dI_\nu}{dl} = -[\alpha_\nu + \sigma_\nu] I_\nu + j_\nu + \frac{1}{4\pi} \int_{\Omega'} \tilde{\sigma}_\nu(\mathbf{k}' \rightarrow \mathbf{k}) I_\nu(\mathbf{k}') d\Omega'$$

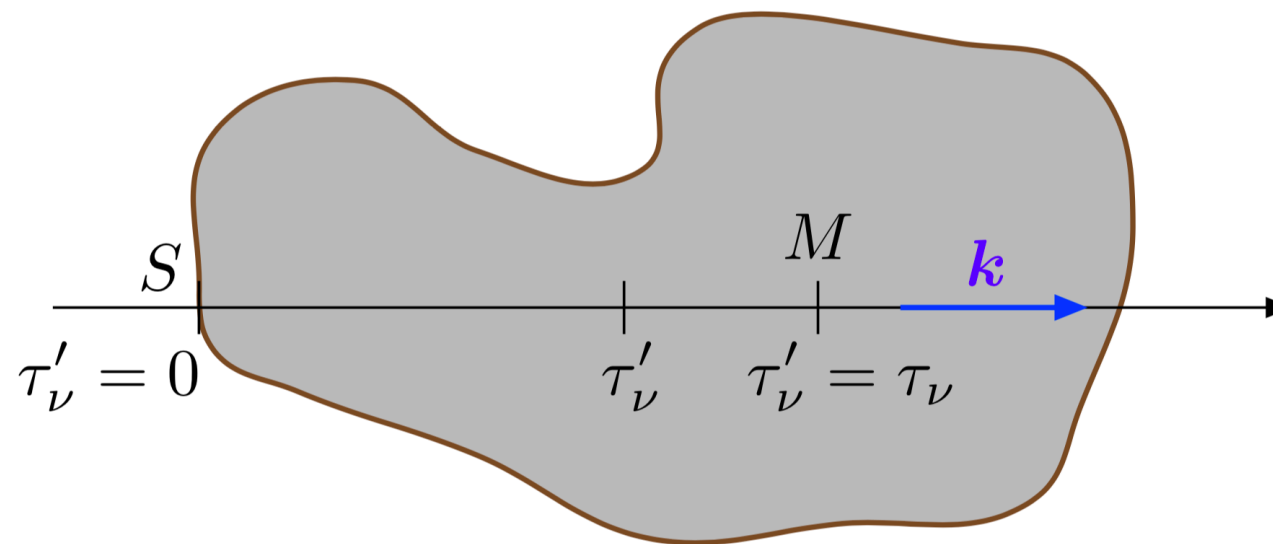
- |                          |  |  |
|--------------------------|--|--|
| • absorption coefficient | $\alpha_\nu = \sum_a n_a s_{\nu,a}$        | $\text{cm}^{-1}$   |
| • diffusion coefficient  | $\sigma_\nu = \sum_d n_d s_{\nu,d}$        | $\text{cm}^{-1}$   |
| • emissivity             | $j_\nu$                                    | $\text{erg s}^{-1} \text{cm}^{-3} \text{Hz}^{-1} \text{sr}^{-1}$ |
| • opacity                | $d\tau_\nu = [\alpha_\nu + \sigma_\nu] dl$ |  |
| • source function        | $S_\nu$                                    | $\text{erg s}^{-1} \text{cm}^{-2} \text{Hz}^{-1} \text{sr}^{-1}$ |



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F. Levrier - radiative transfer lecture

$$\frac{dI_\nu}{d\tau_\nu} = -I_\nu + S_\nu$$

|                             | no diffusion   | isotropic diffusion  |
|-----------------------------|--|--|
|                             | $S_\nu = \frac{j_\nu}{\alpha_\nu}$   | $S_\nu = \frac{j_\nu + \sigma_\nu J_\nu}{\alpha_\nu + \sigma_\nu}$     |
|                             |  | $S_\nu = \omega_\nu J_\nu + (1 - \omega_\nu) \frac{j_\nu}{\alpha_\nu}$ |
| formal solution             | $I_\nu(\tau_\nu) = I_\nu(0)e^{-\tau_\nu} + \int_0^{\tau_\nu} S_\nu(\tau'_\nu)e^{-(\tau_\nu - \tau'_\nu)} d\tau'_\nu$ |  |
| homogeneous source function | $I_\nu(\tau_\nu) = I_\nu(0)e^{-\tau_\nu} + S_\nu(0) [1 - e^{-\tau_\nu}]$   |  |

# Importance of thermodynamic equilibrium

## Outline

- introduction
- statistical mechanics
- Maxwell Boltzmann
- Saha's equation
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- Kirchhoff law
- collisions & chemistry
- conclusions

at high density or high opacity

- thermodynamic equilibrium of the matter
- thermodynamic equilibrium between matter and radiation

known solution for the state of matter

- velocity distribution (Maxwell-Boltzmann)
- chemistry, ionization (Saha's equation)
- level population distribution (Boltzmann)

known solution for the radiative transfer

- photon distribution (Bose Einstein)
- black body radiation (Planck function)

fundamental relations between inverse processes

- emission - absorption
  - ↘ Kirchhoff law
  - ↘ Einstein relations
- chemistry / collision
  - ↘ reaction rates
  - ↘ collision rates

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very brief summary of  
statistical mechanics

# Postulates and thermodynamic equilibrium

## Outline

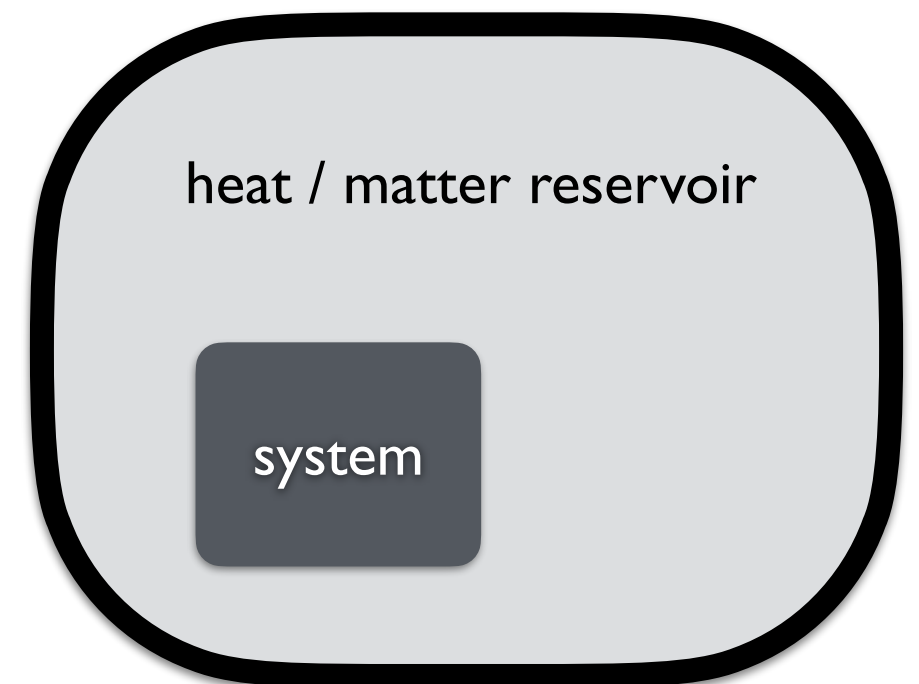
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- *An isolated system at equilibrium is equally likely to be in any of its accessible states*
- *If at some time  $t$ , the system is in state  $s$ , it evolves to other states through interactions between particles*
- *If the system is not at equilibrium, the time to reach equilibrium is given by the interactions between particles*

