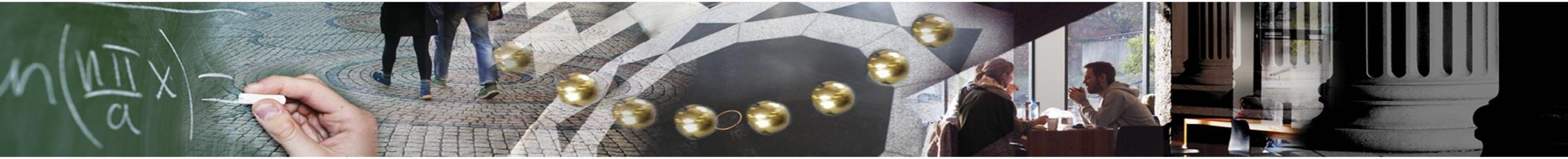


UiO : University of Oslo

Electron gas

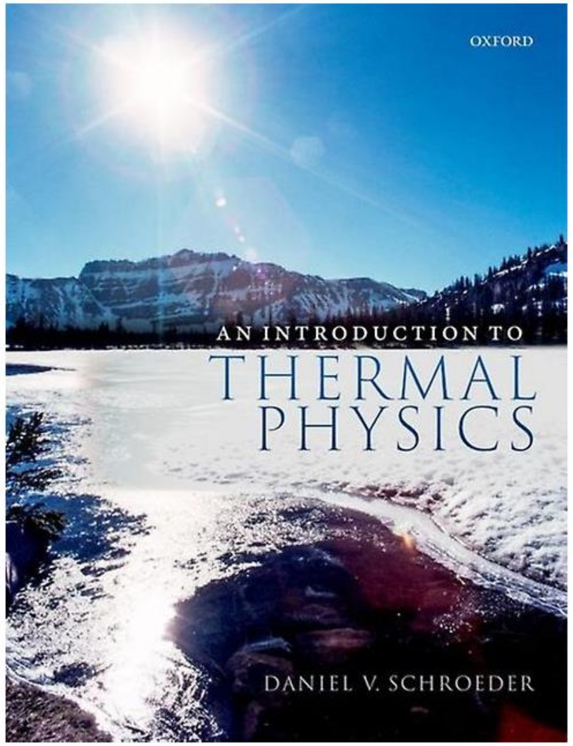
6 Boltzmann Statistics

7 Quantum Statistics

7.1 The Gibbs Factor

7.2 Bosons and Fermions

7.3 Degenerate Fermi Gases



Diffusive equilibrium and chemical potential

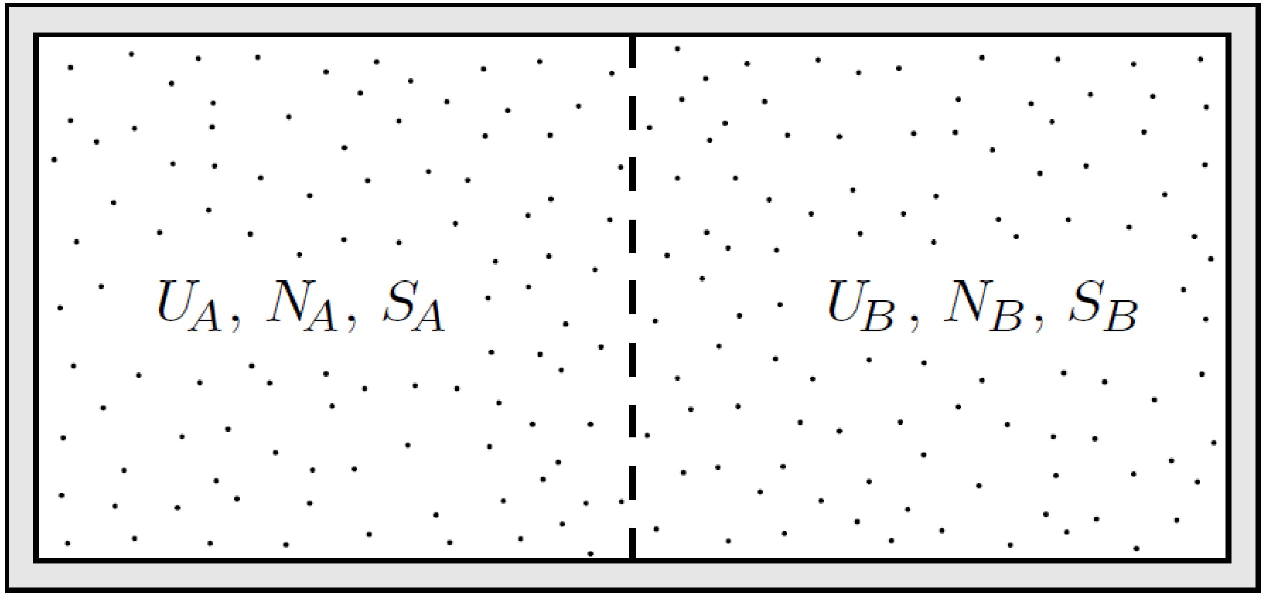
When two systems are in thermal equilibrium, their temperatures are the same. When they're in mechanical equilibrium, their pressures are the same. What quantity is the same when they're in diffusive equilibrium?

$$\left(\frac{\partial S_{total}}{\partial U_A}\right)_{N_A,N_B} = 0 \qquad \left(\frac{\partial S_{total}}{\partial N_A}\right)_{U_A,U_B} = 0$$

$$\frac{\partial S_{total}}{\partial U_A} = \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0$$

$$\frac{\partial S_A}{\partial U_A} = -\frac{\partial S_B}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \qquad \left(\frac{\partial S}{\partial U}\right)_{N,V} \equiv \frac{1}{T}$$

DVS



An example of two systems that can exchange both energy and particles with total energy and number of particles fixed. **At equilibrium, the total entropy is at a maximum.**

At equilibrium:

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \qquad \frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

Constant T

What parameter is constant here?

- Chemical potential is a key for understanding behavior of electron gas.

Diffusive equilibrium and chemical potential

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \qquad -T\frac{\partial S_A}{\partial N_A} = -T\frac{\partial S_B}{\partial N_B}$$

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

μ is chemical potential. In diffusive equilibrium, $\mu_A = \mu_B$.

μ is a parameter which is constant in diffusive equilibrium.

If two systems are not in diffusive equilibrium, then the one with the larger value of $\partial S/\partial N$ will tend to gain particles, since it will thereby gain more entropy than the other loses. Because of the minus sign, this system has the smaller value of μ. Therefore, particles tend to flow from the system with higher μ into the system with lower μ.

Types of interactions

Type of interaction	Exchanged quantity	Governing variable	Formula
thermal	energy	temperature	$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$
mechanical	volume	pressure	$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$
diffusive	particles	chemical potential	$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}$

Generalized thermodynamic identity

Let us change U by dU, V by dV, and N by dN
and see what will happen with S:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{V,U} dN$$

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} \equiv \frac{1}{T} \quad \mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

$$dU = TdS - PdV$$

$$dS = \frac{dU}{T} + \frac{PdV}{T} - \frac{\mu dN}{T}$$

$$TdS = dU + PdV - \mu dN$$

$$dU = TdS - PdV + \mu dN$$

Link to Gibbs free energy

$$\boldsymbol{dU = TdS - PdV + \mu dN}$$

Generalized thermodynamic identity

$$\boldsymbol{dG} = dU - TdS + PdV = \boldsymbol{\mu dN} \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

Chemical potential: different formulas

$$dU = TdS - PdV + \mu dN$$

Fixed U and V: $$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

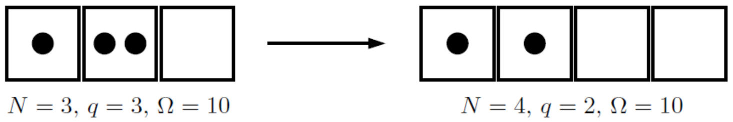
Fixed U and S: $$\mu = P\left(\frac{\partial V}{\partial N}\right)_{U,S}$$

Fixed V and S: $$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Chemical potential is the amount by which a system's energy changes when one adds one particle and keeps the entropy and volume fixed. μ has units of energy.

Chemical potential: an example

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$



DVS

Small Einstein solid with three oscillators and three units of energy $\mathcal{E}$, adding 4th oscillator: k ln 10 ⟶ k ln 20. One unit of energy is necessary to remove $\mu = -\epsilon/1 = -\epsilon$.

