

1. PV Basics

Three generations of photovoltaics

Photovoltaic (PV) technologies are often categorized by a popular, though not entirely distinct, divisions, which refer to the historical evolution and underlying concepts of the associated materials and devices. These are the three generations of solar cells, of which the first two are considered to be more-or-less fleshed out through decades of research, whereas the third is the frontier addressed by current science and engineering. On the other hand, even the most advanced of the current, third-generation technologies at the forefront of the PV research rely heavily on established materials and principles, so expectations of a dramatic paradigm shift remain largely unfulfilled.

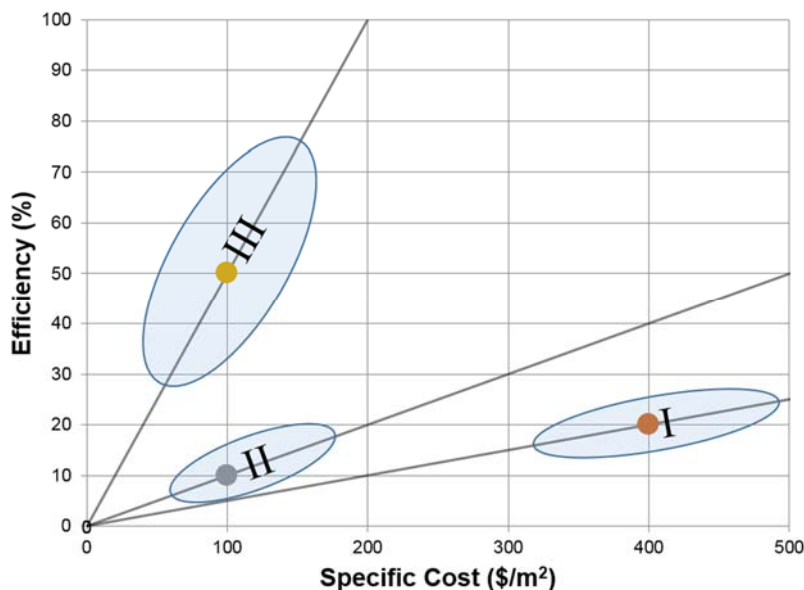
Generation-1 is primarily associated with wafer-based (bulk) silicon, far and away the most enduring and established material for single-junction PV. Despite the earth-abundant Si resources, the absorption of light by Si is fairly weak, and high material quality is needed for devices. The combination of high device fabrication costs and moderate efficiencies (15-25%) remain limitations.

Generation-2 is associated with amorphous and polycrystalline thin films. These are typically strongly absorbing materials that do not require high material quality. But generation-2 efficiencies remain low-to-moderate (8-20%). These cells are generally based on the same physics as generation-1 cells, but can be made with much lower -cost processes.

Generation-3 targets new concepts in PV. The goals are to maintain low materials costs, while improving efficiency.

Efficiency vs. specific costs

The goal is to increase efficiency while reducing specific cost



Another benchmark

We can relate efficiency/specific cost to \$/Watt as follows. The efficiency is

$$\eta = P/P_s$$

where

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P and P_s are the power generated and the solar power supplied, respectively, both of which are measured in watts ($1 \text{ W} = 1 \text{ J/s}$). Consider the cost C (in \$) per unit area A (in m^2) of a PV system – called the specific cost, in $\$/\text{m}^2$. The efficiency per unit specific cost can be written

$$\frac{\eta}{C/A} = \frac{P/P_s}{C/A} = \frac{P}{C \cdot (P_s/A)} = \frac{1}{\left(\frac{C}{P}\right) \cdot I_s}$$

where I_s is the solar power intensity (in W/m^2). Thus, decreasing the cost per unit power is equivalent to increasing efficiency per unit specific cost, i.e.,

$$\frac{\eta}{C/A} \uparrow \Leftrightarrow \frac{C}{P} \downarrow$$

Estimations

A common (though somewhat dated) benchmark to remember that was set by DOE is $\$/\text{W}$. Using

$$\frac{C}{P} = \frac{1}{\left(\frac{\eta}{C/A}\right) \cdot I_s} = \frac{C/A}{\eta \cdot I_s}$$

where $I_s \approx 1000 \text{ W}/\text{m}^2$, we arrive at the following numbers:

Take a generation-1 cell with $\eta \approx 20\%$ and $C/A \approx \$400/\text{m}^2$. Then

$$\frac{C}{P} \approx \frac{\$400/\text{m}^2}{(0.20) \cdot (1000 \text{ W}/\text{m}^2)} = \$2.00/\text{W}$$

A generation-2 cell with $\eta \approx 10\%$ and $C/A \approx \$100/\text{m}^2$ has

$$\frac{C}{P} \approx \frac{\$100/\text{m}^2}{(0.10) \cdot (1000 \text{ W}/\text{m}^2)} = \$1.00/\text{W}$$

Obviously, a generation-3 cell needs to have higher η and lower C/A .

Approaches

What materials/structures are we talking about?

Generation-1 cells are formed of wafers with high-purity, especially crystalline silicon (c-Si), GaAs, or InP. The devices are usually p/n homojunctions. Doping is performed by diffusion or implantation. There are high energy requirement for fabrication and high materials demands.

Generation-2 cells are CdTe, CuInSe₂, a-Si:H, thin-film Si, the CuZnSnS compounds (called kesterites, or stannites). These are formed by evaporation, sputtering, or dip coating on transparent-conducting-oxide (TCO) coated glass. They usually consist of heterojunctions formed with another, wide-bandgap material, such as CdS, or p/i/n structures. An appealing aspect of generation-2 materials is that they are produced by industrially scalable processes.

The scope of generation-3 PV is unlimited, but common targets are semiconductor quantum dots, wires, wells, superlattices, rare-earth, up-converting nanoparticle composites, selective absorbers/emitters, and nanoengineered photonic structures for light trapping.

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The significance of these categories should not be overstated, For example, some technologies, like wafer-based multijunction devices, do not fit entirely within any of these categories. Advances continue to be made for single-junction Si solar cells by incorporating new light and current collection mechanisms within otherwise traditional technologies.

Background

Photovoltaics is the direct conversion of light energy into electrical energy. Light consists of photons (particles) with energy E , but can also be described as waves, with frequency f and wavelength λ . Based on Planck's formulation, Einstein proposed that photons have energy:

$$E = hf$$

The wave satisfies

$$v = f \cdot \lambda_n = \frac{c}{n}$$

where v is the speed of light in medium, c is the speed of light in vacuum and n is the index of refraction. the frequency is constant, so in the vacuum, $c = f \cdot \lambda_1$. We see that

$$\lambda_n = \lambda_1 \cdot \left(\frac{v}{c}\right) = \frac{\lambda_1}{n}$$

For visible light $\lambda_1 \approx 400 - 700$ nm . The photon energy does not change in the medium

$$E = \frac{hv}{\lambda_n} = \frac{hc}{\lambda_1}$$

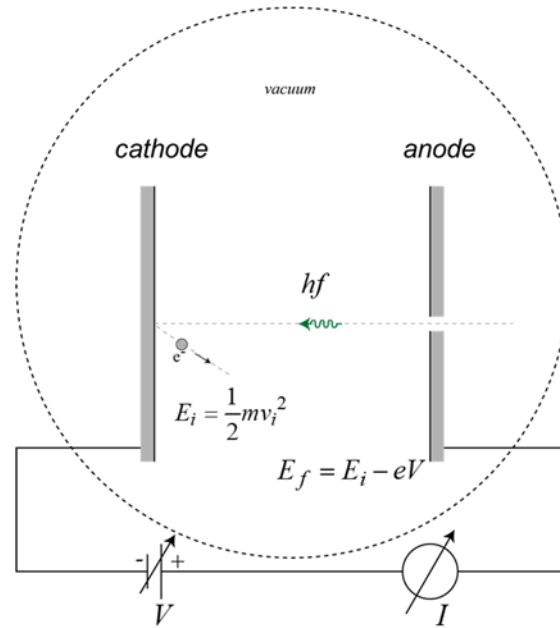
We can use the values of important constants and the definition of the electron volt (eV) to find a useful product

$$\left. \begin{array}{l} h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \\ c = 3.00 \times 10^8 \text{ m/s} \\ 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} \end{array} \right\} \Rightarrow hc = 1240 \text{ eV} \cdot \text{nm}$$