## Thermodynamic equilibrium

isolated system or system in contact with a heat and / or matter reservoir at

- dynamical equilibrium
- thermal equilibrium
- chemical equilibrium



***no need to know the process by which heat is exchanged***

consider a system A with energy  $E$  and  $N$  particles

$\Omega(E, N)$   $\longrightarrow$  number of microstates accessible

$\beta = \frac{1}{kT} = \frac{\partial \ln \Omega}{\partial E}$   $\longrightarrow$  temperature  $T$

$\alpha = -\beta\mu = \frac{\partial \ln \Omega}{\partial N}$   $\longrightarrow$  chemical potential  $\mu$

| canonical   | grand-canonical   |
|---|---|
| interaction - heat reservoir A'                     | interaction heat & matter reservoir A'                          |
| $\longrightarrow$ at equilibrium : $\beta = \beta'$ | $\longrightarrow$ at equilibrium : $\beta = \beta', \mu = \mu'$ |
| $\longrightarrow$ microstate $R : E_R$              | $\longrightarrow$ microstate $R : E_R, N_R$                     |
| $P_R = \frac{e^{-\beta E_R}}{\mathcal{Z}}$          | $P_R = \frac{e^{-\beta(E_R - \mu N_R)}}{\mathcal{Z}}$           |
| $\mathcal{Z} = \sum_R e^{-\beta E_R}$               | $\mathcal{Z} = \sum_R e^{-\beta(E_R - \mu N_R)}$                |

$\mathcal{Z}$  gives all the macro properties of the system ( $S, p, \langle E \rangle, \langle N \rangle, \dots$ )

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# Application 1 : ideal gas of identical particles

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identical *weakly interacting* particles in volume  $V$  in contact with a thermostat  $T$

→  $R =$  complete microstate of the system defined by

- $N_1$  particles in state 1 of energy  $\epsilon_1$
- ...
- $N_f$  particles in state  $f$  of energy  $\epsilon_f$

quantum mechanics: fermions or bosons

$$\rightarrow \overline{N}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} \pm 1} \quad N = \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1}$$

if fixed number of particles

$$\rightarrow \overline{N}_s = \frac{1}{e^{\beta\epsilon_s} - 1}$$

if bosons with indefinite number of particles (photon gas)

in classical mechanics limit (non degenerated gas)

$$\rightarrow \frac{\overline{N}_s}{N} = \frac{e^{-\beta\epsilon_s}}{\sum_i e^{-\beta\epsilon_i}} \quad \zeta = \sum_i e^{-\beta\epsilon_i} = \text{single particle partition function}$$

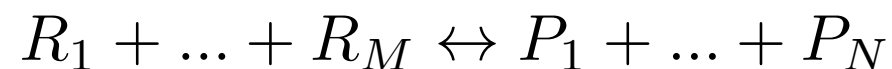
# Application 2 : ideal gas of chemical mixture

## Outline

- introduction
- statistical mechanics
- Maxwell Boltzmann
- Saha's equation
- Planck's law black body
- Kirchhoff law
- collisions & chemistry
- conclusions

*weakly interacting* particles in a volume  $V$  in contact with a thermostat  $T$

- $N(R_1)$  particles of type  $R_1$
- ...
- $N(R_M)$  particles of type  $R_M$
- $N(P_1)$  particles of type  $P_1$
- ...
- $N(P_N)$  particles of type  $P_N$



In the limits of classical mechanics, at thermodynamic equilibrium

→ law of mass action

$$\frac{\prod_{j=1}^N N(P_j)}{\prod_{i=1}^M N(R_i)} = \frac{\prod_{j=1}^N \zeta(P_j)}{\prod_{i=1}^M \zeta(R_i)}$$

$\zeta(X) = \zeta_{\text{trans}}(X)\zeta_{\text{int}}(X)$  → partition function of a single particle including translational & internal states

→ in terms of volume densities

$$\frac{\prod_{j=1}^N n(P_j)}{\prod_{i=1}^M n(R_i)} = \frac{\prod_{j=1}^N \frac{(2\pi m_j kT)^{3/2}}{h^3} \zeta_{\text{int}}(P_j)}{\prod_{i=1}^M \frac{(2\pi m_i kT)^{3/2}}{h^3} \zeta_{\text{int}}(R_i)}$$

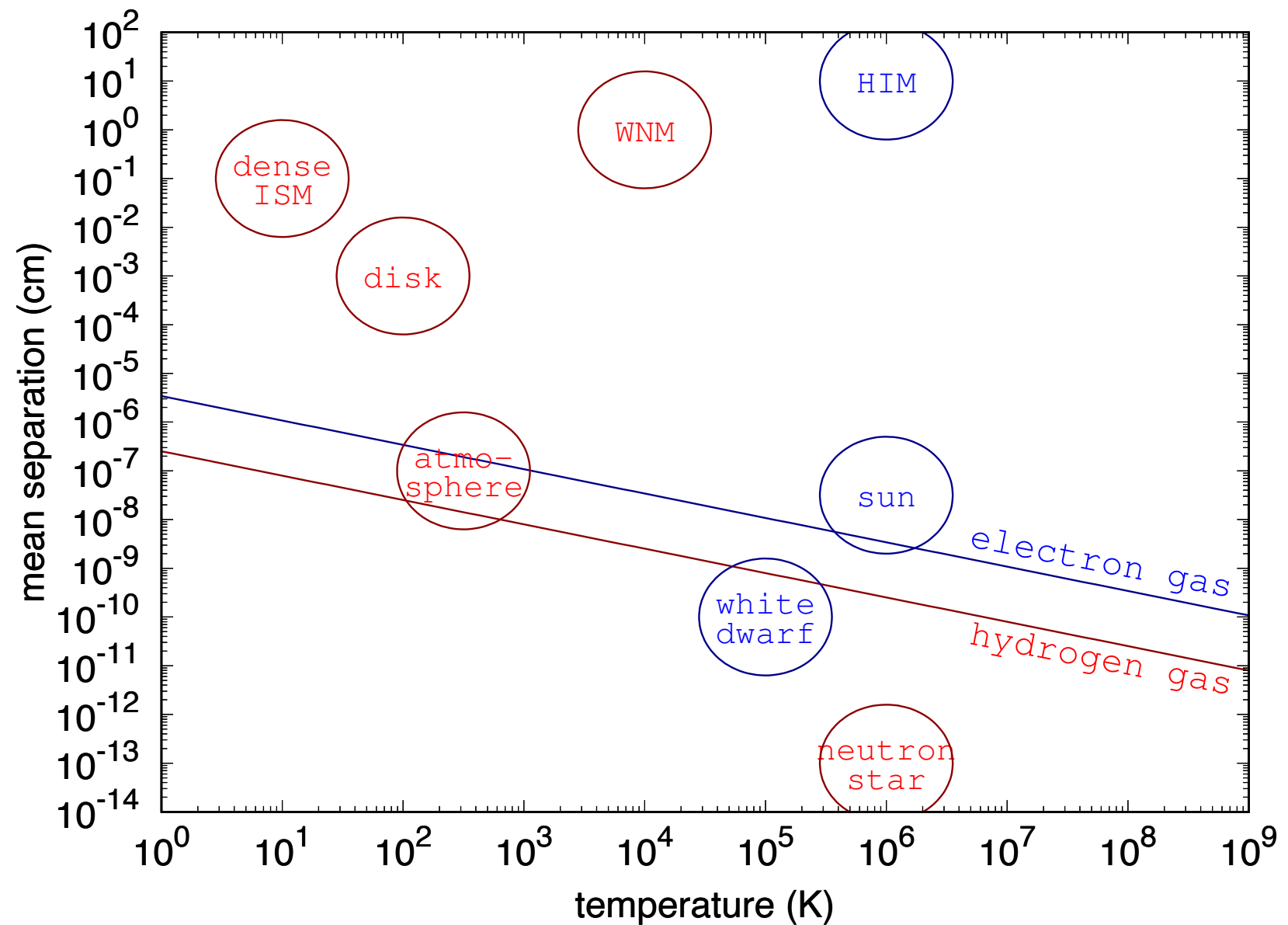
# Application : classical vs quantum mechanics

