



Eq. luminance [lx]

room inside	water	20-40	Weber law (feeling) ~ log (source)
	medium	40-80	
	strong	80-100	
Screen in cinema		80-250	
paper in sunshine		100 000	

E.g. Electric bulb  
 15 W  
 7 W  
 470 nm  $\leftrightarrow$   in 4:30  
 Warm white  
 25000 h

Absorption, Emission, Kirchhoff's Law

Df. absorption   $A(\omega, T) = \frac{\text{absorbed energy at } \omega}{\text{total energy at } \omega}$  [A] = [1]

$A = A(\omega, T, \text{chemistry, colour, phase, etc.})$

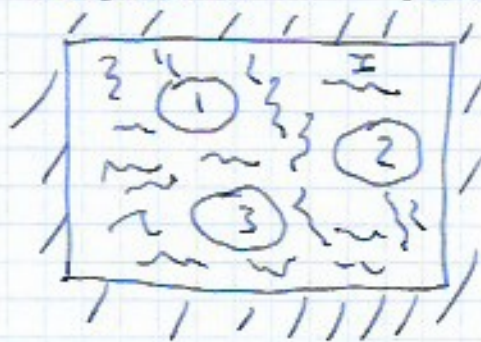
- $A(\omega, T) = 0$  - perfect mirror
- $A(\omega, T) = 1$  - black body
- $A(\omega, T) = \omega \cdot \alpha$  - gray body

Df. emission  $E(\omega, T) = \text{emitted energy at } \omega \text{ per time}$   
 $[E] = [W = \frac{J}{s}]$

# 1859 - Kirchhoff's Law

$$\frac{E(\omega, T)}{A(\omega, T)} = \epsilon(\omega, T) = \text{universal function of } \omega \text{ and } T \text{ for all bodies.}$$

Proof  $n$  - bodies in thermal equilibrium with radiation inside an isolated mirror box.



(\*) Each body emits and absorbs the same amount of energy by  $\Delta S$  and  $\Delta t$  (if not then thermal equilibrium is impossible)

$$E_1(\omega, T) \Delta S_1 \Delta t = A_1(\omega, T) \Delta S_1 \Delta t I(\omega, T)$$

$$E_2(\omega, T) \Delta S_2 \Delta t = A_2(\omega, T) \Delta S_2 \Delta t I(\omega, T)$$

↑ light intensity (the same for all bodies)

$$\Rightarrow \frac{E_1(\omega, T)}{A_1(\omega, T)} = \frac{E_2(\omega, T)}{A_2(\omega, T)} = \dots = I(\omega, T) \equiv \epsilon(\omega, T)$$

□

For a black body ~~radiation~~  $A_{bb}(\omega, T) = 1$

$$\frac{E_{bb}(\omega, T)}{A_{bb}(\omega, T)} = \epsilon(\omega, T) = I(\omega, T) = \frac{c}{4} u(\omega, T)$$

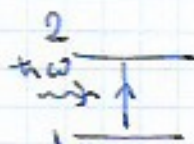
$$\Rightarrow \epsilon(\omega, T) = \frac{c}{4} u(\omega, T) - \text{Planck distribution for all bodies.}$$

↑  
Planck distribution

(\*) A body more radiates if it more absorbs.  
e.g. black copper wool faster than water at the same  $T$ .

# Einstein coefficients

1) absorption

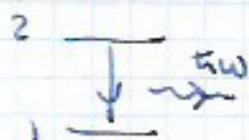


transition rate

$$\left(\frac{dN}{dt}\right)_{ab} = N_1 B_{12} u(\omega)$$

$\uparrow$  occupation of initial states       $\uparrow$  proportionality coefficient       $\uparrow$  density energy

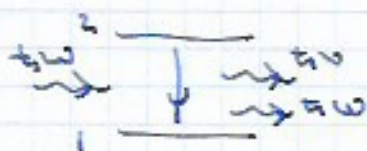
2) spontaneous emission



$$\left(\frac{dN}{dt}\right)_{sp-em} = A N_2$$

$\uparrow$  coefficient       $\uparrow$  occupation of excited state

3) stimulated emission



$$\left(\frac{dN}{dt}\right)_{st-em} = N_2 B_{21} u(\omega)$$

Detailed balance condition

$$\left(\frac{dN}{dt}\right)_{ab} = \left(\frac{dN}{dt}\right)_{sp-em} + \left(\frac{dN}{dt}\right)_{st-em}$$

$$N_1 B_{12} u(\omega) = N_2 A + N_2 B_{21} u(\omega)$$

In thermal equilibrium

$$N_1 = \text{const} e^{-\beta E_1}, \quad N_2 = \text{const} e^{-\beta E_2} \rightarrow \frac{N_1}{N_2} = e^{-\beta(E_2 - E_1)} = e^{-\beta h \omega}$$

$$u(\omega) = \frac{N_2 A}{N_1 B_{12} - N_2 B_{21}} = \frac{A}{B_{21}} \frac{1}{\frac{B_{12}}{B_{21}} e^{\beta h \omega} - 1}$$

