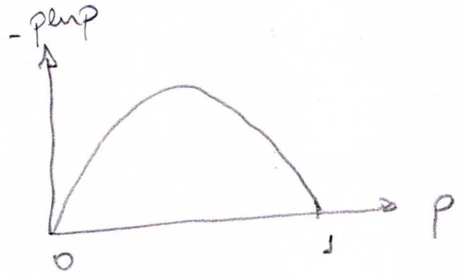
Entropy and etc.

Given any probability distribution P_n, we define its *entropy* as

$$S = -k_B \sum_n P_n \ln P_n \tag{1}$$

In thermodynamics this is called the Gibbs entropy. In probability theory it goes by the name of Shannon entropy and they define it without the k_B.

The entropy is a measure of the *disorder* of the distribution. To see that, note how S is a sum of functions like $-p \ln p$ where $p \in [0, 1]$. this function looks like this



It is zero when $p = 0$ or $p = 1$. Thus, if we have a deterministic distribution, $P_m = 1$ and $P_n = 0$ for $n \neq m$, the entropy will be zero

$$\boxed{S = 0 \text{ for a deterministic distribution}} \tag{2}$$

The entropy is a maximum when all probabilities are equal,

$$p_m = \frac{1}{\Omega} \qquad \Omega = \text{const} \qquad (3)$$

This is called the maximally disordered configuration.

In this case

$$S = -k_B \sum_m \frac{1}{\Omega} \ln(1/\Omega) = -k_B \frac{1}{\Omega} \Omega \ln(1/\Omega)$$

since $\sum_m 1 = \Omega$ by definition. Thus

$$\boxed{S = k_B \ln \Omega} \qquad (4)$$

I will leave for you as an exercise to show that this (3) is indeed the distribution which maximizes S. The calculation is very similar to one we will do later in Eq (23).

Thus, in summary the entropy is zero when there is maximum order and maximum when there is maximum disorder. It therefore serves as a measure of the disorder of the distribution.

Entropy for thermal states

The entropy (1) is a quantity that can be defined for any probability distribution. But for thermal states it acquires a special significance.

Assume

$$P_m = \frac{e^{-\beta E_m}}{Z} \tag{5}$$

Then

$$\ln P_m = -\beta E_m - \ln Z$$

so Eq (1) becomes

$$S = k_B \beta \underbrace{\sum_m E_m P_m}_{U} + k_B \ln Z \underbrace{\sum_m P_m}_{1}$$

Thus, with the definitions

$$U = \sum_m E_m P_m \tag{6}$$

$$F = -k_B T \ln Z \tag{7}$$

we get

$$\boxed{S = \frac{U - F}{T}} \tag{8}$$

This relates the entropy of a thermal state as being the difference between the energy and the free energy.

We can also write this differently as follows. Recall that

$$U = -\frac{\partial}{\partial \beta} \ln Z = k_B T^2 \frac{\partial}{\partial T} \ln Z \qquad (9)$$

Thus

$$S = k_B T \frac{\partial}{\partial T} \ln Z + k_B \ln Z = k_B \frac{\partial}{\partial T} (T \ln Z)$$

Comparing with (7) we see that

$$\boxed{S = -\frac{\partial F}{\partial T}} \qquad (10)$$

Note the similarity between this and the formula for the magnetization

$$M = -\frac{\partial F}{\partial B}.$$

Mag. field and magnetization are related to each other just as temperature and entropy. The field is the stimulus and M is the response. A similar idea holds for T and S: temperature is the stimulus and "disorder" is the response. Of course, we need to be a bit careful with this analysis, as B and T are quantities of different nature.

Entropy and heat capacity

The heat capacity is defined as

$$C = \frac{\partial U}{\partial T} \qquad (11)$$

Let us use (8) to write

$$U = F + TS$$

Then

$$C = \frac{\partial F}{\partial T} + S + T\frac{\partial S}{\partial T}$$

But $\partial F/\partial T = -S$ so the first two terms cancel and we are left with

$$\boxed{C = T\frac{\partial S}{\partial T}} \qquad (12)$$

This is how people measure the entropy of a system:

$$S = \int \frac{C}{T}\, dT + \text{const} \qquad (13)$$

They integrate C/T. Note also that entropy can only be measured up to a constant.