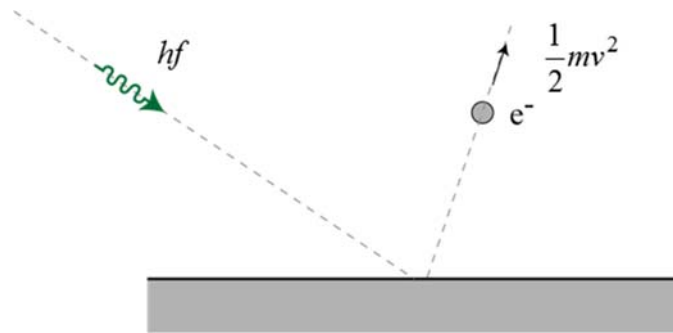
Lastly, note that light undergoes both collisions (in which case we think of it as particles) and interference (when we think of it as waves).

Photoelectric effect (I)

It was observed that electrons were ejected from materials during illumination with short-wavelength light in the experiment depicted below



Say the target (cathode) has work function Φ_c . The kinetic energy of the ejected electron is initially $E_i = mv_i^2/2$. But after crossing the potential barrier, it is reduced to $E_f = E_i - eV$. If $eV > E_i$, no electrons are detected at the anode. Einstein explained that electrons were ejected by individual particles of light (photons).



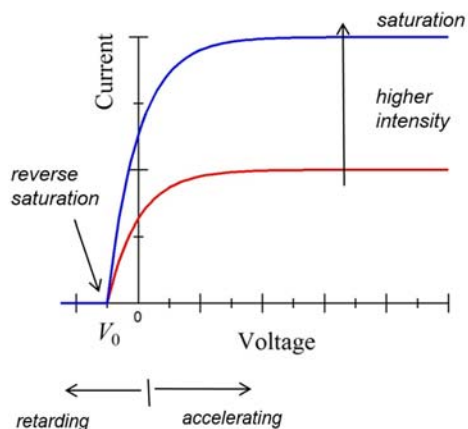
The energy of an ejected electron is

$$\frac{1}{2}mv_i^2 = hf - \Phi_c$$

The reverse saturation voltage is then

$$eV_0 = \frac{1}{2}mv_i^2$$

The current-voltage characteristics with changing potential barrier and light intensity are plotted below.



Increasing the light intensity does not change the reverse-saturation voltage; it only changes the saturation current.

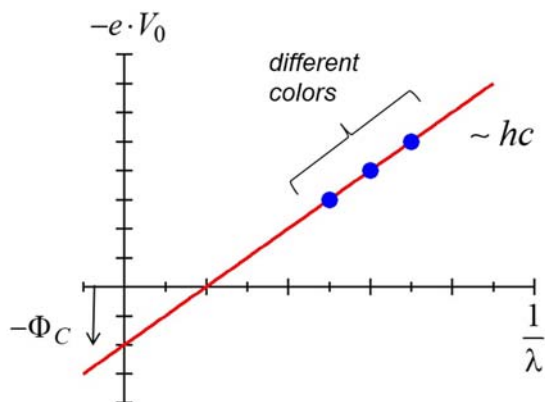
Photoelectric effect (II)

The light used must be of sufficiently short wavelength to overcome the work function of the metal target.