Chemical potential of ideal gas

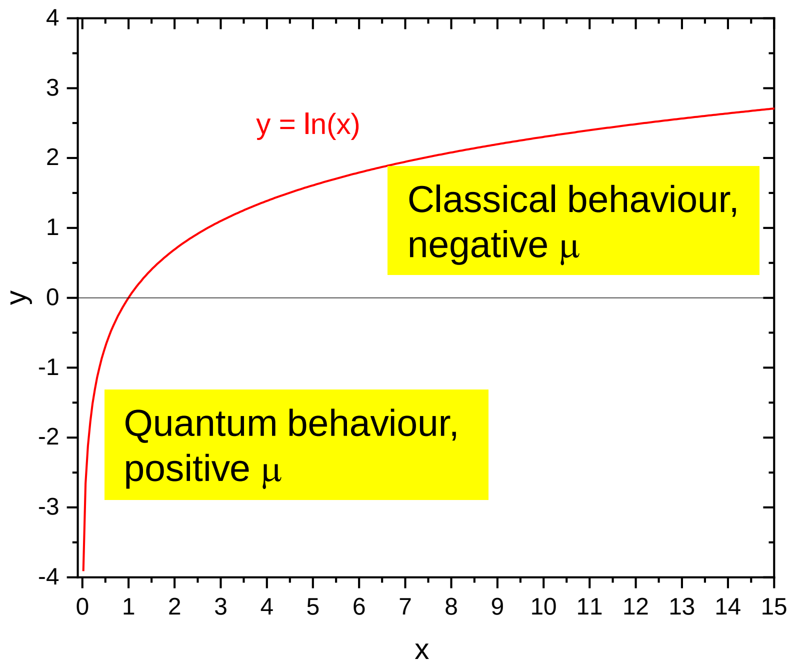
Sackur-Tetrode equation: $$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right].$$

$$\mu = -kTln\left[\frac{V}{N\vartheta_Q}\right]$$

$$\vartheta_Q = l_Q^3 = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3$$



- The sign of chemical potential depends on the ratio of volume per one particle and quantum volume ϑ_Q. μ is negative for $\frac{V}{N} > \vartheta_Q$, or for a non-dense system. A large mass of particles or large T results in a small ϑ_Q.
- Reduction in mass and decrease in temperature results in $\frac{V}{\vartheta_Q N} < 1$ and positive μ.

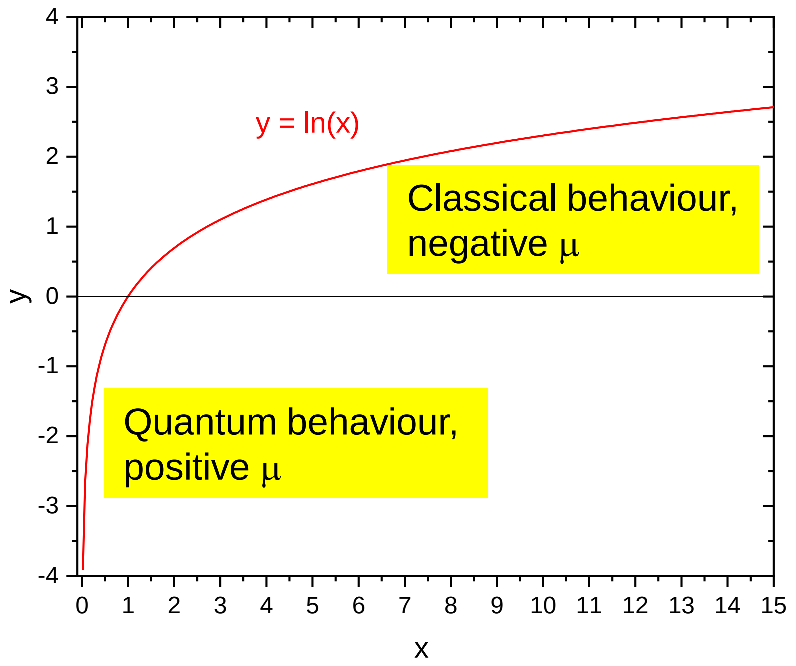
Quantum volume and length

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right].$$

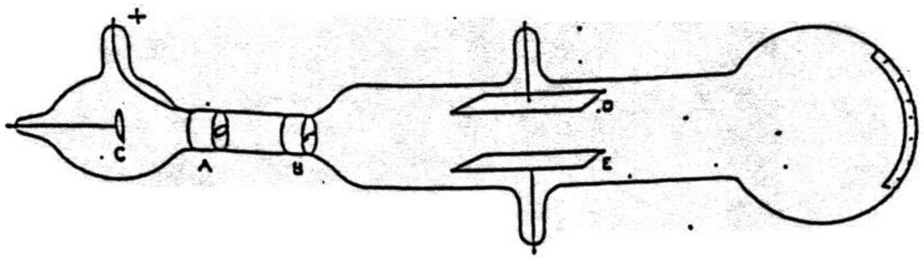
$$\vartheta_Q = l_Q^3 = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3$$

$$\frac{h}{\sqrt{2\pi mkT}} \rightarrow \frac{h}{\sqrt{2\pi m\epsilon}} \xrightarrow{\epsilon = \frac{p^2}{2m}} \frac{h}{p\sqrt{\pi}} \xrightarrow{p = \frac{k\,h}{2\pi}} \frac{2\pi}{k\sqrt{\pi}} \xrightarrow{\frac{2\pi}{k} = \lambda_{dB}} \frac{\lambda_{dB}}{\sqrt{\pi}}$$

- For the air we breathe, the average distance between molecules is about 3 nm while the average de Broglie wavelength is less than 0.02 nm, so condition $\frac{V}{\vartheta_Q N} \gg 1$ is satisfied.
- For an electron at room temperature, because of low mass, the quantum volume is $\vartheta_Q = (4.3\text{ nm})^3$, while the volume per conduction electron is roughly the volume of an atom, $(0.2\text{ nm})^3$. Therefore, **electron gas** in metals at ambient conditions is quantum gas with $\frac{V}{\vartheta_Q N} \ll 1$.



Electron gas



https://en.wikipedia.org/wiki/J._J._Thomson

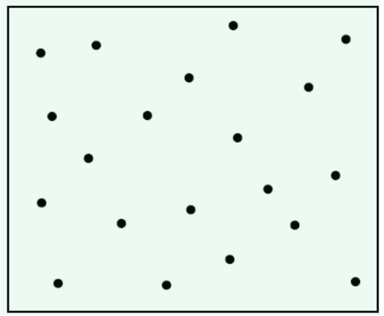
The Nobel Prize in Physics 1906
Joseph John Thomson
"in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases"

'By carefully measuring how the cathode rays were deflected by electric and magnetic fields, Thomson was able to determine the ratio between the electric charge (e) and the mass (m) of the rays. Thomson's result was
$e/m = 1.8\ 10^{11}$ coulombs/kg.
The particle that J.J.Thomson discovered in 1897, the electron, is a constituent of all the matter we are surrounded by. All atoms are made of a nucleus and electrons. He received the Nobel Prize in 1906 for the discovery of the electron, the first elementary particle.'

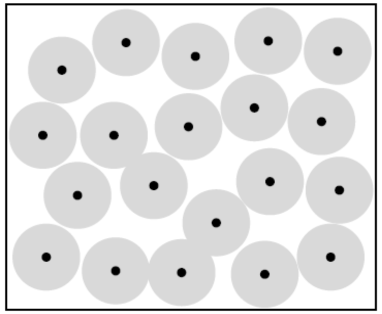
http://www.nobelprize.org/educational/physics/vacuum/experiment-1.html

Cavendish Laboratory

Electron gas in vacuum



Normal gas

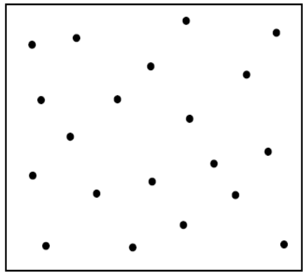


Quantum electron gas

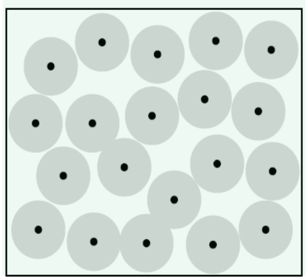
https://en.wikipedia.org/wiki/Vacuum_tube

"The simplest vacuum tube, the diode (i.e. Fleming valve), invented in 1904 by John Ambrose Fleming, contains only a heated electron-emitting cathode and an anode. Electrons can only flow in one direction through the device—from the cathode to the anode. Adding one or more control grids within the tube allows the current between the cathode and anode to be controlled by the voltage on the grids."

