The entropy S

Is a measure of the number of possible microscopic arrangements in a thermodynamic system, i.e. it is a microscopic, statistical description. It is most relevant in physics, biology, chemistry, in information theory, and of course in sensor technology.

2 microstates from 12 particles:

low entropy
low disorder

high entropy
high disorder

The entropy S, as a function of disorder or arrangement of states, can be defined via the occupation probability:

$$S = \tag{3.20}$$

If all N particles or all N states have the same occupation probability $p_i = \frac{1}{N} = \frac{1}{Z}$, the entropy $S = -k \cdot Z \left(\frac{1}{Z} \cdot \ln(\frac{1}{Z}) \right)$ simplifies to

$$S = \tag{3.21}$$

In the example above with $Z = 4.426 \cdot 10^9$, we obtain $S = k_B \cdot \ln(Z) = 22.2 \, k_B$. Correspondingly, the entropic energy is $T \cdot S = 22.2 \, k_B T \approx 8.9 \cdot 10^{-20} \, J$

The difference in entropy is described by the initial and final state (before and after a change)

$$dS = S_f - S_i = \tag{3.22}$$

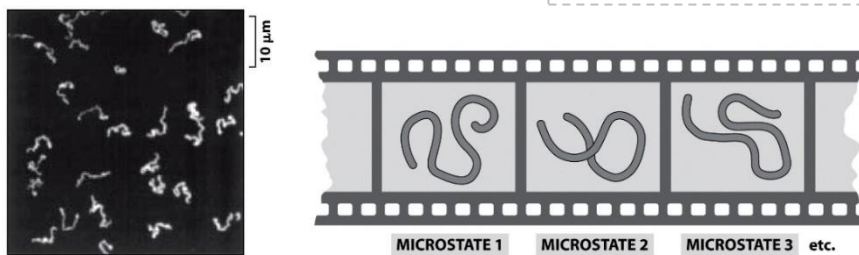MICROSTATE 1   MICROSTATE 2   MICROSTATE 3   etc.

Figure 6.2b Physical Biology of the Cell (© Garland Science 2009)

Figure 2 (by R. Phillips): Microstates of DNA in solution. DNA molecules (and other polymers) jiggle around in solution exploring different conformational states. Each one of these conformations represents a different microstate. Left: Fluorescence microscopy image of λ-DNA confined to a surface. Right: Film strip showing conformations of a single DNA molecule at different instants (from Maier & Rädler, PRL 1999.)

The Helmholtz free energy F

is a another (third) thermodynamic potential the inner energy U minus the energy obtained from the environment:
$$F = U - T \cdot S \tag{3.23}$$

The Gibbs free energy G

is the last (forth) thermodynamic potential and describes how a system is changing over time, i.e. driven by minimizing G(H,T,S). It is the sum of the enthalpic and entropic energy

$$\begin{aligned} G &= H - T \cdot S \\ &= (U + p \cdot V) - T \cdot (k \cdot \ln Z) \end{aligned} \tag{3.24}$$

the Gibbs free energy can be minimized (G → 0) when H ≈ T·S, which can be achieved for many combinations of the three state quantities T, S and H.

Even when the enthalpy H does not become small, G can be minimized by a sufficiently large entropic energy T·S. On it's way to thermal equilibrium, the entropy and the number of possible states is maximized (see diffusion of molecules in chamber).

Reducing the Gibbs free energy by steps dG and the multidimensional way to equilibrium:

$$dG = \quad\quad\quad\quad\quad\quad\quad\quad \text{(3.25)}$$
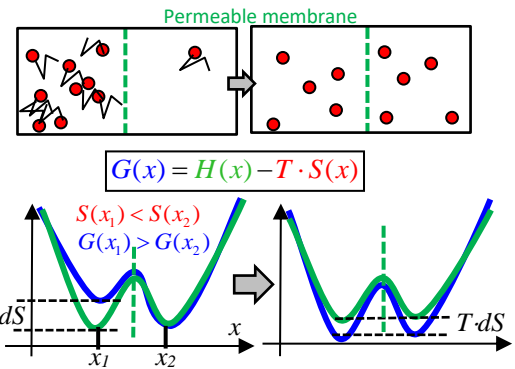
Attention: If you take a movie of a process which has reached thermal equilibrium, you can play the movie backwards without finding any violation of causality. However, if you take a movie of a steady-state process (running water out of a tap), the backward movie will reveal impossible processes.

