# THE GAS and “Gasses”

- probabilistic description of “classical ideal gas”, distinguishable particles
  - probability densities and (cumulative) distribution functions
  - positions, velocities, energies, pressure, heat capacity

- Bose gas
  - blackbody radiation
  - BE condensation in alkali vapors
  - lattice vibrations, heat capacity

- Fermi gas
  - electrons in metals and semiconductors
  - Fermi-Dirac statistics and its classical limit
  - optical response of free electrons and interband transitions
  - surface plasmon resonance

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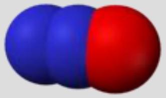
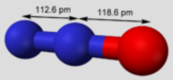
# Classical gas at equilibrium

from probabilities to macroscopic quantities and their fluctuations

The atmosphere in everyday (laboratory) life
- is instrumental in setting the temperature of our samples,
- influences adsorption, desorption, evaporation, ...
- might be important in biosensing





Probability theory applied to

- positions of particles
- pressure

averages (“expectations”) and fluctuations

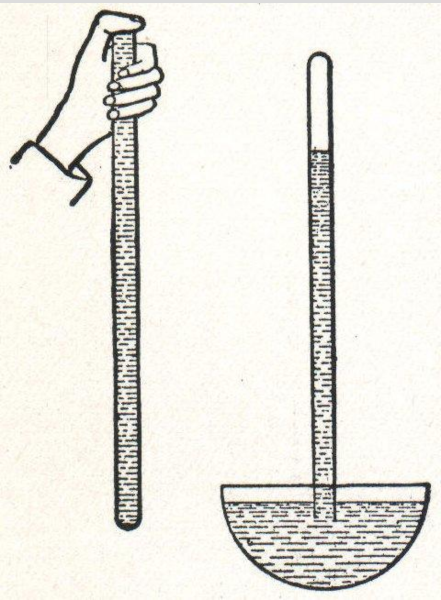
Humphrey Davy 1801

experiment at “Pneumatic institution” in Bristol
$N_2O$ (laughing gas, Lachgas, gas esilarante, rajský plyn)

Free movement of (noninteracting, “small”) particles;

changes of their motion occur only via collisions:

- interparticle,
- hitting (condensed) obstacles, like walls of a container, or a pressure sensor.



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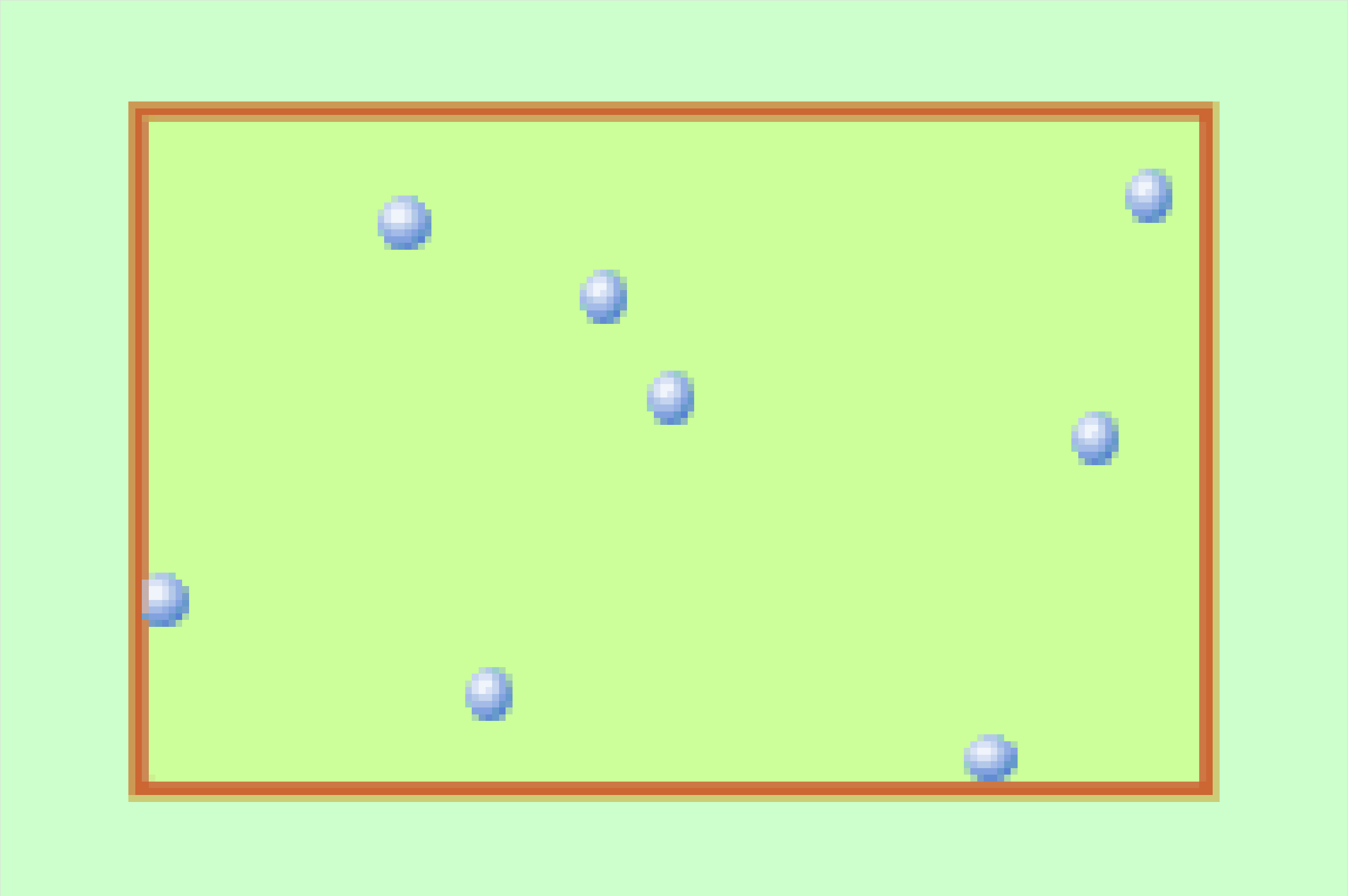
# Collisions: interparticle + walls



# Elastic collisions: interparticle

consider (nonrelativistic) conservation of momentum and energy

$$\vec{p} \equiv m\vec{v}_i + M\vec{V}_i = m\vec{v}_f + M\vec{V}_f$$

$$2E \equiv mv_i^2 + MV_i^2 = mv_f^2 + MV_f^2$$

In 1-dimensional case, the solutions for final velocities are
(1) trivial, no collision:

$$v_f = v_i \quad , \quad V_f = V_i$$

(2)

$$v_f = \frac{(m-M)v_i + 2MV_i}{m+M} \quad , \quad V_f = \frac{(M-m)V_i + 2mv_i}{m+M}$$

(for $m=M$: $v_f=V_i$, $V_f=v_i$)

In 2- and 3-dimensional case, the interaction potential (force) has to be specified

# Large number of particles and unknown initial states → probabilistic description

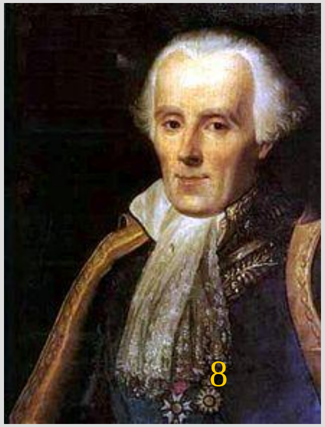
Physical reasoning, supported by relatively simple, but often a bit tricky calculations.

Famous quote by Laplace:

> ...la théorie des probabilités n'est, au fond, que le bon sens réduit au calcul;
>
> ...probability theory is nothing but common sense reduced to calculation.

(Laplace on probability theory)

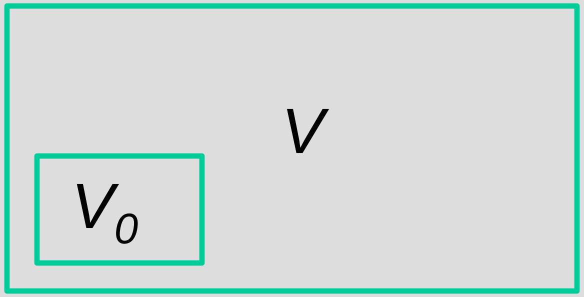
Caution:
usually prone to make errors
in deriving/interpreting
formulae



# Positions and velocities in classical gas

# The probabilistic description

Easy for *positions* of gas particles without external forces:
select volume $V_0$ within the gaseous body contained in $V$



We find that

$$\boxed{p_0 = \frac{V_o}{V} \in \langle 0,1 \rangle}$$ (P0)

is the probability of finding a selected (*i*-th) particle within $V_0$

Assume having *N* distinguishable (classical) particles in total,

$$i = 1, \ldots, N \ ,$$

each of them being placed within $V_0$ with the same probability $p_0$, independently of all the remaining; then the probability

$$P(M \text{ selected particles are found in } V_o) = p_0^M$$

results for any *M=1,...,N* (successive multiplications of $p_0$).

The same reasoning leads to the following probability:

$$\boxed{\begin{aligned} &P(M \text{ selected particles are found in } V_o, \\ &\text{all of the remaining are outside of } V_0) \\ &= p_0^M (1 - p_0)^{N-M} \ . \end{aligned}} \quad \text{(PM)}$$

The set of *M* particles, disregarding their identification (indices), may be realized in the following number of combinations:

$$\boxed{\frac{N!}{M!(N-M)!}\ , \quad N! = 1\cdot 2\cdot 3 \ldots N\ .}$$

(M/N)

The probabilities (with *M=0,1,...,N*)

$$\boxed{\begin{aligned}&P(M \text{ particles are found in } V_o,\\ &\text{the remaining } N-M \text{ are outside of } V_0)\\ &=\frac{N!}{M!(N-M)!}\,p_0^M\,(1-p_0)^{N-M} \equiv P_N(M)\ .\end{aligned}}$$

(Binomial)

form binomial (Bernoulli) distribution, describing the chances of *M* successes in *N* independent trials.

The discrete random variable *M* has the mean value (mathematical expectation)

$$\langle M \rangle = \sum_{M=0}^{N} M \cdot P_N(M) = Np_0 = N \frac{V_0}{V} \ ,$$

the mean density is independent of the selected volume $V_0$

$$\boxed{n \equiv \frac{\langle M \rangle}{V_0} = \frac{N}{V} \ .}$$

(Dens)

These prediction is in agreement with the actual behavior of gasses, as they fill uniformly the available volume.

The irrational “horror vacui” (attributed to Aristotle) is not needed.

We are able to quantify expected deviations of the actually observed values from the mean; the proper quantity to use here is the square root of the dispersion – the second central moment - of (Binomial):

$$\Delta_M \equiv \sqrt{\left\langle \left( M - \langle M \rangle \right)^2 \right\rangle} = \sqrt{N p_0 (1 - p_0)} = \sqrt{N \frac{V_0}{V} (1 - \frac{V_0}{V})} \; .$$

The relative fluctuations of both number of particles and density are

$$\boxed{\frac{\Delta_M}{\langle M \rangle} = \frac{1}{\sqrt{N}} \sqrt{\frac{V - V_0}{V_0}} \; .}$$

(RelFluct)

In spite of typically very large values of *N*, the above results are usable owing to the Moivre-Laplace approximation of binomial probabilities:

$$\boxed{P_N(M) \approx \frac{1}{\sqrt{2\pi\sigma^2}} e^{\frac{-(M-Np_0)^2}{2\sigma^2}} \ , \ \sigma^2 = Np_0(1-p_0)\ .} \qquad \text{(M-L)}$$

We have here an approximation of the discrete probability distribution by a simple (Gaussian) continuous distribution. The standard deviation of the latter allows us to construct confidence intervals; obviously, the probability of finding the actually measured value of *M* in the intervals

$$\langle M \rangle \pm \sigma \quad \text{and} \quad \langle M \rangle \pm 2\sigma$$

is 0.863 and 0.954, respectively.

# Large number of random collisions – independent changes of *velocity* along *x, y, z*

Maxwell 1860: the probabilities of finding velocities in specified intervals
(1) are multiplied for $v_x$, $v_y$, $v_z$ (independence);
(2) depend on the magnitude of the vector of velocity (no preferences in directions)

$$f_x(v_x)dv_x\, f_y(v_y)dv_y\, f_z(v_z)dv_z = g(v^2)dv_x dv_y dv_z \ ,$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Property (1) requires an exponential form of the probability densities,

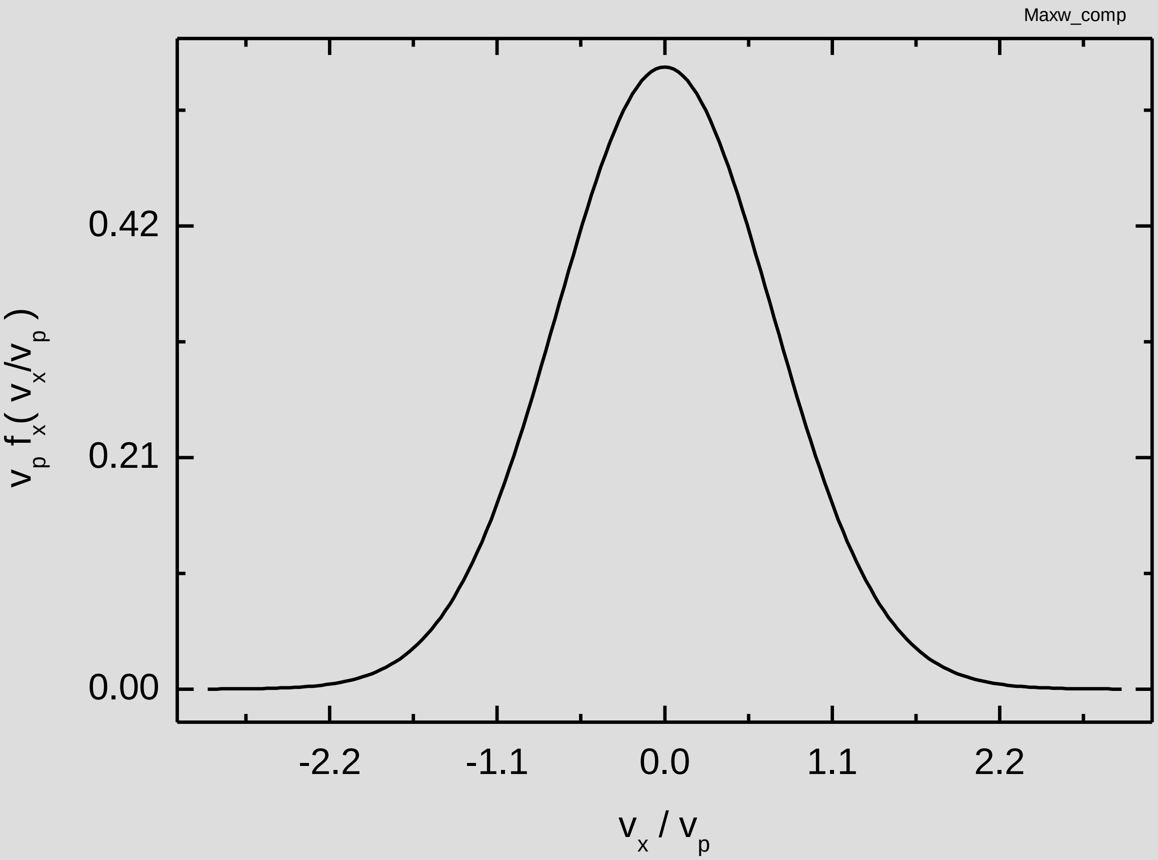
$$f_x(v_x) = const_1 e^{const_2 v_x^2} \ .$$

Using a convenient symbol for the (negative) second constant and setting the first constant to have the density normalized, we arrive at

$$\boxed{f_x(v_x) = \frac{1}{\sqrt{\pi} v_p} e^{-v_x^2/v_p^2} \ .}$$

(Maxw_comp)

The components of velocity are distributed normally; the probability density is $N(0,v_p^2/2)$.