Solid-state transistors



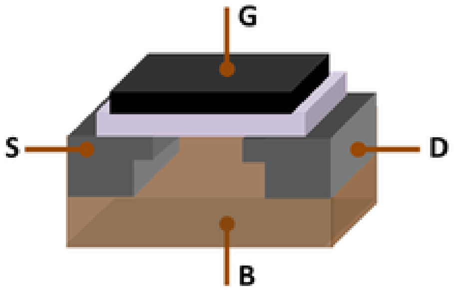
Normal gas

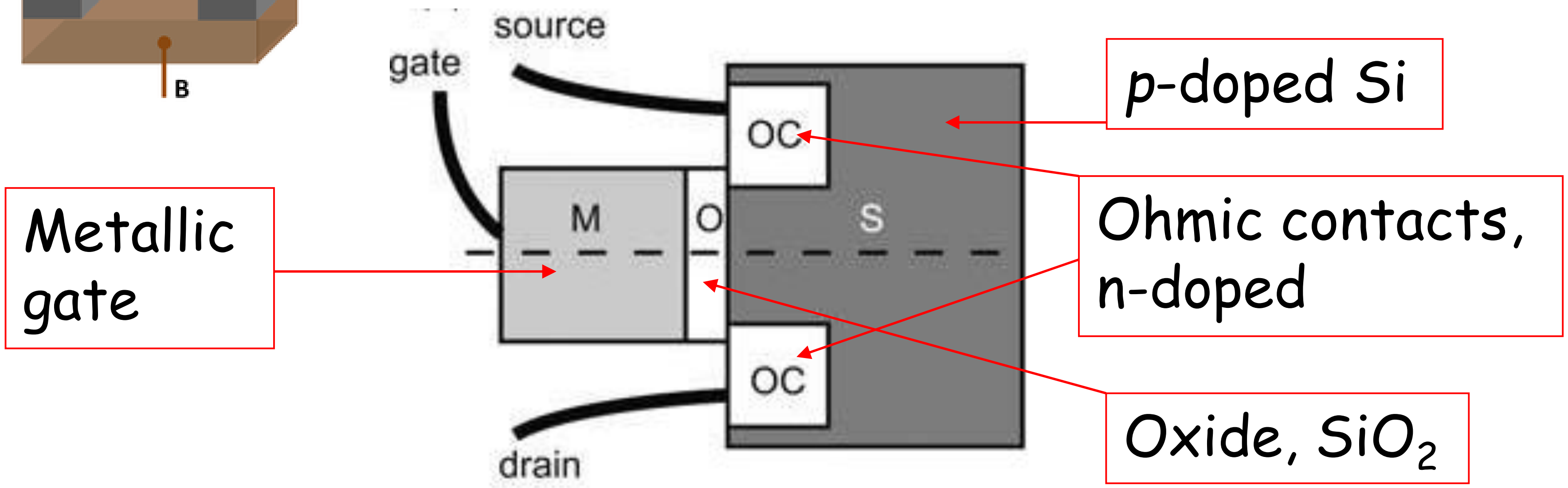


Quantum electron gas

DVS

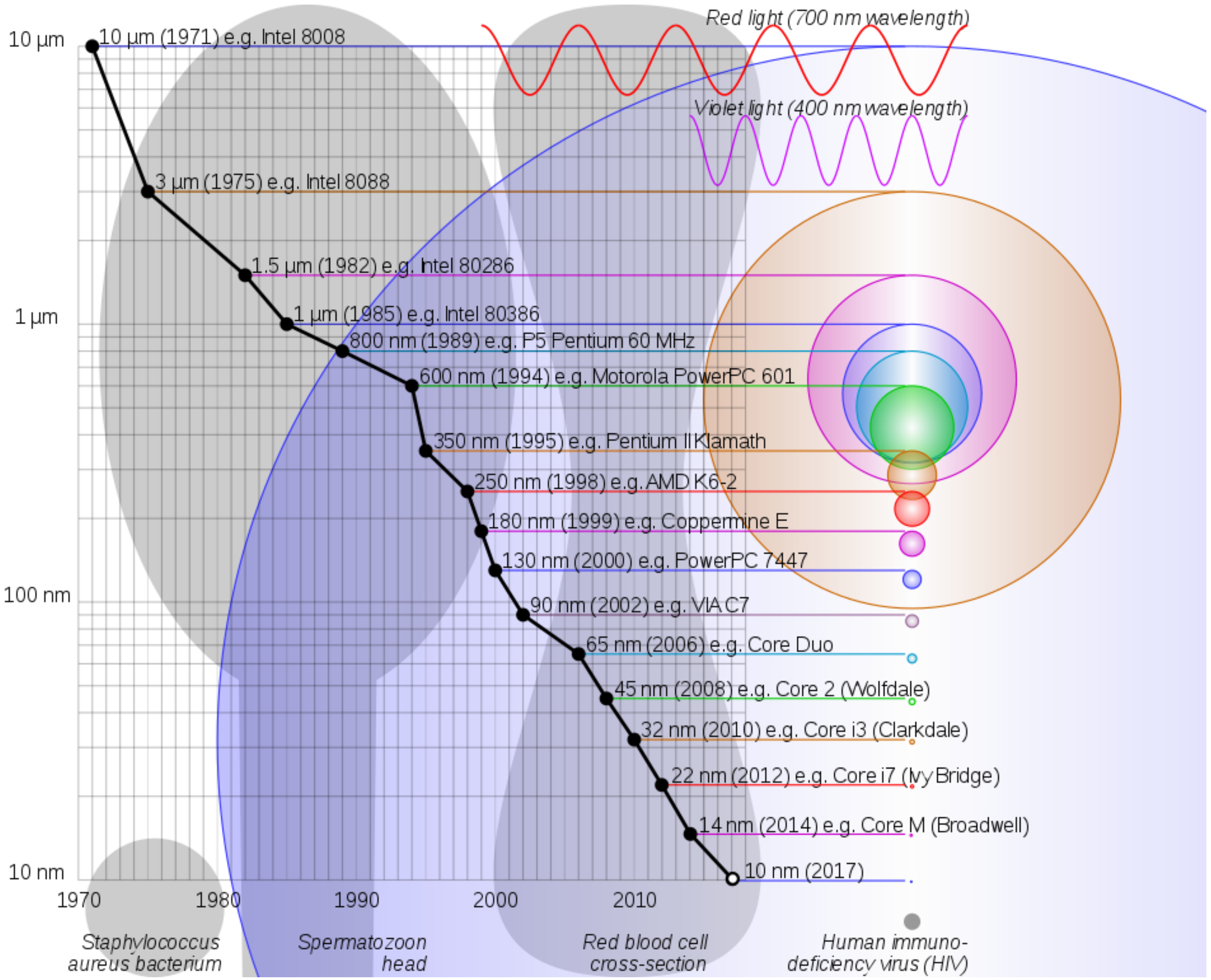
Si-MOSFET





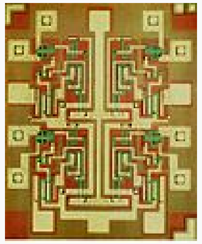
http://en.wikipedia.org/wiki/MOSFET

Progress in miniaturisation



By Cmglee - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=16991155

Semiconductor manufacturing processes



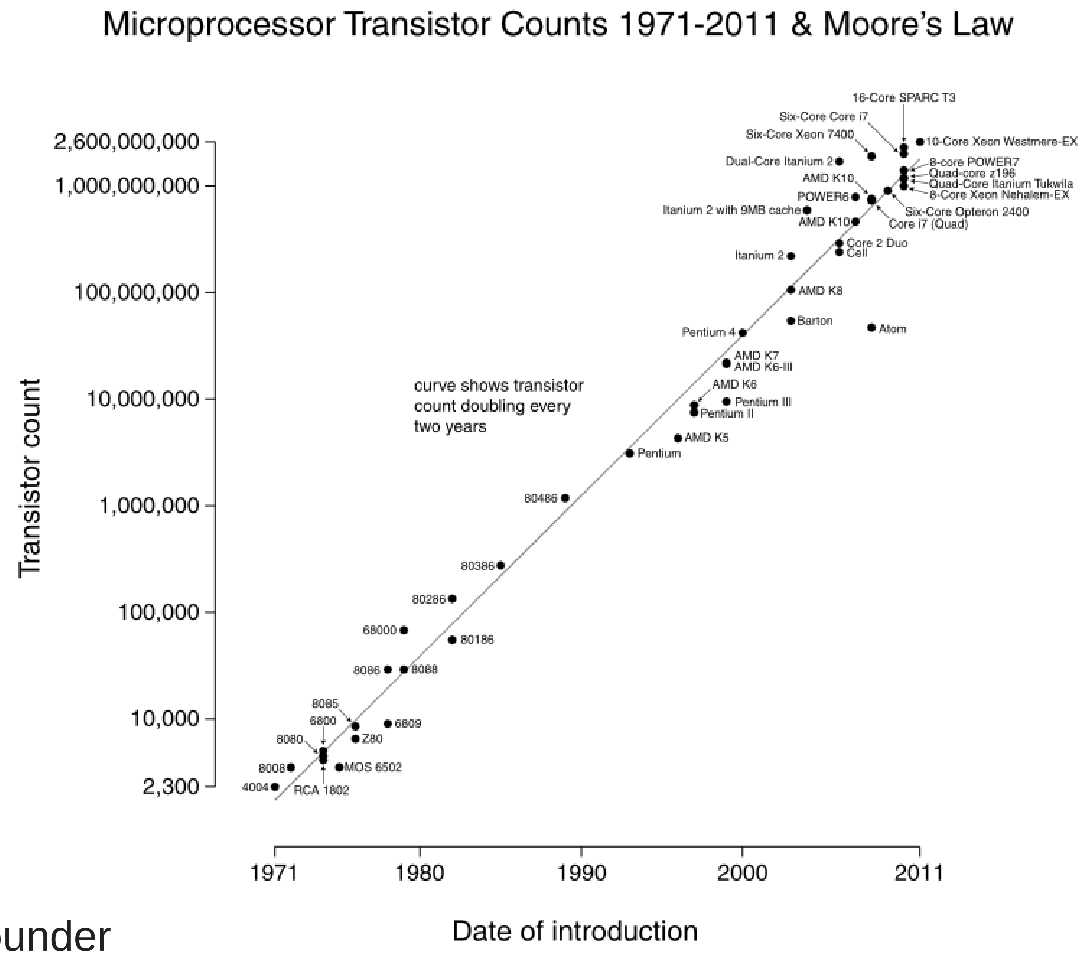
- 10 µm – 1971
- 6 µm – 1974
- 3 µm – 1977
- 1.5 µm – 1982
- 1 µm – 1985
- 800 nm – 1989
- 600 nm – 1994
- 350 nm – 1995
- 250 nm – 1997
- 180 nm – 1999
- 130 nm – 2001
- 90 nm – 2004
- 65 nm – 2006
- 45 nm – 2008
- 32 nm – 2010
- 22 nm – 2012
- 14 nm – 2014
- 10 nm – 2017
- 7 nm – *~2018*
- **5 nm** – *~2020*

Half-nodes

V · T · E

Moor’s law

“Moore's law is the observation that the number of transistors in a dense integrated circuit (IC) doubles about every two years.”