If e.g. 4 from 8 particles are removed (see example above), then the entropy change is negative (the disorder has decreased, i.e. order has increased)

$$dS = S_f - S_i = k \cdot \ln\left(\tfrac{64!}{4!(64-4)!} \Big/ \tfrac{64!}{8!(64-8)!} \right) = -k \cdot 8.849$$
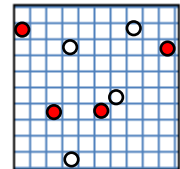
At constant temperature ($dT = 0$), volume ($dV = 0$) and pressure ($dp = 0$) eq. (3.25) becomes $dG = dU - T \cdot dS$, such that the free energy would increase by $dG = k_B T \cdot 8.849 > 0$, making the system slightly hotter until $dG = dU - T \cdot dS = 0$, i.e. until $dU = T \cdot dS$.
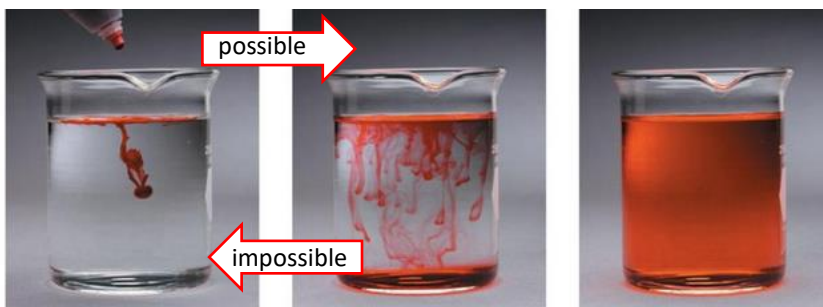
Figure 3: the entropy of the ink-water system increases as the ink mixes with the water. Spontaneous un-mixing is never observed and would violate causality. The Gibbs free energy is decreasing making the glass slightly cooler: $dG = dU - T \cdot dS \approx -T \cdot dS$

Image: Pearson education Inc.

Entropy increase by heating: $dS = S_f - S_i = \quad\quad\quad\quad$ (3.26)

The chemical potential μ $T = \tfrac{1}{3} m v_{rms}^2 / k_B$

is a thermodynamic state quantity that describes the chemical energy of a species of N particles in a system. If the number N_0 of molecules has the chemical energy μ_0, then the chemical potential increases with $N > N_0$ molecules:

$$\mu(N) = \mu_0 + \quad\quad\quad\quad\quad \text{(3.27)}$$

In chemical reactions typically several species (index j) of each N_j molecules are involved, such that the change in Gibbs free energy dG can be described as
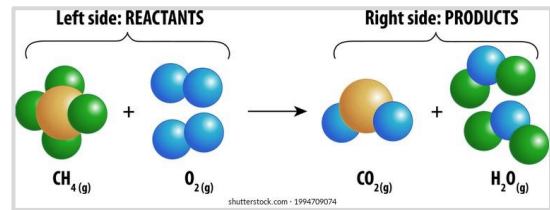
$$dG = dU + p \cdot dV - T \cdot dS + \quad\quad\quad\quad \text{(3.28)}$$

where we assumed constant pressure ($dp = 0$) and constant temperature ($dT = 0$).

An alternative definition of the chemical potential is therefore $\mu_j = \left(\dfrac{dG}{dN_j}\right)_{p,T,N_{j\neq i}}$.

In thermal equilibrium, $dG = \sum_j \mu_j \cdot dN_j = 0$, one obtains for the particle numbers of each species

$$\mu_1 \cdot dN_1 + \mu_2 \cdot dN_2 + \mu_3 \cdot dN_3 + \dots \qquad \text{3.29)}$$
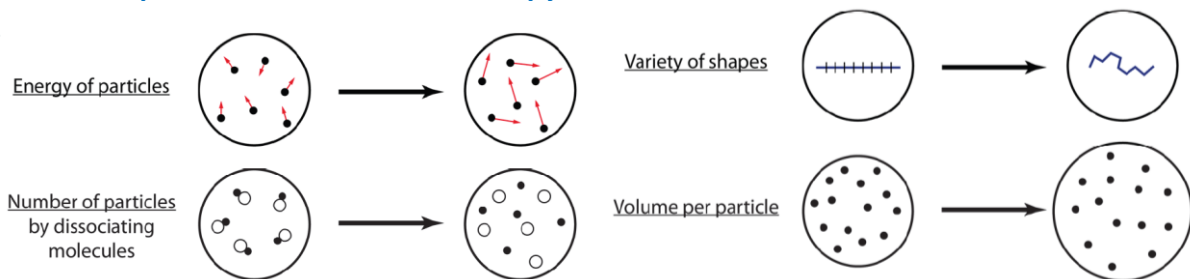

Four examples of how to increase entropy:

Figure 4: Entropy S can be increased by a higher kinetic energy and temperature of the particles, by dissociating (separating) particles, by enabling disordered shapes of filaments, by increasing the volume to give the particle's more possibilities to arrange.