The probability density of the magnitude of velocity results from the integration over all directions; in spherical coordinates,

$$dv_x dv_y dv_z = \mathrm{v}^2 \sin(\theta)\mathrm{dvd}\varphi\mathrm{d}\theta \ ,$$

it results from the probability

$$P(\text{magnitude of the velocity vector is between } v \text{ and } v + \mathrm{d}v) \equiv$$

$$f\,(v)\mathrm{d}v = \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi} \mathrm{d}\theta \; g(v^2) v^2 \sin(\theta)\mathrm{d}v \ .$$

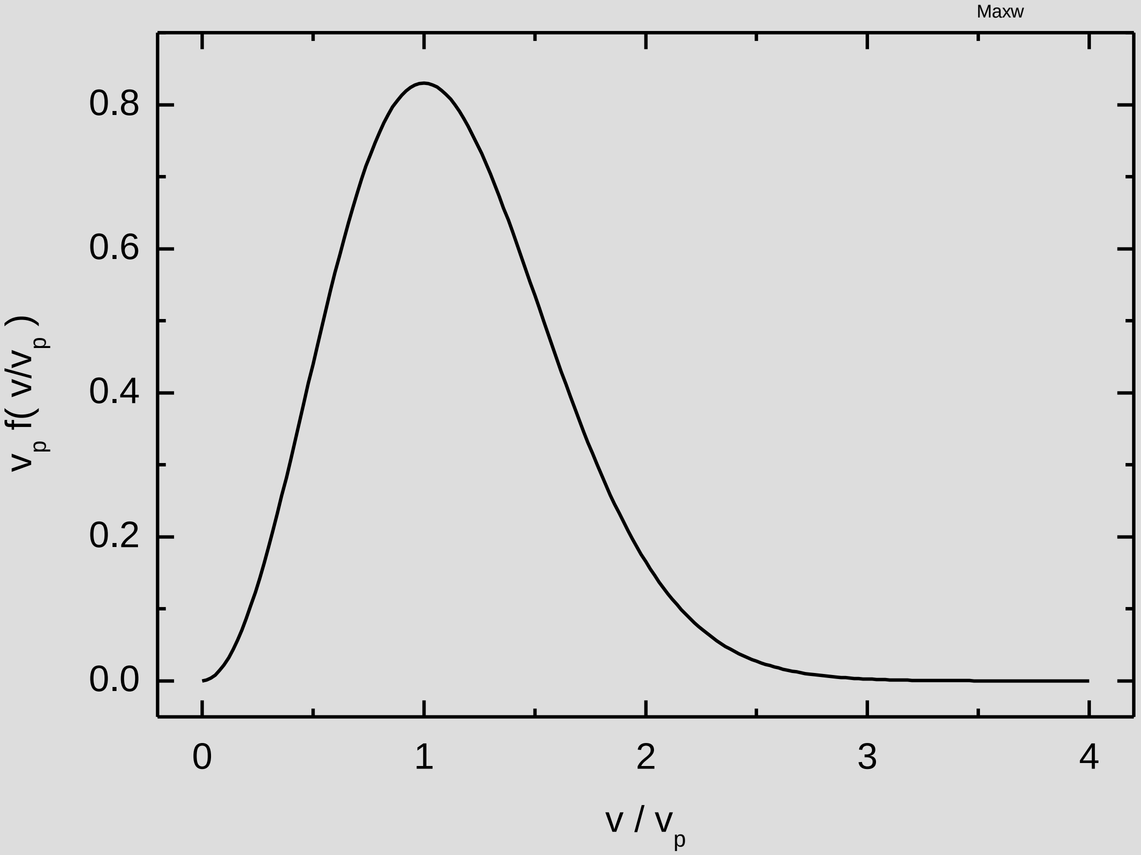
After inserting *g* as the product of three exponentials (Maxw_comp), the famous Maxwell distribution takes the form

$$\boxed{\begin{aligned} & f\,(v) = \frac{4}{\sqrt{\pi}v_p^3} v^2 e^{-v^2/v_p^2} \quad \text{for } v \geq 0 \ , \\ & f\,(v) = 0 \text{ for } v < 0 \ . \end{aligned}}$$

(Maxw)

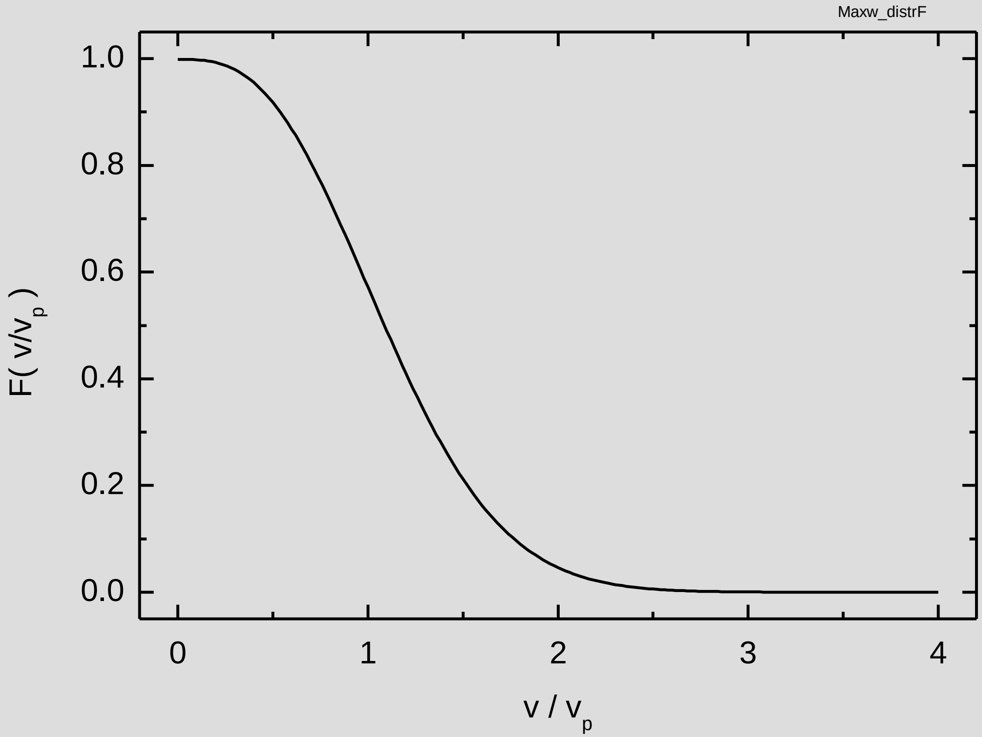
As this density has its maximum for $v/v_p=1$, $v_p$ is usually called the “most probable velocity”, in spite of $P(v=v_p)=0$.

# The magnitude of velocity in the three-dimensional space:

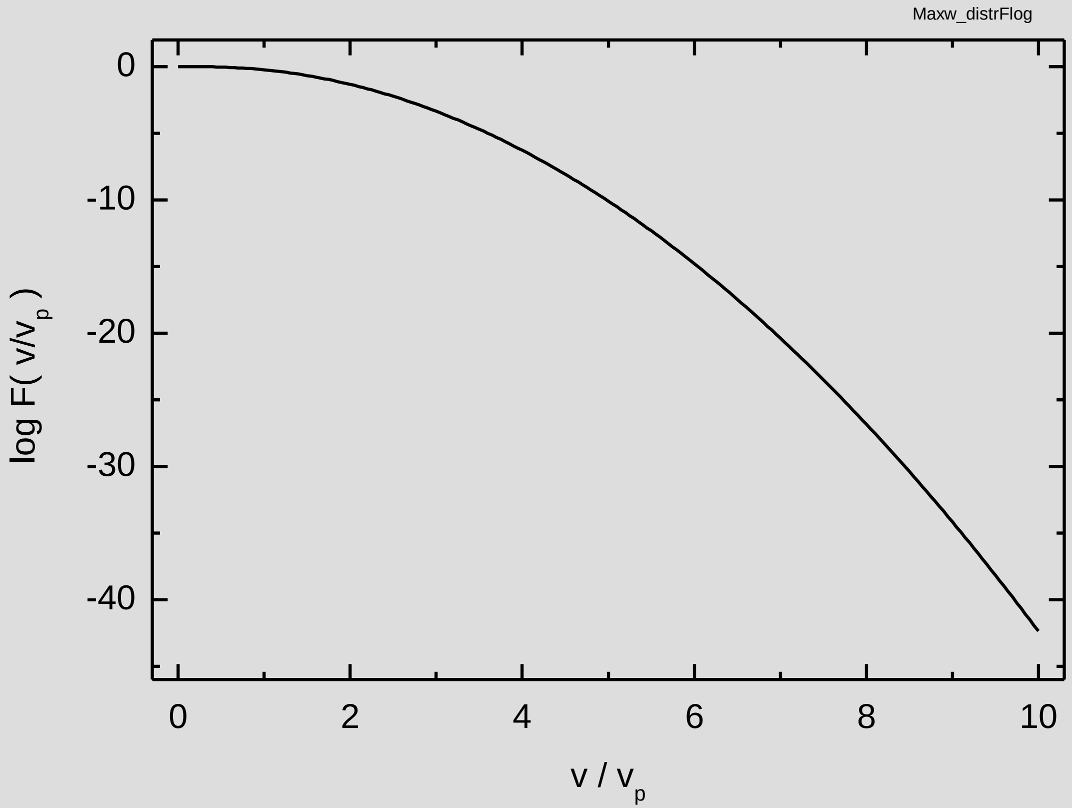


The probability of finding the magnitude of velocity larger than *v*:

$$F = 1 - \int_0^v f(t)dt \; :$$



The probability of finding the magnitude of velocity larger than $v$ - the chances of exceeding 10-times $v_p$ are really small:



An alternative way to Maxwell distribution

invokes the Central Limit Theorem of probability theory:
adding infinite number of independent random changes of any velocity component with (almost) arbitrary distribution produces Gaussian distribution; its mean is zero (no directional preference); denoting its standard deviation by $\sigma_x$, the probability density is

$$\boxed{f_x(v_x) = \frac{1}{\sqrt{2\pi}\sigma_x} e^{-v_x^2/2\sigma_x^2} \quad .}$$

(Maxw_comp)

The standard deviation of velocity component along *y* and *z* is the same; expressed in terms of $v_p$ :

$$\sigma_x = \sigma_y = \sigma_z = v_p / \sqrt{2} \ .$$

The kinetic energy is the linear function of the squares of velocity components are related to kinetic energy,

$$E = \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2) \equiv E_x + E_y + E_z \ .$$

The contribution of the movement along a selected direction to the kinetic energy is the random variable with the probability density obtained from the following probabilistic statement:

$$P(\text{the contribution along } x \text{ is between } E_x \text{ and } E + \mathrm{d}E_x) \equiv$$
$$g_x(E_x)\mathrm{d}E_x = 2 f_x(v_x)\mathrm{d}v_x \ , \ v_x > 0 \ .$$

Note the symmetric contributions of the movements with negative and positive signs of velocities, leading to the factor of 2 in the above relation.

Since

$$\mathrm{d}E_x / \mathrm{d}v_x = mv_x = \sqrt{2mE_x} \quad \text{for } v_x > 0 \ ,$$

the probability density of $E_x$ is

$$g_x(E_x) = \frac{2}{mv_x\sqrt{\pi}v_p} e^{-v_x^2/v_p^2} = \frac{1}{2\sqrt{\pi}E_p\sqrt{E_x/2E_p}} e^{-E_x/2E_p} \ \text{ for } E_x\!>\!0 \ \ ,$$

where $E_p = mv_p^2/4$ .

The probability density $h_x$ of the dimensionless energy $e_x = E_x/E_p$ is

$$h_x(e_x) = \frac{1}{2\sqrt{\pi}\sqrt{e_x/2}} e^{-e_x/2} \ \text{ for } e_x\!>\!0 \ \ ;$$

this is the $\chi^2$ distribution with one degree of freedom.

The probability density of

$E_x$ (1D movement, $n$=1),

$E_x + E_y$ (2D movement, $n$=2),

$E_x + E_y + E_z$ (3D movement, $n$=3),

after normalization to $E_p$, is $\chi^2(n)$:

$$g(x) = \frac{(x/2)^{(n-2)/2}}{2\Gamma(n/2)} e^{-x/2} \ ,$$

$$x > 0, \quad n = 1, 2, \ldots \ ,$$

$$E(x) = n, \ \ D(x) = 2n \ ;$$

Euler integral

of the 2nd kind,

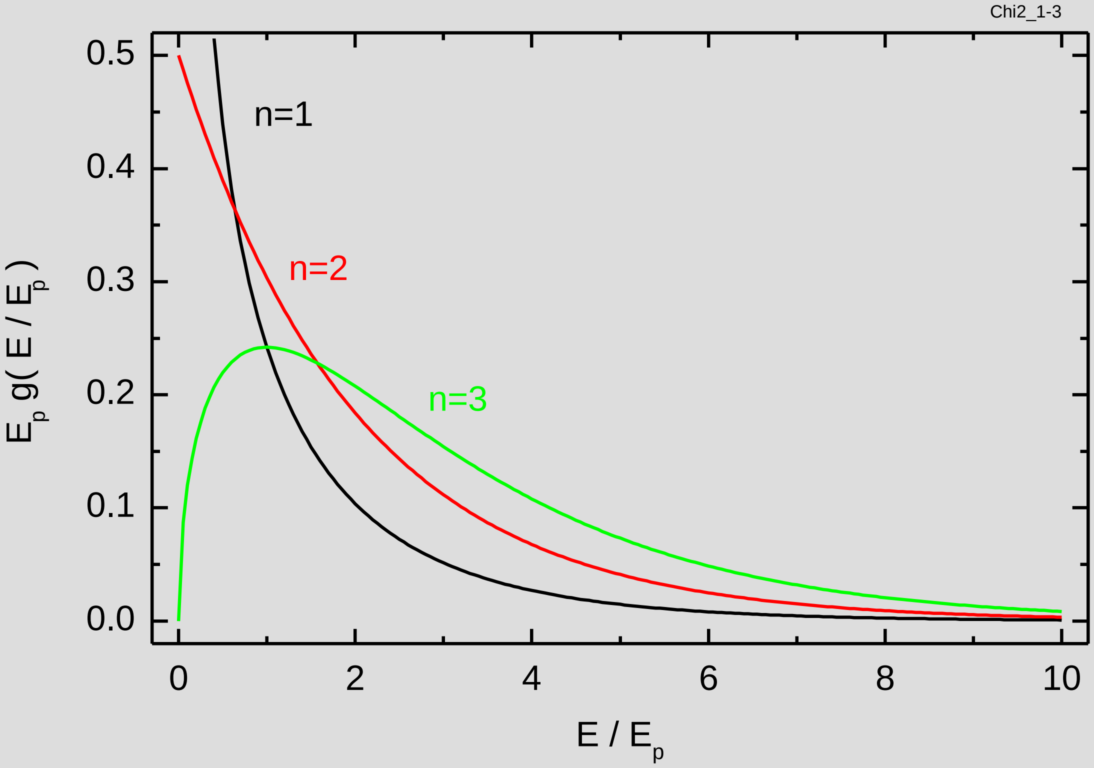
$$\Gamma(t) = \int_0^{\infty} x^{t-1} e^{-x} dx \ ,$$

ensures normalization;

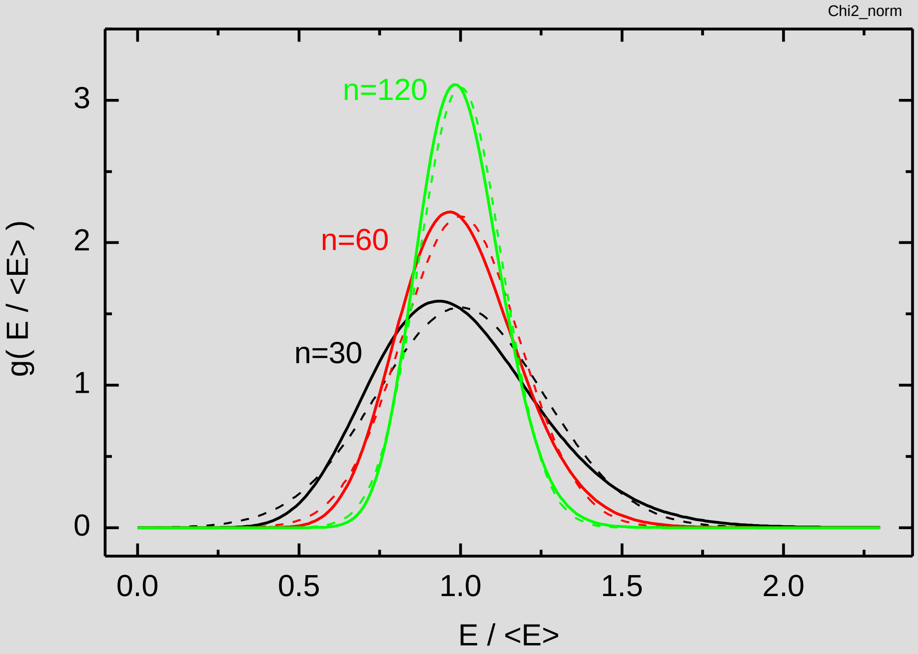
$$\Gamma(1/2) = \sqrt{\pi} \ ,$$

$$\Gamma(1) = 1 \ ,$$

$$\Gamma(t+1) = t\Gamma(t) \ .$$



Adding the energy of many particles leads to the $\chi^2(n)$ probability density with large numbers of freedom:
$\chi^2(n)$ converges (rather slowly) to $N(n, 2n)$ – dashed lines below for 10, 20 and 40 particles in 3D space



Note the narrowness of the distribution for any macroscopic piece of gas; relative fluctuations of the energy are of the order of

$$1/\sqrt{n}\ .$$

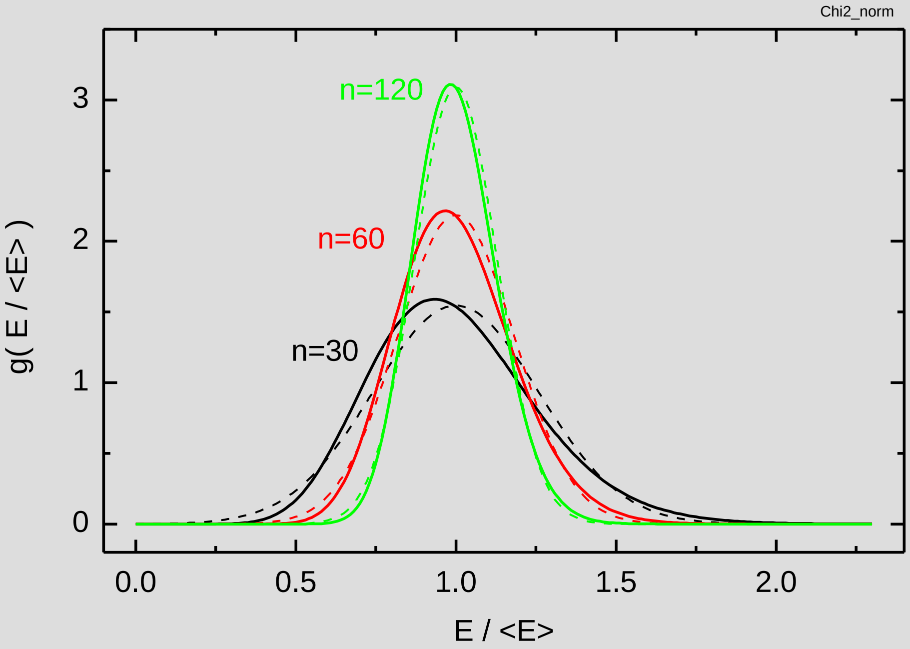
# Digression to “fitting models to data”:

the above exercise with the Gaussian and $\chi^2$ distributions is very useful in assessing the values of “best-fit deviations”, or minimal sum of squares,

$$SSQ = \frac{1}{n-k}\sum_{i=1}^{n}\left(\frac{y_i^{\text{measured}} - y_i^{\text{model}}}{\delta_i}\right)^2 ,$$

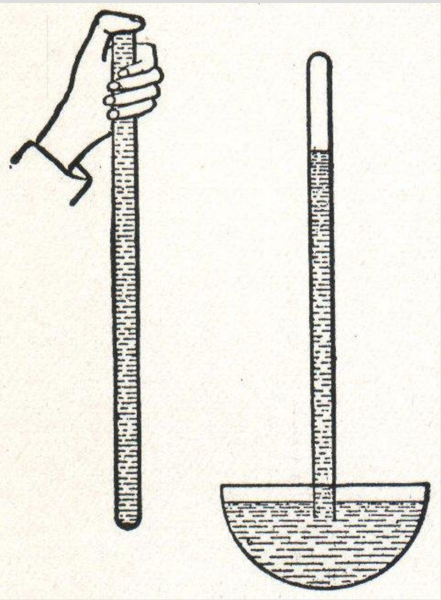
with $n$ data points

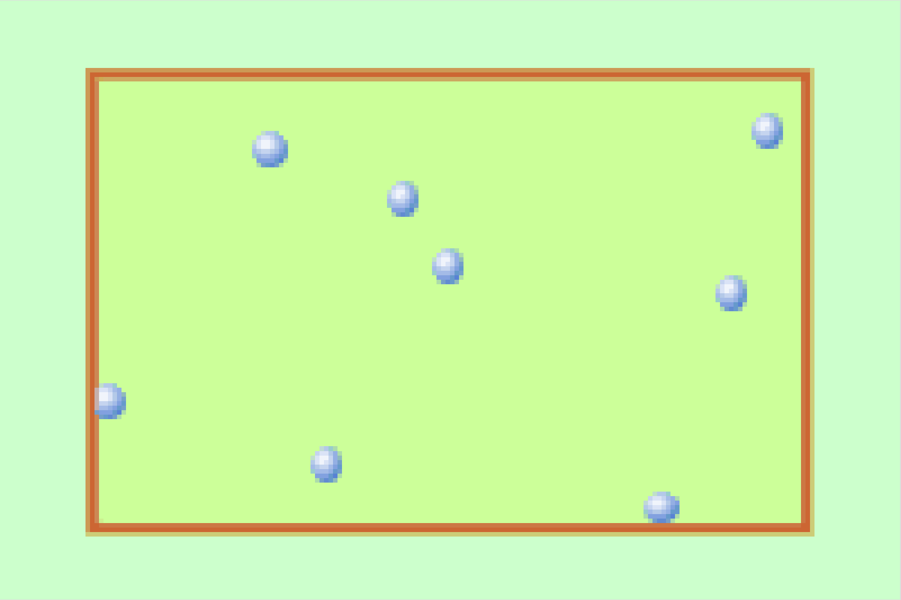
and $k$ model parameters.