The observation is named after Gordon Moore, the co-founder of Fairchild Semiconductor and Intel (and former CEO of the latter).

http://en.wikipedia.org/wiki/Moore's_law

Moor’s law 2.0

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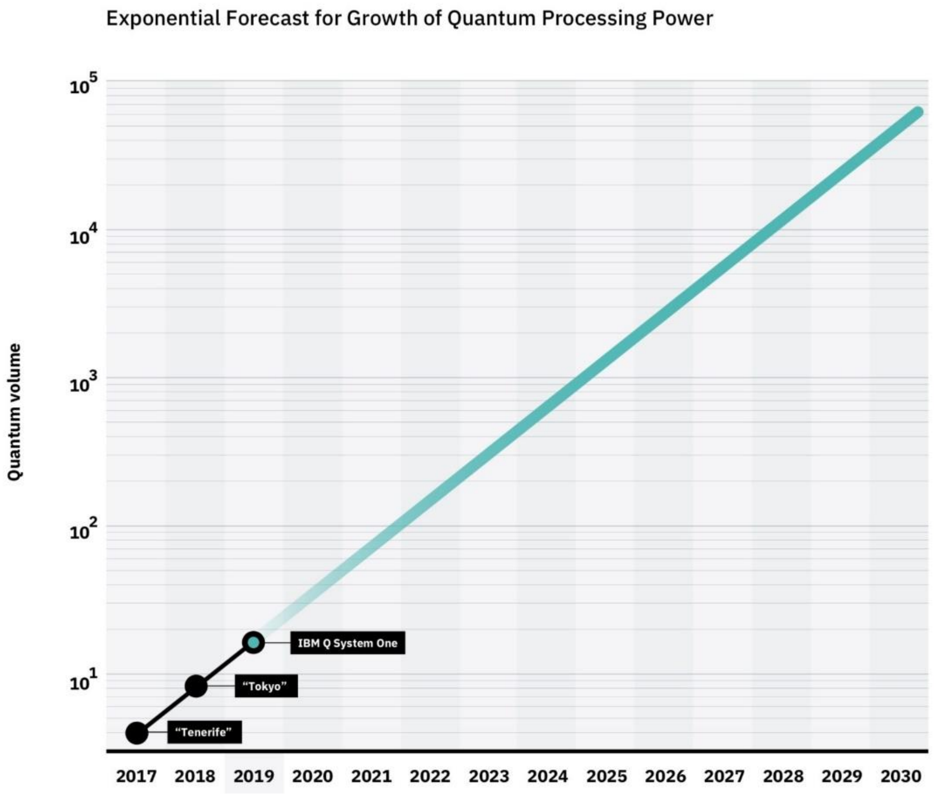
BOSTON, March 4, 2019 /PRNewswire/ -- At the 2019 American Physical Society March Meeting, IBM (NYSE: IBM) unveiled a new scientific milestone, announcing its highest quantum volume to date.



IBM has doubled the power of its quantum computers annually since 2017.

https://newsroom.ibm.com/2019-03-04-IBM-Achieves-Highest-Quantum-Volume-to-Date-Establishes-Roadmap-for-Reaching-Quantum-Advantage#assets_all

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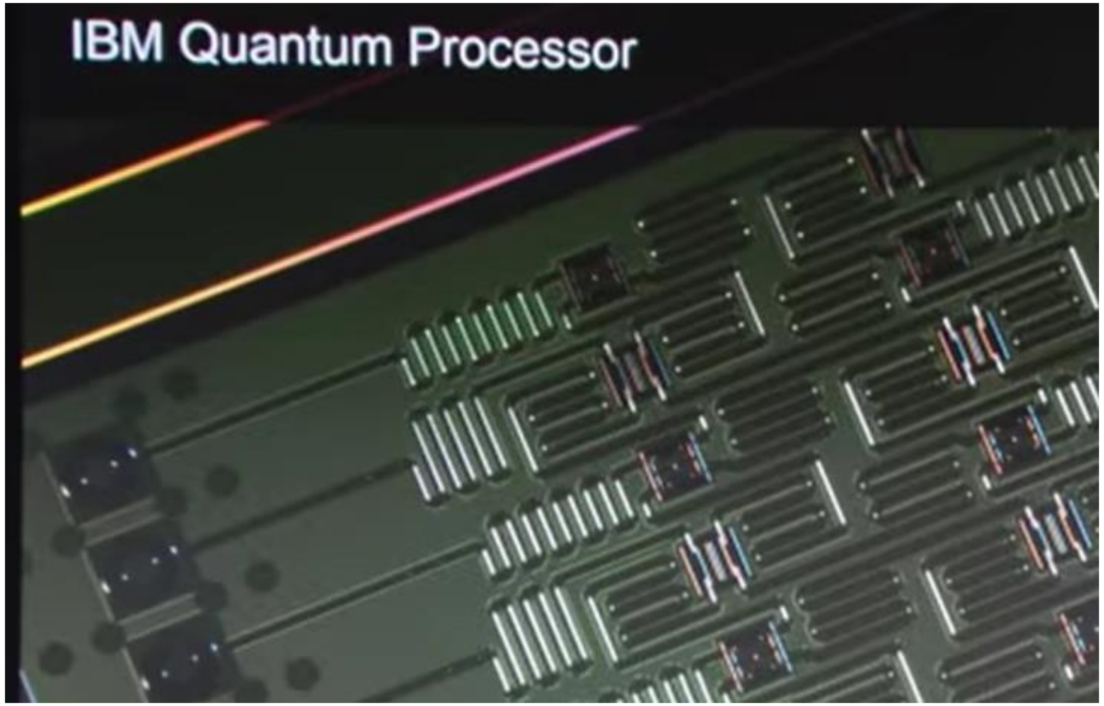
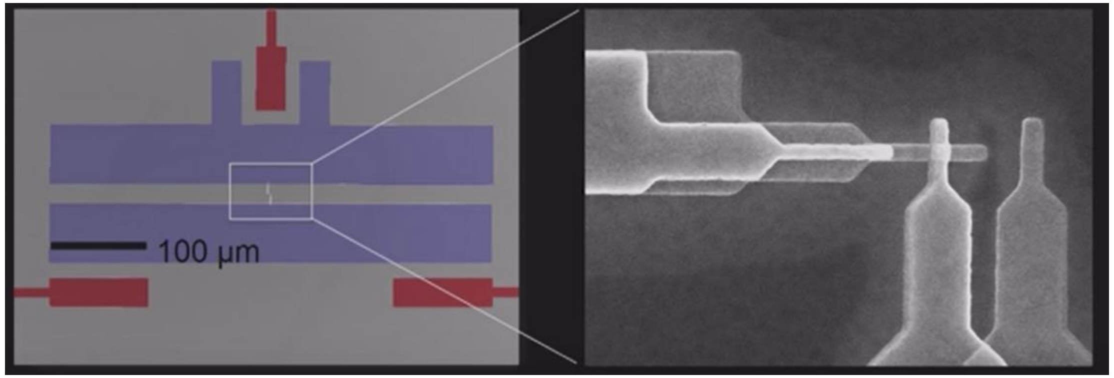
Superconductivity and quantum computing