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classical mechanics valid if

$$\bar{R} = \left( \frac{V}{N} \right)^{1/3} \gg \lambda_{\text{db}} = \frac{h}{\sqrt{3mkT}}$$





## Outline

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well-known  
thermodynamical equilibrium states

# Maxwell velocity distribution

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gas at rest at thermodynamic equilibrium

→ velocity probability distributions

$$dP(\mathbf{v}) = f(\mathbf{v})d^3\mathbf{v} \quad \longrightarrow \quad f(\mathbf{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}$$

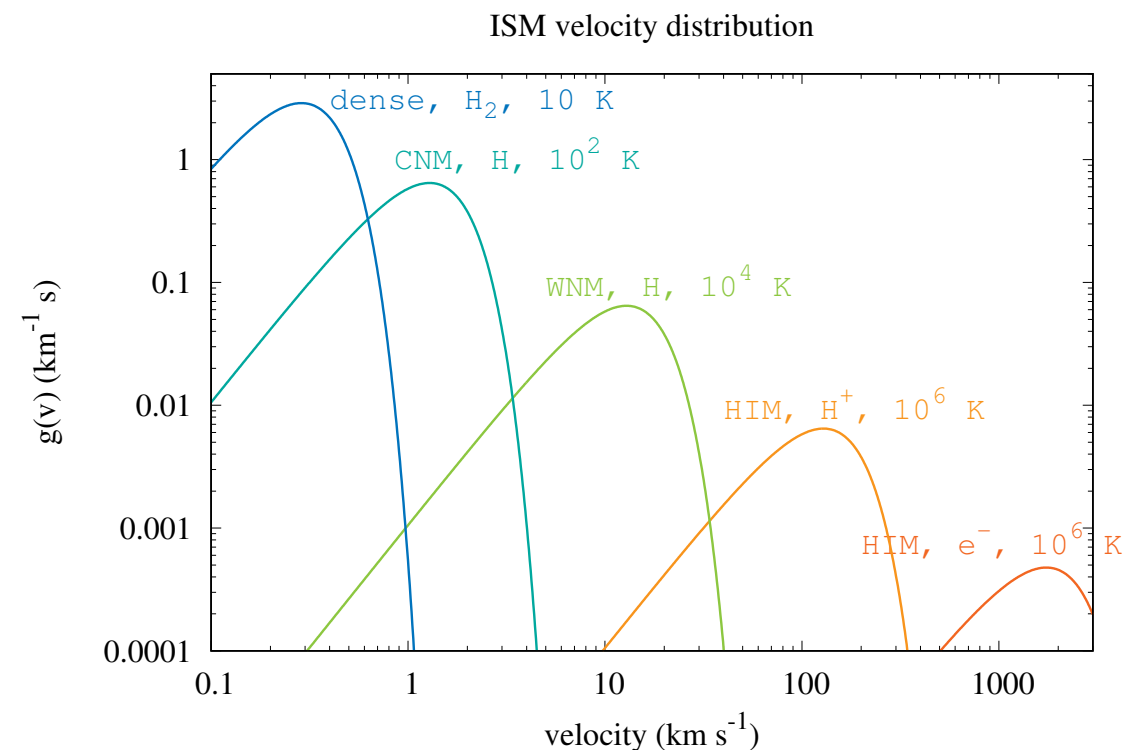
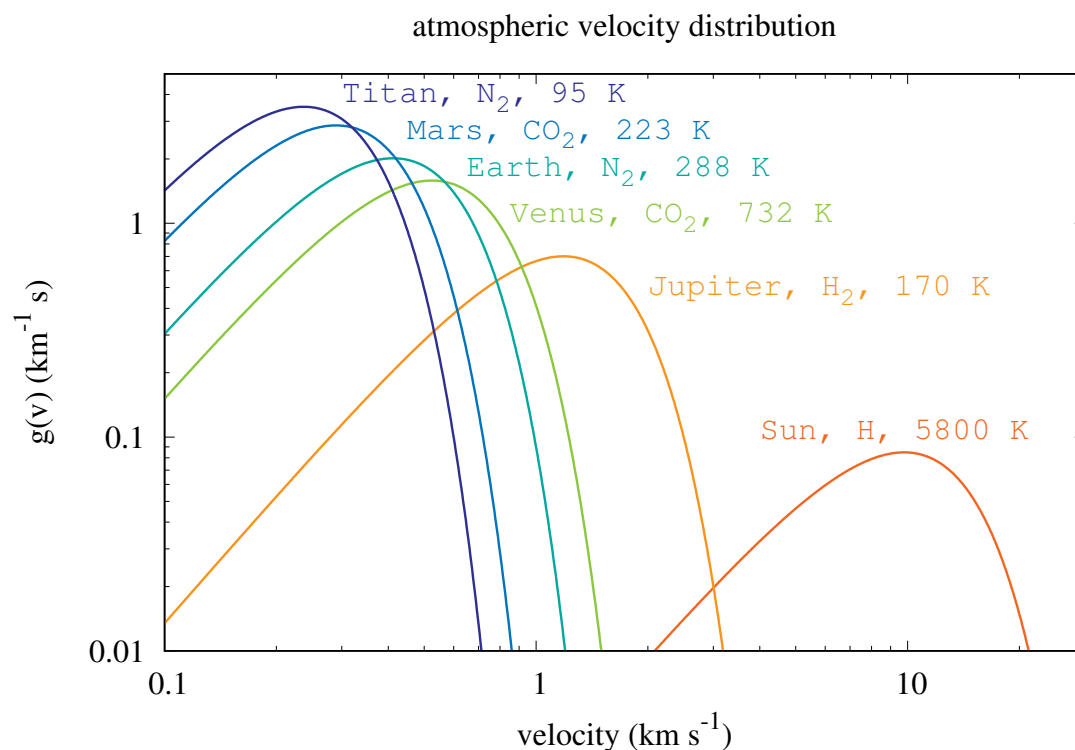
$$dP(|v|) = g(|v|)d|v| \quad \longrightarrow \quad g(|v|) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} 4\pi v^2$$

→ characteristic speeds

$$v_p = \sqrt{\frac{2kT}{m}}$$

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$$

$$\langle v_q \rangle = \sqrt{\frac{3kT}{m}}$$



# Boltzmann energy distribution

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levels populations at thermodynamic equilibrium