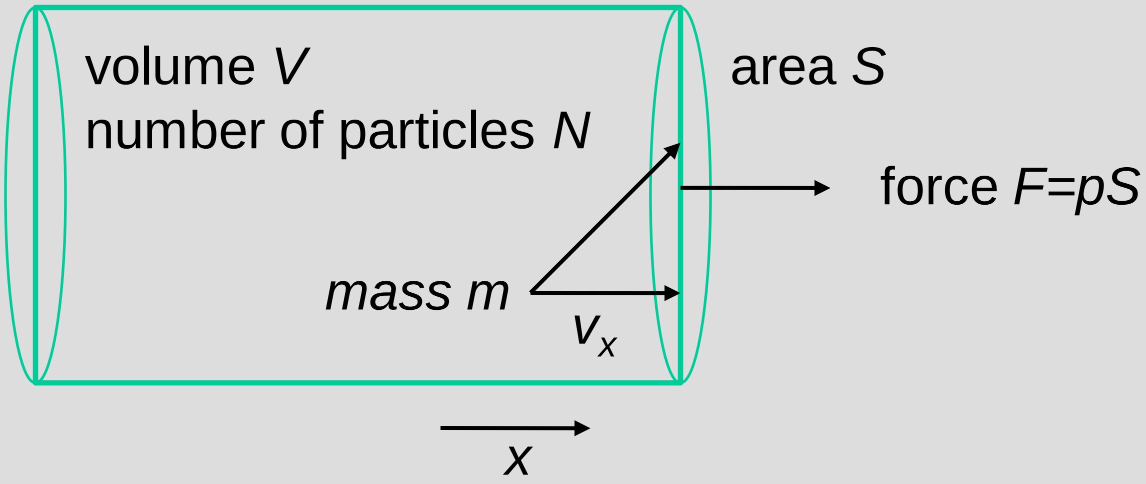
A range of values expected with a “reasonable probability” results from the above probability density.

# Pressure
# in classical gas





Elastic collisions with a pressure gauge, perpendicular to *x*, area S:



volume $V$

number of particles $N$

area $S$

force $F=pS$

mass $m$

$v_x$

$x$

The mean force is the mean momentum passed during $\tau$ divided by the time $\tau$:

$$F = \frac{1}{\tau}\int_0^\infty 2mv_x S\tau v_x \frac{N}{V} f_x(v_x)\mathrm{d}v_x$$

$$= \frac{2mSN}{\sqrt{\pi}V}\int_0^\infty \frac{v_x^2}{v_p}\exp\left(-\frac{v_x^2}{v_p^2}\right)\mathrm{d}v_x = \frac{mSN}{2V}v_p^2 \ .$$

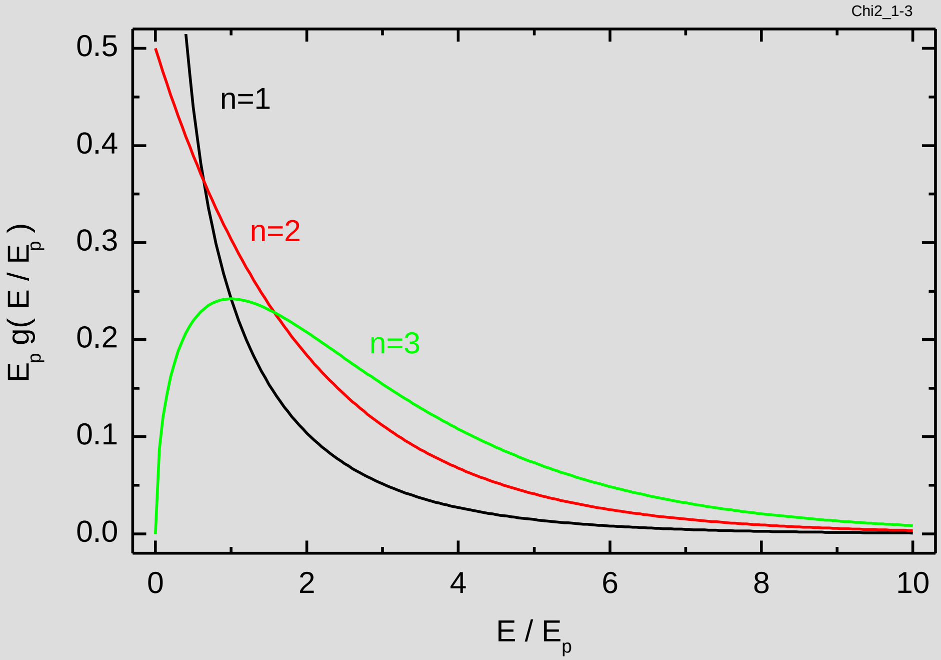
(Force)

Pressure is the force per unit area,

$$p = \frac{F}{S} = \frac{mN}{2V} v_p^2 = \frac{N}{V} \frac{1}{2} m v_p^2 \ ,$$

with the obvious proportionality to the gas density *N/V*.
Looking back at the meaning of $v_p$ and the distribution of energy,

$$E_p = m v_p^2 / 4 :$$



The mean (average, expectation) value of energy is

$E_p$, $2E_p$, and 3 $E_p$

for $n$= 1, 2, and 3, respectively (recall the $\chi^2(n)$ distribution).

The natural temptation is to express the pressure in terms of the mean value of kinetic energy of any single particle,

$$\langle E \rangle = 3E_p = \frac{3}{4} m v_p^2 \ ,$$

leading to

$$\boxed{p = \frac{N}{V}\frac{1}{2} m v_p^2 = \frac{N}{V}\frac{2}{3}\langle E \rangle \ .}$$

(Pressure)

“Pressure of the gas with Maxwellian distribution of velocities is 2/3 of the volume density of kinetic energy.”

Temperature *T* of the gas is *defined* by

$$\langle E \rangle = \frac{3}{2} k_B T \ ,$$

involving the Boltzmann constant $k_B$.

The internal energy (which is state variable) for the gas having *N* particles:

$$U = N\left\langle E \right\rangle = \frac{3}{2} N k_B T \ ,$$

$$U_{1mol} = N_A \left\langle E \right\rangle = \frac{3}{2} RT \ .$$

The probabilistic approach results in the relation between macroscopic (averaged) quantities:

$$\boxed{pV = N k_B T \ .}$$

(Equation of state)

Repeated measurements may reveal "fluctuations", governed by the involved probability distributions.

The microscopic model predicts the heat capacity at constant volume (with vanishing work *pdV*) :

$$\boxed{C\Big|_V \equiv \frac{\delta Q}{\Delta T}\Big|_V = \frac{\Delta U}{\Delta T}\Big|_V = \frac{3}{2} N k_B \ .}$$

(C_V)

It is independent of temperature and the mass of the (pointlike) particles. The numerical value is about 12.5 J/(mol.K).

More generally:
the expectation value of energy per one quadratic term in Hamiltonian is

$$\frac{k_B T}{2} \ ,$$

leading to the contribution to $C_V$ of $\frac{k_B}{2}$ .

This is very often in harsh contradiction with the actual behavior of matter; repaired by using quantum physics instead of the classical.

# Boson gas at equilibrium

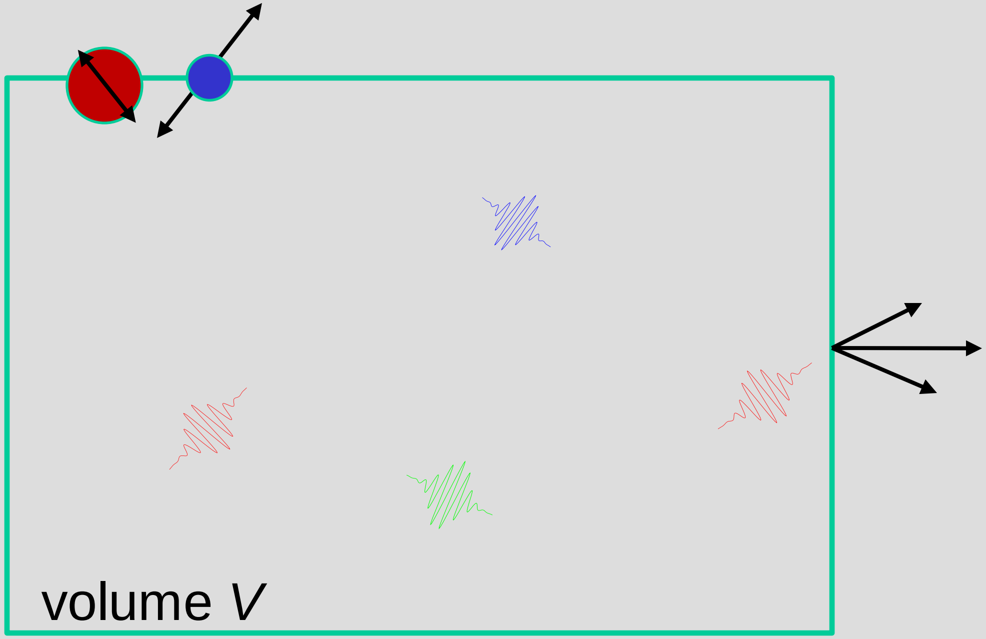
- blackbody radiation

- Bose-Einstein condensation in alkali vapors

- vibrations, heat capacity

# Blackbody radiation – quantum gas

moving charges (electrons and nuclei) in the walls of a cavity produce electromagnetic radiation



volume *V*

a small opening, detector(s)

photon counting possible

The electromagnetic field can be decomposed into modes travelling with the speed of light *c* -
frequency, period, angular frequency, wavelength, wavenumber:

$$f = \frac{1}{T} = \frac{\omega}{2\pi} = \frac{c}{\lambda} = ck \ .$$

The spectral density of modes is

$$D(\omega) \equiv \frac{\text{number of modes with frequency from } \omega \text{ to } \omega + \Delta\omega}{\Delta\omega} = \frac{\omega^2 V}{\pi^2 c^3} \ .$$

In classical physics, each of the modes has the mean energy of $k_B T$ ($k_B T$ /2 for each of the two polarization states); this predicts the diverging spectral density of internal energy

$$\boxed{u(\omega) = \frac{\omega^2 V}{\pi^2 c^3} k_B T \ .}$$

(Rayleigh-Jeans)

# Planck 1900

Energy appears in multiples of quanta,

$$E_n = n\hbar\omega, \;\; n = 0,1,2,\ldots \quad .$$

Each of them occurs with the *canonical* probability *P(E$_n$)*, dependent on its value and the temperature of the thermal bath (the container surrounding the blackbody cavity):

$$\boxed{P(E_n) = \frac{\exp\left(-E_n / k_B T\right)}{\sum_{n=0}^{\infty} \exp\left(-E_n / k_B T\right)} \quad .}$$

(DiscreteE)

The expectation value of the random variable *E$_n$* is

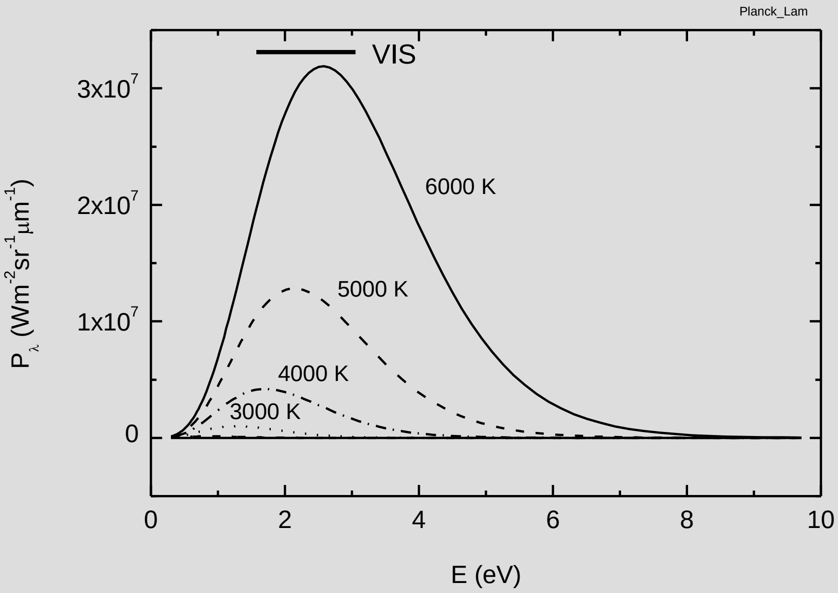
$$\langle E \rangle = \sum_{n=0}^{\infty} E_n P(n) = \frac{\hbar\omega \sum_{n=0}^{\infty} n \exp\left(-E_n / k_B T\right)}{\sum_{n=0}^{\infty} \exp\left(-E_n / k_B T\right)} = \hbar\omega \frac{1}{\exp\left(\hbar\omega / k_B T\right) - 1} \quad .$$

Combined with the spectral density of modes, it leads to the famous Planck formula for the spectral density:

$$\boxed{u(\omega)=\frac{V}{\pi^2c^3}\frac{\hbar\omega^3}{\exp\left(\hbar\omega/k_BT\right)-1}\ .}$$

(Planck)

The corresponding power density for several values of temperature:



We can easily consider the limiting case of neglecting the discrete structure of “energy levels” of the random variable *$E_n$* in (DiscreteE); using a continuous random variable with the exponential probability density

$$f(E)=\frac{\exp\left(-E/k_BT\right)}{k_BT}\ ,\ E>0\ ,$$

the mean of energy is

$$\left\langle E\right\rangle=\int_0^\infty Ef(E)dE=k_BT$$

and we arrive at the classical (Rayleigh-Jeans) formula. The criterion for the possibility to neglect the quantum effects is obvious from the following Taylor expansion:

$$\text{for } \hbar\omega<<k_BT, \exp\left(\hbar\omega/k_BT\right)\approx1+\hbar\omega/k_BT\ , \text{ and}$$

$$\left\langle E\right\rangle\approx k_BT\ .$$

# A nearly perfect blackbody is our Universe – CMB (Cosmic Microwave Background):

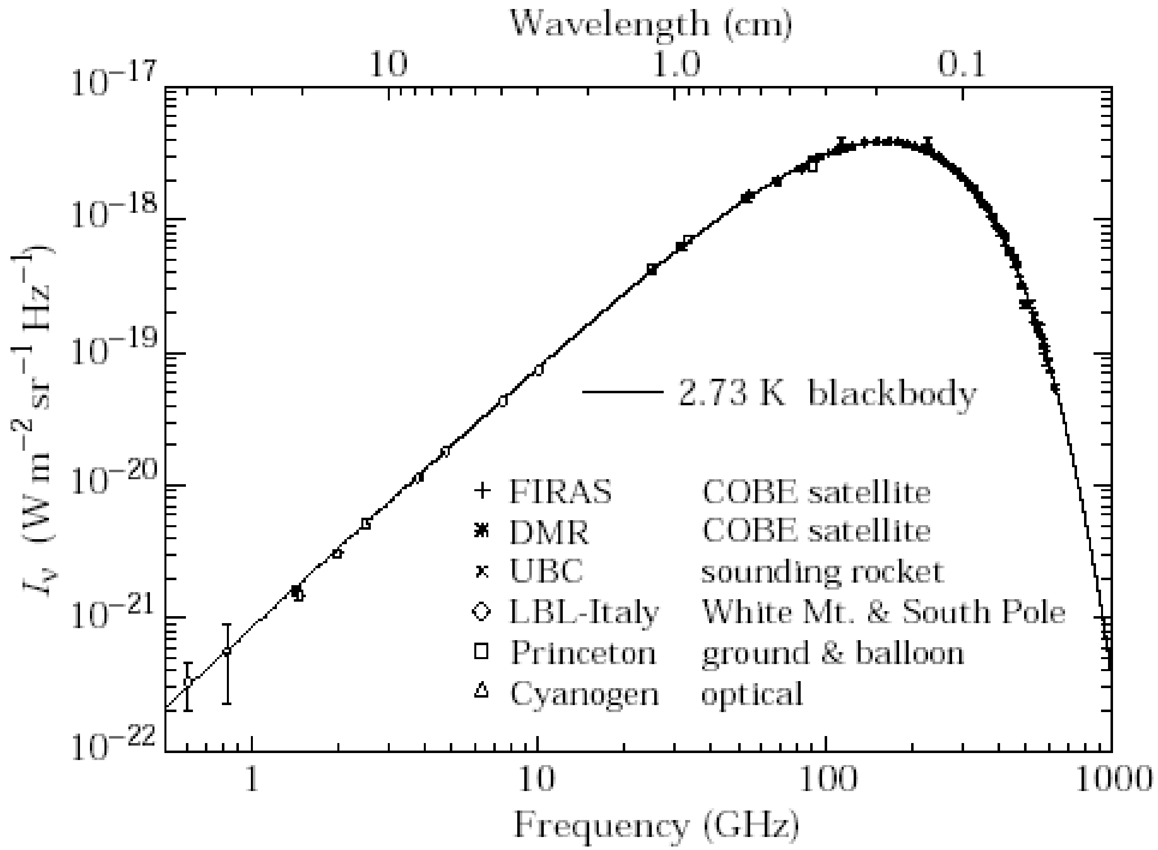


**Figure 1:** Precise measurements of the CMB spectrum. The line represents a 2.73 K blackbody, which describes the spectrum very well, especially around the peak of intensity. The spectrum is less well constrained at 10cm and longer wavelengths. (References for this figure are at the end of this section under "CMB Spectrum References.")