3.3. Diffusion and fluctuation

Principle:

A few micrometer small particle is hit randomly (without correlation) about 10^{20}x per sec by fluid molecules, resulting in a correlated (!) discontinuous motion of the particle.
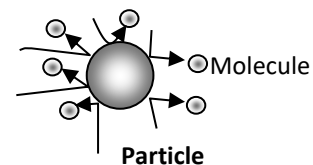
Mathematics:

Brownian motion is a stochastic (Markow-) process, allowing to predict processes in the future from only little information obtained from past processes. With particle mass m this is called a Ornstein-Uhlenbeck process, neglecting the mass this is a Wiener-process.
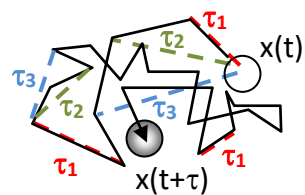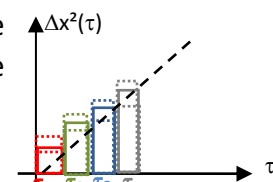

Einstein relation

Einstein was able to derive a principle from the chaotic particle movements: he found that the particle's temporal mean of the square(d) displacement, MSD(τ) = $\langle \Delta \mathbf{r}(\tau)^2 \rangle$, within a certain time interval τ, is proportional to the interval τ:

$$\text{MSD}[\mathbf{r}(t)] = \text{MSD}(\tau) = \langle \Delta \mathbf{r}(\tau)^2 \rangle = \langle (\mathbf{r}(\tau+t) - \mathbf{r}(t))^2 \rangle = \qquad \text{(3.30)}$$

with D = diffusion constant, $[D]$=m²/s, dimension factor M = 1,2,3
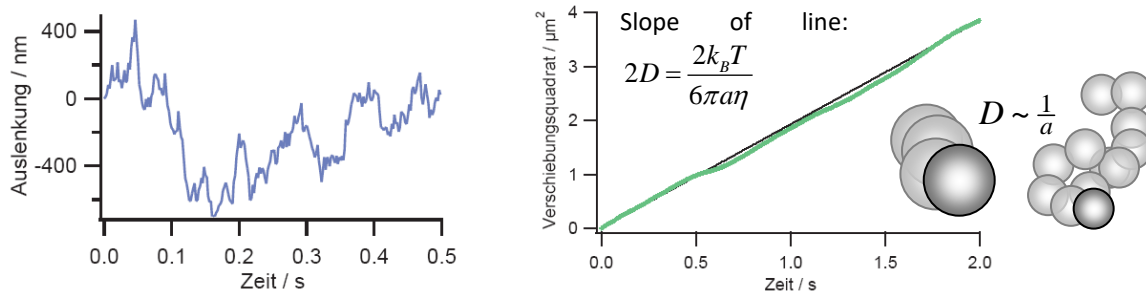
Figure 5: One dimensional particle trajectory x(t) of a and resulting MSD(τ) = $\langle |\Delta x(t, \tau)|^2 \rangle$.

The ingenious achievement from Einstein was to link the microscopic small thermal energy $k_B T$ with the microscopic friction factor γ = F/v:

The Einstein-Smoluchowski relation   (3.31)

Here, $k_B T$ is the thermal energy ($\approx$ 4·pN·nm at T = 300 K) and $k_B = R/N_A$ is the Boltzmann constant, i.e the ratio between the general gas constant R and the Avogadro constant N_A .

$\gamma = 1/\mu$ with μ = mobility, where $\gamma = 6\pi \cdot a \cdot \eta$ for a sphere (**Stokes law**)

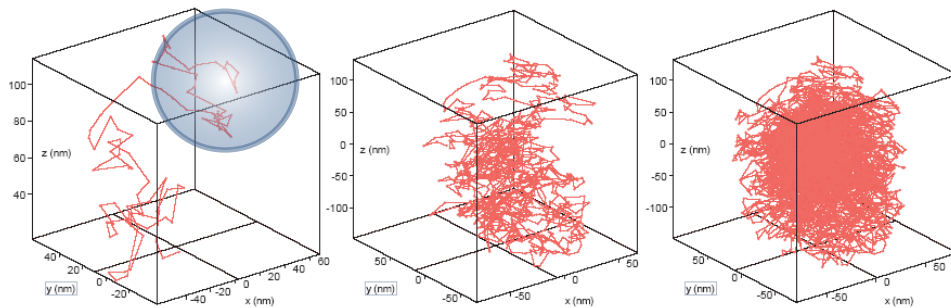$\eta = 1$ mPa s = 1 cP = 250 kT·s/μm³ (T=20°C) viscosity of water, a = sphere radius

Figure 6:
Measured 3D trajectories **r**(t) of an optically trapped sub-micrometer round particle undergoing Brownian motion in time steps of 50μs. Shown are the first 100, 1000 and 5000 center positions. In the center image the particle has sensed the potential the particle is trapped in. On the right image the extent of the potential and the position distribution p(**r**) can be determined.

Thermal noise and stochastic forces

Diffusing particle experience thermal random force $F_{th}(t)$ resulting from molecule collisions from different directions, with temporal mean $\langle F_{th}(t) \rangle = 0$.

