

A. Scheel's lecture notes
Lectures on Stat Phys.
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§8. The Laws of Thermodynamics.

(in the 19th cent.)

Thermodynamics was originally constructed as a purely macroscopic ~~phenomenological~~ phenomenological theory, completely independent of any microphysical understanding of the underlying structure of the physical systems it described.

It rested on a set of postulates ("laws"), which ~~followed~~ ^{from} ~~experimental observations~~ followed experimentally verifiable consequences.

Here we started from a general understanding of how the microphysical information about the nature of the system can be converted into calculation of its bulk properties.

We are now going to reconstruct the laws of thermodynamics (and, therefore, their consequences) from that basis.

8.1 Zeroth Law, ~~temperature~~ temperature

Zeroth Law. If two systems are separately in thermal eq. with a third, then they are also in eq. with each other.

From this, one can ~~also~~ show that some function (called "empirical temperature") exists s.t. two systems in equilibrium are at the same temperature [see, e.g. Kardar §1.2]

In our treatment, we have already introduced a quantity called "temperature" which formally was a Lagrange multiplier that appeared in maximizing entropy for

the canonical ensemble. We then showed that this temperature was related to U and S as follows:

$$\boxed{T = \left(\frac{\partial U}{\partial S} \right)_V} \quad \text{"absolute temperature"}$$

We will now prove that T must indeed be the same for two systems in equilibrium with each other.

Proof. Consider two systems isolated from the rest of the world but in contact with each other. Then

$$U_1 + U_2 = \text{const} \quad (\text{cons. of energy})$$

$$V_1 + V_2 = \text{const} \quad (\text{otherwise the systems will push at the outside world, which will not then remain unchanged})$$

To find the equilibrium state, we must

maximise entropy: \checkmark entropy additive!

$$S = S_1(U_1, V_1) + S_2(U_2, V_2) \rightarrow \text{max}$$

$$dS = dS_1 + dS_2 =$$

$$= \left(\frac{\partial S_1}{\partial U_1} \right)_{V_1} dU_1 + \left(\frac{\partial S_1}{\partial V_1} \right)_{U_1} dV_1 + \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2} dU_2 + \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2} dV_2$$

$$= \left[\left(\frac{\partial S_1}{\partial U_1} \right)_{V_1} - \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2} \right] dU_1 + \left[\left(\frac{\partial S_1}{\partial V_1} \right)_{U_1} - \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2} \right] dV_1 = 0$$

$$+ \left[\left(\frac{\partial S_1}{\partial V_1} \right)_{U_1} - \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2} \right] dV_1 = 0$$

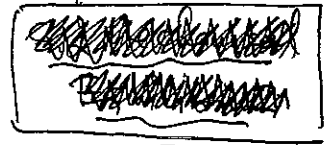
\parallel \parallel
 $\frac{P_1}{T_1}$ $\frac{P_2}{T_2}$

Therefore,

thermal eq.

$$\left(\frac{\partial S_1}{\partial U_1}\right)_{V_1} = \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2} \quad \text{or} \quad \boxed{\frac{1}{T_1} = \frac{1}{T_2}} \quad \text{temperatures equal, q.e.d.}$$

We have also obtained another nice result:



$$\left(\frac{\partial S_1}{\partial V_1}\right)_{U_1} = \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2} \quad \text{What does this mean? (Q)}$$

Recall $dU = TdS - pdV$

$$\text{or } dS = \frac{1}{T}dU + \frac{p}{T}dV$$

$$\text{so } \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \quad \text{as we already know}$$

$$\text{and } \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_U \quad \text{or} \quad \boxed{p = T \left(\frac{\partial S}{\partial V}\right)_U}$$

another nice expression for p .

$$\rightarrow \frac{p_1}{T_1} = \frac{p_2}{T_2} \quad \Rightarrow \quad \boxed{p_1 = p_2} \quad \text{because } T_1 = T_2$$

Thus, pressures are also equal in equilibrium.

(this is called mechanical eq.)

Note that in practice mech. eq. is ~~usually~~ ^{often} achieved faster than thermal because pressure imbalance = uncompensated forces \Rightarrow leads to macroscopic motions, which are often faster than microscopic processes equality T

(recall transport theory: ∇p leads to flows \vec{u} ;

∇T is rectified by diffusion — although we are still to prove that there were the same p and T !)

Some important remarks:

- These arguments are easily generalised to other external parameters, or displacements ($V, l, \vec{B} \dots$) leading to equality of their ~~the~~ response functions, or forces ($p, \tau, M \dots$).
 Note that the former are ~~usually~~ ^{usually} extensive whereas the latter are intensive quantities (but not in the case of \vec{B}, M).