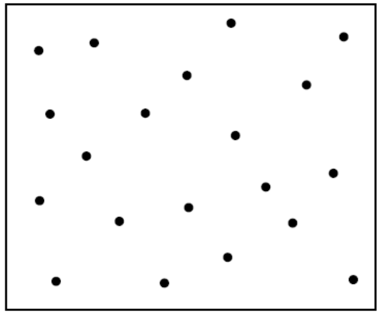


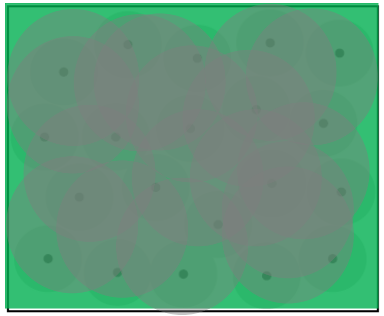
https://techcrunch.com/2017/11/10/ibm-passes-major-milestone-with-20-and-50-qubit-quantum-computers-as-a-service/

https://www.youtube.com/watch?v=yy6TV9Dntlw

Bosons and fermions

Normal gas





Quantum gas

- For a dense system, particles that try to occupy the same state can be divided in two groups.
- Particles that can share a state with another are called bosons. Examples: photons and helium-4 atoms.
- Particles that cannot share a state with another are called fermions. Examples: electrons, protons, neutrons and helium-3 atoms.
- Particles with integer spin (0, 1, 2, etc., in units of $h/2\pi$) are bosons.
- Particles with half-integer spin (1/2, 3/2, etc.) are fermions.

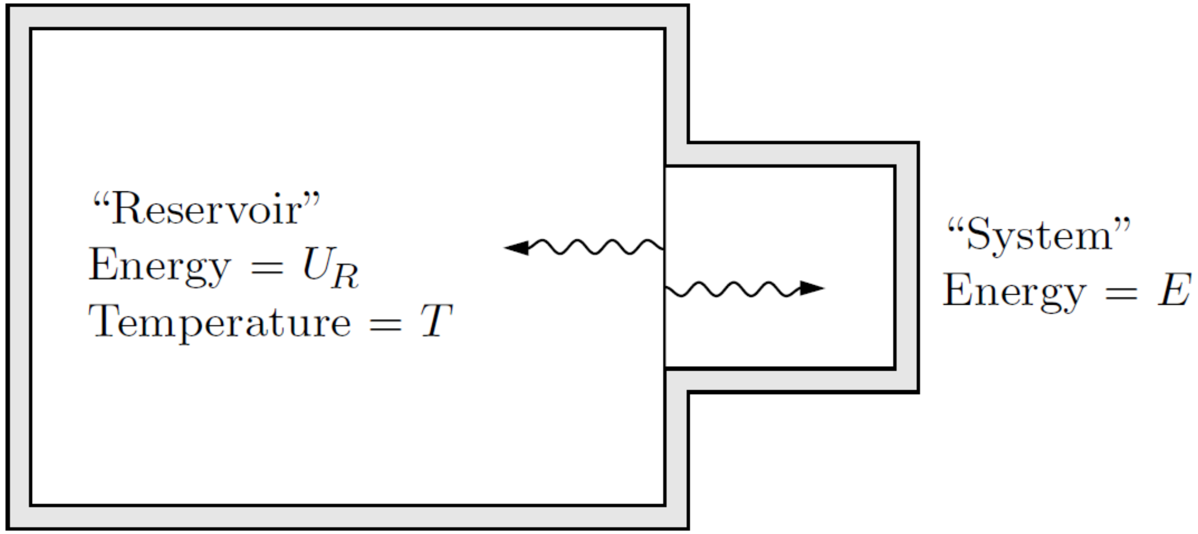
Is electron gas composed of fermions or bosons?

Microcanonical, canonical, and grand canonical ensembles

In isolated systems or microcanonical ensemble, all allowed microstates had the same probability, which is “trivial” probability distribution. In canonical ensemble, members are assigned to states according to the Boltzmann probability distribution. It considers system in thermal contact with a much larger “reservoir” at some well-defined temperature allowing exchange of energy. Grand canonical ensemble allows exchange of particles too.

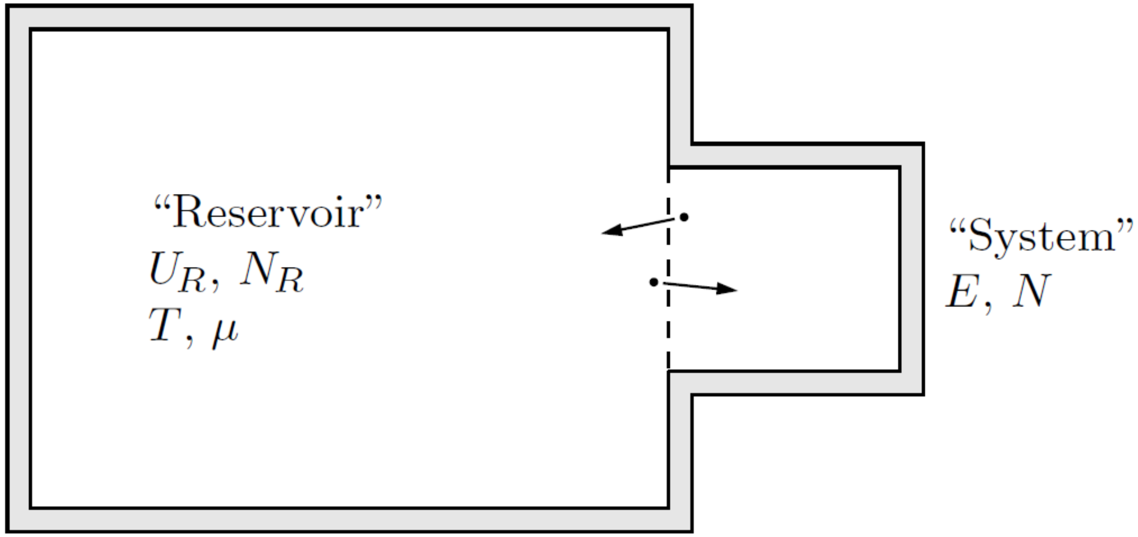
Boltzmann and Maxwell distributions

Fermi-Dirac and Bose-Einstein distributions



DVS

Canonical ensemble



DVS

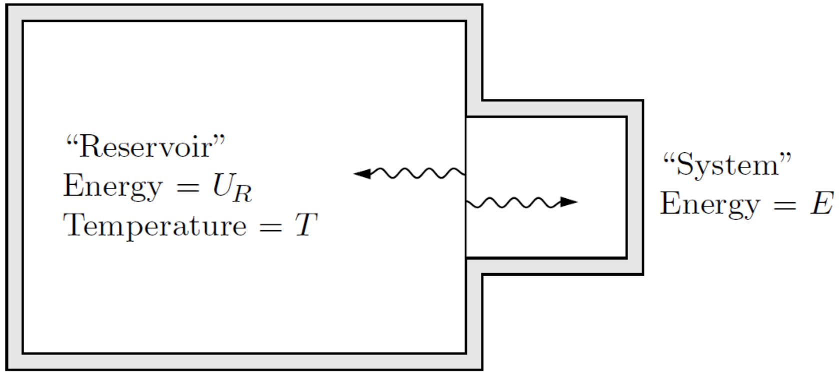
Grand canonical ensemble

- Chemical potential is a key for understanding behavior of electron gas.

