Thermal distributions 3

Entropy and temperature

Modern physics for engineers

David Miller

Entropy

Now we can usefully define a quantity

which we call the "entropy"

$$\sigma(N,U) \equiv \log g(N,U)$$

The key idea of entropy is that

for some given macrostate

it is the log of the multiplicity

Entropy

Though the multiplicity of some combined system is the
product of the multiplicities of the individual systems
because of the logarithm
the entropy of the combined system
is the sum of the entropies

So, for two systems in macrostates
with multiplicities g_1 and g_2 respectively
and hence with entropies $\sigma_1 = \log g_1$ and $\sigma_2 = \log g_2$
the total entropy is

$$\sigma_{tot} = \log\left(g_1 g_2\right) = \log g_1 + \log g_2 = \sigma_1 + \sigma_2$$

Thermal equilibrium

So, with our conclusion that, in thermal equilibrium

$$\left(\frac{\partial \log g_1}{\partial U_1}\right)\bigg|_{N_1} = \left(\frac{\partial \log g_2}{\partial U_2}\right)\bigg|_{N_2}$$

then with our definition of entropy, we have

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

as the condition for thermal equilibrium for two systems in thermal contact

Thermal equilibrium

We can restate the condition

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

as

the rate of change of entropy with energy

is the same for all systems in thermal equilibrium with each other

at least for fixed numbers of particles in each system

Thermal equilibrium

For two systems with temperatures T_1 and T_2

- in thermal equilibrium, we expect $T_1 = T_2$

We have derived the condition $\left(\frac{\partial \sigma_1}{\partial U_1}\right)\bigg|_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)\bigg|_{N_2}$

- so we expect these partial derivatives are related to temperature in some way

We can relate to the existing ideas of temperature if

$$\frac{1}{T} = k_B \left(\frac{\partial \sigma}{\partial U}\right)\bigg|_N$$

Temperature and entropy

In the expression $\frac{1}{T} = k_B \left(\frac{\partial \sigma}{\partial U} \right) \Big|_N$, k_B is Boltzmann's constant

$$k_B \simeq 1.380\ 6488 \times 10^{-23}\ \mathrm{J\,K^{-1}}$$

and it is only there because of our system of units

Sometimes we work with "fundamental temperature", τ

which we can define as

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right) \Big|_N$$

or, equivalently $\tau = k_B T$

Fundamentally, the real unit of temperature is energy

though other units can be more convenient

Temperature and entropy

In classical thermodynamics, we write $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)\Big|_N$

where the thermodynamic entropy S

corresponds with the "fundamental" entropy through

$$S = k_B \sigma$$

We can also write directly

$$\boxed{S = k_B \log g}$$

a key equation by Boltzmann that gave

a tangible meaning to the concept of entropy

An example system

An example system

Two systems, with energies U_1 and U_2, each with two spins

Initially, system 1 has both spins "up"

and system 2 has both spins "down"

A magnetic field B is applied to both systems

so the energies of these systems are

for system 1, $U_1 = -2\mu_s B$

and for system 2, $U_2 = +2\mu_s B$

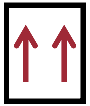
Only one microstate of each system corresponds to these energies

so the starting entropies are each $\log 1 = 0$

An example system

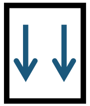
Initial ensemble

System 1



$$\sigma_1 = \log(1) = 0$$

System 2



$$\sigma_2 = \log(1) = 0$$

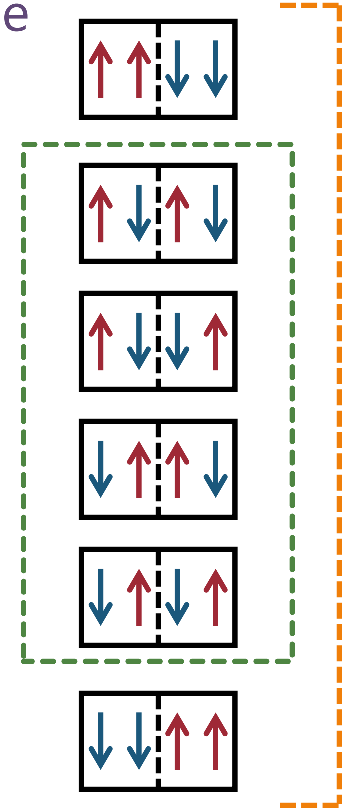
Only one microstate of each system is accessible for the chosen energy for each system

$$\sigma_{tot} = \sigma_1 + \sigma_2 = 0$$

Final ensemble

4 microstates are in the most probable macrostate

$$\sigma_{mp} = \log 4$$



6 microstates are accessible for the same total energy

$$\sigma_{tot} = \log 6$$

An example system

After we allow the systems to exchange energy

- 6 accessible microstates have that same total energy
  - 4 of these are in one macrostate
    - which is the most probable one