If $E_f = 0$, then

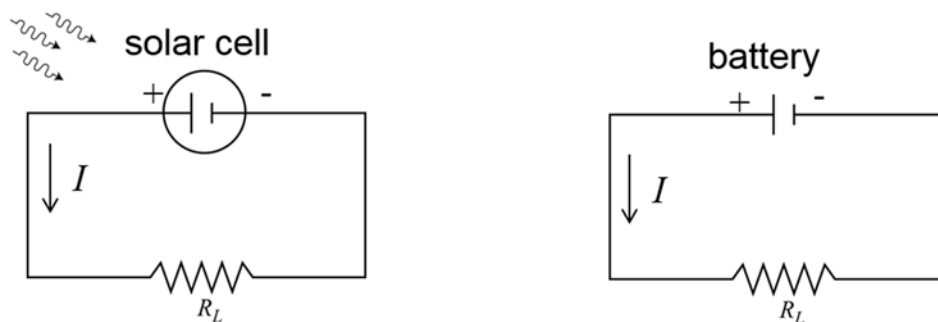
$$-e \cdot V_0 = \frac{1}{2} m v_i^2 = hf - \Phi_c$$

We can measure the work function of the cathode by varying the light wavelength and fitting $-eV_0$ vs. $1/\lambda$.



Solar cell vs. battery (ideal)

The first solar cells were called solar batteries. Both solar cells and batteries provide electrical energy, though the I-V characteristics are not identical.



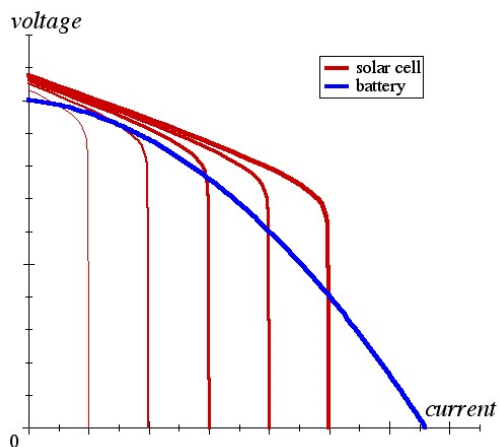
For the solar cell, we will find that the most common behavior is approximately

$$I(V) = I_{photo} - I_{dark}(V)$$

where I_{photo} is the photocurrent and

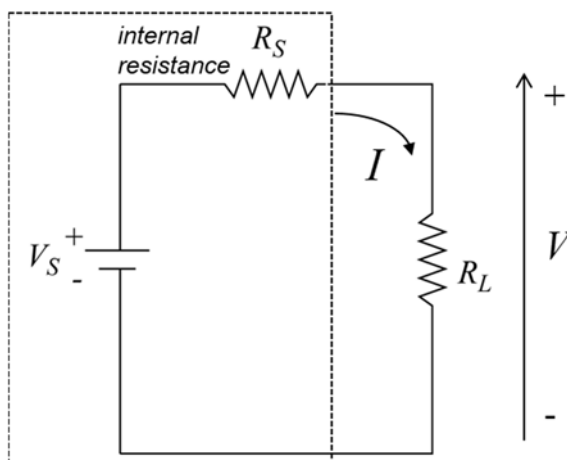
$$I_{dark}(V) = I_0 \cdot (e^{qV/nk_B T} - 1)$$

describes the dark, or diode current. This is different from a battery, which is primarily a voltage source.



Battery: equivalent circuit

A battery with a load resistor R_L can be modeled as shown below



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The battery has some internal resistance R_S in series with the load that must be considered as more power is drawn. The output current is

$$I = \frac{V_S}{R_S + R_L}$$

So, the chemical potential in the battery is divided, reducing the output voltage

$$V = \left(\frac{R_L}{R_S + R_L} \right) \cdot V_S$$

Let's assume the internal resistance increases with current (because of joule heating)

