Thermal distributions 4

The Boltzmann factor

Modern physics for engineers

David Miller

The Boltzmann factor

Suppose a system M

 of moderate size

 is in thermal contact with

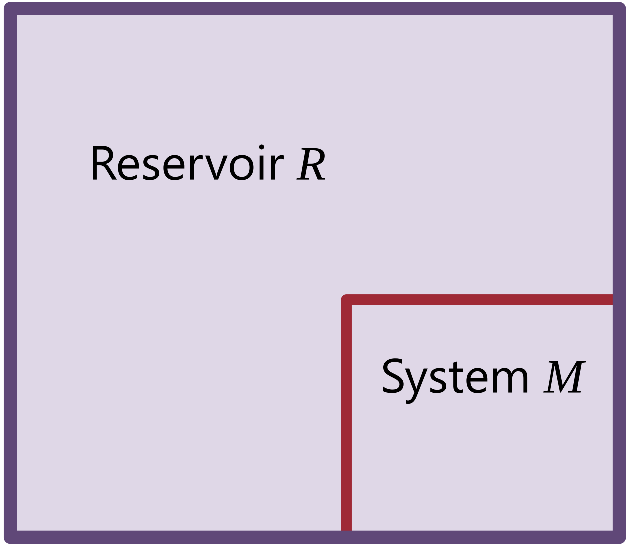
 a very large reservoir, R

Energy can be exchanged

 through the walls between

 system M and reservoir R

 but no particles can be exchanged



The Boltzmann factor

The energy in the total system

is some fixed amount U_o

System M has energy ε

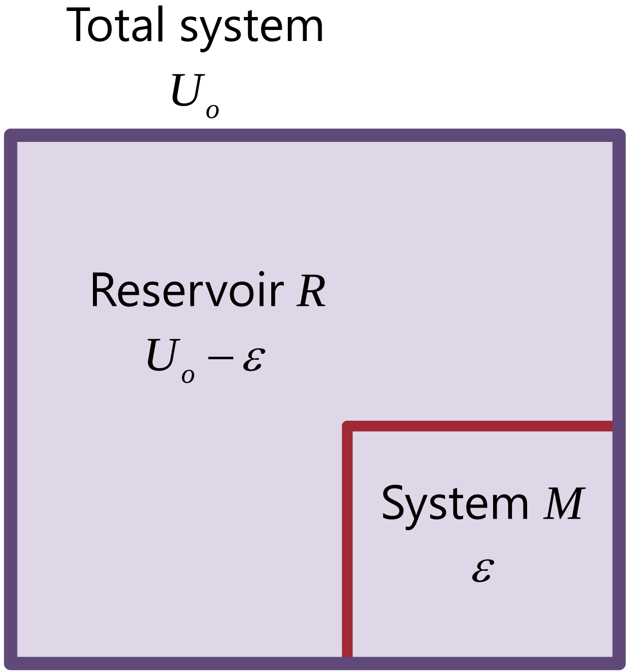
so the energy of reservoir R is $U_o - \varepsilon$

Our goal is to establish the probability

that system M is in some particular quantum state (a microstate of M)