All the microstates in this most probable macrostate

- have the same energy in each (sub) system 1 and 2
  - 2/3 of the microstates are in that macrostate
    - which has most ($\sigma_{mp} = \log 4$) of the entropy, $\sigma_{tot} = \log 6$
- Explicitly, $(\log 4)/(\log 6) \simeq 0.77$ - that is, ~ 77%

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Entropy and heat flow

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Entropy and heat flow

The entropy σ_1 of system or body 1

does not depend on the energy U_2 of body 2

and the entropy σ_2 of system or body 2

does not depend on the energy U_1 of body 1

Changing the energy of body 1 by a small amount ΔU_1

and changing the energy of body 2 by a small amount ΔU_2

therefore gives a change $\Delta\sigma$ in the

total entropy $\sigma = \sigma_1 + \sigma_2$ of the combined system

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

Entropy and heat flow

Suppose we allow a small amount of heat ΔU

to flow from body 1 to body 2

So, body 1 loses energy ΔU, so $\Delta U_1 = -\Delta U$

and body 2 gains energy ΔU, so $\Delta U_2 = \Delta U$

Then

$$\Delta\sigma = \left(\frac{\partial\sigma_1}{\partial U_1}\right)\bigg|_{N_1}(-\Delta U) + \left(\frac{\partial\sigma_2}{\partial U_2}\right)\bigg|_{N_2}(\Delta U) = \left(-\frac{1}{\tau_1} + \frac{1}{\tau_2}\right)\Delta U$$

where we used the definition $\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)\bigg|_N$

Entropy and heat flow

In conventional thermodynamic notation

multiplying both sides by Boltzmann's constant

$$\Delta\sigma = \left(-\frac{1}{\tau_1}+\frac{1}{\tau_2}\right)\Delta U \text{ becomes } \Delta S = \left(-\frac{1}{T_1}+\frac{1}{T_2}\right)\Delta U$$

So, if $T_1 > T_2$

transfer of positive energy or "heat" ΔU

from body 1 to body 2

leads to an increase of entropy overall

Entropy and heat flow

We could rewrite $\Delta S = \left(-\frac{1}{T_1} + \frac{1}{T_2} \right) \Delta U$

as $\Delta S = \Delta S_1 + \Delta S_2$

where ΔS_1 and ΔS_2 are

the changes in entropy of the individual bodies

$$\Delta S_1 = -\frac{\Delta U}{T_1} \qquad \Delta S_2 = \frac{\Delta U}{T_2}$$

So the entropy of "hotter" body 1 has decreased

and the entropy of "colder" body 2 has increased

with entropy increasing overall

An example of entropy and heat flow

Entropy and heat flow

Consider a hot cup of coffee (body 1)

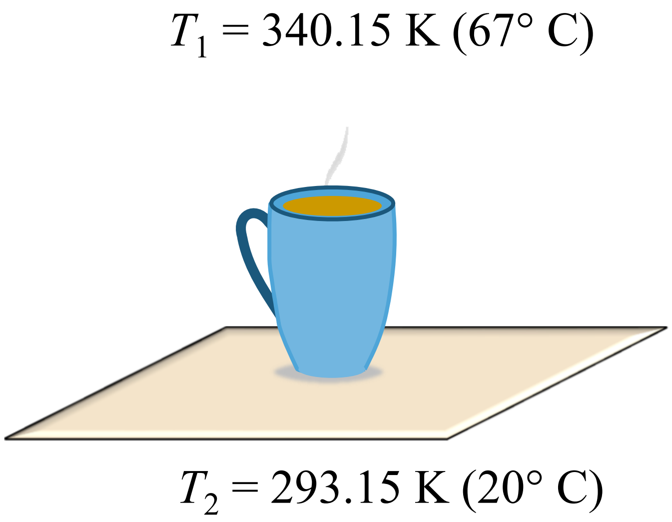
at a temperature of 67° C

so $T_1 = 340.15\ \mathrm{K}$

and a counter-top (body 2)