In the limit  $T \rightarrow \infty$

$$B_{12} = B_{21} = B \Rightarrow M(\omega) = \frac{A}{B} \frac{1}{e^{\beta h \omega} - 1}$$

absorption = stimulated emission

Comparing with Planck distribution

$$\boxed{\frac{A}{B} = \frac{\omega^3 \hbar}{4\pi^2 c^3}}$$

A and B are Einstein coefficients

## Relation to absorption and emission

$$\frac{E(\omega, T)}{A(\omega, T)} = \frac{c}{4} n(\omega, T) = \frac{c}{4} \frac{A}{B} \frac{1}{e^{\beta \hbar \omega} - 1}$$

### Dimensional analysis

$$[A] : \left[ \frac{1}{s} \right] = \left[ \left( \frac{dN}{dt} \right)_{e \rightarrow a} \right] = A N_2 \Rightarrow [A] = \left[ \frac{1}{s} \right]$$

$$[N_2] = 1$$

$$[B] : \left[ \frac{1}{s} \right] = \left[ \left( \frac{dN}{dt} \right)_{s \rightarrow e} \right] = [B N_2 n(\omega)] =$$

$$= \left[ B N_2 \frac{\hbar \omega^3}{4\pi^2 c^3} \frac{1}{e^{\beta \hbar \omega} - 1} \right]$$

$$[B] = \left[ \frac{1}{s} \cdot \frac{\omega^3 / s^3}{2 \cdot s \cdot \frac{1}{s^3}} \right] = \frac{\omega^3}{s} \frac{1}{4\pi \cdot \frac{\omega^2}{s^2} \cdot s} = \frac{m}{kg}$$

$$\Rightarrow \left[ \frac{A}{B} \right] = \left[ \frac{kg}{m \cdot s} \right]$$

On the other hand:

$$\frac{E(\omega, T)}{A(\omega, T)} = \frac{A}{B} \frac{c}{4} \frac{1}{e^{\beta \hbar \omega} - 1}$$

$$\left[ \frac{E}{A} \right] = \left[ \frac{\frac{J}{m^2}}{1} \right] = \left[ \frac{kg \cdot \frac{m^2}{s^2}}{m^2} \right] = \left[ \frac{kg}{s^2} \right]$$

$$\Rightarrow \left[ \frac{A}{B} \right] = \left[ \frac{kg}{s^2} \frac{1}{m/s} \right] = \left[ \frac{kg}{m \cdot s} \right]$$

□

### § 3 SPECIFIC HEAT OF SOLIDS - PHONONS

Def. heat capacity

$$C_x = \left( \frac{\delta Q}{\delta T} \right)_x \quad \left[ \frac{J}{T} \right]$$

at  $x$  - constant during the process, extensive quantity.

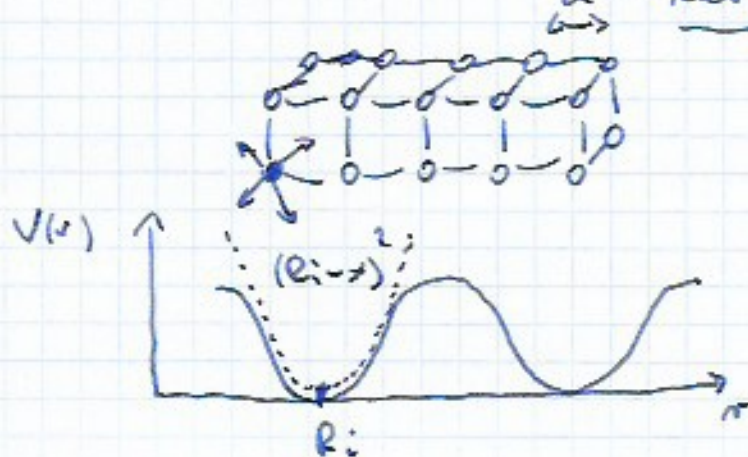
Heat capacities per unit mass or per mole are called specific heats  $\left[ \frac{J}{kg \cdot T} \right]$  and are intensive quantities.