→ probability distribution

$$P_r = \frac{g_r e^{-E_r/kT}}{\sum_r g_r e^{-E_r/kT}}$$

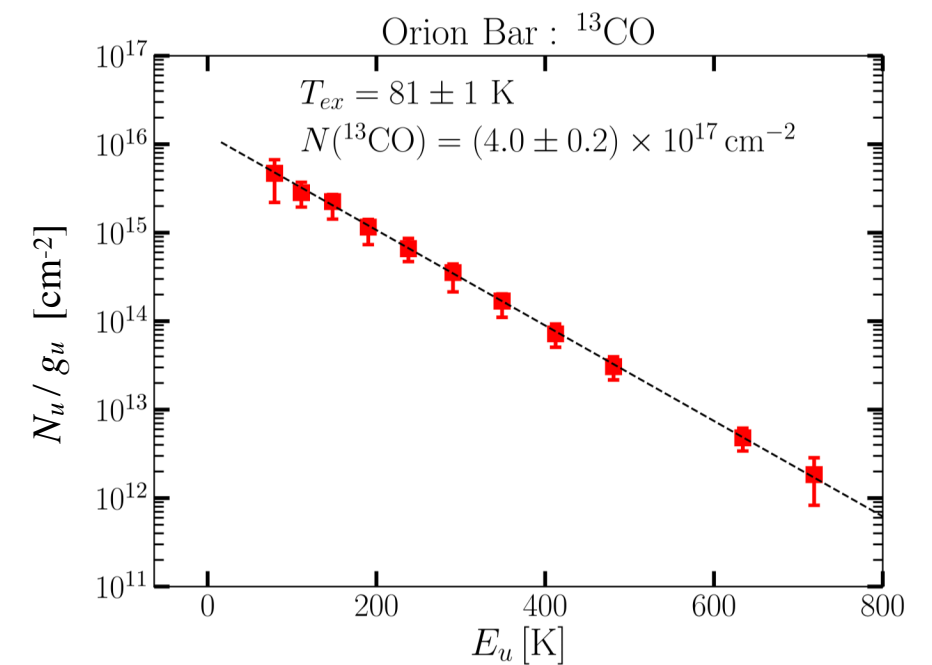
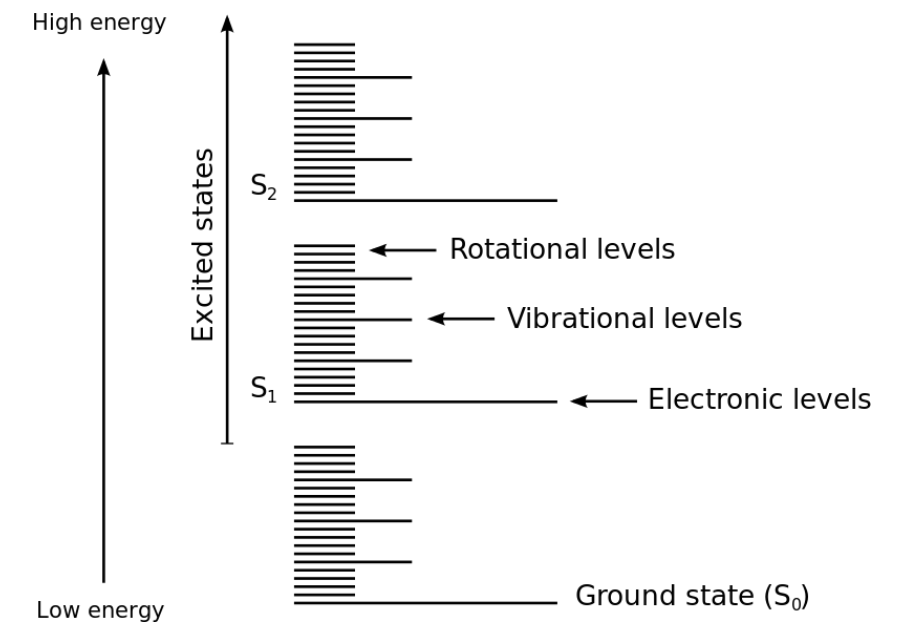
$P_r$  = probability of finding the species in level  $r$

$g_r$  = degeneracy of level  $r$

→ temperature of the thermostat

$$T = \frac{E_b - E_a}{k} \frac{1}{\ln \left( \frac{n_a g_b}{g_a n_b} \right)}$$

independent of a or b



Joblin et al. (2018)

# Boltzmann energy distribution

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levels populations in astrophysics: general case

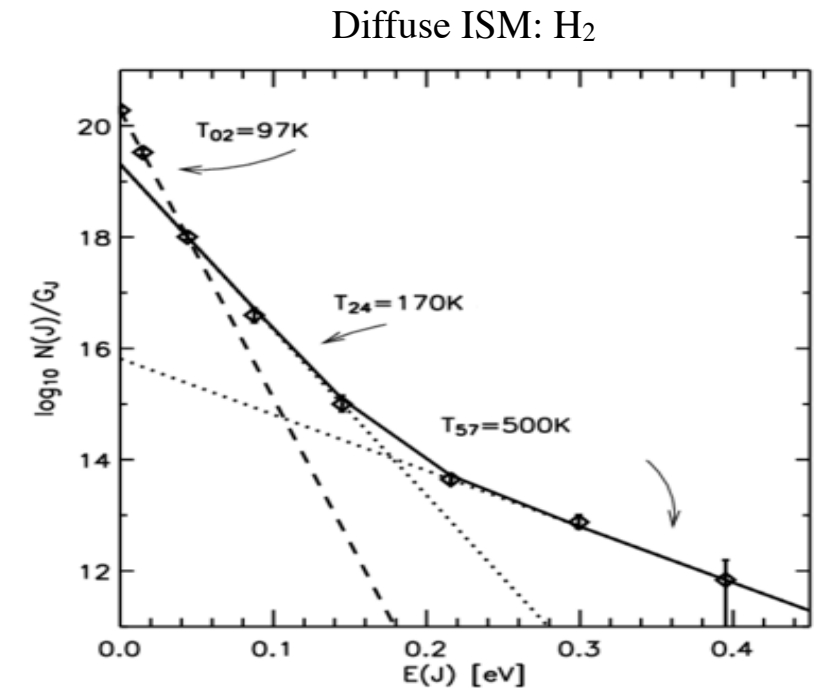
→ excitation temperature

$$T_{\text{ex}}(a, b) = \frac{E_b - E_a}{k} \frac{1}{\ln \left( \frac{n_a g_b}{g_a n_b} \right)}$$

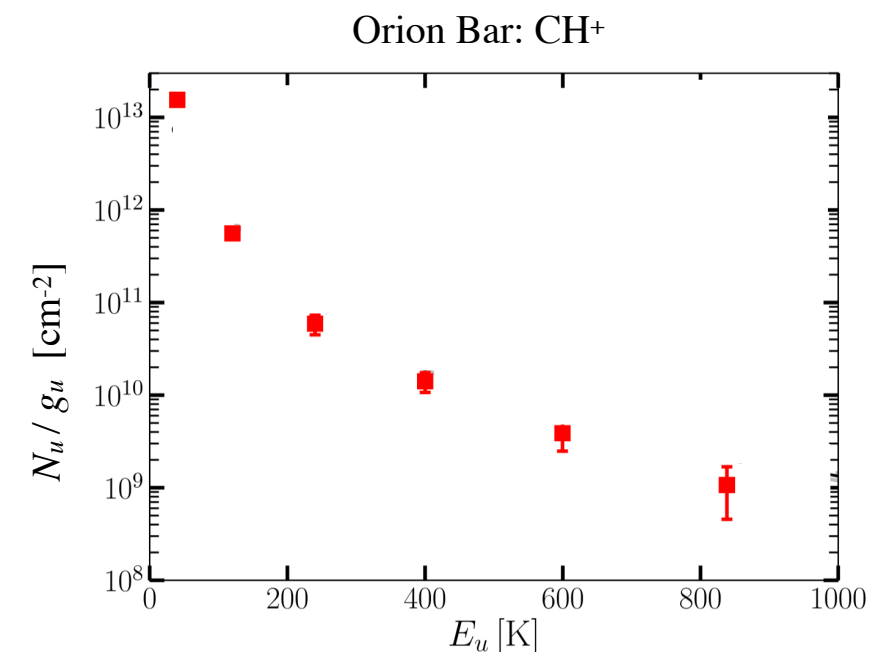
- several components at TE ?
- system out of TE or LTE ?
- several components out of TE or LTE ?