given a temperature $\tau\ (\equiv k_B T)$

for the total system



The Boltzmann factor

Consider two quantum states of M

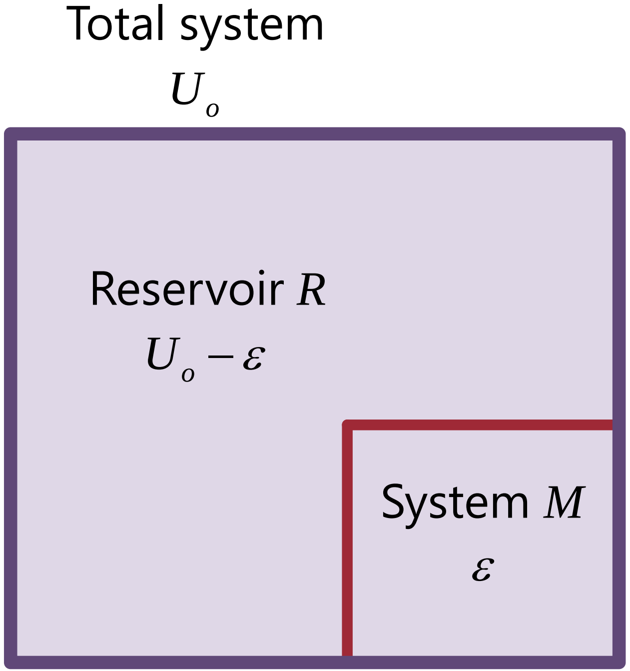
- state 1 and state 2
  - with associated energies ε_1 and ε_2

The probability P_1 that M is in state 1

- is proportional to the multiplicity of the reservoir R
  - when it has energy $U_o - \varepsilon_1$

This multiplicity is the number of ways the total system can exist

- in which system M is in state 1



The Boltzmann factor

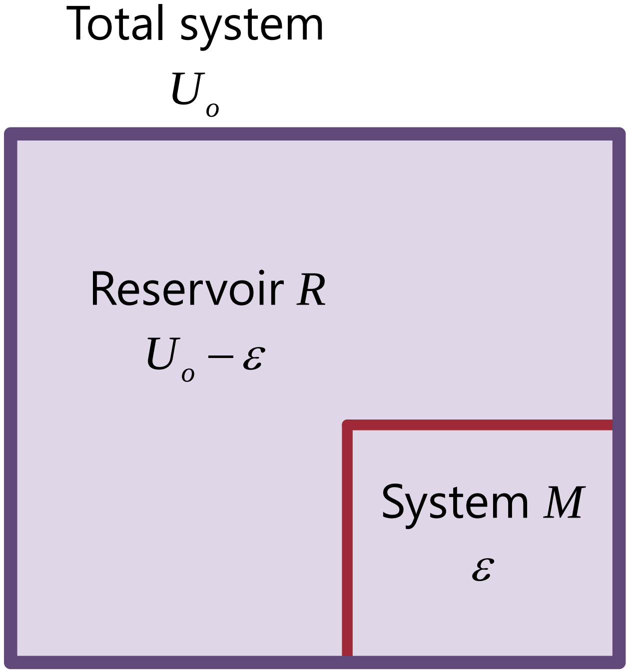
With a similar argument for state 2

and the corresponding probability

P_2 of system M being in state 2

we can write

$$\frac{P_1}{P_2} = \frac{\text{Multiplicity of } R \text{ at energy } U_0 - \varepsilon_1}{\text{Multiplicity of } R \text{ at energy } U_0 - \varepsilon_2}$$