$F_{th}(t)$ can be described only indirectly. Considering only white noise $N_{th}(t)$, which has a constant noise level at all frequencies, one finds for the force kicks from the molecules that $F_{th}(t)$ is uncorrelated for all time differences $\tau = t - t' \neq 0$:
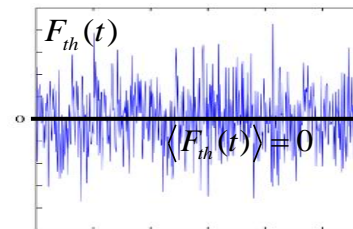
$$AC\left[F_{th}(t)\right] = \langle F_{th}(t) \cdot F_{th}(t+\tau) \rangle =$$ (3.32)

Here, the Kronecker-Delta function is $\delta(t - t') = 1$ if $t = t'$, otherwise $\delta(t - t') = 0$, and M = 1..3 is the number of dimensions. $AC(\tau) = AC[f(t)]$ is the autocorrelation function of $f(t)$.

> **Thought through:** An autocorrelation function $AC(\tau) = AC[x(t)]$ is a memory function or self-similarity function for events $x(t)$ (e.g. a change in position) within the time period $\tau = t'-t > 0$. One investigates what the quantity $x(t)$ at time t has to do with (i.e. correlates with) the quantity at a different time point $t' = t + \tau$, by forming all products $x(t) \cdot x(t+\tau)$. For good statistics, one has to average over many products $\langle x(t) \cdot x(t+\tau) \rangle$ of the same time difference τ. Hence, the trajectory $x(t+\tau)$ is shifted piecewise by τ in the overlap with $x(t)$ is calculated, which is $AC(\tau)$. If for instance the knowledge of a student simply diffuses away with time, his/her corresponding memory function $AC(\tau)$ will decrease linearly.
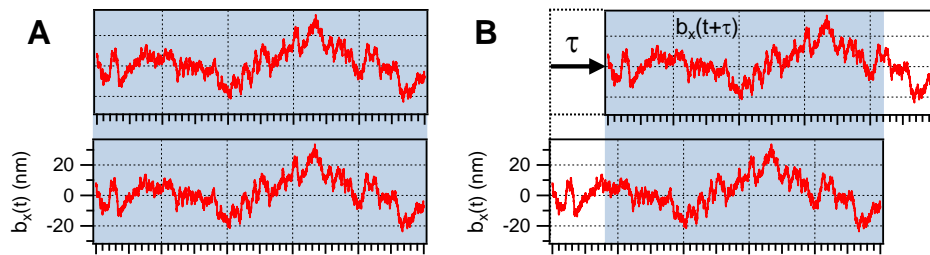

Figure 7: To determine the autocorrelation function $AC[x_j(t)]$ or $AC[b_j(t)]$ the trajectory $b_j(t)$ is shifted successively by τ. Next the temporal averages of overlaps (products) between functions $b_j(t)$ and $b_j(t+\tau)$ are calculated for each time shift τ. The blue region represents the total number of correlated data points, which for larger shifts τ.

Measuring signals on a thermal noise level

A good sensor must to measure signals $s(t)$ with high accuracy and precision, i.e. where the standard deviation Δs is small relative to the average value, $\langle s \rangle \pm \Delta s$. However, even singular peaks (see red ellipse) can contain most significant information, indicating an energy exchange (an interaction) and thereby a measurement.
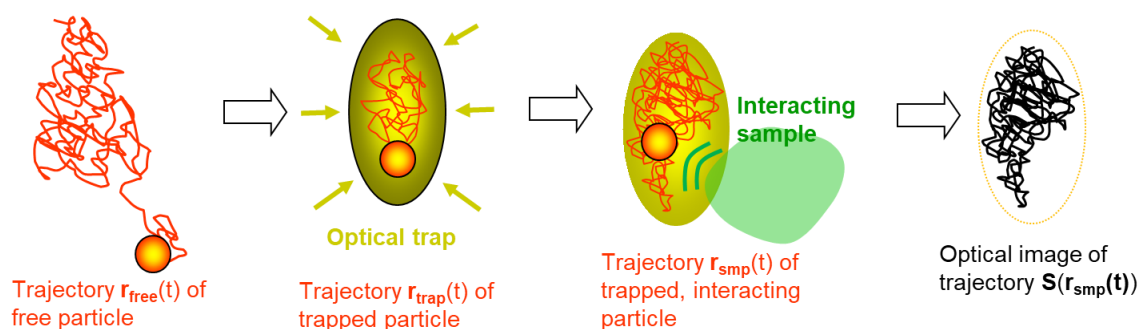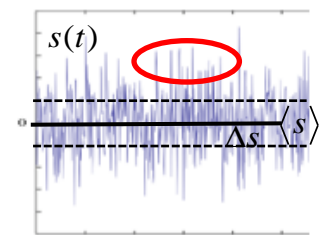

Figure 6: Sensing changes in thermal motion upon interaction with a sample. A freely diffusing particle (left) is captured in an optical trap (laser tweezers), such that Brownian motion is confined. The fluctuating particle trajectory $\mathbf{r}(t) = (x(t),y(t),z(t))$ changes in space and time (2nd figure). Then the optical trap is moved to the interaction partner (sample) and the trajectory changes again in a characteristic manner (3rd figure). A precise high-speed optical sensor (quadrant photodiodes, QPD) measures the particle trajectory (optical image) with reasonable accuracy and precision based on laser interference. The measured particle trajectory is analyzed to reconstruct the interactions with the sample.