at room temperature of, say, 20° C

so $T_2 = 293.15\ \mathrm{K}$



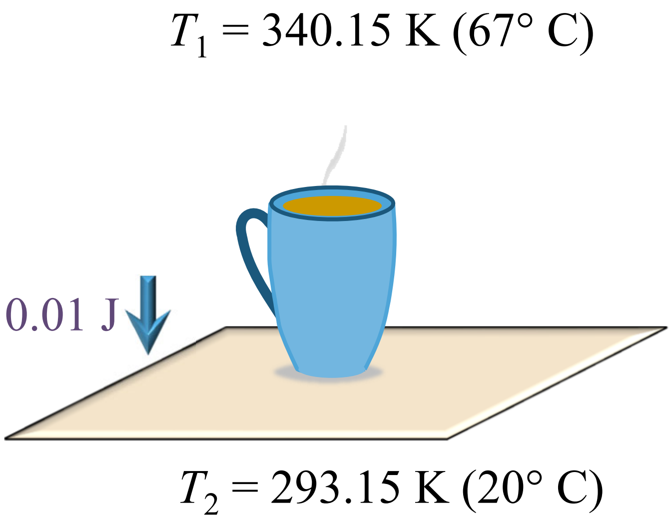
Entropy and heat flow

Suppose we transfer 0.01 J of energy

- from the cup of coffee to the counter-top
  - by briefly laying down the cup of coffee

We presume that both the cup of coffee and the counter-top are sufficiently large that

- this small transfer of energy does not appreciably change the temperature of either of them



Entropy and heat flow

So we have

$$\Delta S_1 = -\frac{0.01}{340.15} \simeq -2.94\times 10^{-5}\ \mathrm{J\,K^{-1}}$$

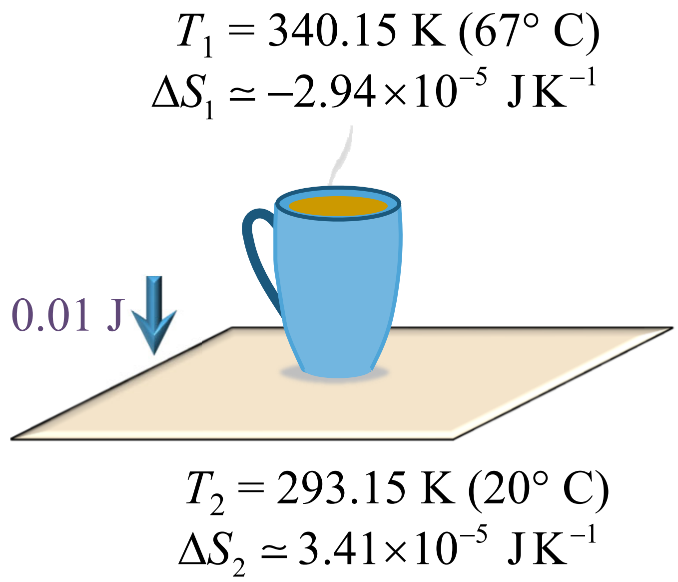
and $\Delta S_2 = \frac{0.01}{293.15} \simeq 3.41\times 10^{-5}\ \mathrm{J\,K^{-1}}$

so the total change in entropy is

$$\Delta S \simeq (3.41 - 2.94)\times 10^{-5} \simeq 4.17\times 10^{-6}\ \mathrm{J\,K^{-1}}$$

which verifies entropy increases

as heat flows from a hotter to a colder body



Entropy and heat flow

Converting back this entropy increase

$$\Delta S \simeq (3.41 - 2.94) \times 10^{-5} \simeq 4.17 \times 10^{-6} \text{ J K}^{-1}$$

to the "fundamental" form

$$\Delta\sigma = \frac{\Delta S}{k_B} \simeq \frac{4.17 \times 10^{-6}}{1.38 \times 10^{-23}} \simeq 3.02 \times 10^{17}$$

we can deduce that the number of microstates

available to the combined system

has increased by

$$\Delta g = \exp\left(3.02 \times 10^{17}\right) \simeq 10^{(\log_{10} e) \times 3.02 \times 10^{17}} \simeq 10^{1.31 \times 10^{17}}$$

