This is the first take-home quiz: Q1

Make a short video (not exceeding 5 minutes), in which using the following slides (the same I used in class) you explain (like I did in class) how we go from Assertion 2 of the Second Law to the definition of Entropy.

Before you make your recording, please prepare your tools in advance, in particular set your device or smartphone so as to record with the smallest resolution, possibly 640x480, so that the size is about 25MB/min.

If you do not find a way to make your image appear all the time during the video next to the viewgraphs, please face the camera at least at the beginning so as to identify yourself.

Of course, if you are unhappy with the recording you made or if it exceeds 5 min, you may try again until you are finally happy with what you submit.

Then, upload it in your Google Drive or other similar webservice and send me an email with the link for me to download your video by just one click.

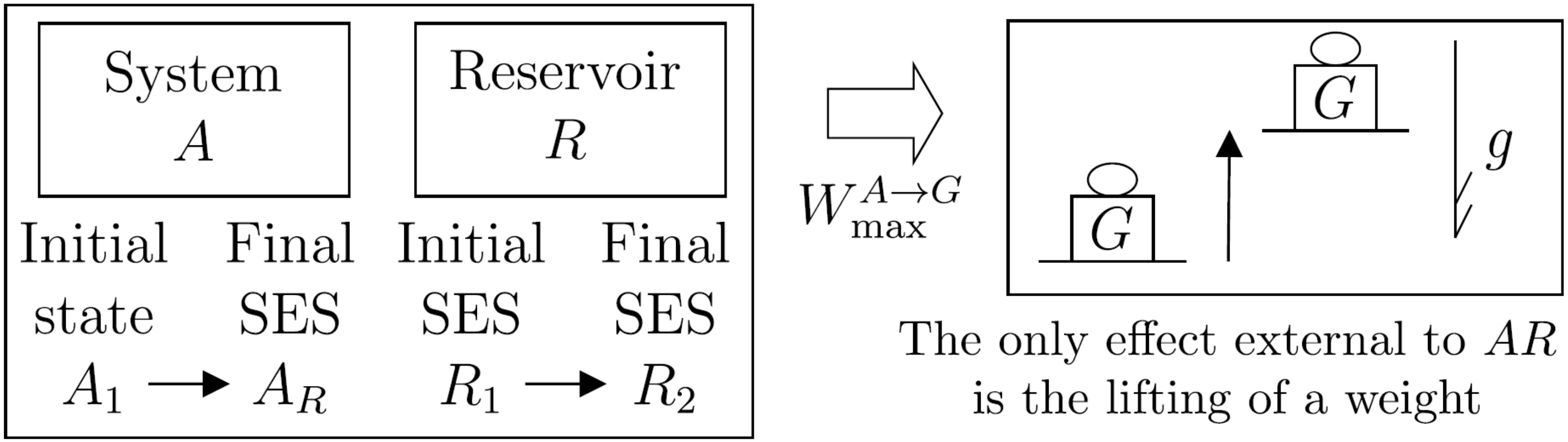
IMPORTANT: please make sure I can download it with no need for me to register for your favorite file exchange service (as I do not want to). Thanks.

Review of basic concepts: importance of the second part of the statement of the Second Law of Thermodynamics

Second Law:

Assertion 1: in the subset of states of a system compatible with given values of the amounts of constituents $\boldsymbol{n}$ and of the parameters $\boldsymbol{\beta}$, there is always one and only one SES for each value of the energy E.

Assertion 2: Starting from any state of the system, it is always possible, through a reversible weight process, to reach a SES with arbitrarily fixed, compatible values of the amounts of constituents and the parameters.