4. Optical components of sensors

4.1. Foundations of optics and radiation

Wave - particle dualism

- Light is a spatially confined package of quantized energy $W_{ph} = h \cdot \upsilon = \hbar \cdot \omega$ and quantized momentum $p = \hbar \cdot \omega / c$ - called photon (with Planck constant h = 6.626·10^{-34}Js, $\hbar = h/2\pi$). It belongs to the particle family of bosons (Spin $\pm$ 1) and does not obey the Pauli exclusion principle (no interaction with other particles). In Quantum Electrodynamics (QED), photons are the exchange quanta of the electromagnetic forces.

- Light is an electromagnetic wave, with the ability to interfere - also with itself. The wave carries energy in a continuous flux of photons provided the number of photons is sufficiently large (high intensity I).

- Light can be approximated as a ray, if the wave nature of light can be disregarded and the extent of the interacting object is large d >> λ. Light is treated as a straight ray or beam undergoing reflection and deflection at interfaces
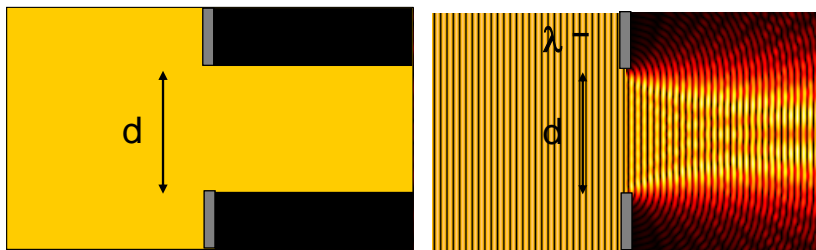

Figure 8: Transmission through an aperture.
Dimensions of ray optics d >> λ (left) and wave optics d ≈ 5λ - 50λ (right).

Where do photons and electromagnetic waves come from?

One uses the idea of a blackbody, which absorbs electromagnetic radiation of all wavelengths λ or frequencies ω = 2π·c/λ. In thermal equilibrium at a specific temperature T, the blackbody body emits an ideal and characteristic radiation spectrum, where the spectral shape is only determined by the temperature.
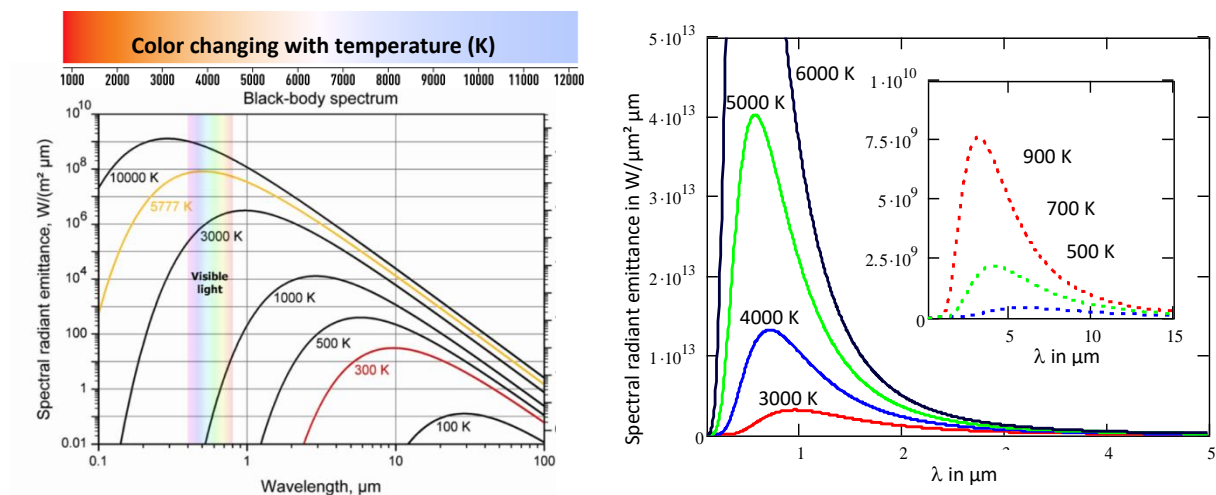

Figure 9: Blackbody radiation spectrum in logarithmic and linear scale. Left: for lower temperatures T the emission maximum shifts to higher wavelengths (Graph: Wikipedia). Right: emission power decreases with T.

The spectrum $L_{BB}(\lambda,T)$ for a blackbody (BB) in thermal equilibrium at temperature T was described in 1901 by Max Planck by his radiation law:

$$\phi'_{BB}(\lambda,T) = 2\pi\, hc_0^2 \cdot \frac{1}{\lambda^5} \cdot \left(\exp\left(\frac{hc_o}{\lambda k_B T}\right) - 1\right)^{-1} \qquad (4.1)$$

The amplitude and thereby the emitted power (area under the curve) strongly increase the temperature by the fifth power. However, to avoid unrealistically high emission at four short wavelengths (ultraviolet catastrophe), Max Planck had to scale the energy of light with frequency $\nu = \omega/2\pi$, which is exactly Planck's constant $h = E/\nu$.