a truly massive number

Entropy and heat flow

If the heat flowed in the opposite direction

from "cold" at 20° C to "hot" at 67° C

leading to an entropy *decrease* of the same size

the system would be changing to a macrostate

with $\exp\left(3.02\times10^{17}\right)$ fewer microstates

Tossing a coin N times leads to 2^N possible outcomes

For $2^N \simeq \exp\left(3.02\times10^{17}\right)$

$$N = \log_2\left(e^{3.02\times10^{17}}\right) = \log_2\left[\left(2^{\log_2 e}\right)^{3.02\times10^{17}}\right] = \log_2\left\{\left[2^{(1/\log_e 2)}\right]^{3.02\times10^{17}}\right\} \simeq 4.4\times10^{17}$$

so asking this heat to flow backwards is like asking for

"all heads" when tossing a coin 4.4×10^{17} times

Entropy and heat flow

Since the universe is ~ 13.8 billion years old

- ~ 4.4×10^{17} seconds old
  - this is like tossing a coin
    - once a second since the Big Bang
      - and asking for it to come up heads every time!

Entropy and heat flow

- This calculation illustrates
  - why heat flows from hot to cold
- There are massively more accessible microstates if the energy flows
  - from the hot body to the cold body
- To flow in the opposite direction
  - would correspond to the number of accessible microstates
    - decreasing by an equally large factor

The second law of thermodynamics

The second law of thermodynamics

- The second law of thermodynamics can be stated in many ways
  - many related to the behavior of heat engines
- Its essence is the “law of increase of entropy”
  - the entropy of a closed system tends to remain constant or to increase

The second law of thermodynamics

- The entropy of parts of a system can decrease
  - Heat flowing out of a hot part of the system
    - decreases its entropy
      - but the entropy of the cold part of the system
        - increases by more

The second law of thermodynamics

The second law is the idea that

- given random processes that change the microstate
- the system will tend to change towards macrostates with larger multiplicity
  - i.e., larger numbers of microstates

There many more ways to do that

- than to change towards lower multiplicity

The second law of thermodynamics

- Because multiplicities increase very fast with system size
  - even for moderate sizes of (closed) systems
    - entropy is overwhelmingly unlikely to decrease by any large amount

The second law of thermodynamics

- The second law is a statistical principle
  - In small systems, we can observe small decreases of entropy sometimes
    - but those systems need to be really small for there to be much chance of seeing this happen

The second law of thermodynamics

- It is also possible to calculate the possibility of small random fluctuations in the system
  - away from the "equilibrium" values
    - Such calculations are an important part of the larger field of statistical mechanics

Thermal distributions 3

Carnot efficiency limit for heat engines

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Limit to heat engine efficiency

All heat engines have a simple
and quite fundamental
limit to their efficiency
Here, efficiency is
the ratio of
work out
to
heat energy in

Limit to heat engine efficiency

This is the Carnot limit

(Sadi Carnot, 1824)

It can be deduced from

conservation of energy overall

the first law of thermodynamics

and the requirement that entropy overall should not decrease

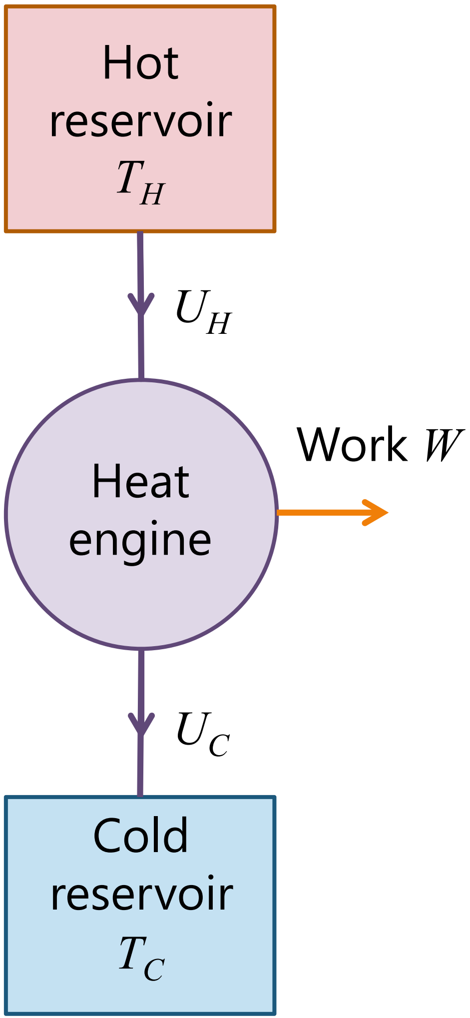
the second law of thermodynamics

Heat engine operation

Heat energy of magnitude U_H
- flows out of the hot reservoir
  - at temperature T_H