*T<sub>ex</sub> can not always be identified to the temperature of a physical thermostat*



Lacour et al. (2004)



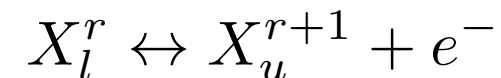
Joblin et al. (2018)

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ideal gas in different ionization states at thermodynamic equilibrium

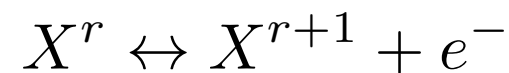
→ consider a species  $X$  in ionization states  $r$  and  $r+1$  and the following ionization process ( $l$  &  $u$  refer to specific internal state)



law of mass action implies

$$\frac{n(X_u^{r+1})n(e^-)}{n(X_l^r)} = 2 \frac{(2\pi m_e kT)^{3/2}}{h^3} \frac{g(X_u^{r+1})}{g(X_l^r)} e^{-(E_u^{r+1} - E_l^r)/kT}$$

→ for the global balance between ionization and recombination



law of mass action implies (Saha's law)

$$\frac{n(X^{r+1})n(e^-)}{n(X^r)} = 2 \frac{(2\pi m_e kT)^{3/2}}{h^3} \frac{\zeta_{\text{int}}(X^{r+1})}{\zeta_{\text{int}}(X^r)}$$

$$\frac{n(X^{r+1})n(e^-)}{n(X^r)} = 2 \frac{(2\pi m_e kT)^{3/2}}{h^3} \frac{\zeta_{\text{int}}^0(X^{r+1})}{\zeta_{\text{int}}^0(X^r)} e^{-I_p(X^r)/kT} \quad I_p(X^r) = E_0^{r+1} - E_0^r$$

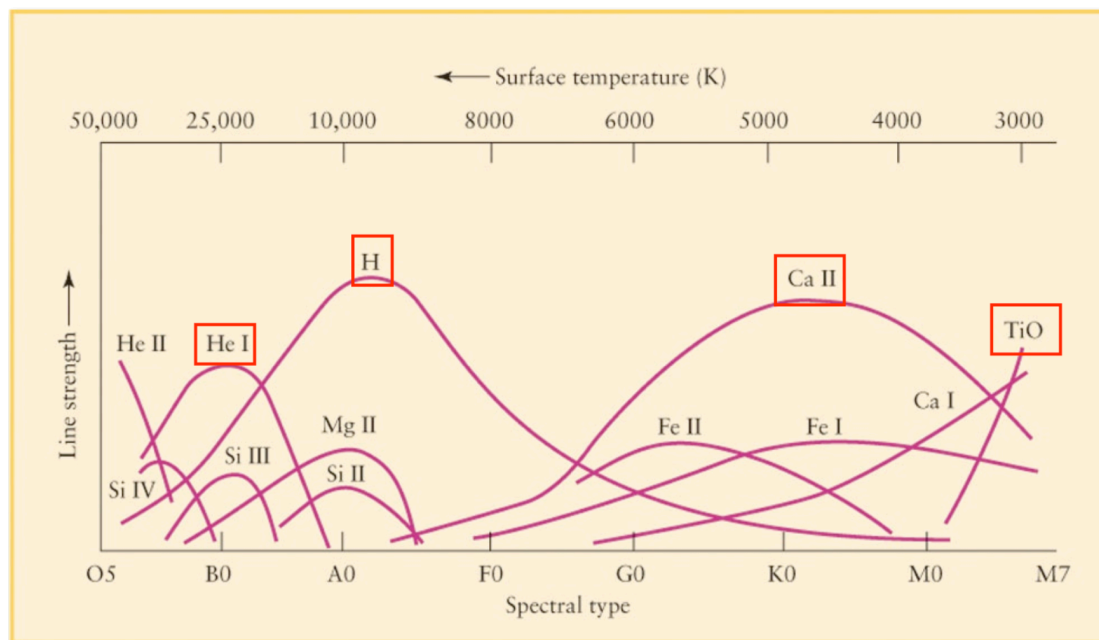
# Saha's law - examples

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spectral classification of stars

- based on absorption lines
  - balmer lines
  - Ca, Fe, Na, He (ionized or not)
  - molecular lines
- Boltzmann energy distribution
- Saha ionization balance



Adam Burrow's webpage  
lecture on stellar atmosphere

matter - radiation decoupling

- Cosmic Microwave Background
- surface of last scattering of photons by free electrons
- estimation of redshift from hydrogen ionization balance

$$T_{\text{CMB}} \propto (1 + z)$$

$$n \propto (1 + z)^3$$

$$\rightarrow z_d \sim 1480$$

simple estimation

# Planck's law

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black body

→ photon gas at thermodynamic equilibrium with a thermostat inside an enclosure

→ 
$$\overline{N_s} = \frac{1}{e^{\beta\epsilon_s} - 1}$$

$$\rho(\nu) = \frac{2\nu^2}{c^3}$$

$$\langle \mathcal{N}_\nu \rangle = \frac{2\nu^2}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$

$$B_\nu = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}$$

$$B_\lambda = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

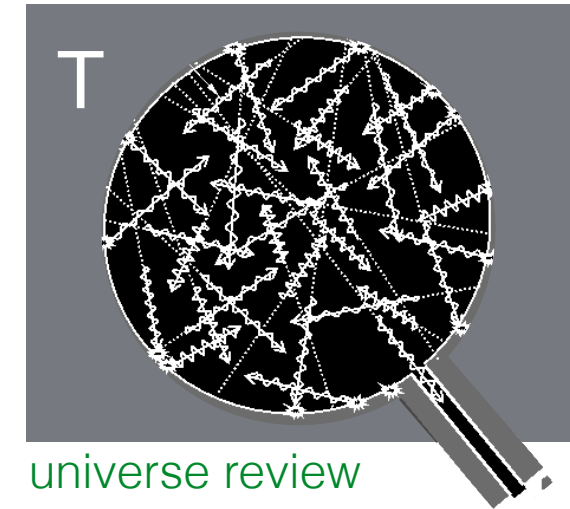
mean number of photons in each accessible state

density of states ( $\text{cm}^{-3} \text{Hz}^{-1} \text{sr}^{-1}$ )

density of photons ( $\text{cm}^{-3} \text{Hz}^{-1} \text{sr}^{-1}$ )

specific intensity ( $\text{erg s}^{-1} \text{cm}^{-2} \text{Hz}^{-1} \text{sr}^{-1}$ )

specific intensity ( $\text{erg s}^{-1} \text{cm}^{-2} \text{cm}^{-1} \text{sr}^{-1}$ )