Boltzmann statistics

Boltzmann statistics calculates probability of the system in the contact with reservoir having energy E . This probability is proportional to multiplicity of reservoir:

$$P(E) = C\Omega_R\ (E)$$



DVS

$$\Omega_R(E) = A\Omega_R\ (0) \quad S_R(E) = k\ \ln\Omega_R(0) + k\ln A$$

$$\Delta S_R = k\ln A \qquad \Delta U = T\Delta S - P\Delta V + \mu\Delta N$$

$$E = -\Delta U_R = -T\Delta S_R \qquad \Delta S_R = -\frac{E}{T}$$

$$P(s) = \frac{1}{Z}e^{-\frac{E(s)}{kT}}$$

$$Z = \sum_s e^{-\frac{E(s)}{kT}}$$

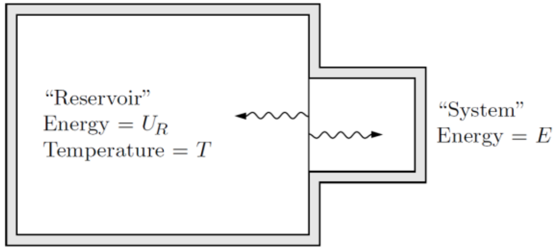
$$A = e^{-E/kT} \qquad P(E) = AC\Omega_R\ (0)$$

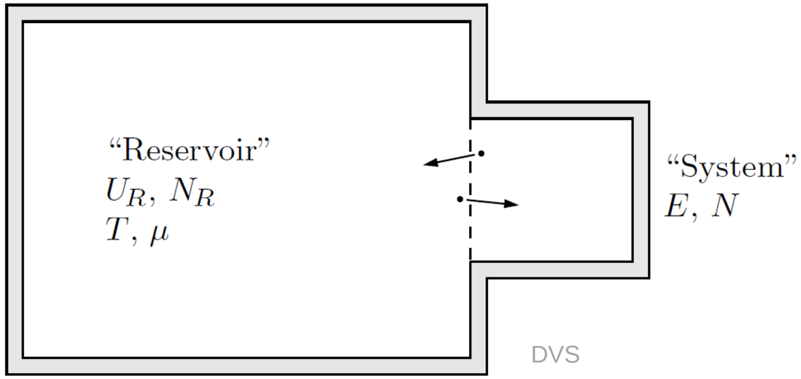
Boltzmann distribution

A is Boltzmann factor $e^{-\frac{E}{kT}}$

$$P(E) = e^{-E/kT}C\Omega_R\ (0) = \frac{1}{Z}e^{-E/kT}.$$

Transition to Gibbs statistics





DVS

Boltzmann statistics calculates probability of the system in the contact with reservoir having energy E . This probability is proportional to multiplicity of reservoir:

$$P(E) = C\Omega_R\,(E)$$

$$\Omega(E) = A\Omega_R\,(0) \qquad S_R(E) = k\,\ln\Omega_R(0) + k\ln A$$

$$\Delta S_R = k\ln A \qquad \Delta U = T\Delta S - P\Delta V + \mu\Delta N$$

$$E = -\Delta U_R = -T\Delta S_R - \mu\Delta N_R \qquad \Delta S_R = -\frac{E - \mu N}{T}$$

$$A = e^{-(E-\mu N)/kT} \qquad \mathcal{P}(E) = AC\Omega_R\,(0)$$

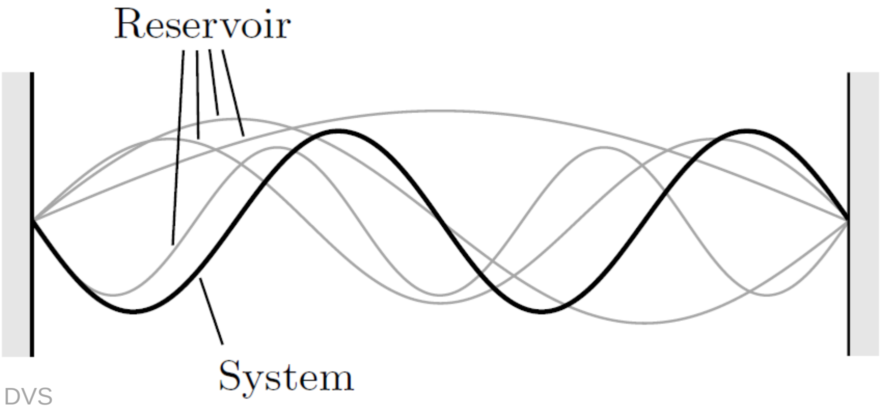
Gibbs distribution

A is Gibbs factor $e^{-\frac{E-\mu N}{kT}}$

$$\mathcal{P}(E) = e^{-(E-\mu N)/kT}\,C\Omega_R\,(0) = \frac{1}{\mathcal{Z}}e^{-(E-\mu N)/kT}$$

Fermi-Dirac distribution

Main idea is to consider a system as combination of states for single-particles and find average number of particles in these states. The energy when a state is occupied by a single particle is ε. When the state is unoccupied, its energy is 0. If it is occupied by n particles, the energy is $n\varepsilon$. The probability of the state being occupied by n particles is:



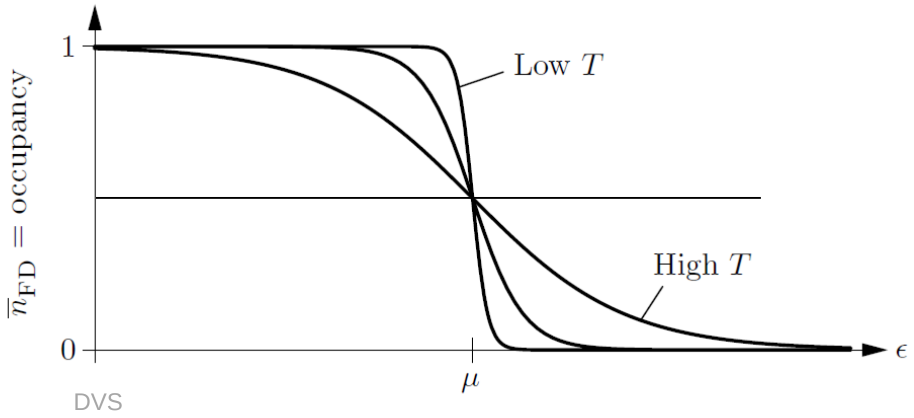
$$\mathcal{P}(n) = \frac{1}{\mathcal{Z}} e^{-\frac{n\epsilon-\mu n}{kT}} = \frac{1}{\mathcal{Z}} e^{-\frac{n(\epsilon-\mu)}{kT}}$$

If the particles are fermions, then n can only be 0 or 1, so the grand partition function is: $\mathcal{Z} = 1 + e^{-\frac{\epsilon-\mu}{kT}}$.

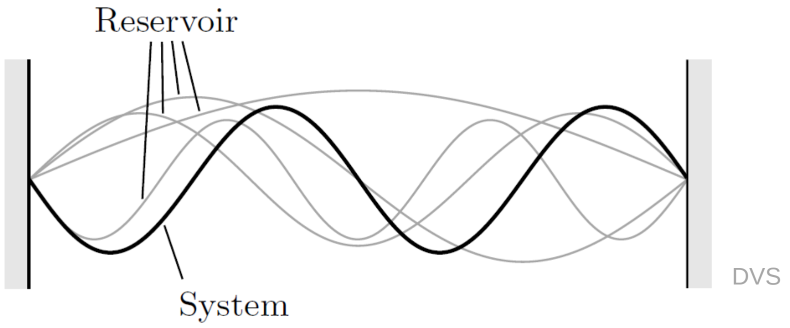
The average number of particles in the state or the occupancy of the state is then:

$$\bar{n} = \sum_n n\mathcal{P}(n) = 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) = \frac{e^{-\frac{\epsilon-\mu}{kT}}}{1 + e^{-\frac{\epsilon-\mu}{kT}}} = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} + 1}.$$

It is the **Fermi-Dirac distribution**: $\bar{n}_{FD} = \frac{1}{e^{\frac{\epsilon-\mu}{kT}}+1}$.