Work of an amount W
- is performed by the heat engine

Heat energy of magnitude U_C
- flows into the cold reservoir
  - at temperature T_C



Heat engine operation

The entropy change of the hot reservoir is

$$\Delta S_H = -\frac{U_H}{T_H}$$

which is a decrease of entropy

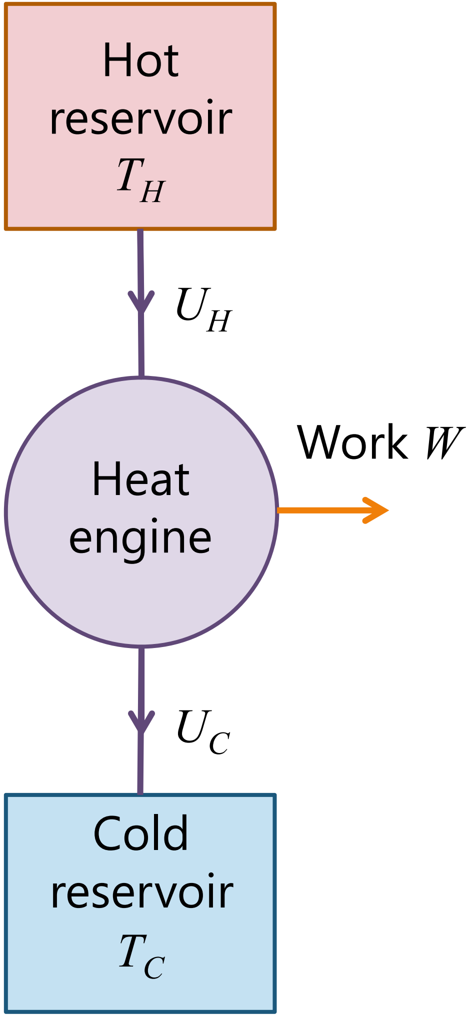
because heat energy has flowed out

The entropy change of the cold reservoir is

$$\Delta S_C = \frac{U_C}{T_C}$$

which is an increase of entropy

because heat energy has flowed in



Heat engine operation

Presuming the engine is to be as efficient as possible

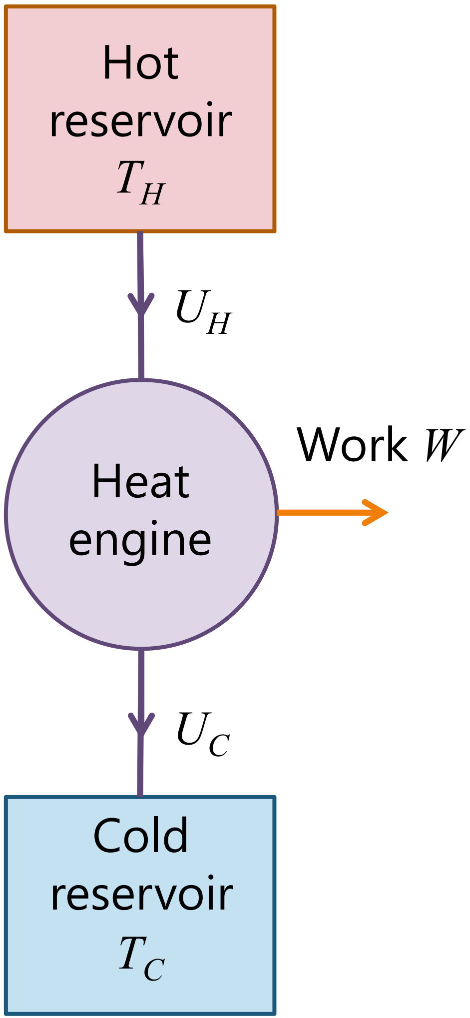
there will be no other loss of energy

so conservation of energy gives

$$U_C = U_H - W$$

So we can rewrite

$$\Delta S_C = \frac{U_C}{T_C} = \frac{U_H - W}{T_C}$$



Heat engine operation

We ask that entropy should not decrease overall

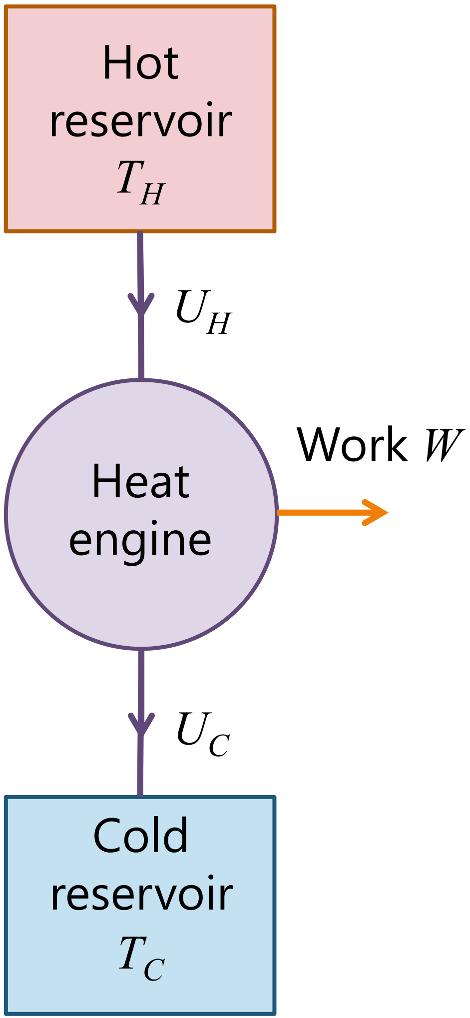