# In a more critical confrontation of the measured data and Planck law:

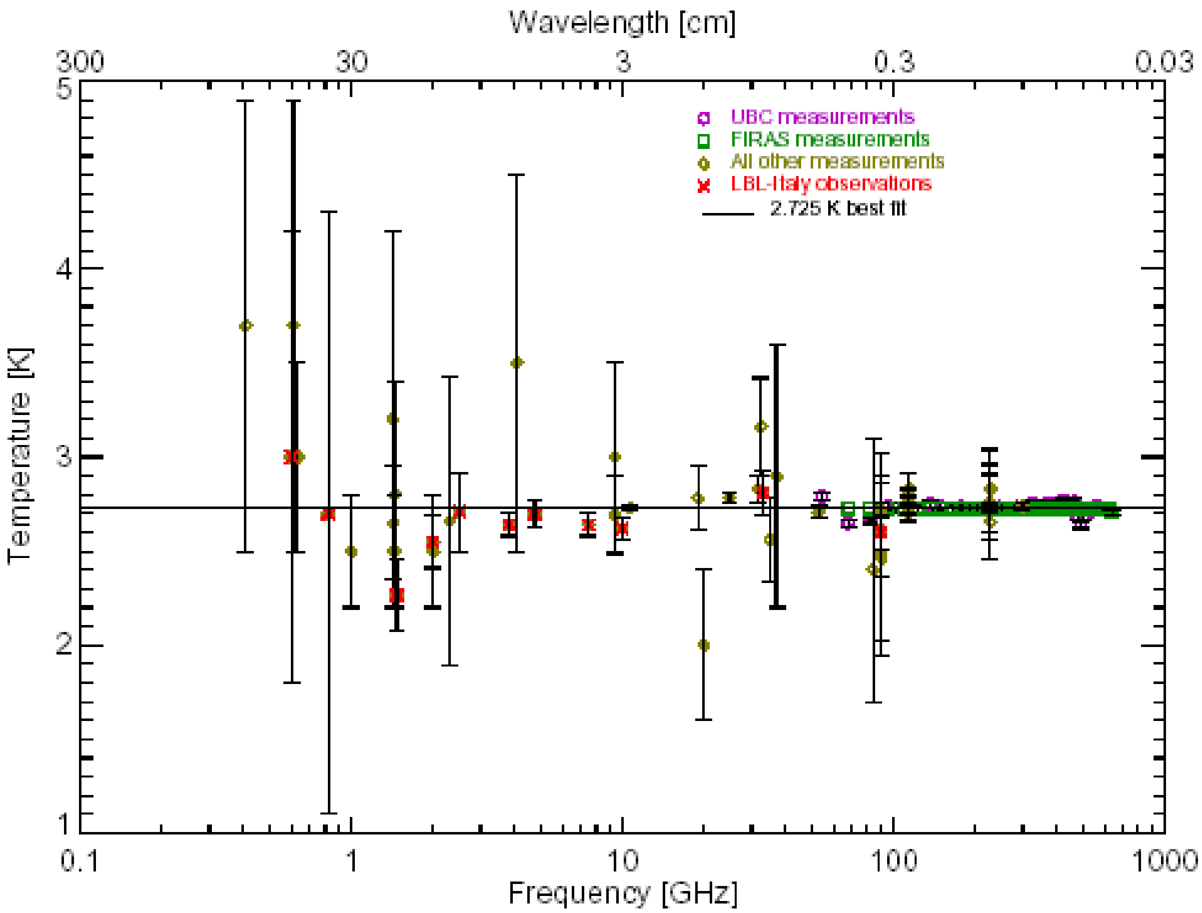
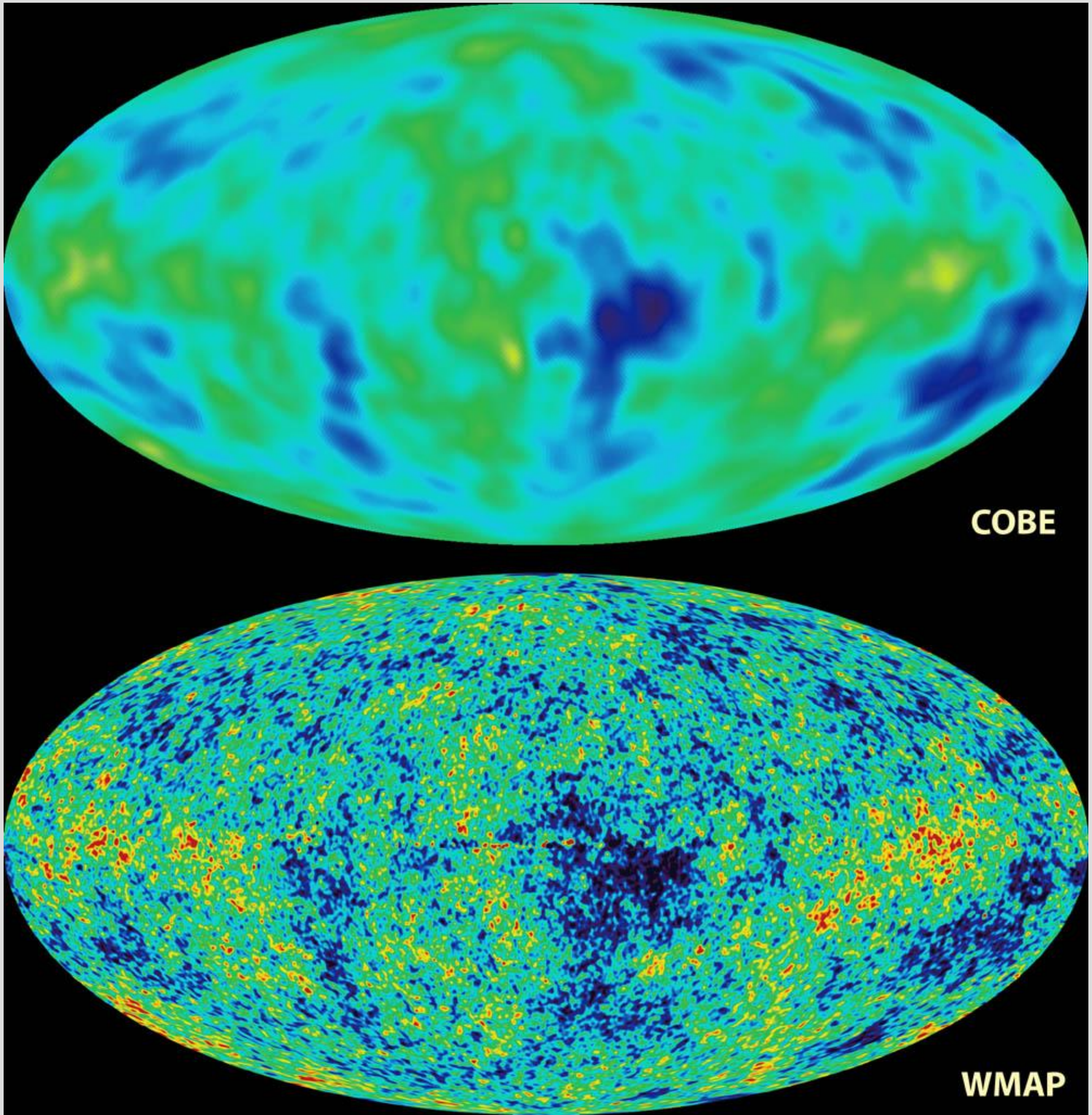
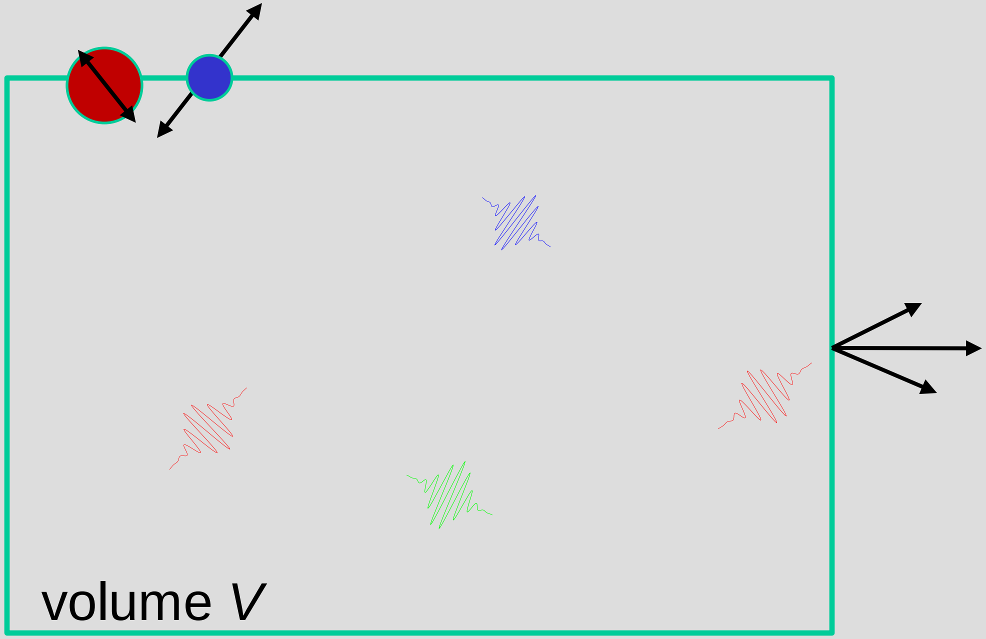


**Figure 2:** Precise measurements of the CMB spectrum, plotted in thermodynamic temperature units (in color). Again the line represents a 2.73 K blackbody, and the references for the experiments can be found at the end.

Even anisotropies of CMB are observable from satellites:



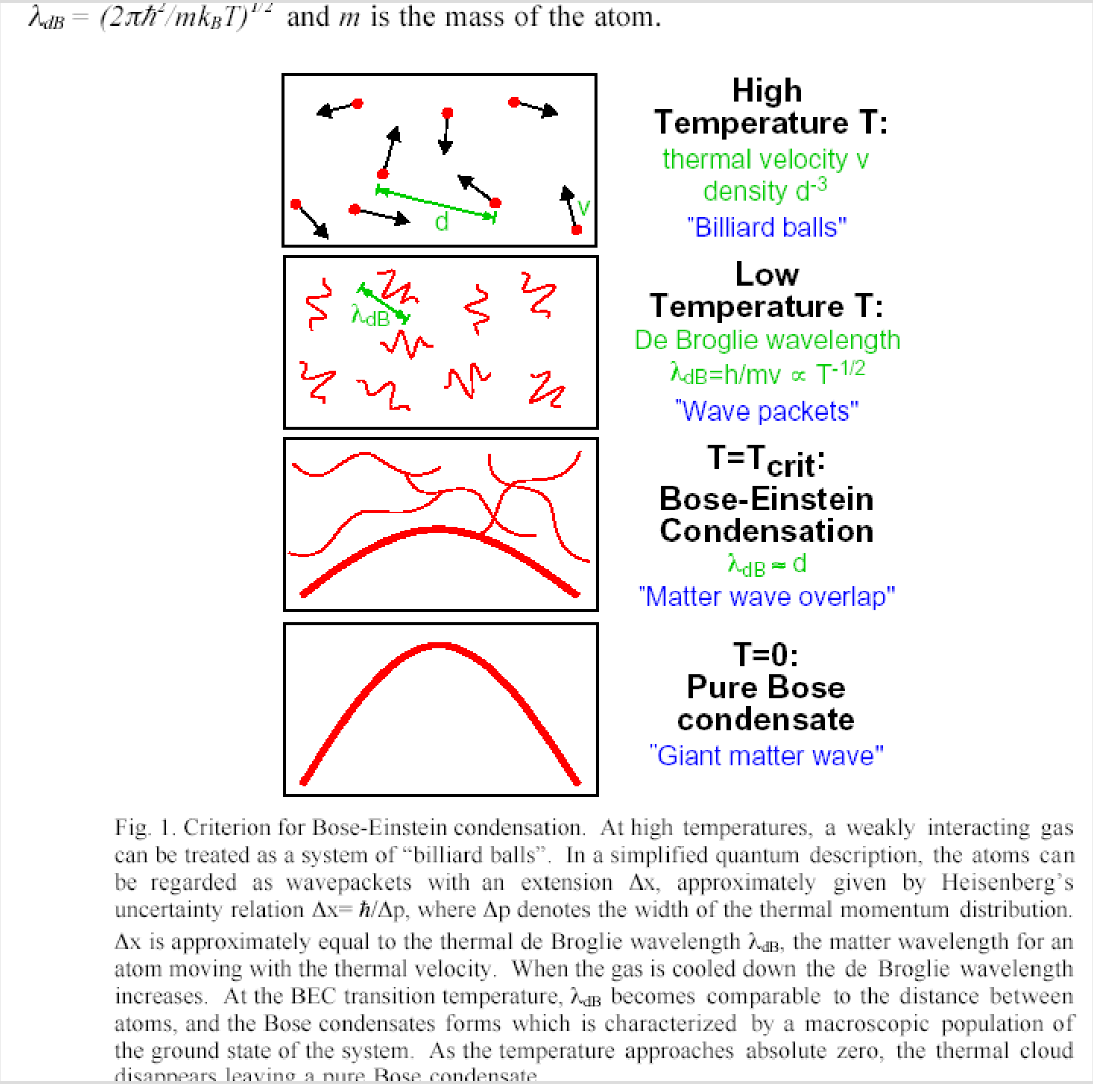
Blackbody radiation shows clearly the wave→particle direction of the quantum-mechanical dualism (in the ultrarelativistic bosonic gas): we can count the photons



a small opening,
detector(s)

photon counting
possible

The opposite direction, particle→wave, of the quantum-mechanical dualism has been confirmed many times; it shows up even in “real” gases in Bose-Einstein condensation of vapors of alkali vapors:



$\lambda_{dB} = (2\pi\hbar^2/mk_BT)^{1/2}$ and $m$ is the mass of the atom.

**High Temperature T:**
thermal velocity v
density $d^{-3}$
"Billiard balls"

**Low Temperature T:**
De Broglie wavelength
$\lambda_{dB}=h/mv \propto T^{-1/2}$
"Wave packets"

**$T=T_{crit}$:**
**Bose-Einstein Condensation**
$\lambda_{dB} \approx d$
"Matter wave overlap"

**T=0:**
**Pure Bose condensate**
"Giant matter wave"

Fig. 1. Criterion for Bose-Einstein condensation. At high temperatures, a weakly interacting gas can be treated as a system of “billiard balls”. In a simplified quantum description, the atoms can be regarded as wavepackets with an extension $\Delta x$, approximately given by Heisenberg’s uncertainty relation $\Delta x = \hbar/\Delta p$, where $\Delta p$ denotes the width of the thermal momentum distribution. $\Delta x$ is approximately equal to the thermal de Broglie wavelength $\lambda_{dB}$, the matter wavelength for an atom moving with the thermal velocity. When the gas is cooled down the de Broglie wavelength increases. At the BEC transition temperature, $\lambda_{dB}$ becomes comparable to the distance between atoms, and the Bose condensates forms which is characterized by a macroscopic population of the ground state of the system. As the temperature approaches absolute zero, the thermal cloud disappears leaving a pure Bose condensate.

Sodium
at MIT,
Rubidium
at Boulder, CO

Nobel prize
2001

from
“Experimental studies of Bose-Einstein condensation”
Durfee and Ketterle, 1998

Very small temperature and large density is required for the significant overlap of the wave functions.