Total system

U_o

Reservoir R

$U_o - \varepsilon$

System M

ε

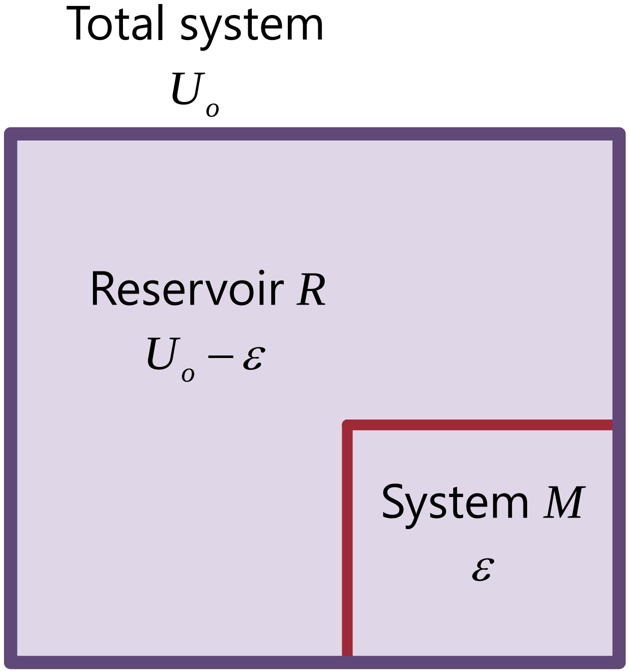
The Boltzmann factor

Note that we are not discussing the probabilities that

the system M has energy ε_1 or ε_2

There could possibly be many different quantum states

that have the same energy ε_1 or ε_2



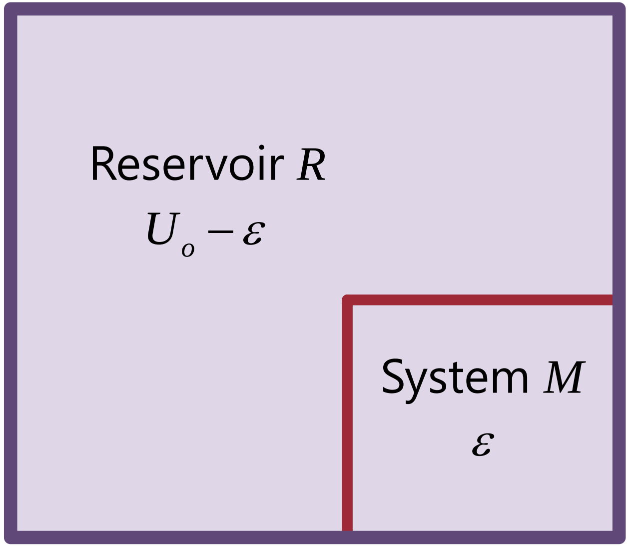
The Boltzmann factor

We are discussing the relative probabilities

- that the system is in a specific quantum state with energy ε_1
- or in another specific quantum state with energy ε_2

Total system

U_o



Reservoir R

$U_o - \varepsilon$

System M

ε

The Boltzmann factor

With $\sigma_R(U)$ as the entropy of the reservoir at some energy U

$$\text{Multiplicity of } R \text{ at energy } U_o - \varepsilon_1$$

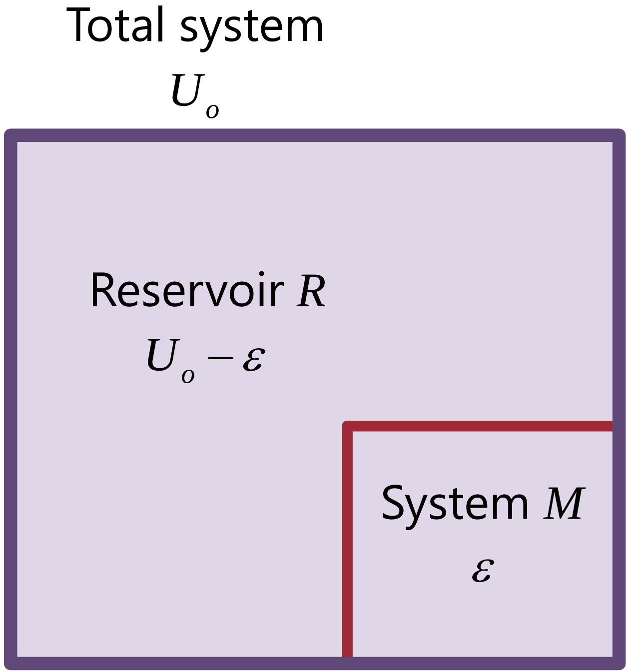
$$= \exp\left[\sigma_R\left(U_o - \varepsilon_1\right)\right]$$