so $$\Delta S_H + \Delta S_C \geq 0$$

Substituting gives

$$-\frac{U_H}{T_H} + \frac{U_H - W}{T_C} \geq 0$$

Rearranging gives

$$U_H\left(\frac{1}{T_C} - \frac{1}{T_H}\right) \geq \frac{W}{T_C}$$



Carnot efficiency limit

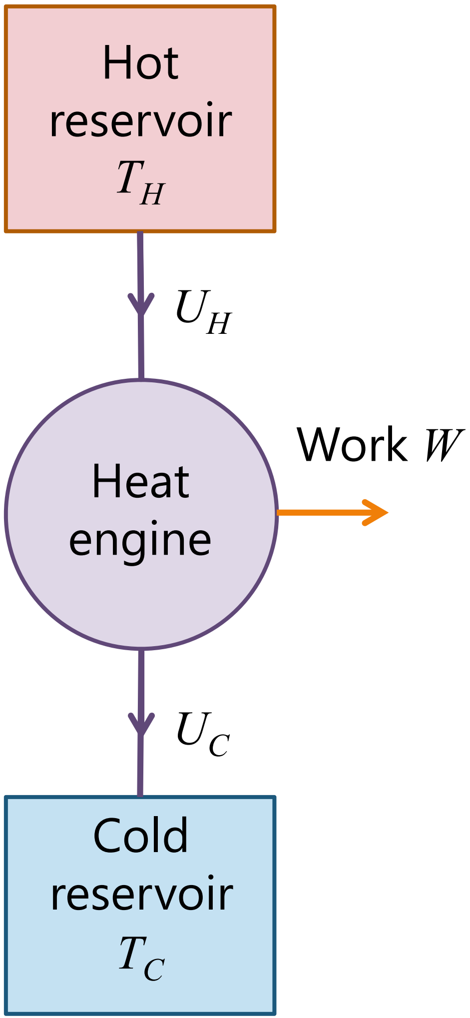
Defining the efficiency η_{engine} as

the work energy out per unit heat energy in

presuming we have to keep replenishing the heat extracted from the hot reservoir

then from $U_H \left(\frac{1}{T_C} - \frac{1}{T_H} \right) \geq \frac{W}{T_C}$

we have $\eta_{engine} \equiv \frac{W}{U_H} \leq 1 - \frac{T_C}{T_H}$



Carnot efficiency limit

$$\eta_{engine} \leq 1 - \frac{T_C}{T_H}$$

This is the Carnot efficiency limit

For given temperatures

- nothing we can do can make a heat engine more efficient than this
  - To do so would require violating either the First or Second Laws of Thermodynamics