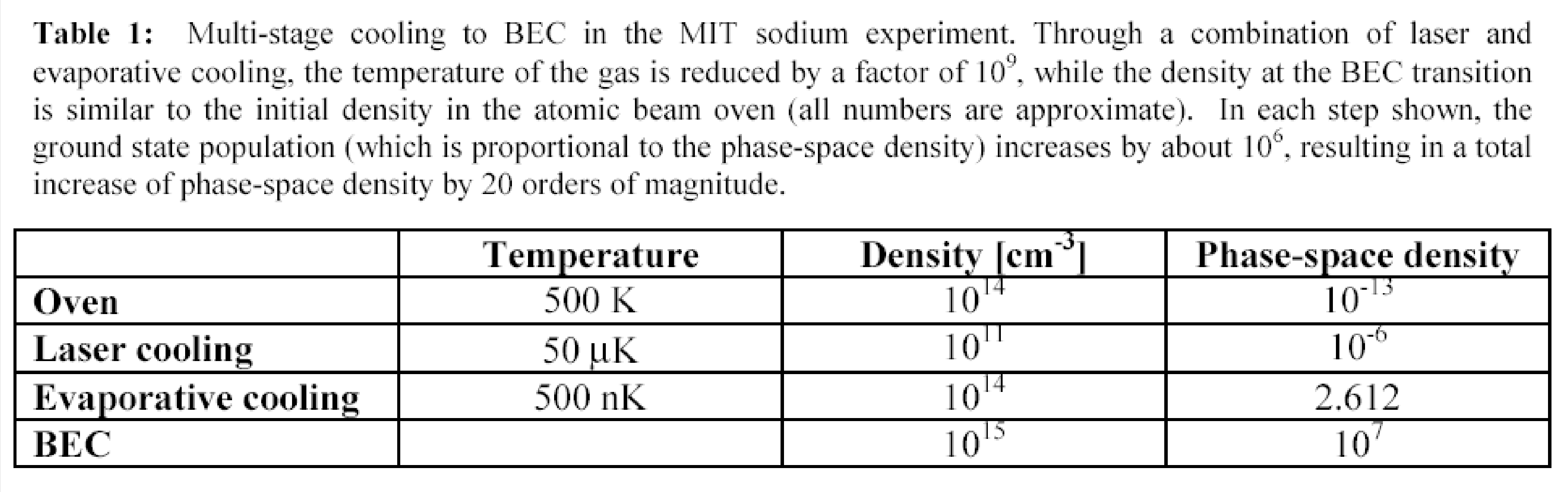
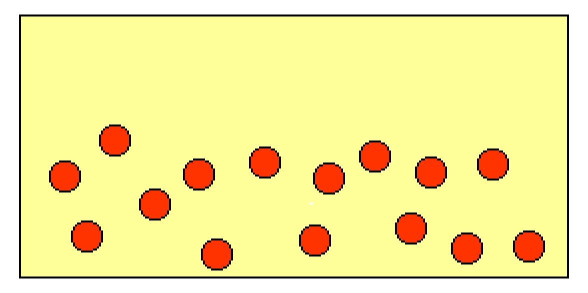


**Table 1:** Multi-stage cooling to BEC in the MIT sodium experiment. Through a combination of laser and evaporative cooling, the temperature of the gas is reduced by a factor of $10^9$, while the density at the BEC transition is similar to the initial density in the atomic beam oven (all numbers are approximate). In each step shown, the ground state population (which is proportional to the phase-space density) increases by about $10^6$, resulting in a total increase of phase-space density by 20 orders of magnitude.

| | **Temperature** | **Density [cm$^{-3}$]** | **Phase-space density** |
|---|---|---|---|
| **Oven** | 500 K | $10^{14}$ | $10^{-13}$ |
| **Laser cooling** | 50 μK | $10^{11}$ | $10^{-6}$ |
| **Evaporative cooling** | 500 nK | $10^{14}$ | 2.612 |
| **BEC** | | $10^{15}$ | $10^{7}$ |

## The phonon gas and lattice heat capacity

in condensed matter (solids and liquids) the internal motion is vibrational



In the harmonic approximation, the energy is a quadratic function of momenta, *p*, and displacements, *q*:

$$H\left(\{q\},\{p\}\right)=\sum_{i=1}^{f}\frac{p_i^2}{2m_i}+\frac{1}{2}\sum_{i,j=1}^{f}\frac{\partial^2 U}{\partial q_i \partial q_j}q_i q_j\ .$$

The crystal symmetry allows us to find a transformation to normal coordinates {*Q*,*P*}, leading to a set of *f* independent harmonic oscillators, with

$$H\left(\{Q\},\{P\}\right)=\sum_{i=1}^{f}\left(\frac{P_i^2}{2M_i}+\alpha_i Q_i^2\right).$$

The (quantum) harmonic oscillators have equidistantly-spaced energies

$$E_n^{(i)} = \hbar\omega_i \left( n + \frac{1}{2} \right) .$$

We have included the zero-point energy

$$E_0^{(i)} = \frac{\hbar\omega_i}{2} \quad .$$

The mathematical expectation of the energy of *i*-th oscillator is

$$\langle E_i \rangle = \frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i}{\exp\left(\hbar\omega / k_B T\right) - 1} \quad ,$$

giving the total internal energy of

$$U \equiv \langle E \rangle = \sum_{i=1}^{f} \left[ \frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i}{\exp\left(\hbar\omega_i / k_B T\right) - 1} \right] .$$

The famous Einstein model gave the correct qualitative result for the vanishing low-temperature heat capacity $C_V$, assuming an identical value of the frequency for all of the oscillators:

$$U = f\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp\left(\hbar\omega/k_BT\right)-1}\right],$$

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = fk_B\left(\hbar\omega/k_BT\right)^2 \frac{\exp\left(\hbar\omega/k_BT\right)}{\left[\exp\left(\hbar\omega/k_BT\right)-1\right]^2}\ .$$

The heat capacity vanishes for vanishing $T$:

$$C_V \approx fk_B\left(\hbar\omega/k_BT\right)^2 \exp\left(-\hbar\omega/k_BT\right) \ \text{ for } \ \hbar\omega >> k_BT\ .$$

The high-temperature behavior of this model leads to the classical (Dulong-Petit) rule, as the mean energy is $k_BT/2$ for each quadratic term in energy:

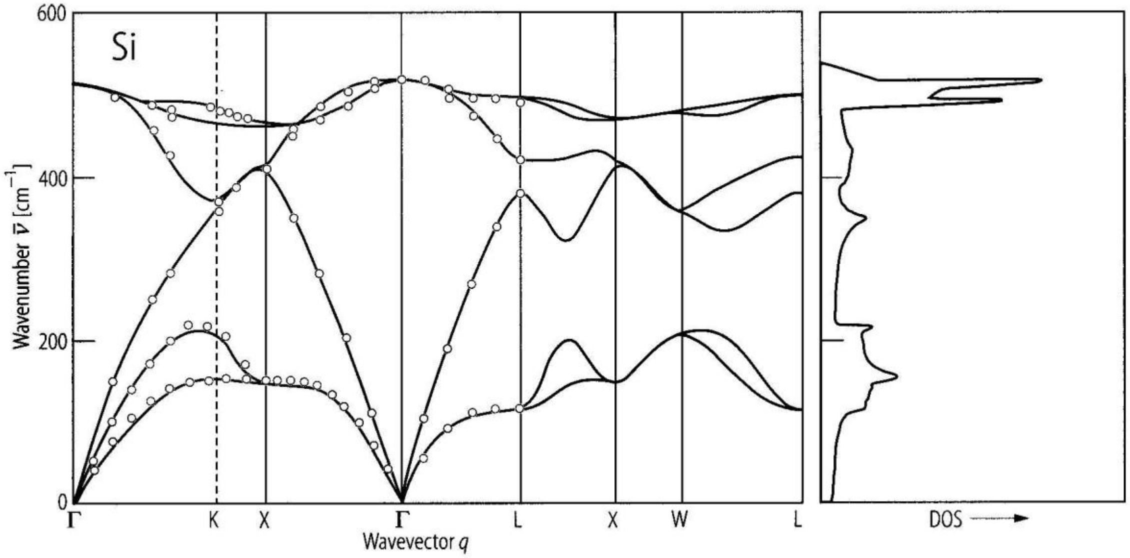
$$C_V \approx fk_B = 3Nk_B \ \text{ for } \ \hbar\omega << k_BT\ .$$

Here $N$ is the number of atoms, each of them contributes 3 to the number of degrees of freedom $f$.

# The actual frequencies, e.g., crystalline silicon:

**Fig. 1.2.8**

Si. Phonon dispersion curves (left panel) and phonon density of states (right panel) [91G]. Experimental data points [63D], [72N2] and ab-initio calculations [91G].



A major improvement here is that of Debye, assuming a spectrum of frequencies from zero to $\omega_{\max}$, which is an empirical parameter of the theory. The quadratic density of vibrational states results from the following development:

$$E_{\max} = \hbar\omega_{\max} \ , \quad E = v\hbar k = vp \ ;$$

$$D(E) = 4\pi\left[\frac{2}{\left(hv_{trans}\right)^3} + \frac{1}{\left(hv_{long}\right)^3}\right]VE^2 \quad \text{, for } \ E \in (0, E_{\max}) \ .$$

Two degenerate (transverse) vibrational branches and one longitudinal branch are assumed to differ in their velocities v. The number of modes is 3-times the number of atoms *N*; consequently

$$3N = \int_0^{E_{\max}} D(E)dE = \frac{4\pi V}{\left(hv_{eff}\right)^3}E_{\max}^3 \quad ,$$

$$\text{with} \quad \frac{1}{v_{eff}^3} = \frac{1}{3}\left(\frac{2}{v_{trans}^3} + \frac{1}{v_{long}^3}\right) \ .$$

This maximum energy is usually expressed in terms of the Debye frequency or Debye temperature:

$$E_{\max} = h v_{eff} \left( \frac{3N}{4\pi V} \right)^{1/3} = \hbar \omega_D = k_B T_D \ .$$

The mean energy (without zero-point vibrations) is

$$\langle E \rangle = \int_0^{E_{\max}} E \frac{D(E)}{\exp\left(E / k_B T\right) - 1} dE = 9 N k_B \left( \frac{T}{T_D} \right)^3 T \int_0^{E_{\max}} \frac{u^3}{\exp\left(u\right) - 1} du \ ,$$

and the vibrational heat capacity

$$C_V = 9 N k_B \left( \frac{T}{T_D} \right)^3 \int_0^{T_D / T} \frac{u^4 \exp\left(u\right)}{\left(\exp\left(u\right) - 1\right)^2} du \ .$$

The low-temperature limit is in accordance with the experimental $T^3$ dependence:

$$C_V \approx \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D}\right)^3 \quad \text{for } T << T_D \ .$$

At high temperatures, the Dulong-Petit rule with a temperature-dependent correction results:

$$C_V \approx\sim 3Nk_B \left[1 - \frac{1}{20}\left(\frac{T_D}{T}\right)^2 + \ldots\right] \quad \text{for } T >> T_D \ .$$

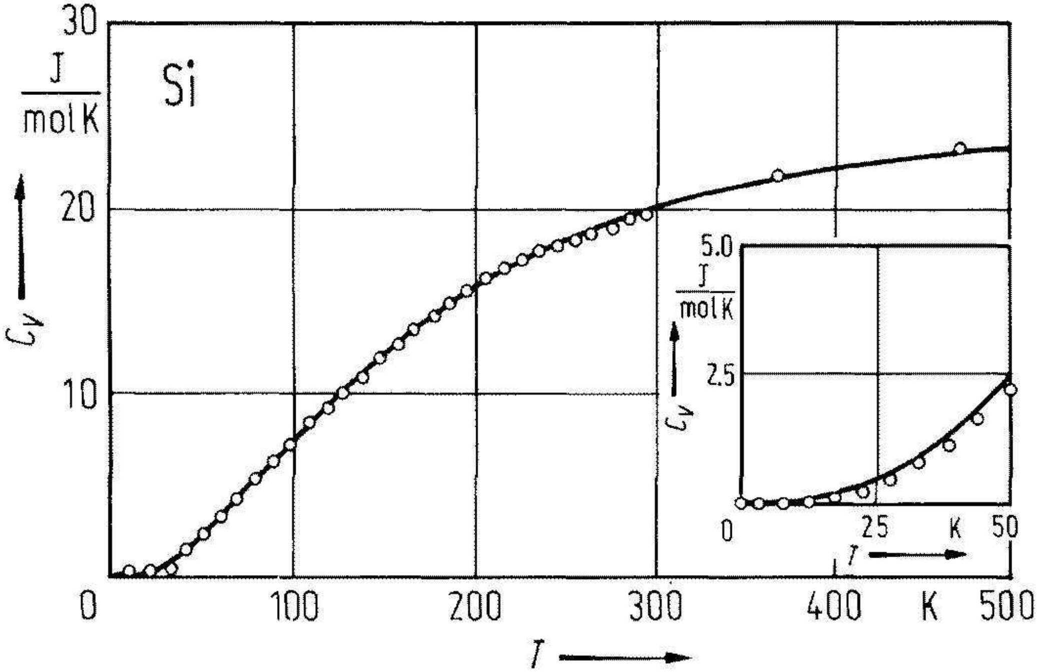
The classical limit of molar heat capacity at constant volume is

$$C_V = 3N_A k_B = 3 * 6.022E23 \ \frac{1}{\text{mol}} * 1.38E-23 \ \frac{\text{J}}{\text{K}} = 24.9 \ \frac{\text{J}}{\text{K}} \ .$$

The measured heat capacity of crystalline silicon. Note that the phonon gas shows pretty much the <u>quantum behavior even at room temperature</u>:

**Fig. 1.2.16**

Si. Heat capacity at constant volume vs. temperature. Fig. from [85K].

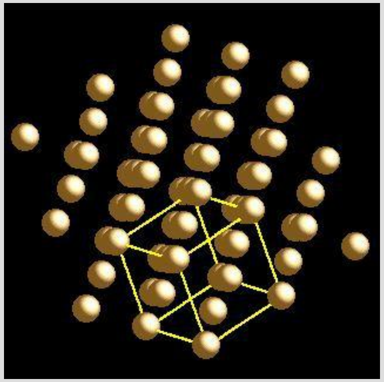


# Fermi gas at equilibrium

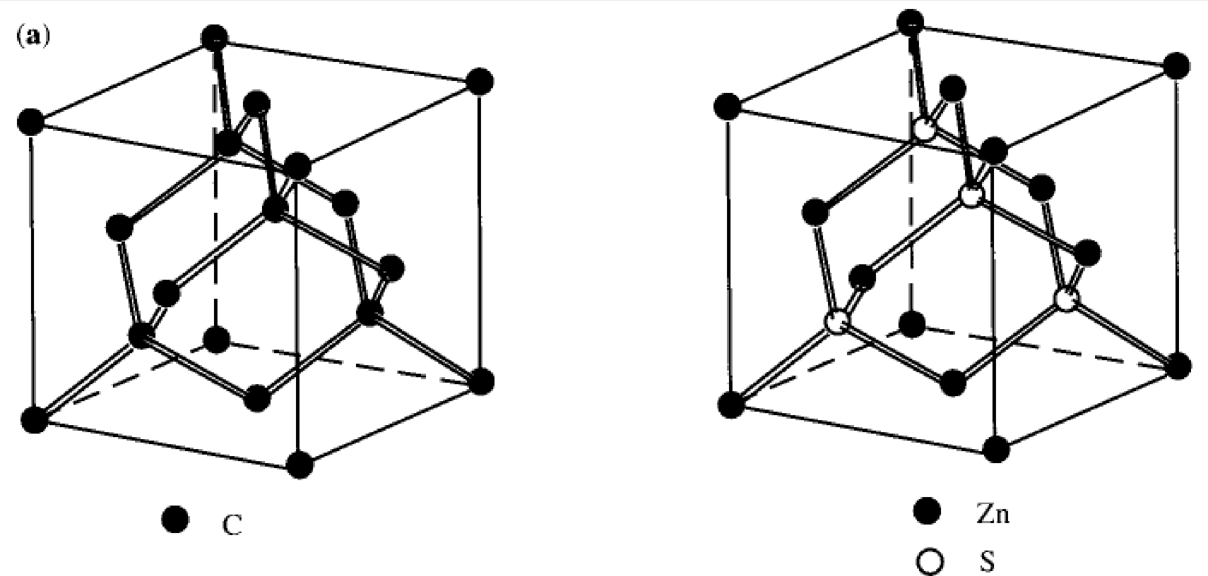
- electrons in metals  and semiconductors
- Fermi-Dirac statistics and its classical limit
- optical response of free electrons and interband transitions
- surface plasmon resonance

# Electrons in solids might be mobile

Metals – mostly cubic (BCC or FCC) lattice, e.g., gold:



Semiconductors – typically diamond and zincblende lattice:

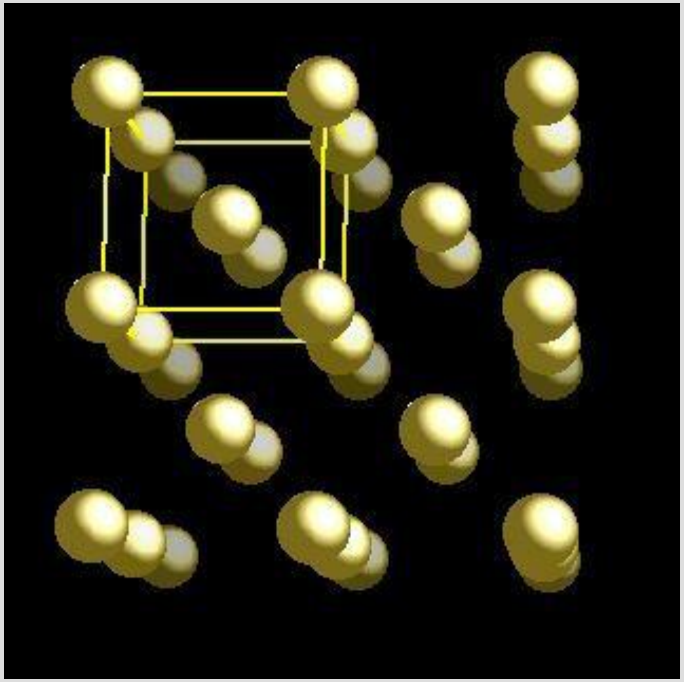


# A textbook metal - Sodium

“the simplest of simple metals”
body-centered cubic structure at RT, a=0.4230 nm

the concentration of atoms (and free electrons, provided the single valence electron of each atom is free):

$$n = \frac{2}{a^3} = 26.4\ \text{nm}^{-3} = 2.64\times10^{22}\ \text{cm}^{-3}$$



# Sodium – the apparent Fermi gas of valence electrons

free (non-interacting) particles, with the momentum and kinetic energy with *effective* mass

$$p = m^* v = \hbar k\ ,\quad E = \frac{p^2}{2m^*} = \frac{\hbar^2 k_F^2}{2m^*}$$

At zero temperature, the available states are occupied up to the Fermi energy

$$E_F = \frac{\hbar^2 k_F^2}{2m_0} = 5.18E-19\ \text{J} = 3.23\ \text{eV} = 0.238\ \text{Ry}$$