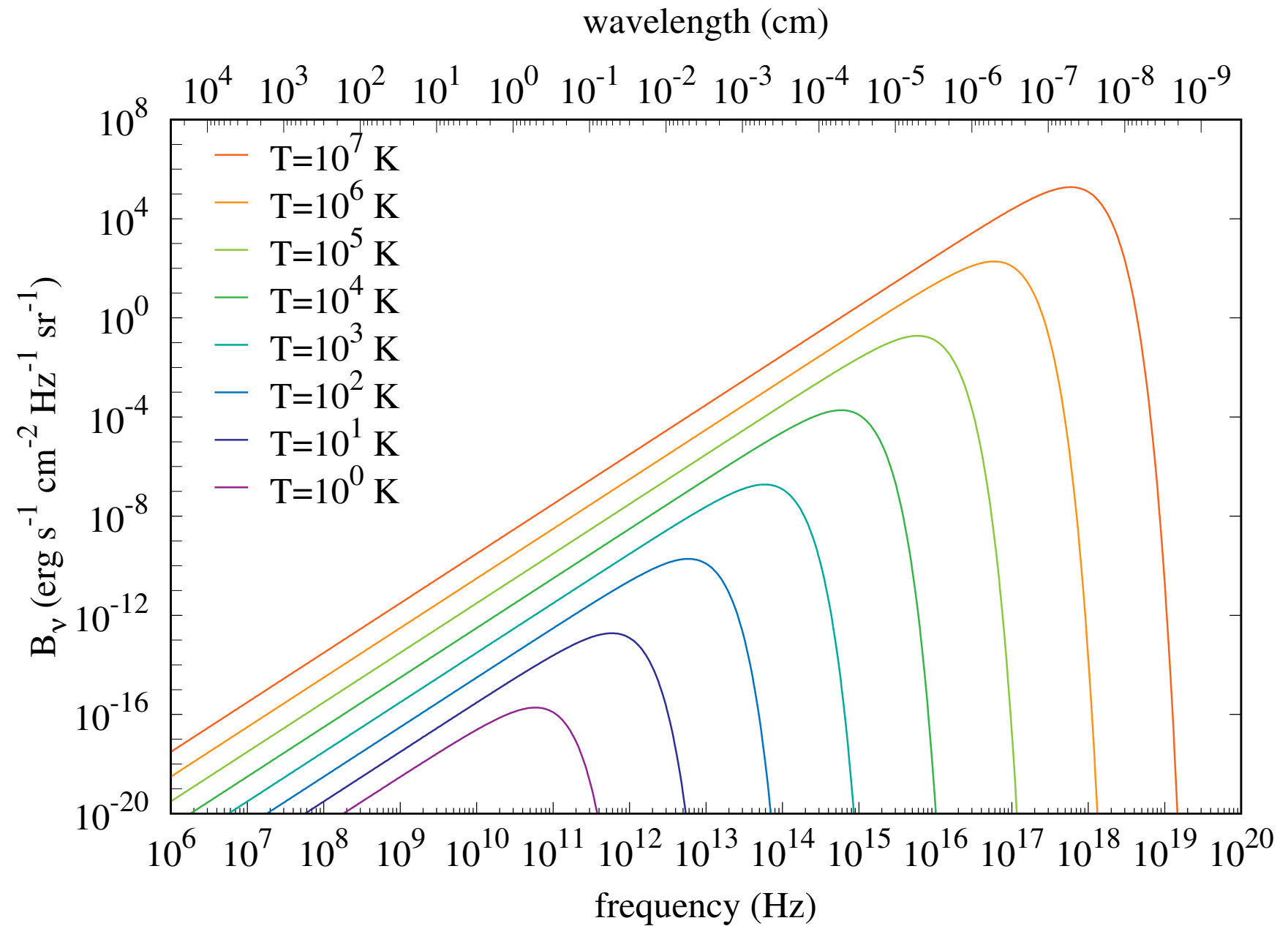




# Planck's law

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Rayleigh-Jeans

$$h\nu \ll kT$$

$$B_\nu \sim \frac{2kT\nu^2}{c^2}$$

Wien

$$h\nu \gg kT$$

$$B_\nu \sim \frac{2h\nu^3}{c^2} e^{-h\nu/kT}$$



# Black body - properties & « observed » temperatures

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| Wien displacement law   | Stefan's law   |
|---|--|
| $\frac{\nu_{\max}}{T} = 5.88 \times 10^{10} \text{ Hz K}^{-1} \rightarrow \text{for } B_{\nu}(T)$ | $F^{+} = 2\pi \int_0^1 \int_0^{\infty} B_{\nu}(T) \mu d\mu d\nu = \sigma_S T^4$    |
| $\lambda_{\max} T = 2.89 \times 10^{-1} \text{ K cm} \rightarrow \text{for } B_{\lambda}(T)$      | $\sigma_S = 5.67 \times 10^{-5} \text{ erg s}^{-1} \text{ cm}^{-2} \text{ K}^{-4}$ |

temperatures used to characterize observations

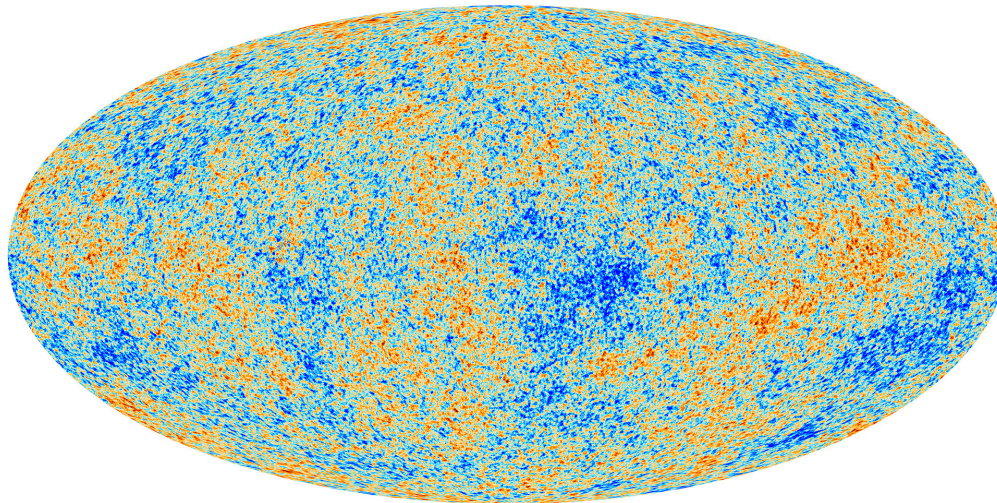
- brightness temperature  $T_b(\nu) = T_{|B_{\nu}(T)=I_{\nu}^{\text{obs}}}$
- radiative temperature  $T_r(\nu) = T_{|B_{\nu}(T)=J_{\nu}^{\text{obs}}}$
- color temperature  $T_c(\nu_1, \nu_2) = T_{|\alpha B_{\nu}(T) \sim I_{\nu}^{\text{obs}} \text{ for } \nu_1 \leq \nu \leq \nu_2}$
- effective temperature  $T_{\text{eff}} = (F^{\text{obs}} / \sigma_S)^{1/4}$

# Black body - examples

## Outline

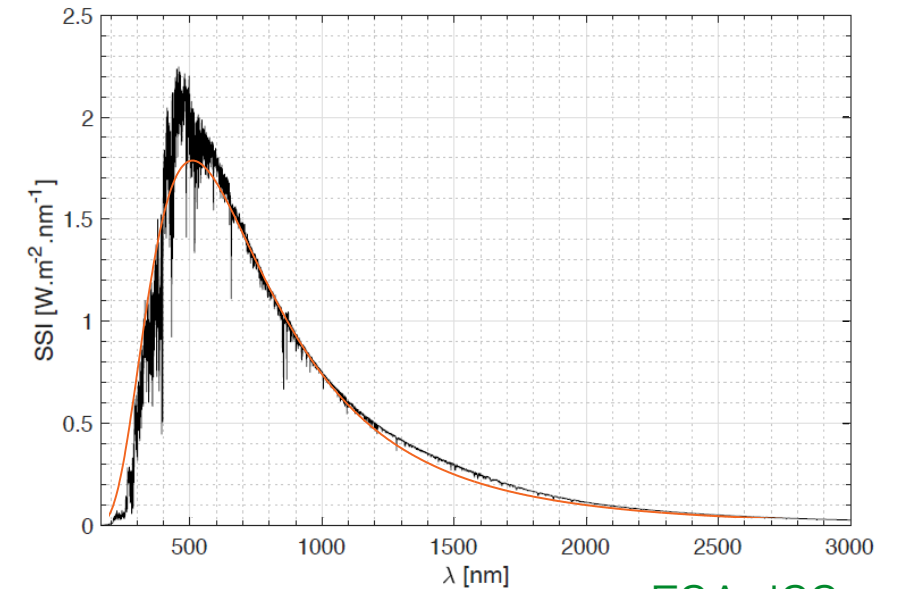
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## cosmic microwave background