Bose-Einstein distribution



If the particles are bosons, then n can be any nonnegative integer, so the grand partition function is:

$$\mathcal{Z} = 1 + e^{-\frac{\epsilon-\mu}{kT}} + e^{-\frac{2(\epsilon-\mu)}{kT}} + \cdots = 1 + e^{-\frac{\epsilon-\mu}{kT}} + \left(e^{-\frac{\epsilon-\mu}{kT}}\right)^2 + \cdots = \frac{1}{1 - e^{-\frac{\epsilon-\mu}{kT}}}$$

$$\mathcal{P}(n) = \frac{1}{\mathcal{Z}} e^{-\frac{n\epsilon-\mu n}{kT}} = \frac{1}{\mathcal{Z}} e^{-\frac{n(\epsilon-\mu)}{kT}}$$

The average number of particles in the state or the occupancy of the state is then:

$$\bar{n} = \sum_n n\mathcal{P}(n) = 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) + 2 \cdot \mathcal{P}(2) + \cdots = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} - 1}$$

This is **Bose-Einstein distribution**: $\bar{n}_{BE} = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} - 1}$

Like the Fermi-Dirac distribution, the Bose-Einstein distribution goes to zero when $\varepsilon \gg \mu$.
Unlike the Fermi-Dirac distribution, it goes to infinity as ε approaches μ from above.

Comparison of distributions

$$F = -kT\ln(Z)$$

$$\mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}$$

$$Z = \frac{Z_1^{\,N}}{N!}$$

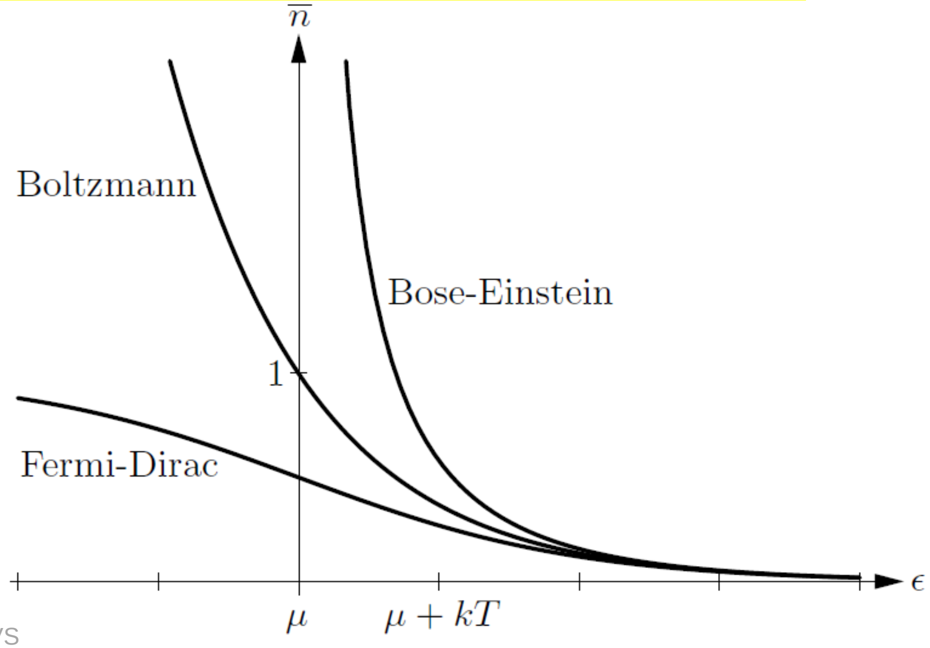
$$\ln N! \approx N(\ln N - 1)$$

For the Boltzmann distribution: $P(s) = \frac{1}{Z_1} e^{-\frac{\epsilon}{kT}}$ $\quad \mu = -kT\ln\left(\frac{Z_1}{N}\right)$

$$\bar{n}_{Boltzmann} = \frac{1}{Z_1} N e^{-\frac{\epsilon}{kT}} = e^{-\frac{\epsilon}{kT}} e^{\frac{\mu}{kT}} = e^{-\frac{(\epsilon-\mu)}{kT}}$$

$$\bar{n}_{Boltzmann} = e^{-\frac{(\epsilon-\mu)}{kT}} \qquad \bar{n}_{FD} = \frac{1}{e^{\frac{\epsilon-\mu}{kT}}+1} \qquad \bar{n}_{BE} = \frac{1}{e^{\frac{\epsilon-\mu}{kT}}-1}$$

When $\varepsilon \gg \mu$, the exponent is very large, one can neglect the 1 in the denominator of Fermi-Dirac and Bose-Einstein distributions, and both are reduced to the Boltzmann distribution. The precise condition for the three distributions to agree is: $\epsilon - \mu \gg kT$.

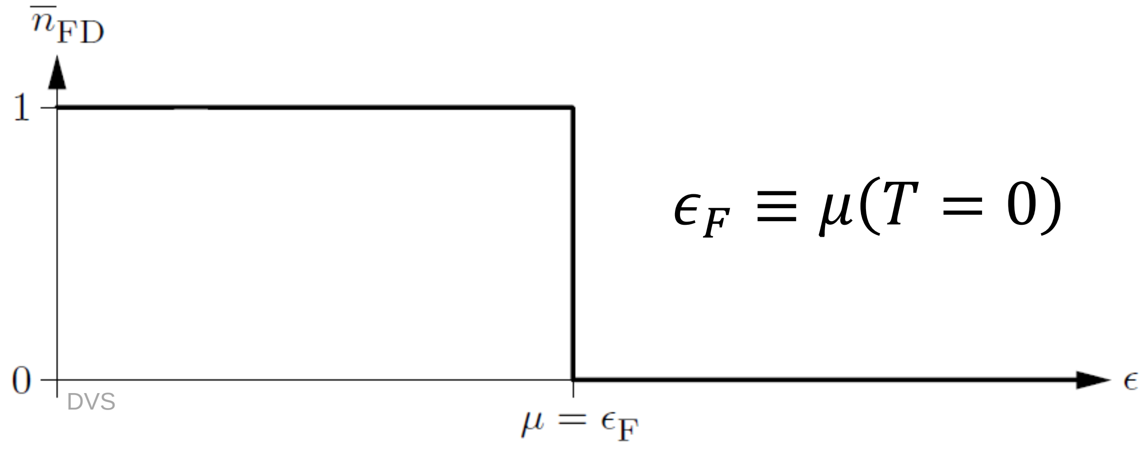


Degenerate Fermi gas

- Gas of fermions is degenerate when nearly all states below μ are occupied and nearly all states above μ are unoccupied, which typically happens at a low temperatures $kT < \epsilon - \mu$.
- At zero temperature, Fermi-Dirac distribution function is a step function. It equals 1 for all states with $\epsilon < \mu$ and equals 0 for all states with $\epsilon > \mu$.
- As a boundary of filled state at $T = 0$, μ is also called Fermi energy: ϵ_F.
- The value of ϵ_F is determined by the total number of electrons.
- All electron states are filled, from the lowest available state to ϵ_F.
- μ is change in total energy at zero temperature when one particle is added to the system.

$$\bar{n}_{FD} = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} + 1}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$



$$\epsilon_F \equiv \mu(T = 0)$$

Counting quantized states in 3D:

$$\epsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}}$$

Properties of degenerate Fermi gas

- The average energy of the electrons is 3/5 the Fermi energy: $U = 3/5\epsilon_F$. Fermi energy for conduction electrons in a typical metal is a few electron-volts. This is much larger than the average thermal energy of a particle at room temperature, $kT \approx 1/40\ eV$, which means electron gas in metals is a degenerate Fermi gas.
- The condition $\epsilon_F \gg kT$ comes from the condition $V/\vartheta_Q \ll N$, which means that quantum statistics is important for the electron gas.
- The large, comparable with kT, Fermi energy justifies approximation of $T \approx 0$.
- Using the formula $P = -(\partial U/\partial V)_{S,N}$, the degeneracy pressure $P = \frac{2U}{3V}$ is found to be few billion N/m^2, sufficient to withstand electrostatic forces. This pressure does not come from the electrostatic repulsion between the electrons. It arises purely from the quantum exclusion principle.
- In degenerate gas, all electron states are filled from the lowest available state to ϵ_F.