Since $S = -\partial F/\partial T$ we can also rewrite (12) as

$$C = -T \frac{\partial^2 F}{\partial T^2}$$

Thus, to summarize, we have 3 equivalent formulas for the heat capacity

$$\boxed{C = \frac{\partial U}{\partial T} = T \frac{\partial S}{\partial T} = -T \frac{\partial^2 F}{\partial T^2}} \quad (14)$$

The limit $T \to 0$

Now I want to understand what happens with P_n, U, S, F, C, ... in the limit $T \to 0$. In this case we must be careful to consider the degeneracy of the ground state.

Suppose that the ground state has degeneracy g (some integer, like 42). This means there are g states with energy E_0. Let us label them by $i = 1, \dots, g$.

We then write

$$E_0 = E_{0,i} < E_1 \leqslant E_2 \leqslant E_3 \quad \dots \qquad (15)$$

Now let's see what happens when $T \to 0$. Consider a ratio like

$$(n \neq 0) \qquad \frac{P_{0,i}}{P_n} = e^{-\beta(E_0 - E_n)}$$

Since $E_0 < E_n$ the quantity $-\beta(E_0 - E_n)$ is positive. And when $T \to 0$ it becomes very large. Thus $e^{-\beta(E_0 - E_n)}$ will be a really really big number, which implies that

$$P_{0,i} \gg P_n \qquad (16)$$

In the limit $T \to 0$ the P_n will become vanishingly small.

$$\lim_{T \to 0} P_n = 0 \qquad n \neq 0 \qquad (17)$$

As for the $P_{0,i}$, we know the Gibbs distribution only depends on the energy. thus, they must all be equally likely. Since there are g states, by normalization we get

$$\boxed{\lim_{T \to 0} P_{0,i} = \frac{1}{g}} \qquad (18)$$

the internal energy $U = \sum_n E_n P_n$ will tend to the ground-state value

$$\boxed{\lim_{T \to 0} U = E_0} \qquad (19)$$

As for the entropy, it will tend to

$$S = -k_B \sum_{i=1}^{g} \frac{1}{g} \ln(1/g)$$

since the P_n, with $n \neq 0$, do not contribute. whence

$$\boxed{\lim_{T \to 0} S = k_B \ln g} \qquad (20)$$

These results form the basis of the <u>third law</u> <u>of thermodynamics</u> :

> 3rd law : the entropy of a physical system tends to a constant when $T \to 0$

what "tends to a constant" means is that it remains finite. Another way to put it is as follows. Since $C = T \frac{\partial S}{\partial T}$ and $\frac{\partial S}{\partial T}$ is finite, then $C \to 0$. thus

> 3rd law : the heat capacity of a physical system tends to zero when $T \to 0$

Most of the times the degeneracy g is a finite number, like 2 or 17. then the entropy per particle will tend to zero when N becomes large

$$\frac{S}{N} = \frac{k_B \ln g}{N} \to 0$$

In older books people used to state the third law as saying that the entropy per particle tends to zero when $T \to 0$.

But there are some materials, like the spin glasses, where the degeneracy scales like $g \sim \lambda^N$, for some constant λ. Then

$$\frac{S}{N} = \frac{k_B \ln \lambda^N}{N} = k_B \ln \lambda$$
$$= \text{finite}$$

Thus, it is more correct to always say "the entropy tends to a constant". In many cases this constant is zero. But it can also not be.

Equilibrium is the configuration which minimizes the free energy

When $T = 0$ we saw that the system tends to the ground state; that is, it tends to the configuration with the smallest energy.