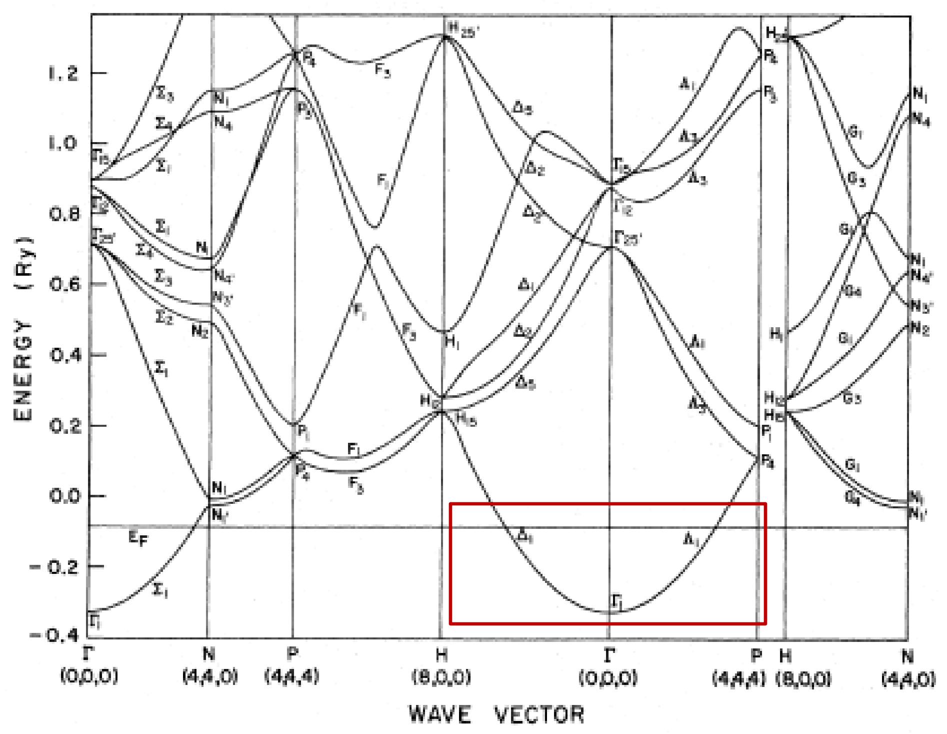
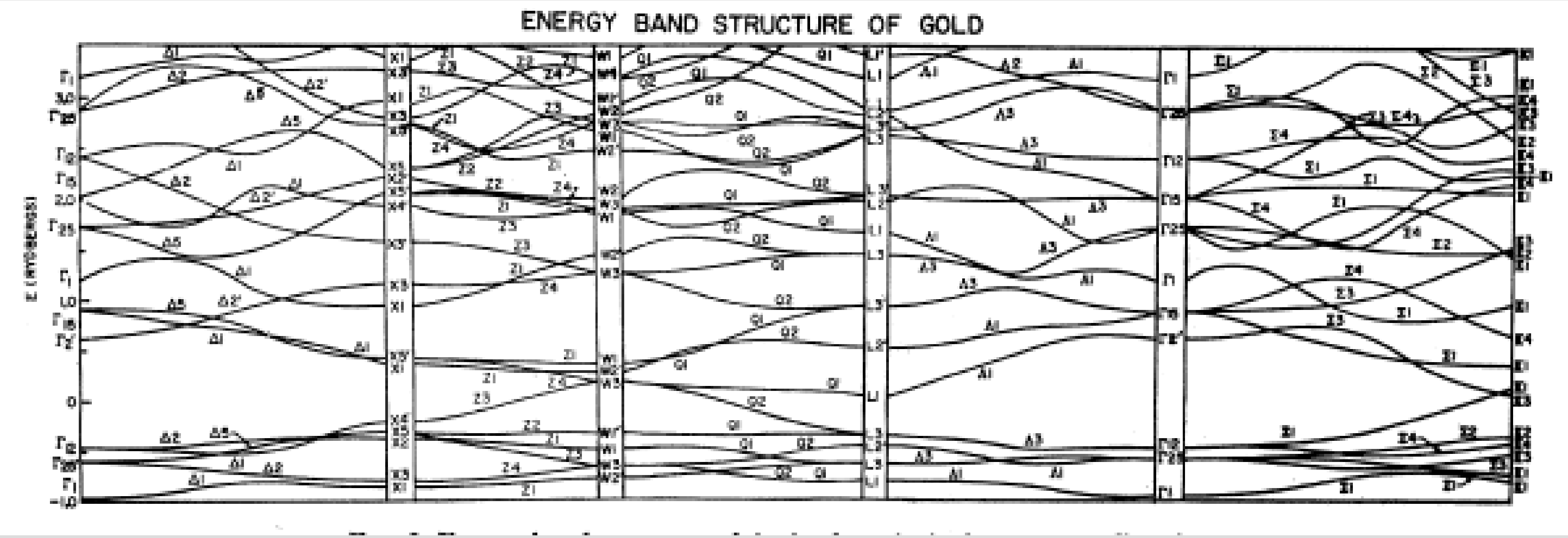


FIG. 1. Energy bands in sodium along symmetry directions.

| | $m_{eff}/m_0$ |
|---|---|
| Li | 1.33 |
| Na | 0.97 |
| K | 0.86 |
| Rb | 0.78 |
| Cs | 0.73 |

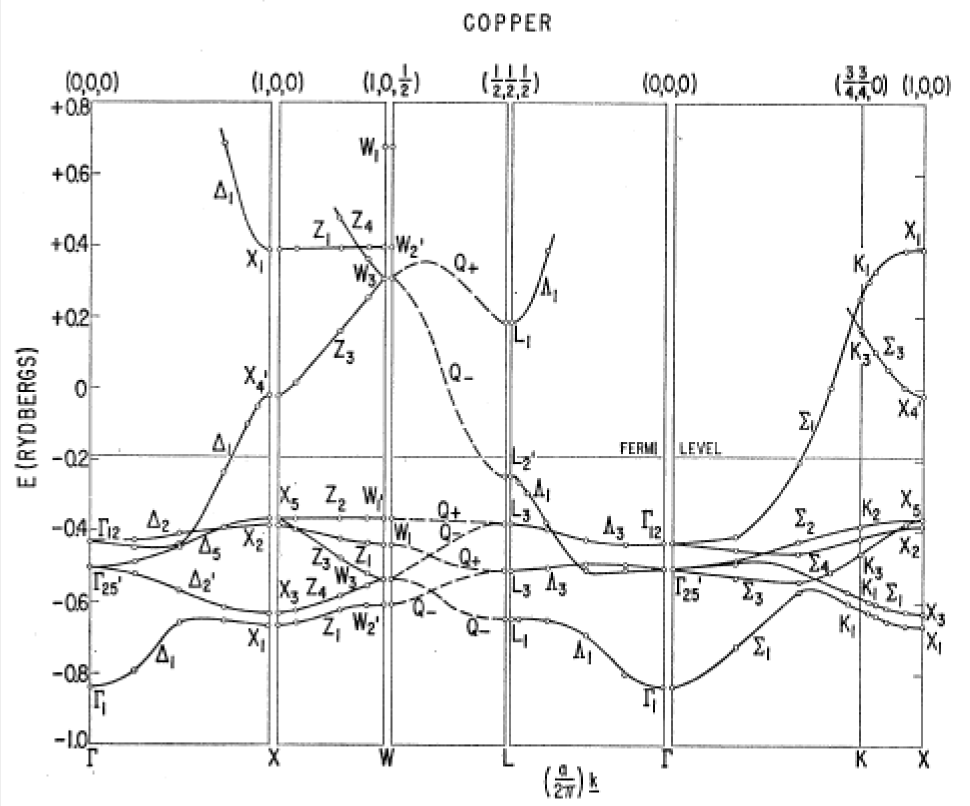
# Bandstructure of Au (FCC)

many bands with nonparabolic dispersion



# Bandstructure of Cu (FCC)

many bands with nonparabolic dispersion



# Ideal Fermi gas – basic description

Macroscopic (thermodynamic) conservation of energy,

$$dU = TdS - \delta A + \mu dN \ ,$$

where *TdS* is heat acquired by the gas from the environment, *A is* the work performed by the gas, and $\mu dN$ is the change of energy given by a change of the number *N* of particles; *S* is entropy, $\mu$ the chemical potential of the gas.

Microscopic model is based on the probabilities of occupation of available states, indexed by their energies and numbers of particles:

$$w(E_a, N_a) = \frac{1}{Z} \exp\left( -\frac{E_a - \mu N_a}{k_B T} \right) \ , \ Z = \sum_a \sum_{N_a} g_a \exp\left( -\frac{E_a - \mu N_a}{k_B T} \right) .$$

The normalization factor *Z* is called partition function, possible degeneracy of states is included by their multiplicity $g_a$. The grandcanonical potential is

$$\Omega = -k_B T \ln(Z) \ .$$

# Ideal Fermi gas – basic description

The independent (noninteracting), indistinguishable fermions obey the Pauli exclusion principle (the maximum occupation number of any state is one). Their Hamiltonian is the sum of single-particle contributions:

$$\hat{H} = \sum_{i=1}^{N} \hat{H}_i \ , \hat{H}_i \left|\psi_i\right\rangle = E_i \left|\psi_i\right\rangle \ .$$

The state vector of the gas is antisymmetric with respect to the exchange of ant two fermions. The energy eigenvalues can be degenerate (e.g., several states in a band scheme of a crystal can have the same energy). Consequently, we have to introduce an additional indexing symbol. The probability

$$w_{i,\alpha_i} = \frac{1}{Z_{i,\alpha_i}} \exp\left(-\frac{E_i - \mu}{k_B T} n_{i,\alpha_i}\right) \ , \ Z_{i,\alpha_i} = \sum_{n_{i,\alpha_i}} \exp\left(-\frac{E_i - \mu}{k_B T} n_{i,\alpha_i}\right) \ ,$$

depends on the occupation numbers $n_{i,\alpha i}$ of the states with the energy $E_i$.

# Ideal Fermi gas – basic description

The random occupation of available states of *different* particles is independent, i.e., the corresponding probabilities are *multiplied*, as well as the normalizing factors in the partition function.
The (random) occupation number has only two possible values, 0 and 1.
The expectation (mean) is

$$\left\langle n_{i,\alpha_i} \right\rangle = \sum_{n_{i,\alpha_i}} n_{i,\alpha_i} w_{i,\alpha_i} = -\frac{\partial \Omega_{i,\alpha_i}}{\partial \mu} = \frac{1}{\exp\left(\frac{E_i - \mu}{k_B T}\right) + 1} = f_{FD}\left(\frac{E_i - \mu}{k_B T}\right) ,$$

since

$$\Omega_{i,\alpha_i} = -kT \ln\left[1 + \exp\left(\frac{E_i - \mu}{k_B T}\right)\right] .$$

The average occupation number is called Fermi-Dirac statistics,

$$f_{FD}(x) = \frac{1}{\exp(x) + 1} .$$

# Ideal Fermi gas – basic description

The available spectrum of energies is usually (quasi)continuous; using the density of states *D*, the number of particles with the energies between *E* and *E+dE* is

$$f_{FD}\left(\frac{E-\mu}{k_B T}\right)D(E)dE \ ,$$

and the expectation values of the total number of particles and total energy are

$$\langle N\rangle = \int_{-\infty}^{\infty} f_{FD}\left(\frac{E-\mu}{kT}\right)D(E)dE \ ,$$

$$\langle E\rangle = \int_{-\infty}^{\infty} Ef_{FD}\left(\frac{E-\mu}{kT}\right)D(E)dE \ .$$

Further predictions depend on the functional form of the density of states.

# Ideal Fermi gas – basic description

For the anisotropic dispersion

$$E\left(\vec{k}\right)=\frac{\hbar^2}{2}\left(\frac{k_x^2}{m_x}+\frac{k_y^2}{m_y}+\frac{k_z^2}{m_z}\right)$$

and the two-fold spin degeneracy, the density of states in volume *V* is

$$D(E)=V\,\frac{\sqrt{2}}{\pi^2}\,\frac{\sqrt{m_x m_y m_z}}{\hbar^3}\sqrt{E}\ .$$

The concentration can be expressed in terms of a special function called Fermi-Dirac integral:

$$n=\frac{\langle N\rangle}{V}=\frac{\sqrt{2}}{\pi^2}\,\frac{(m^*)^{3/2}}{\hbar^3}\int_0^\infty f_{FD}\left(\frac{E-\mu}{kT}\right)\sqrt{E}\,dE$$

$$=\frac{\sqrt{2}}{\pi^2}\,\frac{(m^* kT)^{3/2}}{\hbar^3}\int_0^\infty \frac{t^{1/2}dt}{\exp(t-z)+1}\ , \qquad z=\frac{\mu}{kT}\ ,$$

where $m^*=(m_x m_y m_z)^{1/3}\ .$

# Ideal Fermi gas – basic description

In general, several macroscopic (averaged) quantities in the present context can be expressed in terms of the Fermi integrals

$$F_j(z) = \int_0^\infty \frac{t^j\,dt}{\exp(t-z)+1}\;, \quad j > -1\,,$$

satisfying the recursion

$$\frac{d}{dz}F_j(z) = jF_{j-1}(z)\;.$$

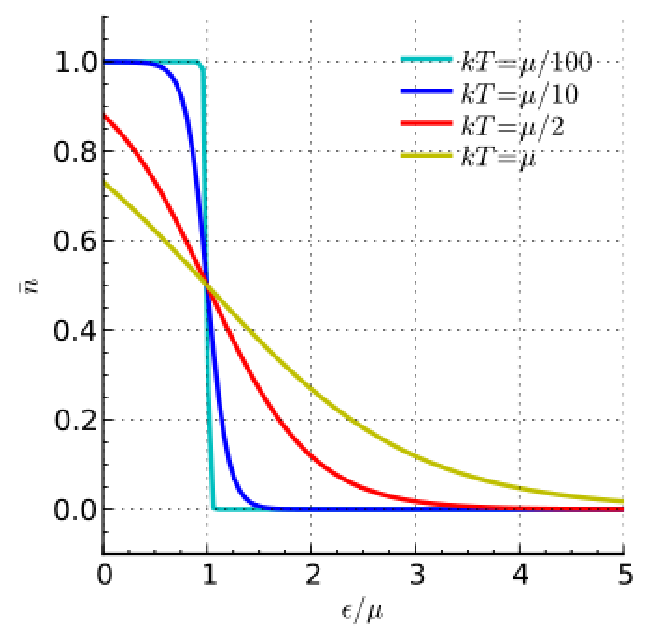
The following simplification is often advantageous:

$$F_j(z) \to \exp(z)\int_0^\infty t^j \exp(-t)\,dt = \exp(z)\Gamma(j+1) \quad \text{for} \quad z \to -\infty\;,$$

where $\Gamma$ is the Euler integral of the second kind.

# Ideal Fermi gas – basic description

energy dependence of the mean occupation number

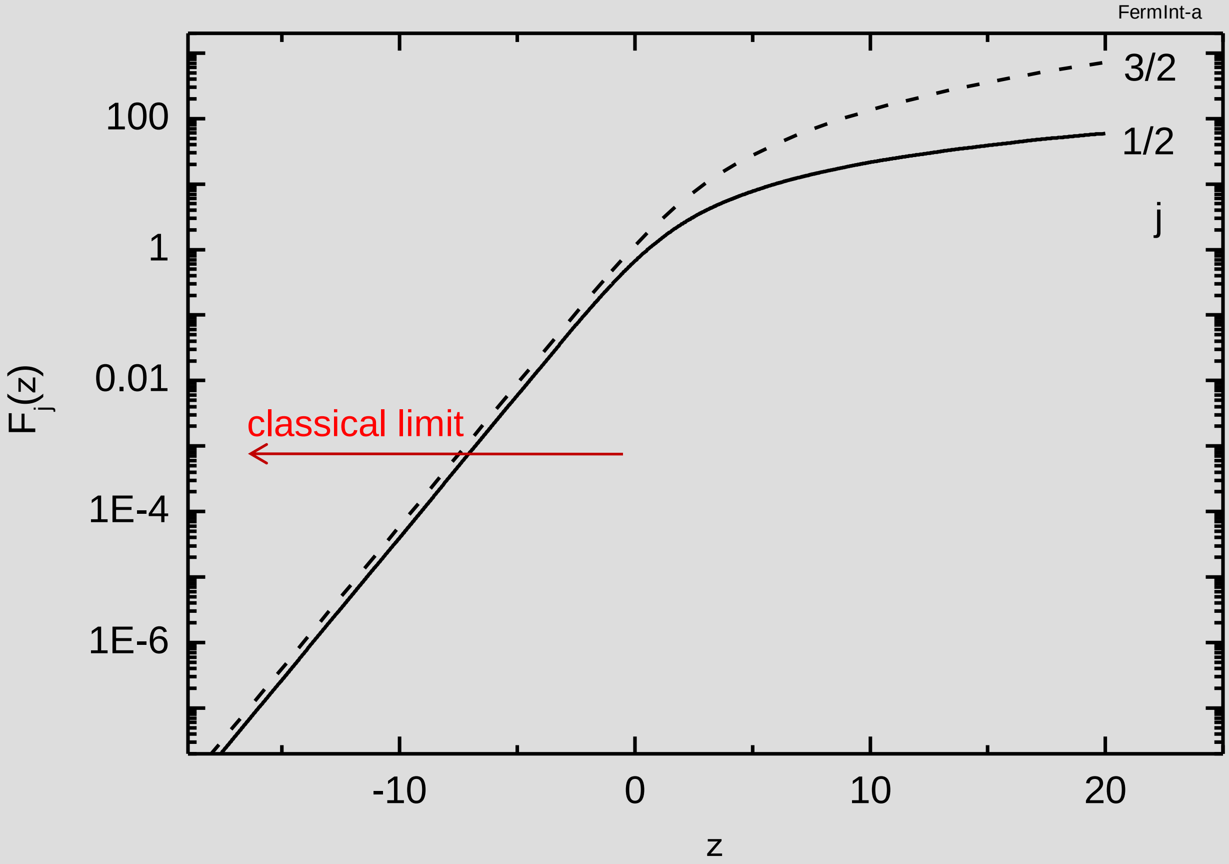


Note that $\left\langle n_{i,\alpha_i} \right\rangle = f_{FD}\left(\frac{E_i - \mu}{k_B T}\right)$

is the probability $p_{occ}$ of the state being occupied, as

$$\left\langle n_{i,\alpha_i} \right\rangle = 1 * p_{occ} + 0 * (1 - p_{occ}) \; .$$

# Ideal Fermi gas – basic description



# Ideal Fermi gas – the classical limit

Whenever the chemical potential is much smaller than the smallest energy *E* (which is zero for the above density of states), the Fermi-Dirac statistics is approximated by the classical Boltzmann $f_B$:

$$f_{FD}\left(\frac{E-\mu}{k_BT}\right) \approx f_B\left(\frac{E-\mu}{k_BT}\right) = \exp\left(\frac{\mu}{k_BT}\right)\exp\left(-\frac{E}{k_BT}\right) .$$

The concentration reduces to

$$n = 2\frac{(2\pi m^* kT)^{3/2}}{8\pi^3\hbar^3}\exp\left(\frac{\mu}{k_BT}\right).$$

This approximation can be interpreted in the following way. Using

$$\exp\left(\frac{\mu}{k_BT}\right) = n\frac{1}{2}\frac{8\pi^3\hbar^3}{(2\pi m^* k_BT)^{3/2}} = \frac{\langle N\rangle}{V}\frac{1}{2}\lambda_T^3 \ ,\ \lambda_T^3 = \frac{h}{\sqrt{2\pi m^* k_BT}} \ ,$$

we identify $\lambda_T$ with the de Broglie wavelength associated with the particle having the energy $k_BT$ and mass $m^*$.