So

$$\frac{P_1}{P_2} = \frac{\text{Multiplicity of } R \text{ at energy } U_o - \varepsilon_1}{\text{Multiplicity of } R \text{ at energy } U_o - \varepsilon_2}$$

gives

$$\frac{P_1}{P_2} = \frac{\exp\left[\sigma_R\left(U_o - \varepsilon_1\right)\right]}{\exp\left[\sigma_R\left(U_o - \varepsilon_2\right)\right]} = \exp\left[\sigma_R\left(U_o - \varepsilon_1\right) - \sigma_R\left(U_o - \varepsilon_2\right)\right]$$



Total system

U_o

Reservoir R

$U_o - \varepsilon$

System M

ε

The Boltzmann factor

Now, we presume that

compared to the energy of the very large reservoir

the energy ε of the specific state of the system M

is very small

So, we expand the entropy of the reservoir

in a Taylor series about the point U_o

$$\sigma_R\left(U_o-\varepsilon\right)=\sigma_R\left(U_o\right)-\varepsilon\left(\frac{\partial\sigma_R}{\partial U}\right)\bigg|_{U=U_o}+\frac{1}{2}\varepsilon^2\left(\frac{\partial^2\sigma_R}{\partial U^2}\right)\bigg|_{U=U_o}+\cdots$$

The Boltzmann factor

In $$\sigma_R(U_o-\varepsilon)=\sigma_R(U_o)-\varepsilon\left(\frac{\partial\sigma_R}{\partial U}\right)\bigg|_{U=U_o}+\frac{1}{2}\varepsilon^2\left(\frac{\partial^2\sigma_R}{\partial U^2}\right)\bigg|_{U=U_o}+\cdots$$

the derivatives are being taken at constant numbers of particles in both the reservoir and the system M

so $$\left(\frac{\partial\sigma_R}{\partial U}\right)\bigg|_{U=U_o}=\frac{1}{\tau}$$

where $\tau\ (\equiv k_B T)$ is the reservoir temperature

Presuming negligible change of reservoir temperature

we drop all higher derivatives

The Boltzmann factor

So retaining only the first derivative term

$$\sigma_R\left(U_o-\varepsilon\right)=\sigma_R\left(U_o\right)-\frac{\varepsilon}{\tau}$$

and using this in

$$\frac{P_1}{P_2}=\frac{\exp\left[\sigma_R\left(U_o-\varepsilon_1\right)\right]}{\exp\left[\sigma_R\left(U_o-\varepsilon_2\right)\right]}=\exp\left[\sigma_R\left(U_o-\varepsilon_1\right)-\sigma_R\left(U_o-\varepsilon_2\right)\right]$$

gives

$$\frac{P_1}{P_2}=\frac{\exp\left(-\varepsilon_1/\tau\right)}{\exp\left(-\varepsilon_2/\tau\right)}=\exp\left[-\frac{\left(\varepsilon_1-\varepsilon_2\right)}{\tau}\right]\equiv\exp\left[-\frac{\left(\varepsilon_1-\varepsilon_2\right)}{k_BT}\right]$$

The Boltzmann factor

So, for a system M in thermal contact

with a large reservoir at temperature $\tau \,(\equiv k_B T)$

the relative probability

under conditions of constant numbers of particles

of the system M being

in a specific quantum state of energy ε_1

rather than one of energy ε_2

is given by $$\frac{P_1}{P_2} = \exp\left[-\frac{(\varepsilon_1 - \varepsilon_2)}{k_B T}\right]$$

The Boltzmann factor

This factor

$$\boxed{\exp\left(-\frac{\varepsilon}{k_B T}\right)}$$

that expresses this

relative probability of occupation of states

separated by energy ε

in thermal equilibrium

is called the Boltzmann factor

The Boltzmann factor

This factor

$$\exp\left(-\frac{\varepsilon}{k_B T}\right)$$

and closely related ones

appear in a wide range of situations

They form the basis for the distributions of particles

among quantum mechanical states

in systems in thermal equilibrium

Thermal distributions 4

Chemical potential

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Chemical potential

Now we extend by one more step

allowing particles to move between the system M and the reservoir R

through a permeable membrane

instead of a thermally conducting wall

Such “diffusion” processes can occur

even if the temperature is the same on both sides

Chemical potential

The joint system should now settle down

in what we can call

diffusive equilibrium

to some situation that maximizes entropy overall

Chemical potential

- Presume for the moment that this movement of particles
  - does not itself change the energy of either system
    - For example
      - we could turn off the magnetic field on the spins
        - then every spin would have zero energy anyway