Reversible weight process for AR ending with A and R in MSE

System A

Reservoir R

Initial state A_1 → Final SES A_R

Initial SES R_1 → Final SES R_2

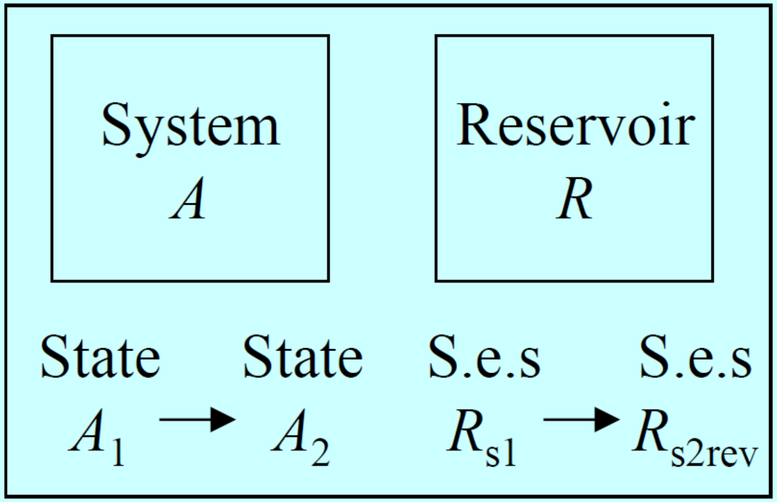
$W_{\max}^{A\to G}$

The only effect external to AR is the lifting of a weight

Review of basic concepts: Consequences of the (First&)Second Law:

Feasibility for arbitrary A, A_1, A_2, R, R_{s1} of the following

Standard reversible weight process for *AR*

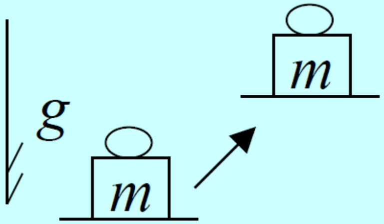


System A

Reservoir R

State A_1 → State A_2

S.e.s R_{s1} → S.e.s R_{s2rev}



This is the only effect external to *AR*.

Our statement of the Second Law warrants the feasibility of such process for arbitrary states A_1 and A_2 and any initial s.e.s. R_{s1} (these determine uniquely the final state R_{s2rev}).

We are interested in measuring the change in energy of the reservoir in this process, that we denote by

$$\left(E^R_{\mathrm{s2rev}} - E^R_{\mathrm{s1}}\right)_{A_1 R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R_{\mathrm{s2rev}}}$$

Review of basic concepts: Consequences of the (First&)Second Law:

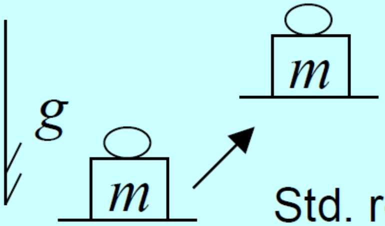
Measurement procedure defining the “constant temperature of a thermal reservoir”

System
A
auxiliary to
this measure

Reservoir
R
the object of
this measure

State $A_1 \rightarrow$ State A_2

S.e.s $R_{s1} \rightarrow$ S.e.s R_{s2rev}



Std. rev. w.p. for *AR*
Measure the change in E^R

$$\frac{\left(E^{R}_{s2rev}-E^{R}_{s1}\right)_{A_1R_{s1}\underset{w,rev}{\Rightarrow}A_2R_{s2rev}}}{\left(E^{R^o}_{s2rev}-E^{R^o}_{s1}\right)_{A_1R^o_{s1}\underset{w,rev}{\Rightarrow}A_2R^o_{s2rev}}}$$

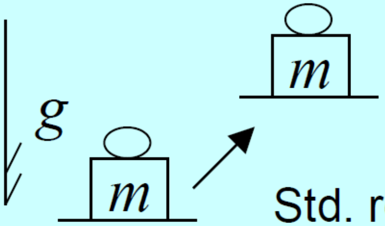
Repeat for the same A_1 and A_2, but with a reference reservoir R^0 *(water at the triple point)*

System
A
the same
as above

Reference
reservoir
R^o

State $A_1 \rightarrow$ State A_2

S.e.s $R^o_{s1} \rightarrow$ S.e.s. R^o_{s2rev}



Std. rev. w.p. for *AR*^{o}
Measure the change in E^R

Review of basic concepts: Consequences of the (First&)Second Law: Measurement procedure defining the "constant temperature of a thermal reservoir"