• Note that T to S is what p is to V .

In HT, we'll encounter another such pair:

chemical potential μ and # of particles N

(leading to the concept of chemical equilibrium and the Grand-canonical ensemble)

- The property of T to be the same between two systems in eq. means we can measure T by putting any system in contact with some standard reference system (thermometer) in which the scale from hot to cold can be set ~~up~~ up in terms of some monotonically dependent on T property (e.g. ~~length~~ expansion of mercury etc.)

• We expect $T \geq 0$ and $P \geq 0$. These conditions basically follow from stability requirements:

a system with $T < 0$ would seek equilibrium by blowing itself apart ~~by blowing itself apart~~ (converting internal energy into motion of parts);

$$\left(\frac{\partial S}{\partial U}\right)_V < 0$$

a system with $p < 0$ would seek equilibrium by shrinking to nothing

$$\left(\frac{\partial S}{\partial V}\right)_U < 0$$

Further note on stability (see LL§10,13). 13: see pp 61b-c.
CHW problem)

Subdivide system into parts, indexed by i , each with momentum \vec{p}_i and mass m_i .

Entropy ~~can~~ of each part can only a function of internal energy [because of Galilean invariance, p_i 's in each part cannot be a function of how fast the part is moving as a whole].

Since entropy is additive, $S = \sum_i S_i(U_i - \frac{p_i^2}{2m_i})$
(in a closed system, $\sum_i \vec{p}_i = 0$ and also $\sum_i \vec{r}_i \times \vec{p}_i = 0$) (*)

If $\left(\frac{\partial S_i}{\partial U_i}\right)_{V_i} = \frac{1}{T_i} < 0$, then all S_i 's would be maximised by making $U_i - \frac{p_i^2}{2m_i}$ as small as possible - so p_i 's would be as large as possible, subject to $\sum_i \vec{p}_i = 0$ - parts of system would fly apart.

Note. BTW, by maximising S subject to conditions (*), one can prove that in eq. a closed system can only have uniform motion and uniform rotation, but not any internal macroscopic motions. Ex! (LL§10)
[recall transport theory: viscosity relaxes gradients in \vec{u}]

$p < 0$ would mean $\left(\frac{\partial S}{\partial V}\right)_U < 0$ - spontaneous shrinkage (while $p > 0$ means systems want to expand - but are opposed by surroundings).

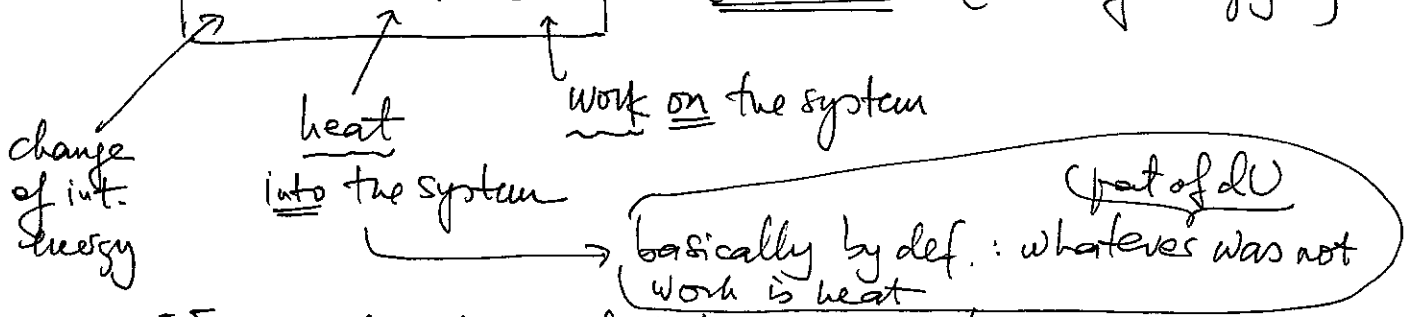
In fact, can have $p < 0$ in metastable states (to be discussed in HT)

8.2 First Law

It has been intuitively clear for centuries (and explicitly pointed out in 1789 by Count Rumford, who watched canons being bored) that ^(internal) energy can be imparted to a body both by doing work on it (e.g. friction) and by putting it in contact with a hotter body. This simple insight can be ~~more~~ expressed as

$$\Delta U = \Delta Q + \Delta W$$

first law (cons. of energy!)