Chemical potential

So we examine a relation for the change in entropy

- for systems 1 and 2
  - with changes of particle numbers N_1 and N_2
    - at constant energies U_1 and U_2

Chemical potential

So we have $$\Delta\sigma = \left(\frac{\partial\sigma_1}{\partial N_1}\right)\Bigg|_{U_1} \Delta N_1 + \left(\frac{\partial\sigma_2}{\partial N_2}\right)\Bigg|_{U_2} \Delta N_2$$

Presuming conservation of particle number overall

so ΔN particles are moving from system 1 to system 2

then $\Delta N_1 = -\Delta N$ and $\Delta N_2 = \Delta N$

At diffusive equilibrium, we presume maximum entropy

so small transfers result in vanishing entropy changes

$$0 \simeq -\left(\frac{\partial\sigma_1}{\partial N_1}\right)\Bigg|_{U_1} \Delta N + \left(\frac{\partial\sigma_2}{\partial N_2}\right)\Bigg|_{U_2} \Delta N$$

Chemical potential

With $$0 \simeq -\left(\frac{\partial \sigma_1}{\partial N_1}\right)\Bigg|_{U_1} \Delta N + \left(\frac{\partial \sigma_2}{\partial N_2}\right)\Bigg|_{U_2} \Delta N$$

we conclude that in diffusive equilibrium

$$\left(\frac{\partial \sigma_1}{\partial N_1}\right)\Bigg|_{U_1} = \left(\frac{\partial \sigma_2}{\partial N_2}\right)\Bigg|_{U_2}$$

So the quantity represented by such a derivative is equalized under diffusion of particles from one system to the other

Chemical potential

Conventionally in thermodynamics

we use the chemical potential $\mu_C = -\tau \left(\frac{\partial \sigma}{\partial N} \right) \Big|_U$

This is simply (minus) the (fundamental) temperature τ

× the derivative that is equalized in diffusive equilibrium

Presuming we are operating at some temperature

then diffusive equilibrium for some "species" of particle

means the same chemical potential for that species in both systems

We can generalize to multiple species

with separate chemical potentials for each species

Thermal distributions 4

Chemical potential and the Gibbs factor

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The Gibbs factor

- Now we can consider
  - the exchange of both particles and energy
- We can derive another useful factor
  - called the Gibbs factor
- This is analogous to the Boltzmann factor
  - which arose when we considered only the exchange of energy

The Gibbs factor

Consider now a system M in

thermal and diffusive contact with a large reservoir R

Now, in addition to being able to transfer energy

we can also transfer particles

The entire closed system of reservoir R and system M

has N_o identical particles, and has energy U_o

When the system M has N particles

then the reservoir has $N_o - N$ particles

and when the system M has energy ε_M

the reservoir has energy $U_o - \varepsilon_M$

The Gibbs factor

Just as for the derivation of the Boltzmann factor

- we consider the system M to be in a particular state
  - in which it has energy ε_M and N particles