At $T \neq 0$ this is no longer true since now there are thermal fluctuations. We are now going to show that in this case the system tends to the state which minimizes the free energy. Since $S = (U-F)/T$, we can write

$$\boxed{F = U - TS} \tag{21}$$

Thus, the free energy is a competition between energy U and thermal disorder $-TS$.

Using (5) and (6) we can write

$$\boxed{F = \sum_m \{ E_m P_m + k_B T P_m \ln P_m \}} \tag{22}$$

In principle we could use this as a general definition of free energy, valid for any distribution P_m.

What I want to show is that the distribution P_m which minimizes F is exactly the Gibbs distribution.

To do that we need to minimize F with respect to each P_m. But this minimization must be subject to the constraint that $\sum_m P_m = 1$. To do that we introduce a Lagrange multiplier

$$F' = \sum_m \{ E_m P_m + k_B T P_m \ln P_m \} + \alpha \left(\sum_m P_m - 1 \right) \qquad (23)$$

Then $\partial F'/\partial \alpha = 0$ gives

$$\frac{\partial F'}{\partial \alpha} = \sum_m P_m - 1 = 0$$

which is the normalization. The value of α is fixed in the end to ensure that $\sum_m P_m = 1$.

Differentiating F' with respect to P_m we get

$$\frac{\partial F'}{\partial P_m} = E_m + k_B T \ln P_m + k_B T + \alpha = 0$$

Thus

$$\ln P_m = -\frac{E_m}{k_B T} - \frac{\alpha}{k_B T} - 1$$

or

$$P_m = e^{-\beta E_m} \, e^{-\beta\alpha - 1}$$

Now we choose α to ensure normalization. that is,

we choose $e^{-\beta\alpha - 1} = \frac{1}{Z}$, which gives

$$P_\mu = \frac{e^{-\beta E_\mu}}{Z}$$

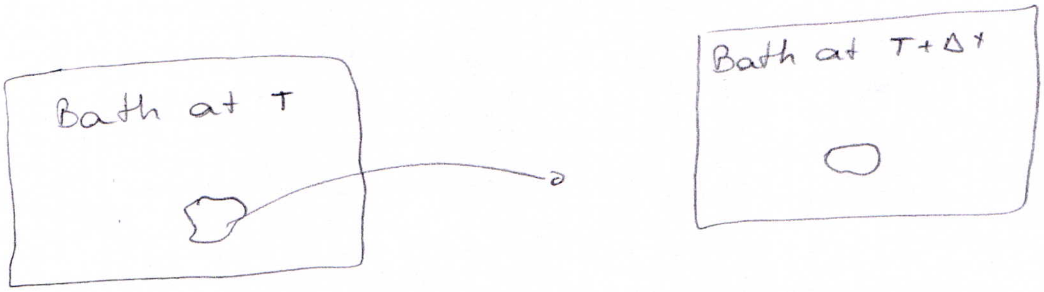
Conclusion: thermal equilibrium is the configuration which minimizes the free energy.

Heat

Suppose you have a system connected to a bath at a temperature T. Its probabilities are $P_m(T)$ and its internal energy will be

$$U(T) = \sum_m E_m P_m(T) \tag{24}$$

Now we take this system away from this bath and put it in another bath at a temperature $T + \Delta T$



What will happen is that the system will initially exchange some energy with its new bath until it eventually settles at a new equilibrium configuration, with probabilities $P_m(T+\Delta T)$ and internal energy

$$U(T+\Delta T) = \sum_m E_m P_m(T+\Delta T) \tag{25}$$

the difference in energy is called the heat exchanged with the new bath

$$\boxed{\Delta Q = U(T+\Delta T) - U(T)} \tag{26}$$

when ΔT is small we may use the Taylor series expansion

$$f(x+\Delta x) \simeq f(x) + \frac{\partial f}{\partial x}\Delta x \tag{27}$$

we then get

$$\boxed{\Delta Q = \frac{\partial U}{\partial T}\Delta T = C(T)\,\Delta T} \tag{28}$$