# Ideal Fermi gas – degeneracy

Another useful approximation results for large concentrations, small temperatures and small effective masses. For chemical potential much larger than $k_B T$, the FD statistics can be replaced by the step function, we obtain the concentration in the following form:

$$n = \frac{\sqrt{2}}{\pi^2} \frac{(m^* k_B T)^{3/2}}{\hbar^3} \int_0^{\frac{\mu_0}{k_B T}} t^{1/2} dt = \frac{(2m^*)^{3/2}}{3\pi^2 \hbar^3} \mu_0^{3/2} \ .$$

Conversely, the $T$=0 limit of the chemical potential (usually called Fermi energy, is

$$\mu_0 = \left(\frac{3}{8\pi}\right)^{2/3} \frac{h^2}{2m^*} n^{2/3} \ .$$

The volume density of mean energy is independent of temperature

$$\frac{\langle E \rangle}{V} = \frac{\sqrt{2}}{\pi^2} \frac{(m^*)^{3/2}}{\hbar^3} \int_0^{\mu_0} E^{3/2} dE = \frac{3}{5} \frac{(2m^*)^{3/2}}{3\pi^2 \hbar^3} \mu_0^{5/2} = \frac{3}{5} n \mu_0 \ .$$

This is to be compared with the much smaller classical value ($3nk_B T/2$).

# Ideal Fermi gas – degeneracy

The dense packing of degenerate gas, characterized by the mutual intolerance of fermions, leads to the strong increase of energy.

The condition for complete degeneracy is the reverse of the classical limit:

$$\frac{V}{\langle N \rangle} << \lambda_T^3 \ , \ \lambda_T^3 = \frac{h}{\sqrt{2\pi m^* k_B T}} \quad .$$

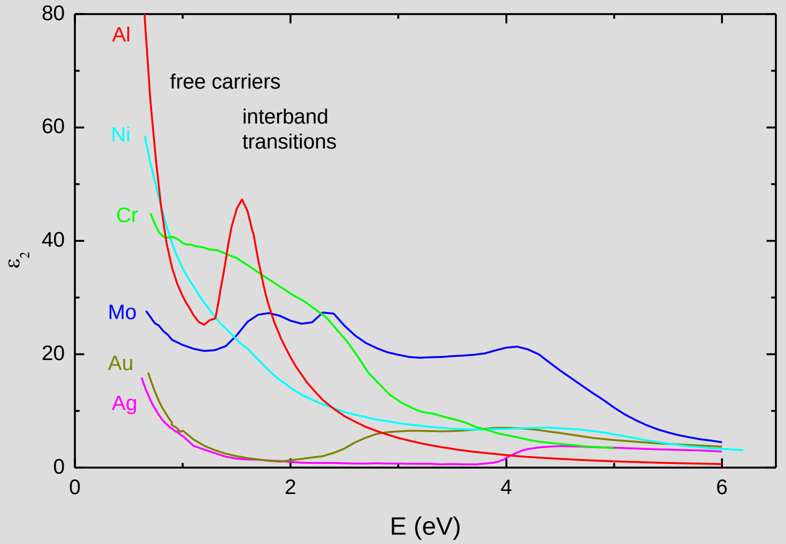
It is easily fulfilled in usual metals up to very high temperatures; we can express the Fermi energy in terms of the Fermi temperature:

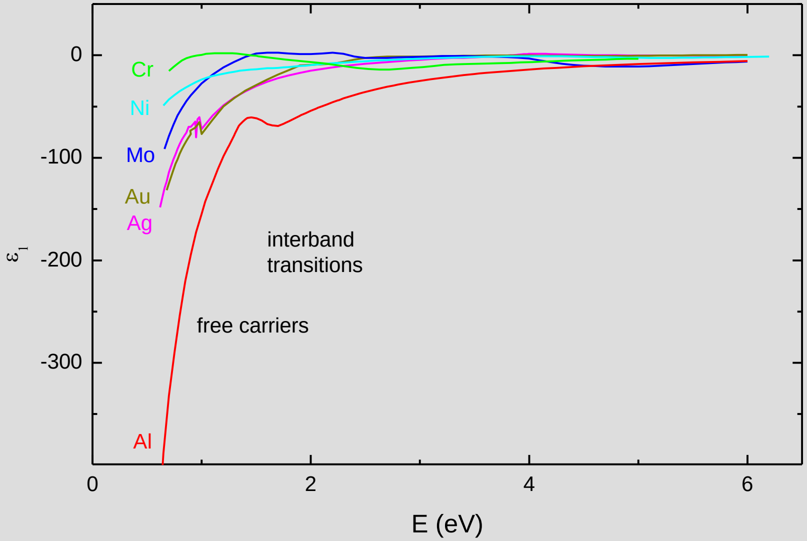
$$T_F = \frac{\mu_0}{k_B} \ ;$$

the typical values for metals are of the order of $10^4$ K.

On the other hand, reaching degeneracy in semiconductors requires typically heavy doping and low temperatures.

# Gas of free electrons in the optical response of metals





metals:

free electrons
dominate in IR,

overlap with
interband transitions

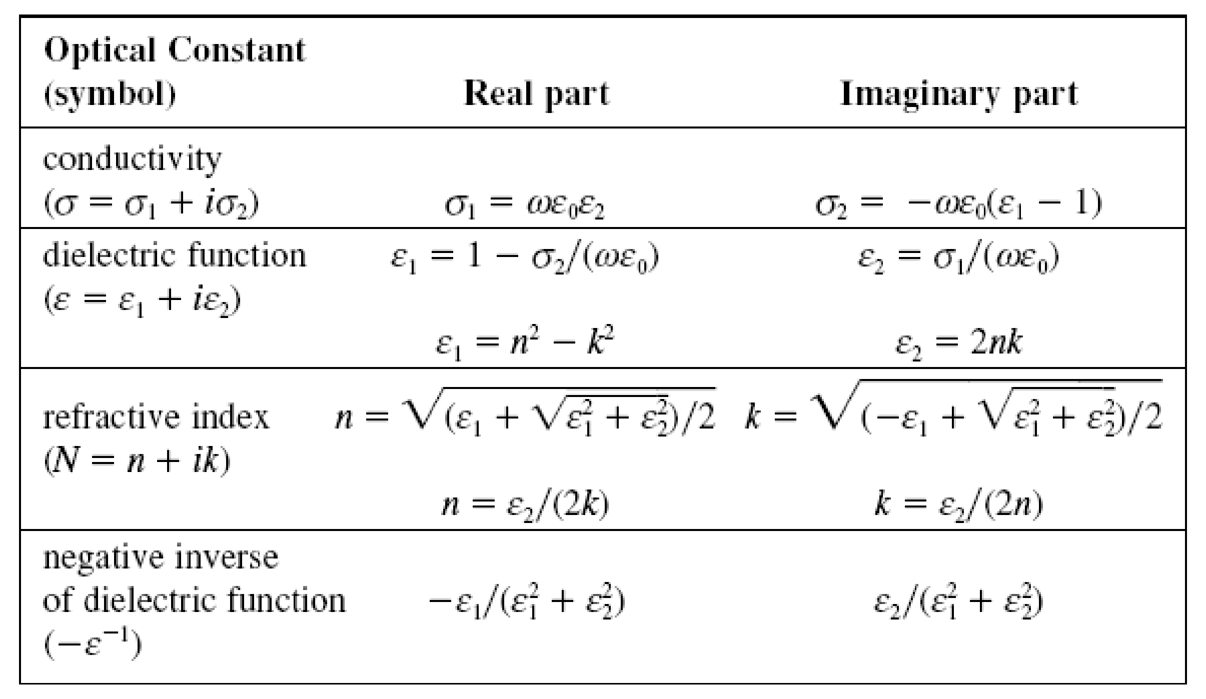
# Gas of free electrons in the optical response of metals

The (macroscopic) electric field of an optical wave moves the free elctrons and creates the induced polarization and current:

$$\vec{D} \equiv \varepsilon_0 \vec{E} + \vec{P} = (1 + \hat{\chi})\varepsilon_0 \vec{E} = \hat{\varepsilon}\varepsilon_0 \vec{E} \ ,$$

$$\vec{j} = -i\omega\vec{P} = \sigma\vec{E} \ .$$

Models and/or measurements provide several sets of interrelated response functions (“optical constants”):



| **Optical Constant (symbol)** | **Real part** | **Imaginary part** |
|---|---|---|
| conductivity ($\sigma = \sigma_1 + i\sigma_2$) | $\sigma_1 = \omega\varepsilon_0\varepsilon_2$ | $\sigma_2 = -\omega\varepsilon_0(\varepsilon_1 - 1)$ |
| dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) | $\varepsilon_1 = 1 - \sigma_2/(\omega\varepsilon_0)$<br>$\varepsilon_1 = n^2 - k^2$ | $\varepsilon_2 = \sigma_1/(\omega\varepsilon_0)$<br>$\varepsilon_2 = 2nk$ |
| refractive index ($N = n + ik$) | $n = \sqrt{(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2})/2}$<br>$n = \varepsilon_2/(2k)$ | $k = \sqrt{(-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2})/2}$<br>$k = \varepsilon_2/(2n)$ |
| negative inverse of dielectric function ($-\varepsilon^{-1}$) | $-\varepsilon_1/(\varepsilon_1^2 + \varepsilon_2^2)$ | $\varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2)$ |

# Gas of free electrons in the optical response of metals

The classical Drude model for a gas of free electrons/holes predicts the following spectral dependence of the complex permittivity,

$$\varepsilon(\omega) = 1 - \frac{4\pi N e^2}{m^* V} \frac{1}{\omega(\omega + i/\tau)},$$

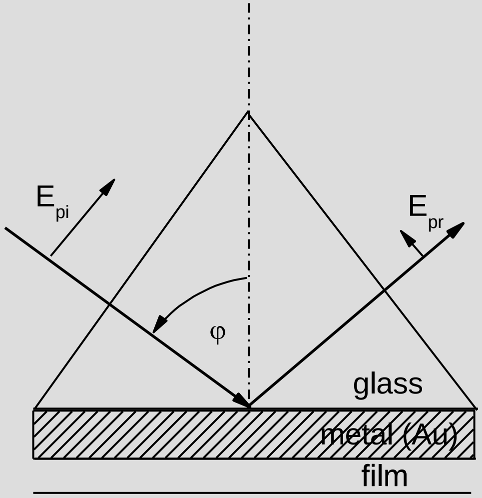
for the concentration of carriers *N/V*, their effective mass *m**, and the scattering rate $1/\tau$ (the number of collisions destroying the drift velocity acquired in the time interval $\tau$). The imaginary part of $\varepsilon$ diverges towards zero frequency, while the real part is finite and negative, the real part of conductivity is finite and positive:

$$\mathrm{Re}\{\varepsilon(0)\} = 1 - \frac{4\pi N e^2 \tau^2}{m}, \qquad \sigma_1(0) = \frac{e^2 \tau}{m} \ .$$

# Surface plasmon resonance in metallic films

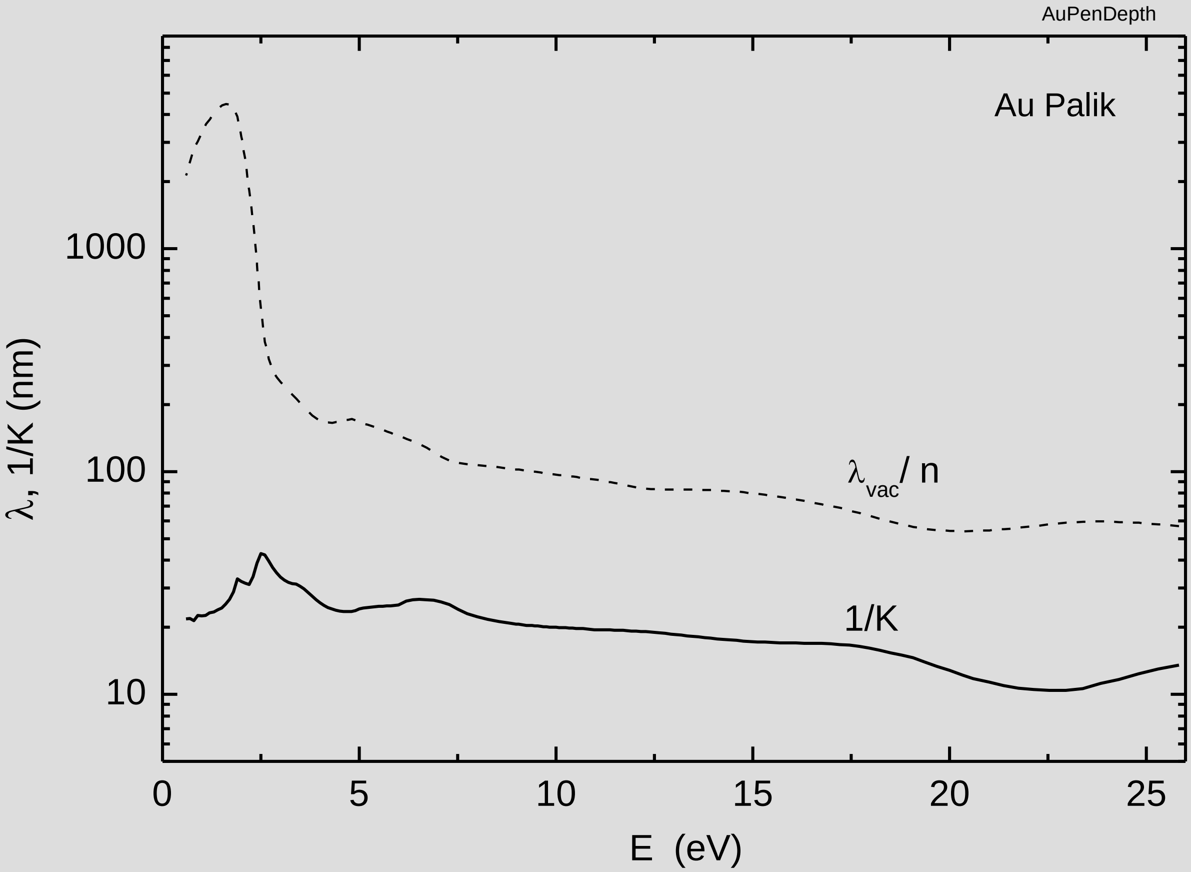
The Drude-like behavior of metals supports the surface-plasmon-resonance in a thin metallic film surrounded by insulators.

Namely, the evanescent wave occurring at oblique incidence of the p-polarized light (the electric vector of the wave lies in the plane of incidence, and therefore has a non-vanishing component perpendicular to the interfaces) can have substantially enhanced strength. This typically leads to strong variations of reflected intensity with varying frequency or angle of incidence.



# Surface plasmon resonance in metallic films

the tradeoff in choosing the thickness and material of the film;
gold is very popular