Its total emitted power $\phi_{BB}(T) = \int \phi'_{BB}(\lambda,T)\, d\lambda$ is described by the emissivity, which is $\mathcal{E} = 100$ %. $\mathcal{E}$ is the ratio of the actual radiant flux emitted from a surface relative to that from an ideal (blackbody) emitter ($\mathcal{E} = 1$) having the same temperature T:

$$\mathcal{E}(\lambda,T) = \frac{\phi(\lambda)}{\phi_{BB}(T)} < 1 \qquad (4.2)$$

For most materials as gases in the atmosphere the spectrum becomes distorted with characteristic photon absorption bands.

Figure 10: Nonideal, here terrestrial and extra-terrestrial emission spectrum relative to the black body spectrum.
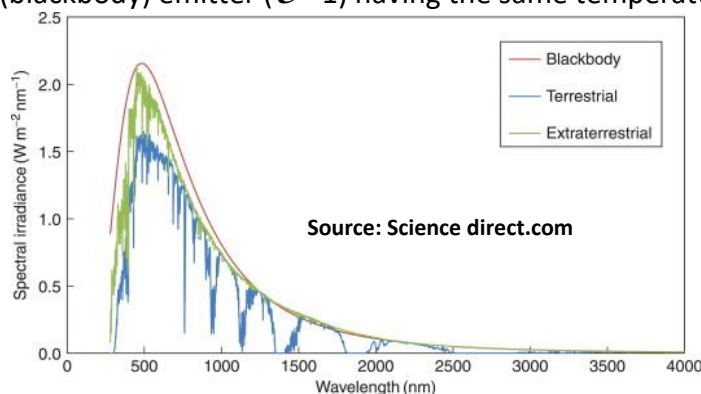
Radiation at different wavelengths

The average energy of vibrating particles (atoms or molecules) is represented by temperature. The vibrating atom has an electron cloud, i.e. orbiting electric charge around the nucleus with oscillation frequency ω.

According to the laws of electrodynamics (Maxwell equations), a moving electric charge is associated with a variable electric field **E** that produces an alternating magnetic field **B**. In turn, when the magnetic field changes, it produces a changing electric field, and so on. Thus, a vibrating particle is a source of electromagnetic field, which propagates outwardly with the speed of light and is governed by the laws of optics, i.e. electromagnetic waves can be reflected, filtered, focused, etc.
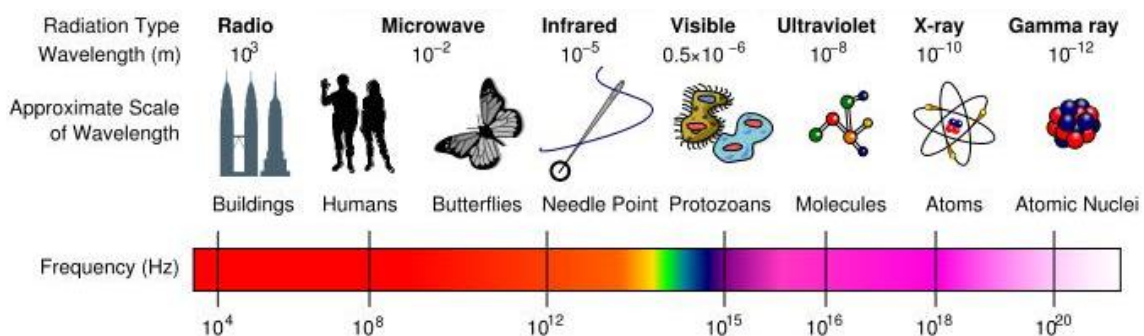

Figure 11: Radiation wavelengths, frequencies relative to objects for different radiation types (Source: Wikipedia)

Flux of photons in numbers and transport of energy and momentum

Irradiance: A light source emits the radiant flux $P = W/t$ (in Watt = Joule/s = J/s). The irradiance $I = P / A$ is defined by the radiant flux per area A (with units $[\hat{I}] = $ W/m²).

The **Poynting-vector S** describes the directional transport of energy density W/A per time t (i.e. the radiant flux per area $[|\mathbf{S}|] = \frac{J}{m^2 \cdot s} = \frac{W}{m^2}$) of an electromagnetic wave at the speed of light c. $\mathbf{S} = \mathbf{E} \times \mathbf{H} = \mathbf{E} \times \mathbf{B}/\mu_0$ is the vector product of the electric field $\mathbf{E} = \mathbf{E}_0 \cdot \cos(\phi(\mathbf{r},t))$ and the magnetic field.

We find $|\mathbf{S}| = S = P/A = E \cdot H = E \cdot B/\mu_0 = E \cdot E/(c\mu_0)$ with $B = \frac{1}{c} \cdot E$.