This explains why $C(T)$ is called the "heat capacity". Note also that $C(T) \geq 0$. Thus, Q will have the same sign as ΔT :

$\Delta T > 0 \rightarrow Q > 0 \rightarrow$ Heat enters the system

$\Delta T < 0 \rightarrow Q < 0 \rightarrow$ Heat leaves the system

Using Eq (12) we may also write

$$\Delta Q = T \frac{\partial S}{\partial T} \Delta T$$

or, what is even better

$$\boxed{\Delta Q = T \Delta S} \qquad (29)$$

This establishes a famous relation in thermodynamics, between heat and entropy changes. We will learn later that this continues to be true when work is performed in the system.

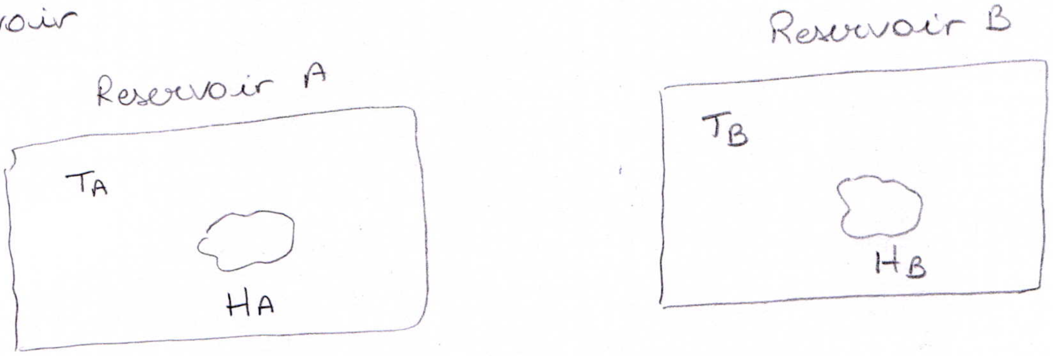
Eq (29) can also be used to define an <u>adiabatic process</u>; i.e., a process for which no heat flows through the system. We see, in terms of (29), that this is a synonym of a process which occurs at constant entropy.

The Jarzynski - Wójcik fluctuation theorem

Now I want to discuss a quite new and remarkable result. We all know that "heat flows from hot to cold". I want to demonstrate this. And I will only need 2 ingredients: the Gibbs formula and time-reversal invariance

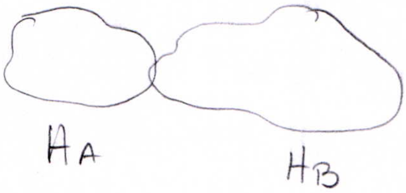
These calculations are based on Phys. Rev. Lett 92, 230602 (2004). I will do it for classical dynamics. In the paper they also do it in the quantum case. The final result is the same.

The basic setup is the following. Suppose you have two arbitrary systems, each connected to its own reservoir



Initially the two systems are completely decoupled from each other.

Now, at $t=0$ we disconnect them from their baths and put them in contact with each other.



Then, for $t>0$ the systems will start to exchange energy.

Let y_A denote the set of microstates of system A and similarly for y_B and system B. For $t>0$ we can describe the total energy of A+B as

$$H(y_A, y_B) = H_A(y_A) + H_B(y_B) + V(y_A, y_B) \tag{30}$$

where $V(y_A, y_B)$ is the *interaction energy*. We will assume that this interaction is weak

$$V << H_{A,B} \tag{31}$$

which is known as the *weak coupling approximation*. This is usually true in most systems since H_{AB} are volumetric quantities, whereas V depends on the surface of the systems (the number of atoms in the surface is much smaller than on the bulk).

Let $y = (y_A, y_B)$ and denote by y_t the microstate at time t. At $t=0$ the systems were coupled to heat baths so y_0 is a random variable with probability

$$P(y_0) = \frac{e^{-\beta_A H_A(y_{A,0})}}{Z_A} \frac{e^{-\beta_B H_B(y_{B,0})}}{Z_B} \tag{32}$$

But for $t>0$ we have decoupled the systems from their baths. So the evolution of y_t will be deterministic, according to Newton's law. We thus have a deterministic evolution with random initial conditions.