They measure how the system responds to the uptake of heat from its surroundings - thermodynamic response function

Solid Crystals - ions vibrate around equilibrium positions, lattice sites.

(not move around the volume like in gas or liquid)

$a$  - lattice constant



- ) Amplitudes of vibrations are small  $|x| \ll a$ .
- ) A G of  $3N$  body system oscillates

•••) In this small amplitude limit we have a set of  $3N$  harmonic oscillators

Energy of a harmonic crystal

$$\mathcal{H}(p, p) = \sum_{n=1}^{3N} \left( \frac{p_n^2}{2m_n} + \frac{1}{2} m_n \omega_n^2 p_n^2 \right)$$

$m_n, \omega_n$  - constants in harmonic approximations  
 $p_n, P_n$  - generalized coordinates

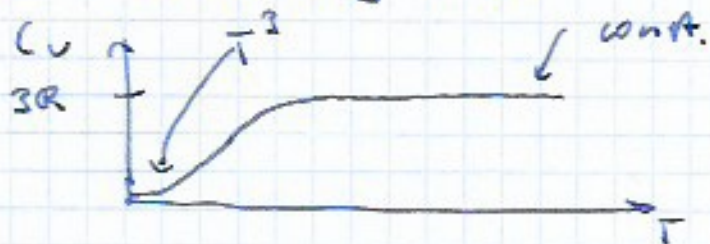
History:

o) Classical statistical physics predicted that

$$\begin{cases} U = \langle \mathcal{H} \rangle = 3Nk_B T & \text{for one mole} \\ C_V = \left( \frac{dU}{dT} \right)_V = 3Nk_B = 3R = \text{const.} \end{cases}$$

[ Dulong - Petit Law (1819) ]

∴ in second half of 19<sup>th</sup> it was shown experimentally that



∴ Einstein model (1907) - used Planck distribution to describe crystal vibrations

∧<sub>n</sub>  $\omega_n = \omega$  - each atom is the same oscillator  
 $m_n = m$

$$U = 3N_A \langle \mathcal{E} \rangle = 3N_A \left[ \frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\frac{\hbar \omega}{k_B T}} - 1} \right]$$

Einstein temperature

$$\boxed{T_E = \frac{\hbar \omega}{k_B}}$$

$$C_V = \frac{dU}{dT} = 3R \left( \frac{T_E}{T} \right)^2 \frac{e^{\frac{T_E}{T}}}{(e^{\frac{T_E}{T}} - 1)^2}$$

$$C_V \sim \begin{cases} 3R & T \gg T_E \\ 3R \left( \frac{T_E}{T} \right)^2 e^{-\frac{T_E}{T}} & T \ll T_E \end{cases}$$

exponential decay at low T

• v) P. Debye (1912) model - took more general model, where each modes can have different frequencies (linear)

$$W = W_x + W_y + W_z = W \bar{\omega}$$

and assumed that frequency is quasi-continuous.  
 In a range  $[\omega, \omega + d\omega]$  there are  $\rho(\omega) d\omega$  normal modes  
 [ density of states.

Now,  $\omega \leq \omega_{max}$

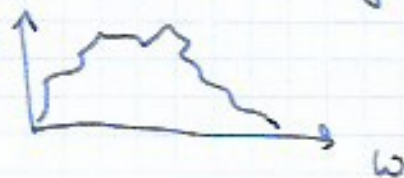
$$U = \int_0^{\omega_{max}} \frac{\hbar \omega}{2} \rho(\omega) d\omega = \int_0^{\omega_{max}} \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \rho(\omega) d\omega$$

$\omega_{max}$  - maximal frequency of vibrations.

Proof:

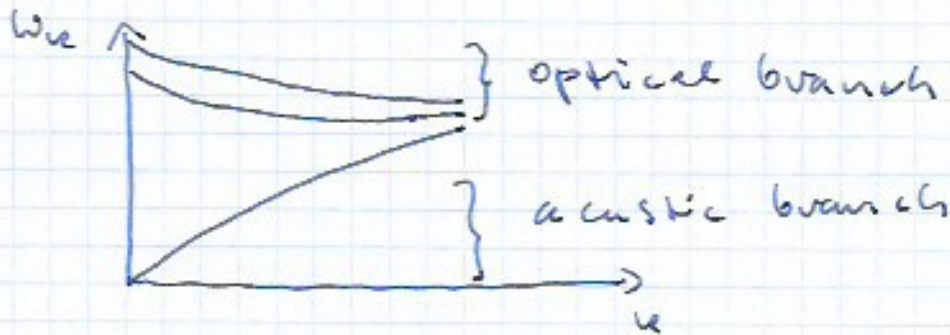
$$\sum_{\vec{k}} \frac{\hbar \omega_{\vec{k}}}{e^{\beta \hbar \omega_{\vec{k}}} - 1} = \int d\omega \underbrace{\frac{2}{\hbar} \delta(\omega - \omega_{\vec{k}})}_{\rho(\omega)} \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \quad \square$$

Practically, DOS  $\rho(\omega)$  is determined numerically (density functional theory or neutron scattering)



Finding  $\rho(\omega)$  is equivalent to know  $\omega_{\vec{k}}$  or  $\omega_{\vec{k}}$ .