Fermi gas at small nonzero temperatures

- At finite temperature T, normal particles would get energy about kT. However, degenerate electron gas is special. Most of the electrons cannot acquire such energy, because all the states that they might jump in are already occupied.
- The only electrons that can acquire some energy (thermal) are those that are already within kT of the Fermi energy. Only they can jump up into unoccupied states above ϵ_F.
- The number of electrons that can be affected by the increase in T is proportional to T. This number must also be proportional to N. Thus, the additional energy at finite T is doubly proportional to T: $\Delta U(T) \propto NkT \cdot kT$.
- Coefficient proportionality can be guessed from dimensionality units. It must have unit of one over energy, and the only energy available in this model is ϵ_F.
- Knowing this, allows to calculate heat capacity of electron gas. It is going to zero as $T \to 0$.

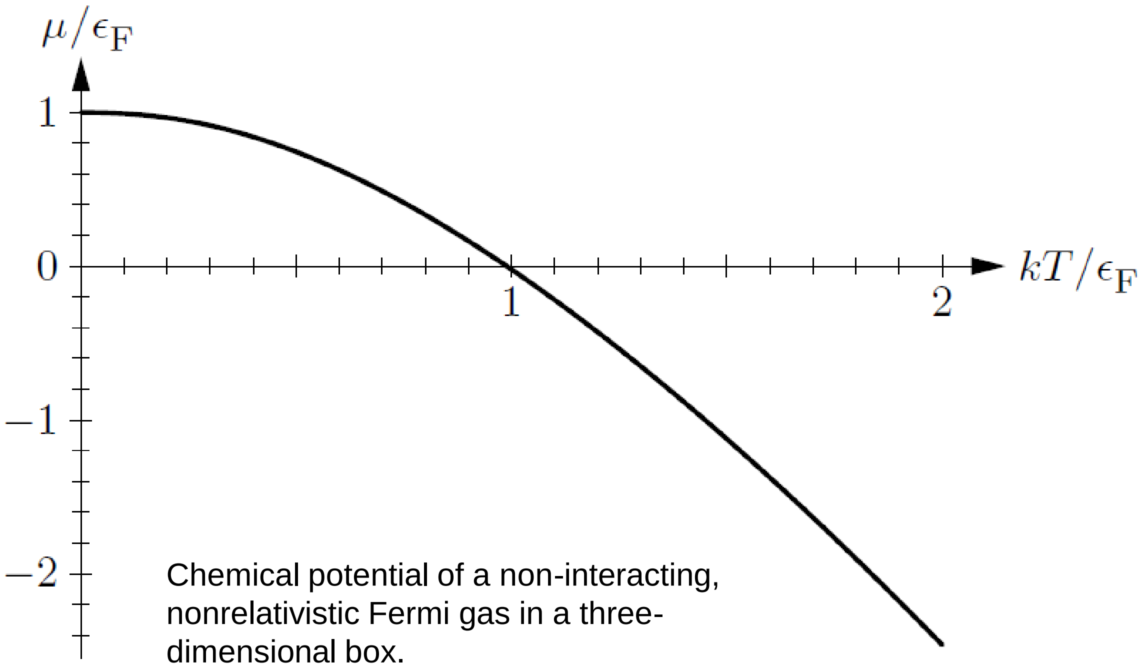
$$U = \frac{3}{5}N\epsilon_F + A\frac{NkT \cdot kT}{\epsilon_F} \qquad A = \frac{\pi^2}{4} \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\pi^2 Nk^2 T}{2\epsilon_F}$$

Chemical potential of degenerate Fermi gas

- The chemical potential, μ, is the point where the probability of a state being occupied is exactly 1/2.
- At $T = 0$, $\mu = \epsilon_F$.
- The chemical potential decreases with increase of T.
- At high temperatures, μ becomes negative and approaches the form for an ordinary gas obeying Boltzmann statistics.

Chemical potential of ideal gas:

$$\mu = -kTln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$



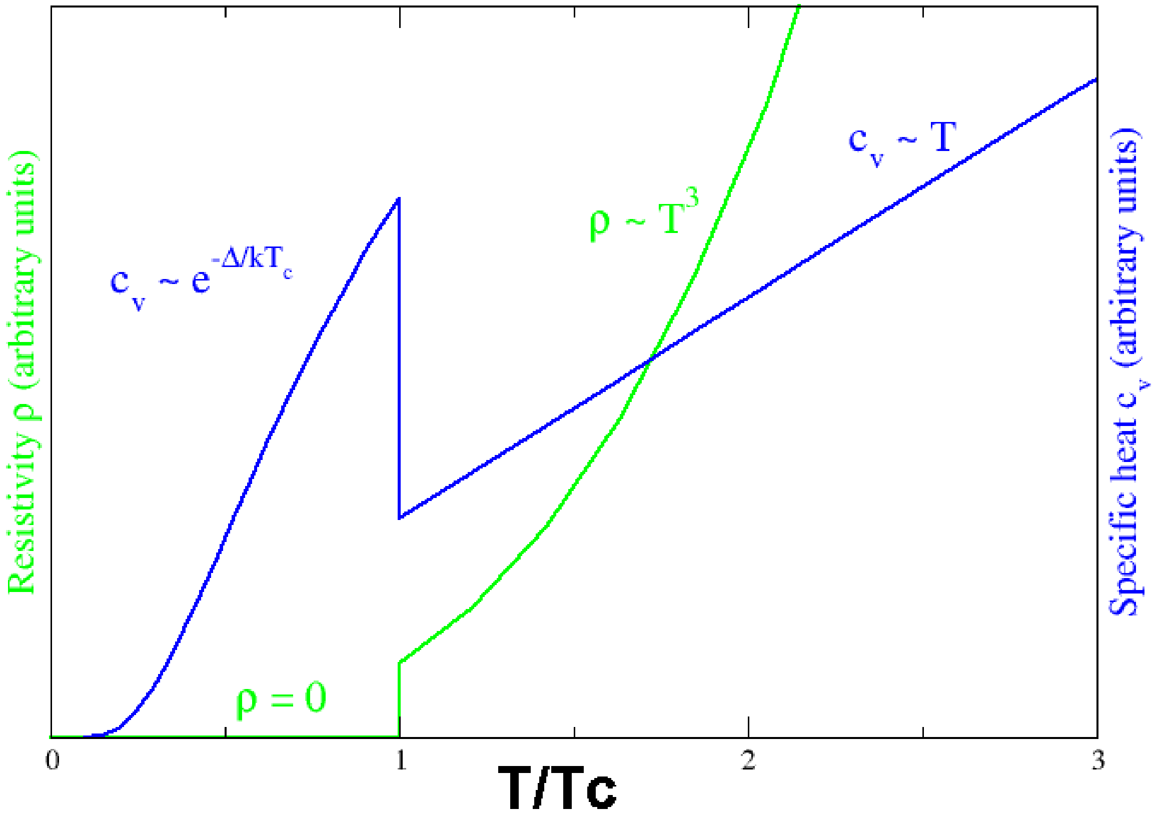
Chemical potential of a non-interacting, nonrelativistic Fermi gas in a three-dimensional box.

Bose-Einstein condensation and superconductivity

- Superconductivity is the result of Bose-Einstein condensation taking place when fermions form bosons being united into Cooper pairs.
- As a result, electron gas acquires property of superfluidity dropping resistance to absolute zero.
- Superconductors have unique quantum properties allowing multiple uses in modern technology.

Fermi gas: $$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\pi^2 N k^2 T}{2\epsilon_F}$$

Superconductor:



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Summary

- Chemical potential is a key for understanding behavior of electron gas.
- Chemical potential changes from negative to positive at a transition from classical to quantum behavior.
- Electrons in a metal behave quantum mechanically with positive chemical potential.
- Quantum behavior results in quantum statistics: Bose-Einstein and Fermi-Dirac.
- Electrons in a metal at room temperature are well described by a model of degenerate Fermi-Dirac gas. In this gas, all states are filled at energies below the Fermi energy ϵ_F and empty above.
- Chemical potential of degenerate Fermi-Dirac gas changes from positive to negative when kT becomes higher than ϵ_F.
- Electrons can be Bose-Einstein particles when they are united into Cooper pairs, which leads to phenomenon of superconductivity.