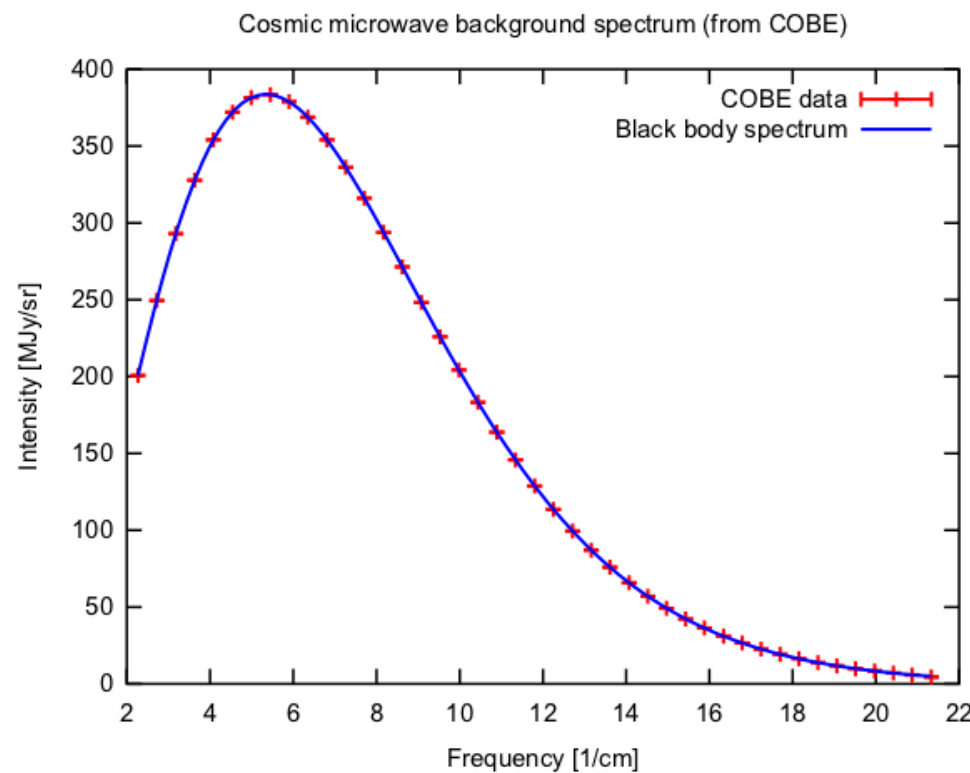
ESA - Planck

## stars

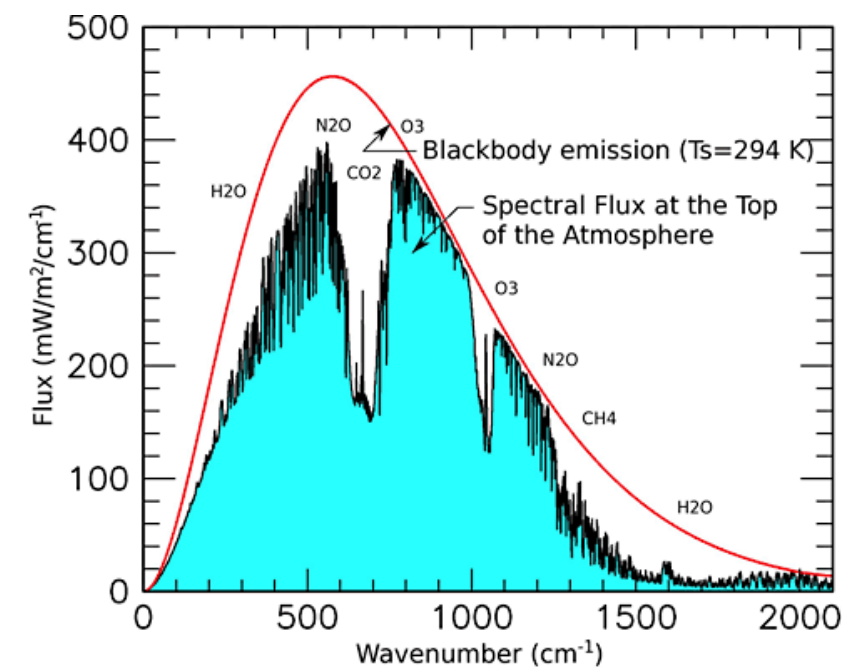


sun - ESA, ISS

## planets



NASA - COBE



NASA - GISS

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fundamental relations between  
inverse processes

# Kirchhoff law from detailed balance

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question : what is the power radiated by a body at a given temperature T

→ thought experiment

- body placed in enclosure at same T
- shield that absorb radiation except over  $dS, d\Omega, d\nu$

→ Thermal equilibrium implies

$$\mathcal{P}_{\text{emi}}(-\mathbf{k}, \nu) = \mathcal{P}_{\text{abs}}(\mathbf{k}, \nu) = a(\mathbf{k}, \nu) \mathcal{P}_{\text{inc}}(\mathbf{k}, \nu) \quad \forall \mathbf{k}, \nu, d\Omega, d\nu, dS$$

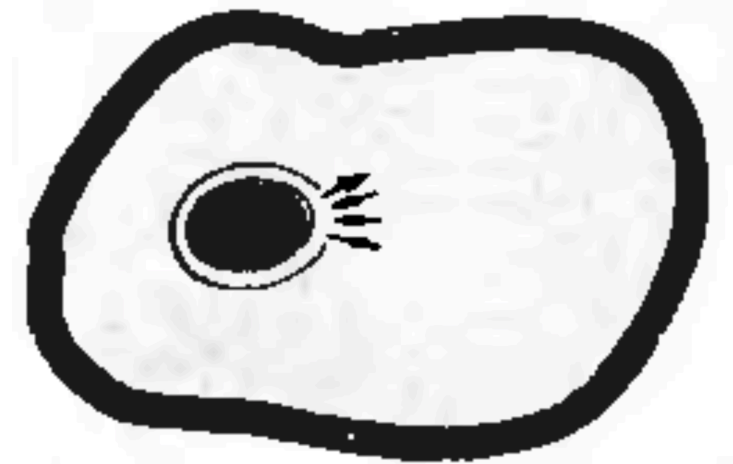
$a$  = fraction of photon absorbed

$$I_{\nu}^{\text{emi}}(T, -\mathbf{k}) = a(\mathbf{k}, \nu) B_{\nu}(T)$$

$$I_{\nu}^{\text{emi}}(T) = a(\nu) B_{\nu}(T) \quad \text{if isotropic absorption}$$