At low wave vector  $\vec{k}$ :



There exists one mode with linear dispersion relation  $\omega_{\vec{k}} = v|\vec{k}|$

Goldstone theorem: broken of continuous symmetry  $\rightarrow$  one zero mode

translational symmetry



gas,  
liquid



discrete symmetry



Solid

### Debye model

$$\omega_n = v|\vec{k}| = v \frac{\pi}{L} |n| \quad n = \sqrt{n_x^2 + n_y^2 + n_z^2}$$

$$\sum_n (\dots) = \frac{3}{8} \int_0^{n_{max}} 4\pi n^2 (\dots) dn \quad \left[ \begin{array}{l} \text{like in} \\ \text{cavity} \\ \text{radiation} \\ \text{but ...} \end{array} \right]$$

3 - # of polarization

$n_{max}$  - there are 3N degrees of freedom (finite number of atoms, infinite number of photons)



$$\frac{1}{2} \pi n_D^3 = 3N$$

$$n_D \equiv n_{max}$$



$$3 \cdot \frac{1}{8} \cdot \frac{4}{3} \pi n_D^3 = 3N$$

interpretation:

$$k_D = \frac{2\pi}{L} n_D \sim \frac{\sqrt[3]{N}}{L} = \frac{2\pi}{\lambda_D}$$

$$\lambda_D \sim \frac{L}{\sqrt[3]{N}} \sim a \quad - \text{ lattice constant}$$

The shortest wave length cannot be shorter than the interatomic distance

$\lambda_D$  - Debye length

$k_D$  - Debye wave vector

$\omega_D$  - Debye frequency

$$\omega_D = v k_D$$

## Internal energy

$$U = \sum_n \frac{\hbar \omega_n}{e^{\beta \hbar \omega_n} - 1} = \frac{3}{8} \int_0^{\omega_D} \hbar \omega^2 \frac{\hbar \omega \frac{\omega}{L}}{e^{\beta \hbar \omega \frac{L}{v}} - 1} d\omega =$$

$$\left\{ x = \beta \hbar \frac{v}{L} \omega \right\} = \frac{3 \hbar^4 v}{8} \left( \frac{L}{\hbar \beta \hbar v} \right)^4 \frac{\hbar \omega}{L} \int_0^{x_D} \frac{x^3}{e^x - 1} dx =$$

$$x_D \equiv \frac{\pi \hbar v \omega_D}{L k_B T}$$

$$= \frac{3 \pi^2 \hbar v}{2 L} \left( \frac{k_B T L}{\hbar \hbar v} \right)^4 \int_0^{x_D} \frac{x^3}{e^x - 1} dx$$

$$x_D \equiv \frac{\Theta}{T} = \frac{k_B \Theta}{k_B T}, \quad \boxed{k_B \Theta = \left( \frac{\hbar v}{k_B} \right) \left( \frac{6 \sqrt{2} N}{v} \right)^{1/3}} \quad \text{Debye temperature}$$

At low  $T \ll \Theta$

$$\int_0^{x_D} \frac{x^3}{e^x - 1} dx \approx \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

$$U = \frac{3 \pi^4 N k_B T^4}{5 \Theta^3} \quad T \ll \Theta$$

$$C_V = \left( \frac{dU}{dT} \right)_V = \frac{12 \pi^4 N k_B}{5} \left( \frac{T}{\Theta} \right)^3$$

$T^3$  - Debye law

$\Theta$ [K]	470	343	105	645	374	287	225	165
	Fe	Cu	Pb	Si	Ge	As	Ag	Au
	metal			semiconductor				

Phonons - quanta of crystal lattice

vibrations - quasiparticles similar to photons, emergent particles

$$1 + 1 \neq 2$$

Science 177, 393 (1972)

P. W. Anderson

More is different

Emergent properties - Fundamentally new phenomena in complex systems (quasiparticles) not deduced (predicted a priori) from the knowledge of elementary particles of the system.