Units: $[S = E \cdot H] = V/m \cdot A/m = $ W/m² where $[B] = $ Tesla $= V \, s \, /m^2$
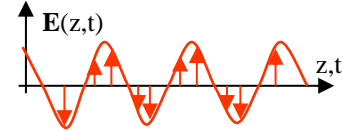
The irradiance corresponds to the amplitude of the Poynting vector $\mathbf{S} = c^2 \varepsilon_0 \cdot \mathbf{E} \times \mathbf{B}$, which is time averaged ($\langle \cos(\phi(\mathbf{r},t)) \rangle = \frac{1}{2}$) over the measurement time $\tau \gg 2\pi/\omega = 1/\nu \cong 10^{-15}$s

$$I(\mathbf{r}) = \tag{4.3}$$
$$=$$

Example: A laser pointer with $I = \frac{c \varepsilon_0}{2} \cdot |\mathbf{E}|^2 = 1 \frac{mW}{mm^2}$ has an electric field $E = 0.87$ V/mm.

Δt is the integration time of the detector (Camera, Eye, etc.) which measures a photo current. Additional integration over the detector area A and measurement time Δt provides the applied energy measured by a sensor

$$W(\Delta t) = \tag{4.4}$$

The flux P sensed by our eye is measured in lumen (lm). At $\lambda = 550$nm, P = 1000 mW $\triangleq$ 680 lm. The speed of light c $\approx$ 300.000 km/s is directly related to the natural constants ε_0 and μ_0,

$$\frac{1}{\varepsilon_0 \cdot \mu_0} = c^2 = \left(3 \cdot 10^8 \frac{m}{s}\right)^2 \text{ in vacuum and by } \frac{1}{\varepsilon \cdot \mu} = \frac{c^2}{\varepsilon_r \cdot \mu_r} = v^2 < c^2 \text{ in matter} \tag{4.5}$$

The speed of light is slowed down by a factor $\sqrt{(\varepsilon_r \cdot \mu_r)}$ in matter by the material constants ε_r, μ_r (r = relative), which allow to define

- the electric permittivity $\varepsilon = \varepsilon_r \cdot \varepsilon_0$; with relative permittivity ε_r, and vacuum permittivity $\varepsilon_0 = 8.85 \cdot 10^{-12}$ C²/(N·m²)

- the magnetic permittivity or permeability $\mu = \mu_r \cdot \mu_0$; with relative permeability μ_r ; and vacuum permeability $\mu_0 = 4\pi \cdot 10^{-7}$ Ns²/C²

Optical forces and radiation pressure

| Flash lamp! |

The radiant flux, i.e. optical power or radiant power P exerts

a radiation pressure $p =$ (4.6)   and an optical force $F =$ (4.7)

on the area A. *See the lecture experiment with the flash lamp.*

More precise: $F = Q \cdot P/c$, where Q is a momentum efficiency factor with $Q = 1$ for full absorption and $Q = 2$ for full reflection

Interesting:

i) **The radiation pressure of the sun** is used to control the position and orientation of satellites in the orbit.

ii) **Optical tweezers** (simply generated by a focused laser beam) suffer from radiation pressure which presses a particle in light propagation direction (F_{scat}). The gradient force pulls the particle towards the focus center (F_{grad}).
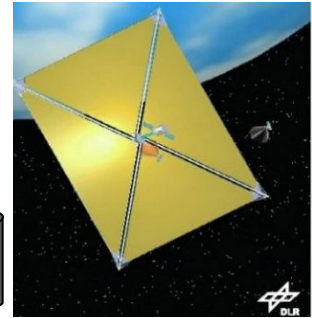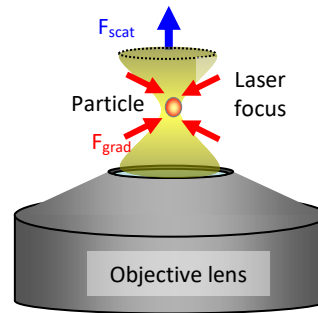
The optical force is described more precisely through the electromagnetic force, i.e. the sum of the electrostatic force $q \cdot E$ and the Lorentz force $q \cdot (v \times B)$, which both act on a charge distribution q moving with **v**, such that

$$\mathbf{F} = q \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \tag{4.8}$$

In contrast to the radiant flux, the photon flux is independent of wavelength or frequency ν

Photon flux (in photons per second)

$$\phi = \frac{}{V} \tag{4.9}$$

with photon energy $W_{ph} = h \cdot \nu = h \cdot c / \lambda = 4 \cdot 10^{-19}$ Nm for visible light at $\lambda = 0.5 \mu m$