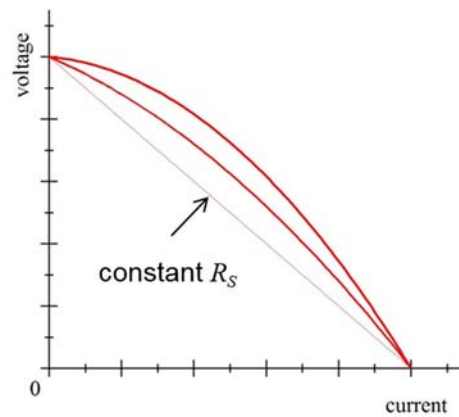
$$R_S = R_0 + R_1 \cdot \left(\frac{I}{I_{\max}} \right)$$

Then the maximum current is

$$I_{\max} \equiv \frac{V_S}{R_0 + R_1}$$

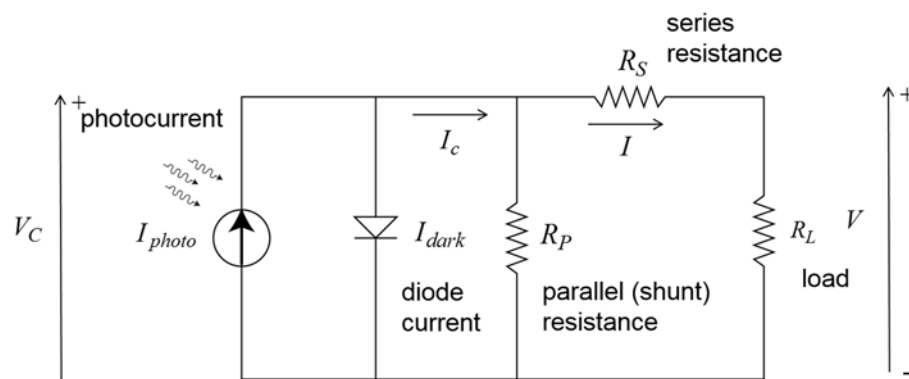
The voltage provided to the load is only

$$V = V_S - I \cdot R_S$$



Solar cell: equivalent circuit

A simple equivalent circuit for a solar cell is shown below



This depicts the equation

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$$I_C(V_C) = I_{photo} - I_{dark}(V_C)$$