The Gibbs factor

We will consider two specific microstates of system M

State 1

- in which system M has energy ε_1 and N_1 particles

State 2

- in which system M has energy ε_2 and N_2 particles

The Gibbs factor

The ratio of the probabilities of M being in state 1 or 2 is

$$\frac{P(N_1,\varepsilon_1)}{P(N_2,\varepsilon_2)} = \frac{g(N_o - N_1, U_o - \varepsilon_1)}{g(N_o - N_2, U_o - \varepsilon_2)}$$

where g in each case is the corresponding multiplicity

of the whole system when M is in the given state

Rewriting using entropies gives

$$\frac{P(N_1,\varepsilon_1)}{P(N_2,\varepsilon_2)} = \frac{\exp\left[\sigma(N_o - N_1, U_o - \varepsilon_1)\right]}{\exp\left[\sigma(N_o - N_2, U_o - \varepsilon_2)\right]} = \exp(\Delta\sigma)$$

where $\Delta\sigma = \sigma(N_o - N_1, U_o - \varepsilon_1) - \sigma(N_o - N_2, U_o - \varepsilon_2)$

The Gibbs factor

Just as we did for the Boltzmann factor derivation

we expand $\sigma\left(N_o - N, U_o - \varepsilon\right)$ in a Taylor series

now about the values N_o and U_o

where now we need to expand

in two variables, N and ε, to obtain

$$\sigma\left(N_o - N, U_o - \varepsilon\right) = \sigma\left(N_o, U_o\right) - N\left(\frac{\partial\sigma}{\partial N_o}\right)_{U_o} - \varepsilon\left(\frac{\partial\sigma}{\partial U_o}\right)_{N_o} + \cdots$$

Assuming that the reservoir is very large

we neglect all higher order terms in the expansion

The Gibbs factor

So, with $\sigma\left(N_o - N, U_o - \varepsilon\right) \simeq \sigma\left(N_o, U_o\right) - N\left(\frac{\partial\sigma}{\partial N_o}\right)_{U_o} - \varepsilon\left(\frac{\partial\sigma}{\partial U_o}\right)_{N_o}$

$$\Delta\sigma = \sigma\left(N_o - N_1, U_o - \varepsilon_1\right) - \sigma\left(N_o - N_2, U_o - \varepsilon_2\right)$$

becomes $\Delta\sigma = -\left(N_1 - N_2\right)\left(\frac{\partial\sigma}{\partial N_o}\right)_{U_o} - \left(\varepsilon_1 - \varepsilon_2\right)\left(\frac{\partial\sigma}{\partial U_o}\right)_{N_o}$

Using our definitions $\mu_C = -\tau\left(\frac{\partial\sigma}{\partial N_o}\right)$ $\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U_o}\right)$

then $\Delta\sigma = \frac{\left(N_1 - N_2\right)\mu_C}{\tau} - \frac{\left(\varepsilon_1 - \varepsilon_2\right)}{\tau}$

The Gibbs factor

So, with $\Delta\sigma = \dfrac{(N_1 - N_2)\mu_C}{\tau} - \dfrac{(\varepsilon_1 - \varepsilon_2)}{\tau}$

$$\frac{P(N_1,\varepsilon_1)}{P(N_2,\varepsilon_2)} = \frac{\exp\left[\sigma(N_o - N_1, U_o - \varepsilon_1)\right]}{\exp\left[\sigma(N_o - N_2, U_o - \varepsilon_2)\right]} = \exp(\Delta\sigma)$$

becomes

$$\frac{P(N_1,\varepsilon_1)}{P(N_2,\varepsilon_2)} = \frac{\exp\left[(N_1\mu_C - \varepsilon_1)/\tau\right]}{\exp\left[(N_2\mu_C - \varepsilon_2)/\tau\right]}$$

The Gibbs factor

In $$\frac{P(N_1,\varepsilon_1)}{P(N_2,\varepsilon_2)}=\frac{\exp\left[\left(N_1\mu_C-\varepsilon_1\right)/\tau\right]}{\exp\left[\left(N_2\mu_C-\varepsilon_2\right)/\tau\right]}$$

the factor that expresses this relative probability
of occupation of states separated by
energy ε and population difference N

is called the Gibbs factor $$\boxed{\exp\left[\frac{\left(N\mu_C-\varepsilon\right)}{\tau}\right]}$$

an un-normalized probability that the system M can be
in a state of energy ε and particle number N