Counting photons means to extinct photons (counting or measuring is usually realized by absorption in the electron shell). Photons can be counted if the illumination intensity is reduced to a minimum (see figure without (left) and with (right) attenuators)
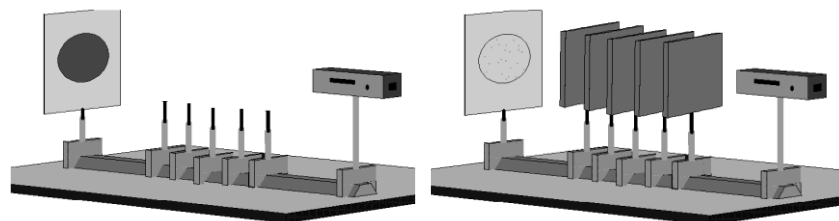
Examples: N photons hit the eye pupil with 2 mm diameter:
- HeNe laser (2.5 mW): N = 10^{16}/s   - Bright sunlight: N = 10^{16}/s - Room light: N = 10^{14}/s   - Moon light: N = 10^{10}/s   - Star light: N = 10^8/s

Detecting and sensing single photons

Two Principle questions:

Can a single photon pass through 2 adjacent slits at the same time? Answer: Y

Are then two photons detected on the screen behind?

Answer: i.e. to the photon that excites an atom of the detector screen!
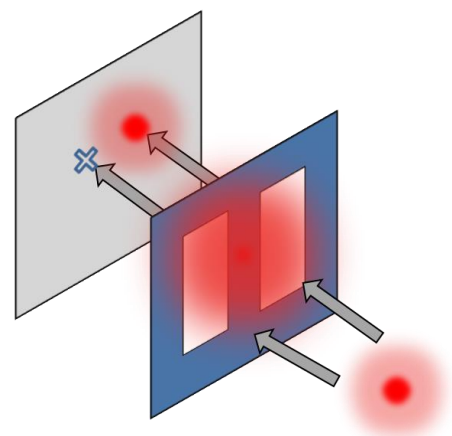
Albert Einstein (1879-1955)

So, what is light?

Einstein doesn't know it, but he states:

*„Light is born as a particle, it lives as a wave and it dies as a particle"*

This might help to understand the answers *Yes* and *No* above!?

4.2. Optical interaction at interfaces

Sensors are only partly absorptive - the emissivity

While wavelengths of the radiated IR light are temperature dependent, the magnitude of radiation is also a function of the surface property, emissivity $\mathcal{E}$ or absorption A.

In 1860 Gustav Kirchhoff found that emissivity and absorption are the same, i.e. $\mathcal{E}(\lambda) = A(\lambda)$. Both measured on a scale from 0 to 1. Hence also A is the ratio of the actual radiant flux relative to the ideal absorption $A(\lambda) = \frac{\phi(\lambda)}{\phi_{BB}} < 1$
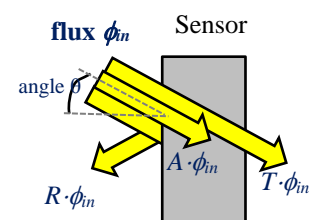
Hence 100% of the radiation is split into the fractions absorption A < 1, transparency T < 1, and reflectivity R < 1. The wavelength dependent parameters specify the object interface:

$$ \tag{4.10}$$

For opaque (non-transparent) objects (T=0) we find that the emissivity $A(\lambda) = 1 - R(\lambda)$ decreases with larger reflectivity.

The Lambert-Beer law describes the exponential decay of the transmitted intensity $I_{tr}(z) = \frac{c\varepsilon_0}{2} \cdot \left| E_{tr}(z) \right|^2$ in an absorbing (and weakly scattering) medium in direction z

$$ I_{tr}(z,\lambda) = \Big(\tag{4.11}$$
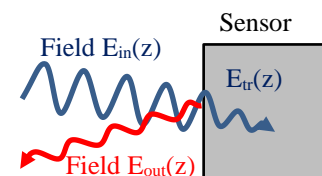
Here $\mu_{ext}(\lambda) = \mu_{abs}(\lambda) + \mu_{sca}(\lambda)$ is the extinction coefficient consisting of the absorption and scattering coefficient measured in units of cm^{-1}. The term $exp(-\mu_{ext}\cdot z)$ describes the behavior of ballistic (unscattered) photons propagating in z-direction.
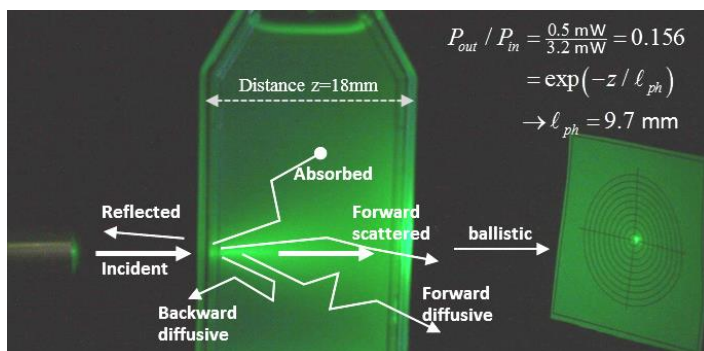

Figure 12: Left: Photon propagation in scattering media. Separation in ballistic, scattered and absorbed photons depends on the wavelength.