It can be proved that the ratio:

$$\frac{\left(E^{R}_{\mathrm{s2rev}} - E^{R}_{\mathrm{s1}}\right)_{A_1 R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R_{\mathrm{s2rev}}}}{\left(E^{R^o}_{\mathrm{s2rev}} - E^{R^o}_{\mathrm{s1}}\right)_{A_1 R^o_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R^o_{\mathrm{s2rev}}}}$$

- is positive
- is independent of the initial states R_{s1} , $R^0{}_{s1}$ of the reservoirs
- is independent of the choice of the auxiliary system A and of its states A_1 and A_2
- it depends therefore only on the pair of reservoirs R and R^0
- for a reference R^0 fixed once and for all, it is a *constant* property of reservoir R
  (it has the same value in all the stable equilibrium states of R)
- being a dimensionless number that emerges from the comparison with a reference reservoir, this property defines a new dimension and requires the choice of a new unit of measure
- this defines the property **temperature of reservoir** R:

$$T_R = T_{R^o} \frac{\left(E^{R}_{\mathrm{s2rev}} - E^{R}_{\mathrm{s1}}\right)_{A_1 R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R_{\mathrm{s2rev}}}}{\left(E^{R^o}_{\mathrm{s2rev}} - E^{R^o}_{\mathrm{s1}}\right)_{A_1 R^o_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R^o_{\mathrm{s2rev}}}}$$

For R^0 chosen to be water at the triple point, we obtain the S.I. unit, the **kelvin**, defined by

$$T_{R^0} = 273.16\ \mathrm{K}$$

Review of basic concepts: Consequences of the (First&)Second Law:

Measurement procedure defining the “constant temperature of a thermal reservoir”

Notice that from

$$T_R = T_{R^o} \frac{(E^R_{\mathrm{s2rev}} - E^R_{\mathrm{s1}})_{A_1 R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R_{\mathrm{s2rev}}}}{(E^{R^o}_{\mathrm{s2rev}} - E^{R^o}_{\mathrm{s1}})_{A_1 R^o_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R^o_{\mathrm{s2rev}}}}$$

it follows that the ratio

$$\frac{(E^R_{\mathrm{s2rev}} - E^R_{\mathrm{s1}})_{A_1 R_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R_{\mathrm{s2rev}}}}{T_R} = \frac{(E^{R^o}_{\mathrm{s2rev}} - E^{R^o}_{\mathrm{s1}})_{A_1 R^o_{\mathrm{s1}} \underset{\mathrm{w,rev}}{\Rightarrow} A_2 R^o_{\mathrm{s2rev}}}}{T_{R^o}}$$

- is independent of reservoir R and of its initial state R_{s1}
- It depends therefore only on system A and the pair of states A_1 and A_2

This observation prompts the following definition for the entropy difference between the states A_1 and A_2 of system A.

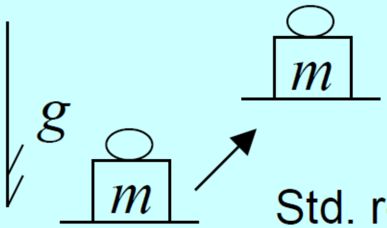
Review of basic concepts: Consequences of the (First&)Second Law: definition of property Entropy

System A
the object of this measure

Reservoir $\boldsymbol{R}$
auxiliary to this measure

State A_1 → State A_0

S.e.s R_{s1} → S.e.s R_{s0rev}



Std. rev. w.p. for *AR*
Measure the change in E^R

state A_0 is an arbitrarily chosen state to which we assign the arbitrary reference value S_0

The ratio:

$$\frac{(E^R_{s0rev} - E^R_{s1})_{A_1R_{s1} \underset{w,rev}{\Rightarrow} A_0R_{s0rev}}}{T_R}$$

- is independent of reservoir R and of its initial state R_{s1}
- It depends therefore only on system A and the pair of states A_1 and A_0

Hence it defines a property:

$$S_1 = S_0 + \frac{(E^R_{s0rev} - E^R_{s1})_{A_1R_{s1} \underset{w,rev}{\Rightarrow} A_0R_{s0rev}}}{T_R}$$

2.43 Advanced Thermodynamics
Spring 2024