Determinism

$$1 + 1 = 2$$

reductionism

(Democritus)

Emergency

$$1 + 1 \neq 2$$

Darwin, Boltzmann, Landau, Anderson

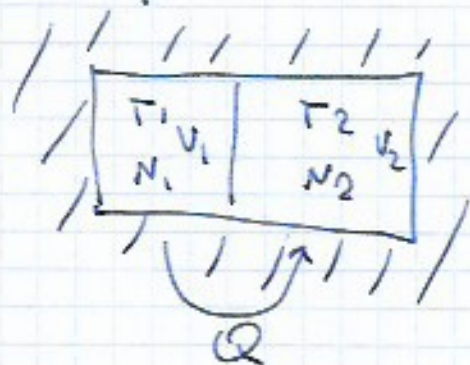
Geometric Example

•	point
••	points
—	segment / line ( $\infty$ points)
//	concept of parallel
X	concept of angle
□	concept of area
□	concept of volume

# IV GRAND CANONICAL ENSEMBLE

## § 1. CHEMICAL POTENTIAL

→ We investigated systems in thermal interaction (contact) with exchanging an energy



$$T_1 > T_2$$

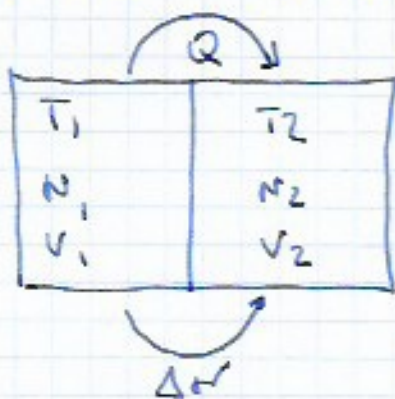
heat  $Q$  "flows" from ① to ② under

$$T_1 = T_2$$

$$\frac{1}{T_1} = \left( \frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} = \left( \frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2} = \frac{1}{T_2}$$

From the maximization of the microdynamic probability  $S = k_B \ln \Omega$

→ now we add a chemical interaction (contact) with exchanging particles apart of thermal interaction



$$T_1 > T_2$$

thermal + diffusive contact

A system is in thermal and in chemical equilibrium if

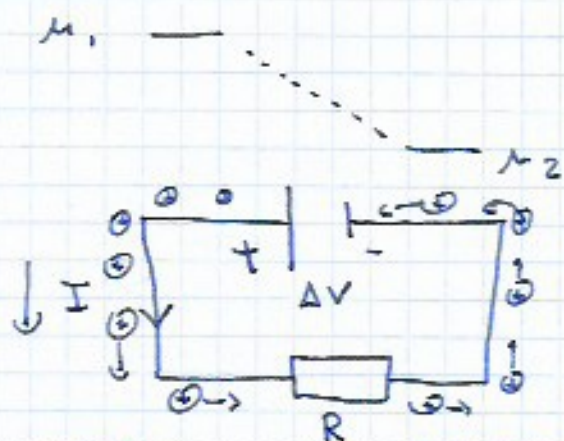
$$\begin{aligned} T_1 &= T_2 \\ \mu_1 &= \mu_2 \end{aligned}$$

What is  $\mu_1$

A chemical potential powers a flow of particles, e.g. a battery

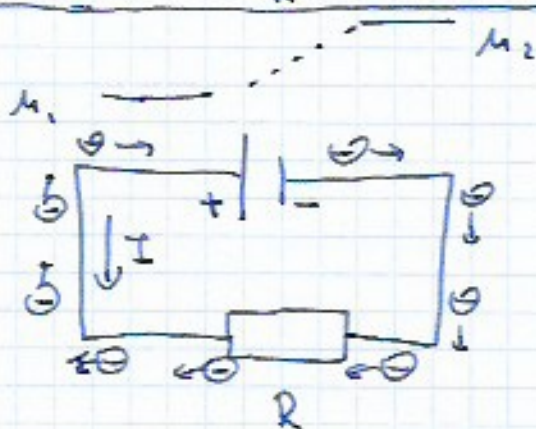
here an electric potential  $\Delta V$

$\mu_1 > \mu_2 \Rightarrow$  flow of current  $I$



$$\mu_1 - \mu_2 = q\Delta V$$

motion of positive  $q > 0$  charges from  $\mu_1$  to  $\mu_2$ .



$$\mu_1 - \mu_2 = q\Delta V$$

motion of negative  $q < 0$  charges from  $\mu_2$  to  $\mu_1$

How to define a chemical potential in thermodynamics?