The current delivered to the load is

$$I = I_C(V_C) - \frac{V_C}{R_P} = \frac{V_C - V}{R_S}$$

The cell voltage is

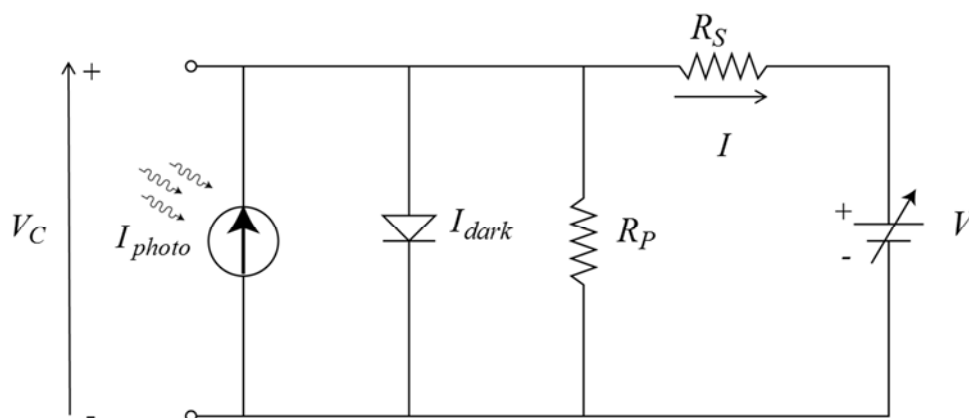
$$V_c = I \cdot (R_S + R_L)$$

The output voltage is somewhat less

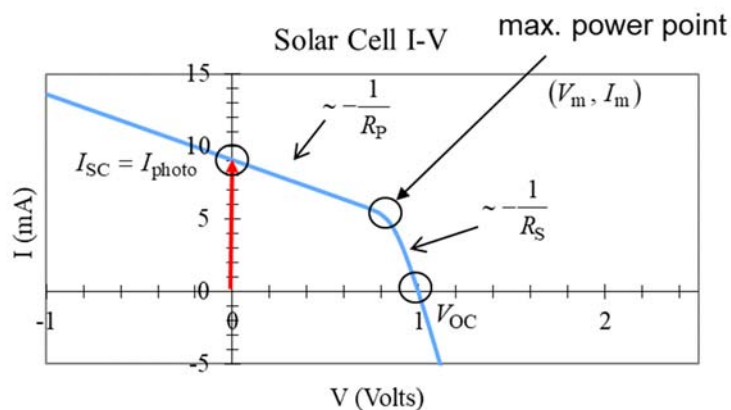
$$V = I \cdot R_L$$

Solar-cell testing

Testing of solar cells is usually done with a variable voltage source



Typical I-V characteristics of an imperfect solar cell are shown below. Near open circuit ($I = 0$), the slope is given by the series conductance $1/R_S$. Near short circuit ($V = 0$), the slope is determined by the parallel (shunt) conductance $1/R_P$.



I-V algorithm

An iterative algorithm for finding the current delivered by a solar cell with parasitic resistance for a given applied voltage is outlined below.


```

//Initialize
I = 0      VC = V
tol = 10-12  done=false
while(not(done))
  improved = false
  { V'+ = fV(VC + δV)      V'- = fV(VC - δV)
    if (|V'+ - V| < δbest)    if (|V'- - V| < δbest)
      {                          {
        δbest = |V'+ - V|      δbest = |V'- - V|
        VC → VC + δV      VC → VC - δV
        improved = true      improved = true
      }                          }
  if(improved) δV → (1.5) · δV
  else δV → δV/2
  if (δbest < tol) done=true
}

```

$$f_V(V_C) \equiv V_C \cdot \left(1 + \frac{R_S}{R_P}\right) - I_C(V_C) \cdot R_S$$

Thermal distribution functions

From the first law of thermodynamics, the change in internal energy of a system is related to changes in entropy S and the number of particles N :

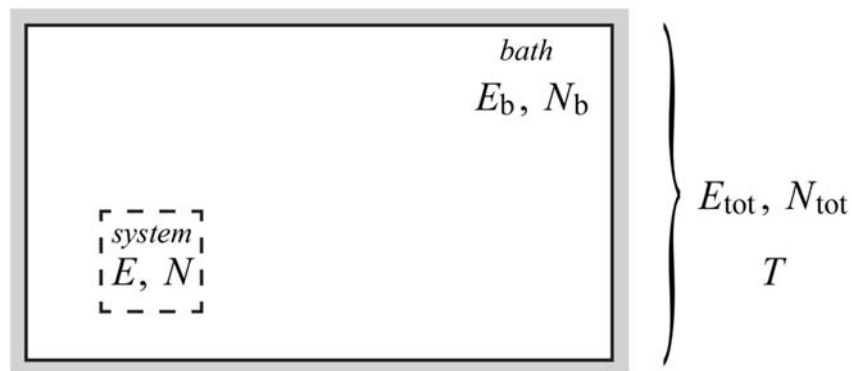
$$dE = T \cdot dS + \mu \cdot dN$$

where T is temperature and μ is chemical potential.

Statistical mechanics relates the entropy to the number of microstates $\Omega(E, N)$ for a given E and N :

$$S = k \cdot \ln[\Omega(E, N)]$$

Consider a microscopically small system embedded within a much larger bath of particles. The entire system is in equilibrium and there is no partition, so energy and particles can move freely between the bath and system.