# Optical response of Au (Aspnes)

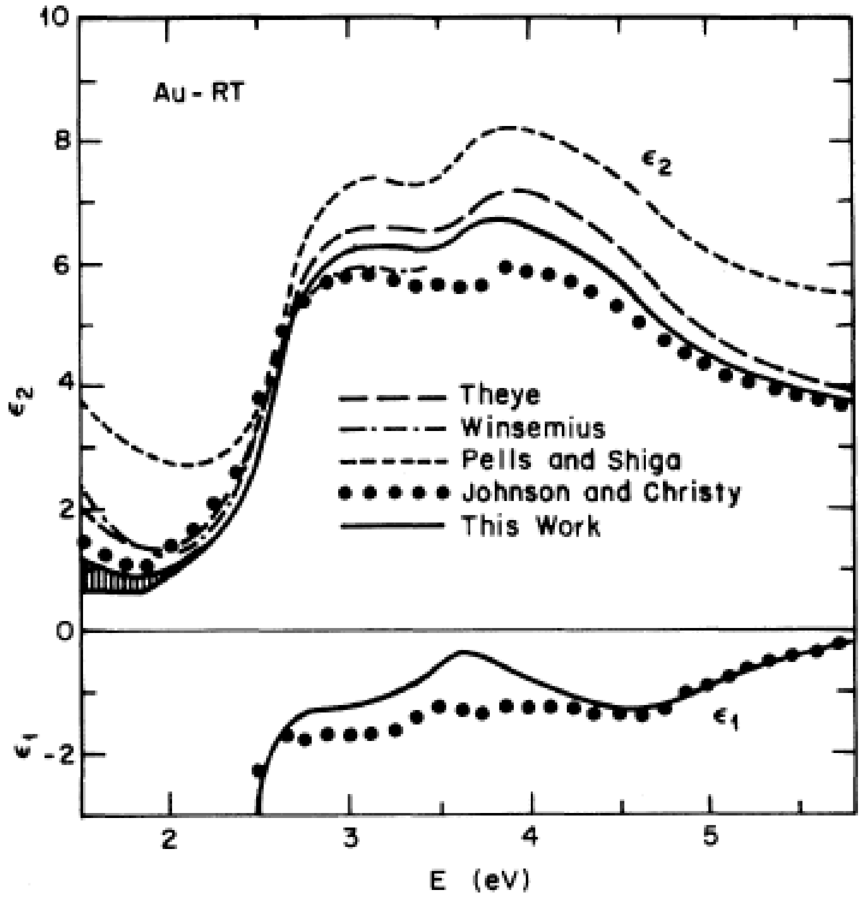
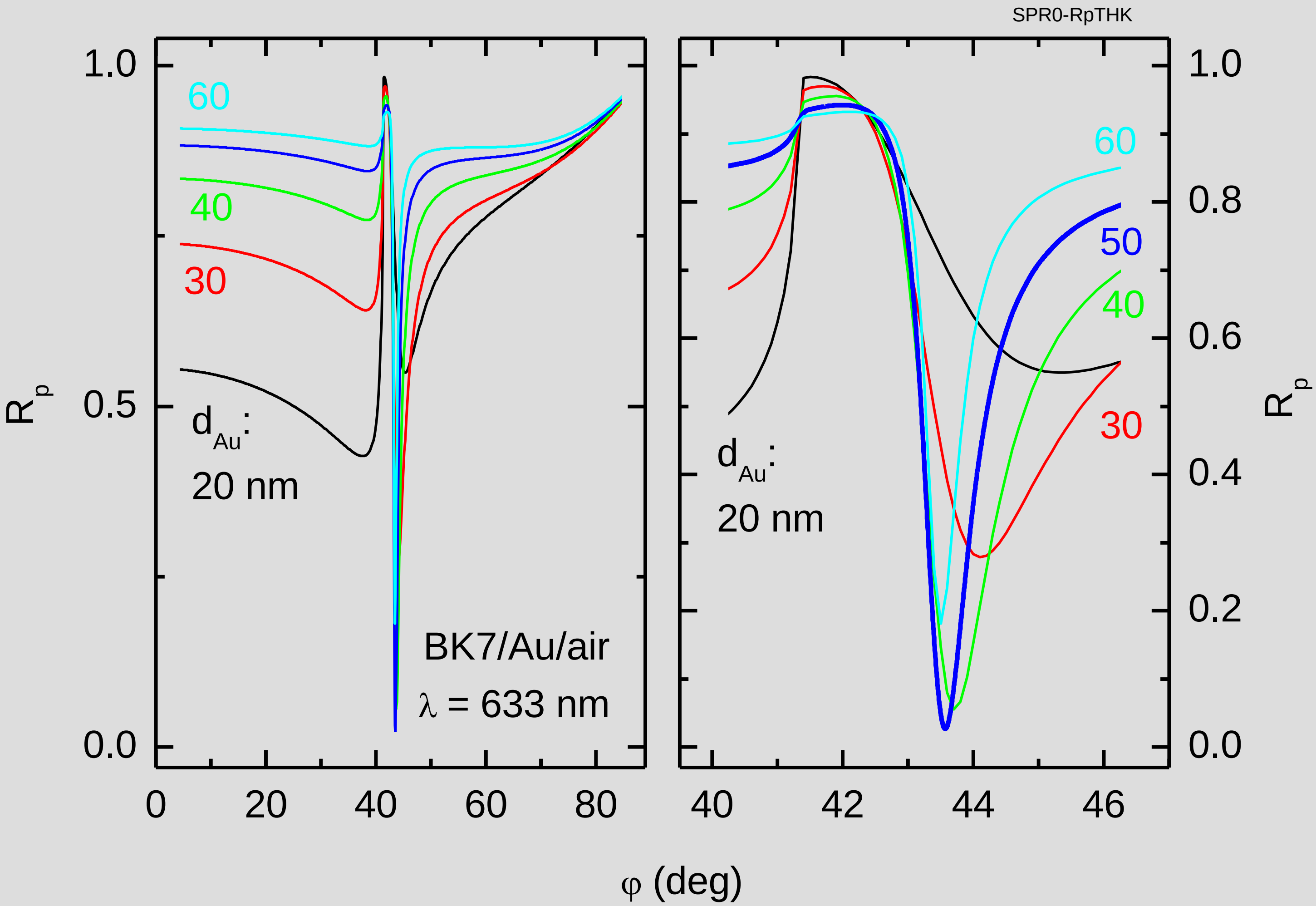
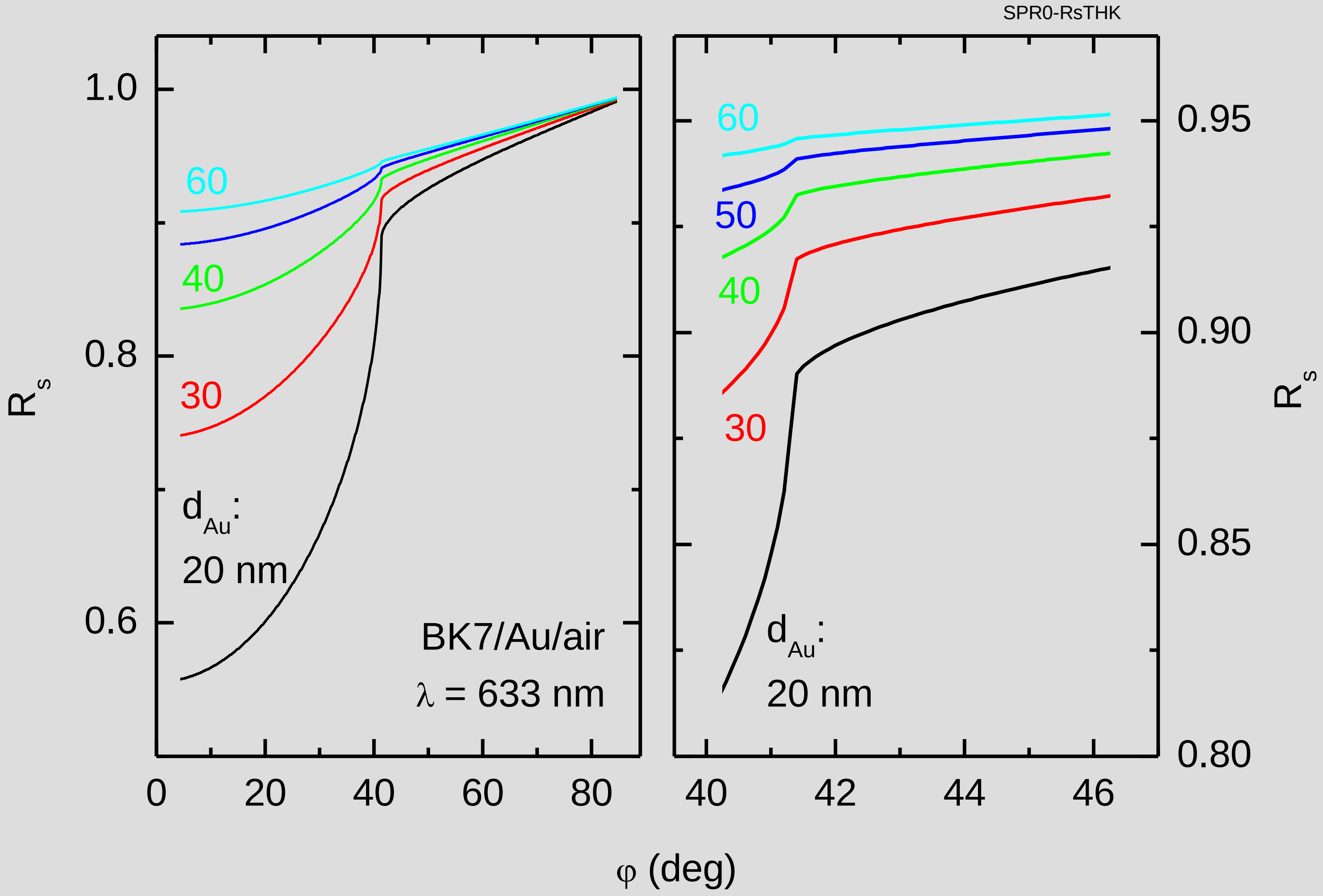


FIG. 1. Representative dielectric-function data for Au: Thèye (Ref. 14), thin film, UHV evaporated and annealed; Winsemius (Ref. 25), bulk polycrystal, UHV annealed; Pells and Shiga (Ref. 21), as Winsemius; Johnson and Christy (Ref. 15), unannealed thin film; this work, electron-beam evaporated thin film.

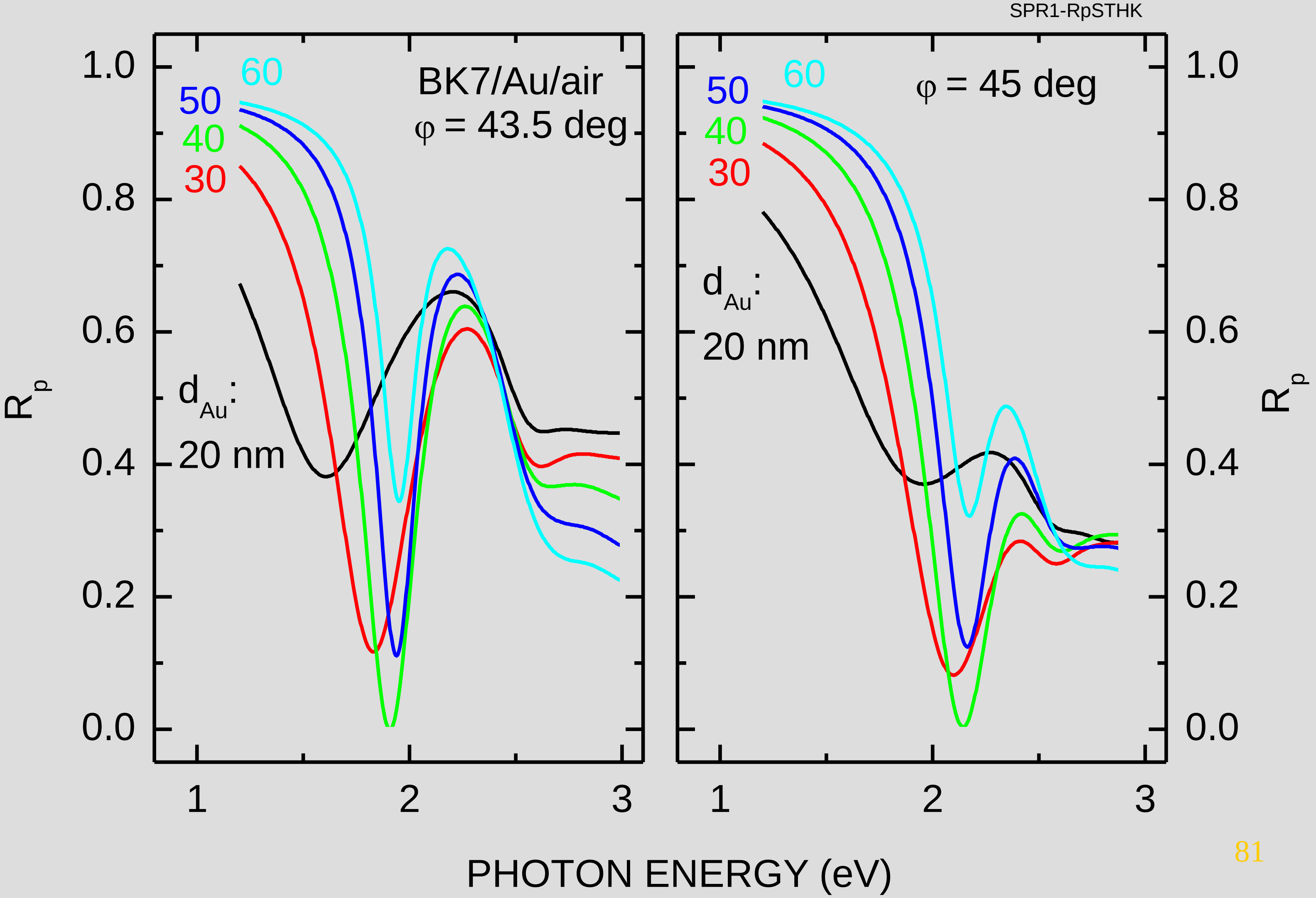
# SPR, angular dependence



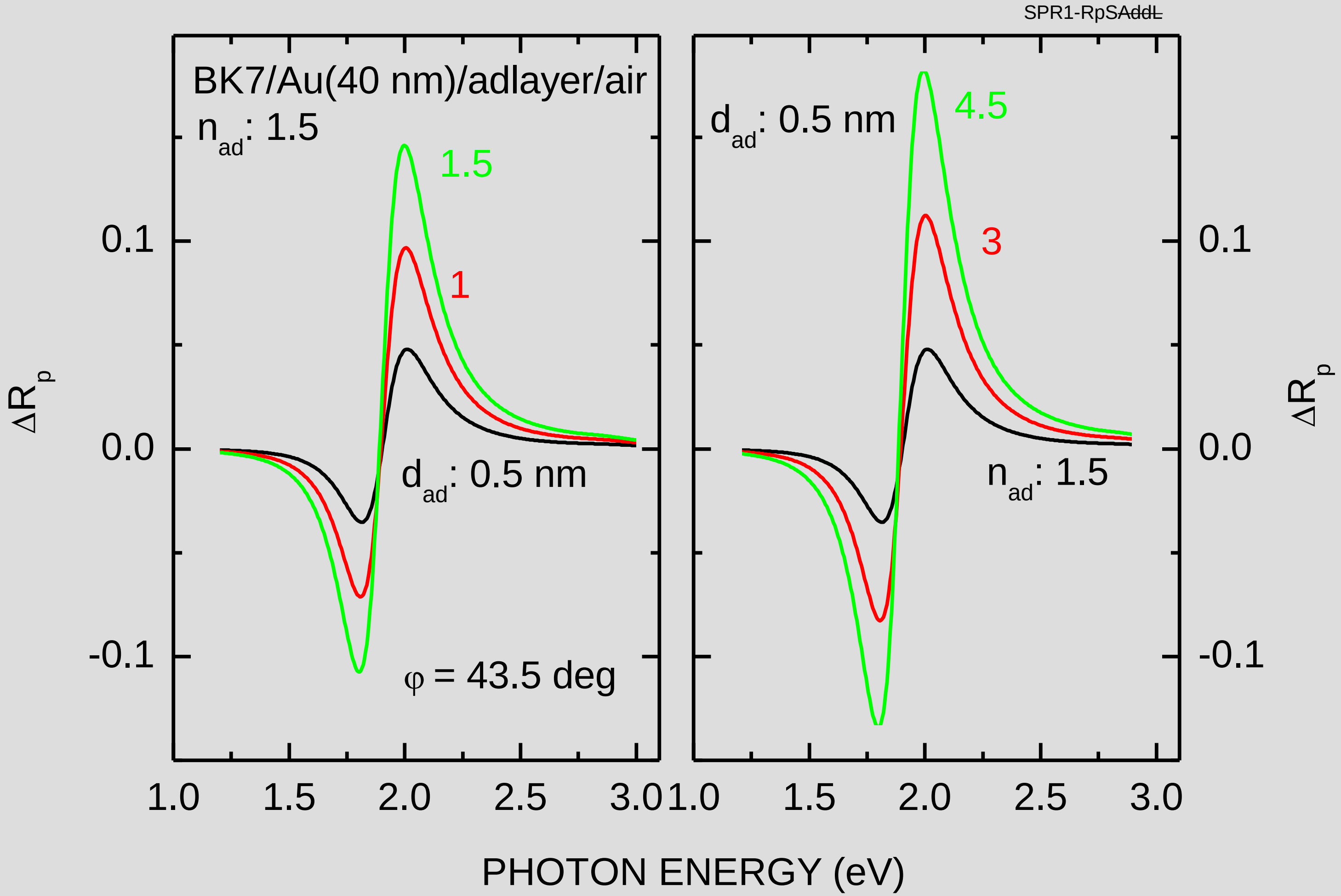
# s-polarized reflectivity – detects the critical angle
no enhancement of the light field within the Au film



# SPR for fixed angle, spectral dependence



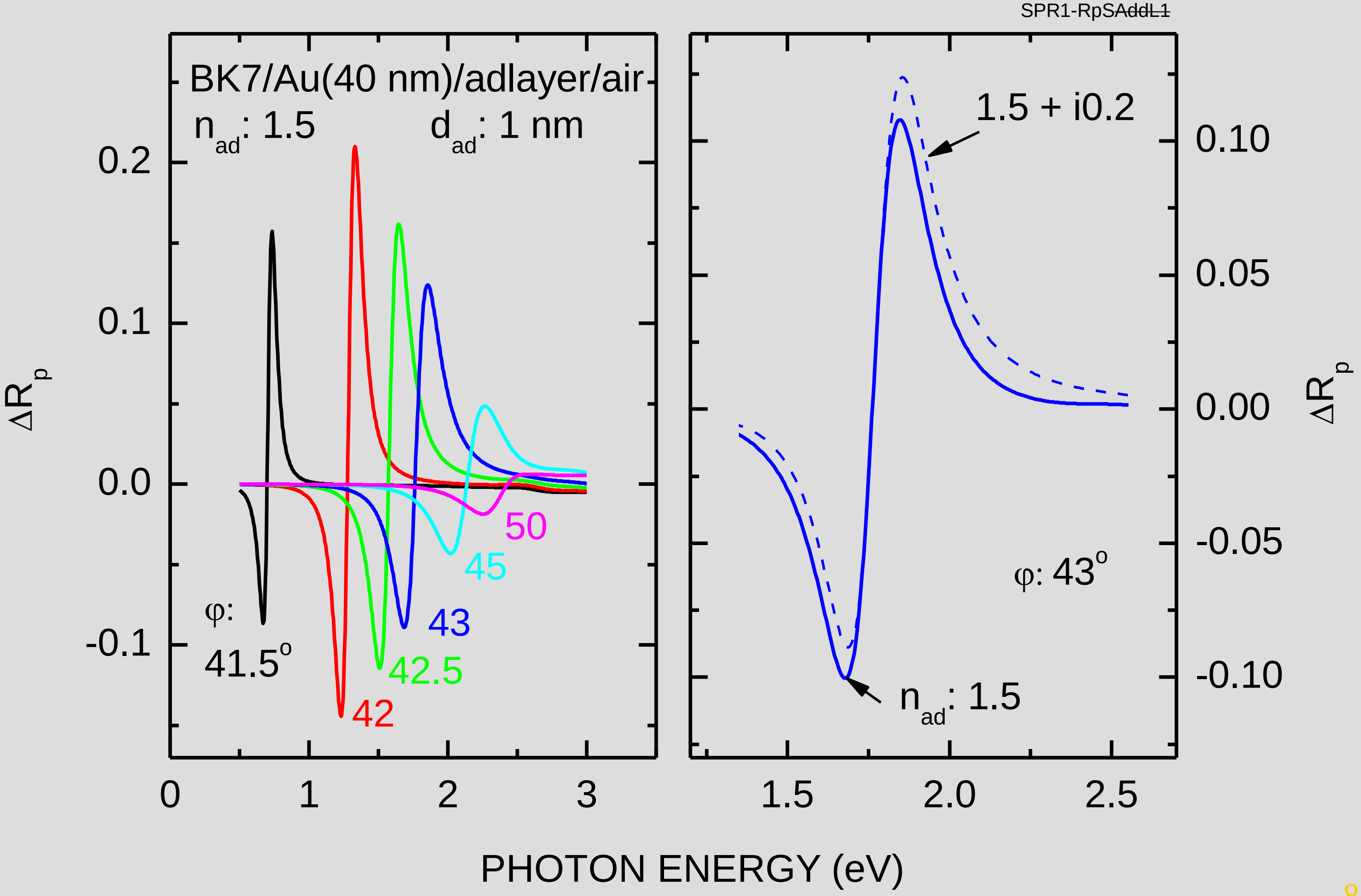
# SPR – sensitivity to added layer



# SPR – sensitivity to added layer

for different angles of incidence

slightly absorbing layer



# A selection of very interesting topics in ideal Fermi gases
# in semiconductors

- creating fermionic gas by doping, shallow impurities
- cyclotron resonance of electrons and holes
- statistics of electrons/holes/excitons
- screening of interface charges, MOS structures
- metal-insulator transition

- 2D, 1D  !!