→ *A good emitter of radiation is a good absorber and vice versa*

*Best emitter for  $a = 1$  → black body*



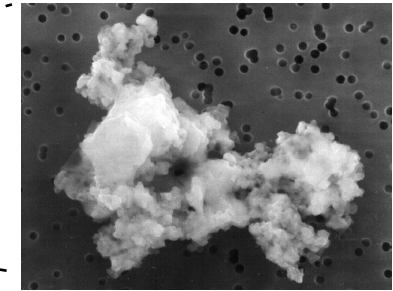
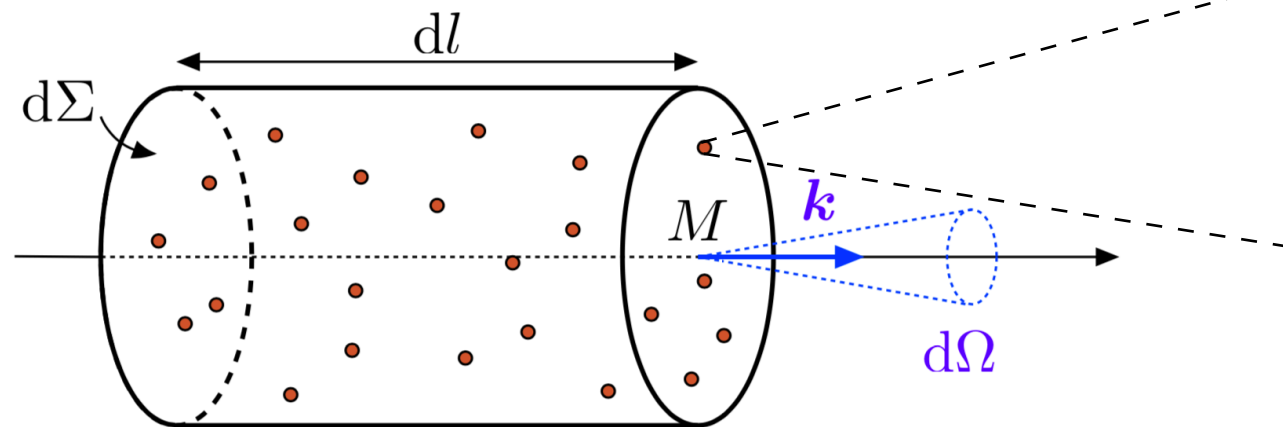
Reif (1965)



# Application - dust

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NASA - stardust

F. Levrier - radiative transfer lecture

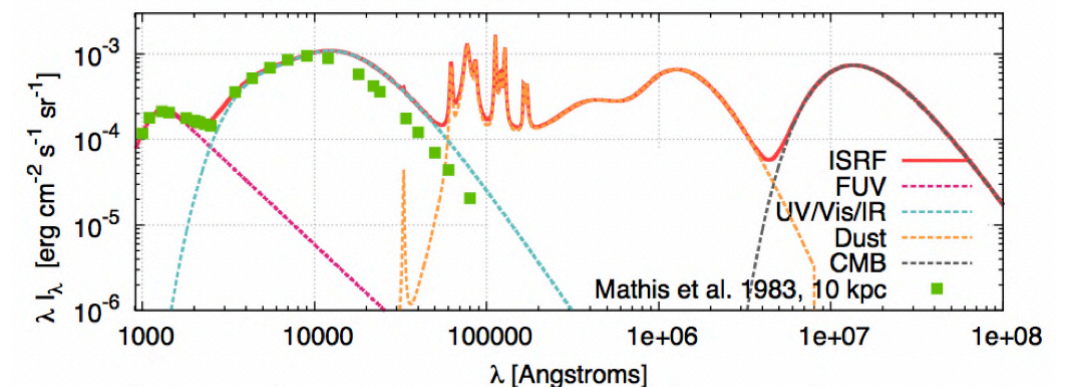
→ consider interstellar dust grains at temperature  $T_d$

$$\left. \begin{aligned} da(\nu) &= \alpha_\nu dl \\ dI_\nu^{\text{emi}}(T_d) &= j_\nu dl \end{aligned} \right| \longrightarrow \boxed{j_\nu = \alpha_\nu B_\nu(T_d)}$$

the emissivity of grains depend on their absorption efficiency

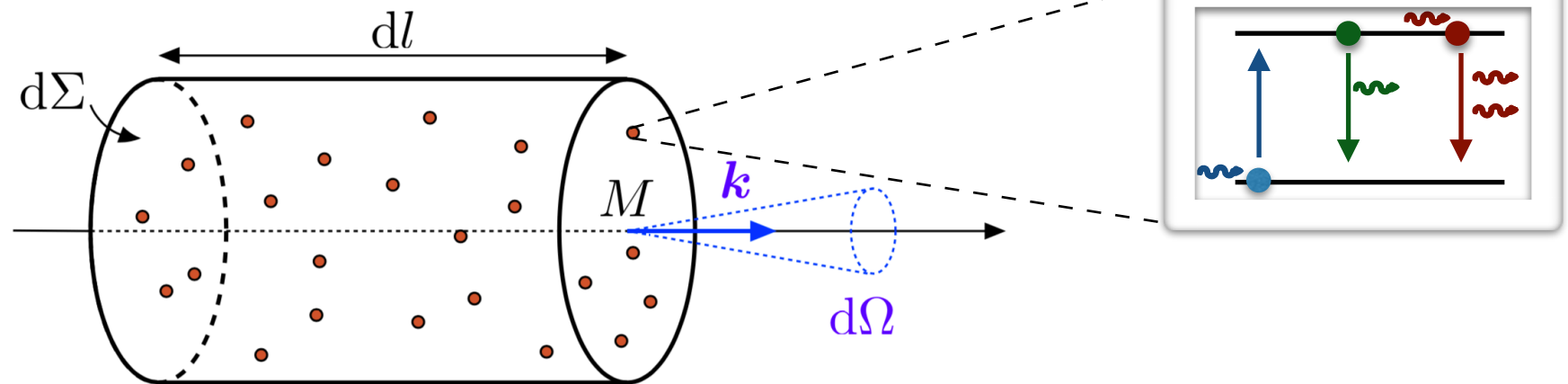
→  $T_d$  can be computed at equilibrium with surrounding RF by solving

$$\int \alpha_\nu J_\nu d\nu = \int \alpha_\nu B_\nu(T_d) d\nu$$



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F. Levrier - radiative transfer lecture

→ consider a gas of a single species with two energy levels  
**if the gas is at thermodynamical equilibrium at  $T_g$**

$$\left. \begin{aligned} da(\nu) &= \alpha_\nu dl \\ dI_\nu^{\text{emi}}(T_g) &= j_\nu dl \end{aligned} \right| \longrightarrow \boxed{j_\nu = \alpha_\nu B_\nu(T_g)}$$

the absorption of a two level system is given by its emissivity

→ Einstein relations (see next lecture)

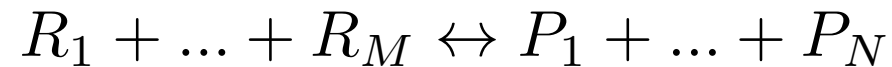
$$g_l B_{lu} = g_u B_{ul} \qquad A_{ul} = \frac{2h\nu^3}{c^2} B_{ul}$$

# Forward and reverse reaction rates

## Outline

- introduction
- statistical mechanics
- Maxwell Boltzmann
- Saha's equation
- Planck's law black body
- Kirchhoff law
- collisions & chemistry
- conclusions

The law of mass action implies strong restrictions on rate coefficients



$k_f$  = forward rate

$k_r$  = reverse rate

$$\frac{k_f}{k_r} = \frac{\prod_{j=1}^N \frac{(2\pi m_j kT)^{3/2}}{h^3} \zeta_{\text{int}}(P_j)}{\prod_{i=1}^M \frac{(2\pi m_i kT)^{3/2}}{h^3} \zeta_{\text{int}}(R_i)}$$

application to inelastic scattering (see next lecture)



$$\frac{\langle \sigma v \rangle_{lu}}{\langle \sigma v \rangle_{ul}} = \frac{g_u}{g_l} e^{-(E_u - E_l)/kT}$$

$$(E_u - E_l + E) \sigma_{lu}(E_u - E_l + E) = \frac{g_u}{g_l} E \sigma_{ul}(E) \quad \forall E > 0$$

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### Thermodynamic equilibrium

- perfect system (isolated at dynamical, thermal, & chemical equilibrium)
- entirely described by statistical & quantum mechanics
- macro-properties and statistical micro-properties known  
Maxwell-Boltzmann, Planck distributions
- gives fundamental relation between inverse processes

### In astrophysics

- TE or LTE is rare (CMB, stars)
- systems may partly be in thermodynamic equilibrium  
i.e. behave partly as in TE with a heat reservoir

***goal : learn to identify these cases and the associated heat reservoir***