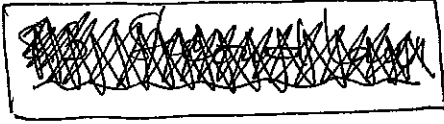
NB: U is a function of state and so dU is an exact differential, $dU = U_{\text{final}} - U_{\text{initial}}$, ind. of ~~route~~ path.

Q and W are not functions of state - how much work is done or how much heat changes hands depends on the history ^(path) between the initial and final states - so ΔQ and ΔW are used to indicate inexact differentials. Alternative notation: $\oint Q$ and $\oint W$ (they are not derivatives!).

How do we determine heat in practice?

Earlier (p.66) we had a useful device - an adiabatic process (i.e. very slow work), in which W was ind. of path between

states: $\Delta W_{\text{ad}} = \Delta U_{\text{ad}} = -PdV$, so $\Delta W_{\text{ad}} = - \int_{\text{initial}}^{\text{final}} PdV$



8.3 $T \geq 0$

→ This can also be argued from stability (U&S10-see p.73)

entropy of Universe always goes up → thermal death of the Universe.

Let us consider two systems in contact with each other but isolated from everything else (this can be thought as a system and its surroundings, the two systems thus comprising the entire Universe). Let them exchange heat and (maybe) do work on each other. Then, as we have argued,

$\delta Q_1 \leq T_1 dS_1$ heat into 1

$\delta Q_2 \leq T_2 dS_2$ heat into 2

But they only exchange heat with each other, so

$\delta Q_1 + \delta Q_2 = 0$

Therefore $0 \leq T_1 dS_1 + T_2 dS_2 \leq T_2 (dS_1 + dS_2)$, because, without loss of generality, $T_2 \geq T_1$.

IF $T_2 \geq 0$, this gives

$dS_1 + dS_2 \geq 0$

So the entropy of the Universe cannot decrease by interaction between two systems. This is in fact not news to us because as the combined system strives to move to equilibrium it must maximise its total entropy, so S cannot go down,

45 ~~but~~ we can ^{then} argue from the above that $dS_1 + dS_2 \geq 0 \Rightarrow [T_2 \geq 0]$

NS

8.4 Reversible Processes

What is interesting is to ~~work~~ work under what conditions the entropy stays the same?

$$dS_1 + dS_2 = 0 \Rightarrow T_1 dS_1 + T_2 dS_2 = 0$$

$$(T_1 - T_2) dS_1 = 0 \Rightarrow T_1 = T_2 = T$$

This then means that

$$\begin{cases} \delta Q_1 \leq T dS_1 \\ \delta Q_2 \leq -T dS_1 \\ \text{"} \\ -\delta Q_1, \text{ so } \delta Q_1 \geq T dS_1 \end{cases}$$

so you can't have any temp. gradients (recall transport: ∇T get smoothed by diffusion)

Thus, $\delta Q_1 = T dS_1$ and $\delta Q_2 = T dS_2$

and so $\delta W_1 = -P_1 dV_1$ and $\delta W_2 = -P_2 dV_2$

absolute minimum work is done. (entropy stays same, so all int. points are eq.)

The process is clearly quasistatic and what's more, it is reversible because it connects two eq. states ~~of~~ of the Universe that have the same entropy and so it is OK for the Universe to move between them in either direction.

Thus, the equalities $\delta W = -PdV = dW_{rev}$
 $\delta Q = TdS = dQ_{rev}$

are achieved for reversible processes.

NB: Not every quasistatic process is reversible

(e.g. anything involving ∇T or, say, friction is not)

These considerations are intimately connected to the 2nd law of thermodynamics, whose main consequence is the existence of a function of state S such that in a reversible process,

$$dQ_{rev} = TdS \quad (\text{with } T \text{ defined via 0th law})$$

(and that this function cannot decrease for the Universe).

We did not need to prove S existed as we started with its explicit microphysical definition and the principle that it must be maximised in equilibrium. Under this scheme, the 2nd law is in fact a provable consequence:

Clausius's formulation. No process is possible whose sole result is transfer of heat (energy) from a colder to a hotter body.

Pf. Consider two systems in thermal contact (and nothing else happening). From p.71,

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 \geq 0 \quad \text{— entropy must increase as they equilibrate.}$$

$$0 < T_1 < T_2 \Rightarrow dU_1 \geq 0$$

so energy is transferred to the colder system. g.e.d.

In thermodynamics, it is then ~~proven~~ proven that this is equivalent to

Kelvin's formulation. No process is possible whose sole result is conversion of heat into work (perpetuum mobile). L9 ended here.