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Say the bath and system have parameters E_b , N_b and E , N , respectively. The total energy and number of particles are:

$$E_{\text{tot}} = E_b + E \quad N_{\text{tot}} = N_b + N$$

The total number of microstates is the product of those in the bath and system. We find that the entropy is then extensive:

$$\begin{aligned} \Omega_{\text{tot}}(E_{\text{tot}}, N_{\text{tot}}) &= \Omega_b(E_b, N_b) \cdot \Omega(E, N) \\ S_{\text{tot}} &= k \ln[\Omega_{\text{tot}}(E_{\text{tot}}, N_{\text{tot}})] \\ &= k \ln[\Omega_b(E_b, N_b)] + k \ln[\Omega(E, N)] \\ S_{\text{tot}} &= S_b + S \end{aligned}$$

Consider the entropy of the bath $S_b = S_{\text{tot}} - S$. Then

$$e^{S_b/k} = e^{S_{\text{tot}}/k} \cdot e^{-S/k}$$

Because the system is extremely small, we can let $S \rightarrow dS$, $E \rightarrow dE$, and $N \rightarrow dN$. So

$$dS = (dE - \mu \cdot dN)/T$$

for the system, and we have

$$\Omega_b(E_{\text{tot}} - dE, N_{\text{tot}} - dN) = e^{S_{\text{tot}}/k} \cdot e^{-(dE - \mu \cdot dN)/kT}$$

This is proportional to the probability that the bath has energy $E_{\text{tot}} - dE$ and $N_{\text{tot}} - dN$ particles, which equals the probability that the system has energy dE and dN particles. The first factor on the right is constant. Referring to the total system parameters as E and N :

$$P(E, N) \propto e^{-(E - \mu \cdot N)/kT}$$

The smallest possible system would have a single energy level ε that contains N particles, so $E = N \cdot \varepsilon$. The probability that this state has a given number of particles N is then:

$$P(N) = \frac{e^{-N(\varepsilon - \mu)/kT}}{\sum_n e^{-n(\varepsilon - \mu)/kT}}$$

The average number of particles in the state is:

$$\langle N \rangle = \sum_n n \cdot P(n) = f_\mu(\varepsilon)$$

Defining $x \equiv e^{-(\varepsilon - \mu)/kT}$, we can write:

$$f(x) = \frac{\sum_n n \cdot x^n}{\sum_n x^n}$$

Two important cases are distinguished by the quantum statistics governing the allowed numbers of identical particles in a single state:

case 1: Bose-Einstein statistics

Particles such as photons are bosons. Any number can share a quantum state. The sum is over all $n = 0, 1, 2, 3, \dots, \infty$

$$f(x) = \frac{\sum_{n=0}^{\infty} n \cdot x^n}{\sum_{n=0}^{\infty} x^n}$$

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Defining the denominator as:

$$S = \sum_{n=0}^{\infty} x^n$$

we have

$$(1-x) \cdot S = 1 \Rightarrow S = \frac{1}{1-x}$$

The denominator can be found using

$$\sum_{n=0}^{\infty} n \cdot x^n = x \cdot \sum_{n=0}^{\infty} n \cdot x^{n-1} = x \cdot \frac{dS}{dx} = \frac{x}{(1-x)^2}$$

Thus,

$$f(x) = \frac{x}{1-x} = \frac{1}{\frac{1}{x} - 1}$$

This gives the Bose-Einstein distribution function.

$$f^{(BE)}(\varepsilon - \mu) = \frac{1}{e^{(\varepsilon - \mu)/kT} - 1}$$

case 2: Fermi-Dirac statistics

Particles such as electrons are fermions. No more than one may occupy a single quantum state. Thus $n = 0, 1$. Here

$$f(x) = \frac{\sum_{n=0}^1 n \cdot x^n}{\sum_{n=0}^1 x^n} = \frac{x}{1+x} = \frac{1}{\frac{1}{x} + 1}$$

This gives the Fermi-Dirac distribution function, or fermi function.

$$f^{(FD)}(\varepsilon - \mu) = \frac{1}{e^{(\varepsilon - \mu)/kT} + 1}$$

In the limit $\varepsilon - \mu \gg kT$, both the BE and FD distributions reduce to the Maxwell-Boltzmann distribution:

$$f^{(MB)}(\varepsilon - \mu) = e^{-(\varepsilon - \mu)/kT}$$