At a certain time τ, the energy of each system will be $H_A(y_{A,\tau})$ and $H_B(y_{B,\tau})$. We define

$$\begin{aligned} \Delta E_A &= H_A(y_{A,\tau}) - H_A(y_{A,0}) \\ \Delta E_B &= H_B(y_{B,\tau}) - H_B(y_{B,0}) \end{aligned} \tag{33}$$

Due to the weak coupling approximation, it follows that

$$\Delta E_A \approx -\Delta E_B \tag{34}$$

meaning all energy which leaves A must enter B. This allows us to define the heat exchanged between the two systems as

$$Q(y_0) = \Delta E_B \simeq -\Delta E_A \tag{35}$$

We define it such that $\hat{Q}>0$ means energy has entered system B.

But since y_0 is a random variable, the heat $\hat{Q}(y_0)$ will also be a random variable. That is why I put a hat in it.

We may thus speak about a <u>distribution</u> of <u>heat</u>

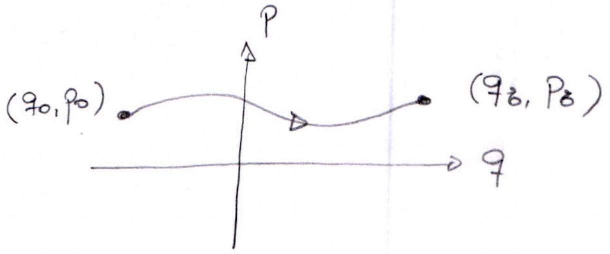
$P_\tau(Q)$ = prob. that a heat Q has flown between the systems after a certain time τ.

We can define it using what we know about changing variables:

$$\boxed{P_\tau(Q) = \int dy_0 \; P(y_0)\, \delta\left[Q - \hat{Q}(y_0)\right]} \qquad (36)$$

Now comes the main ingredient we are going to need; <u>time-reversal</u> <u>invariance</u>: Newton's law (and Schrödinger's Eq) are invariant if you play the movie backwards.

what this means is as follows. Consider a single particle with q_t and p_t, and let's look at the evolution of this particle from time $t=0$ to time τ

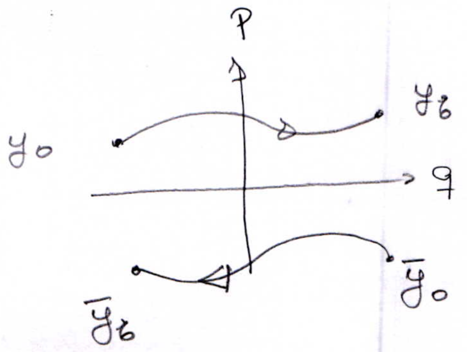


the trajectory (q_t, p_t) are solutions of Newton's Eqs.

Now consider the *time* *reversed* *trajectory*, obtained as

$$\bar{y}(t) = (q_{\tau-t}, -p_{\tau-t}) \tag{37}$$

this trajectory must also be a solution of Newton's Eq



we change the sign of p because $p \propto \frac{dq}{dt}$ and to play the movie backwards we must put $t \to -t$.

The Hamiltonian of any physical system must be invariant under time reversal. that is, if we change $q \to q$ and $p \to -p$, we keep H unchanged. we thus get, based on the picture in the previous page

$$H(y_t) = H(\bar{y}_0)$$

$$H(y_0) = H(\bar{y}_t) \qquad (38)$$

Thus, if we look at the energy exchanged in the reversed trajectory we get

$$\hat{Q}(\bar{y}_0) = H_B(\bar{y}_{B,t}) - H_B(\bar{y}_{B,0})$$

$$= H_B(y_{B,0}) - H_B(y_{B,t})$$

$$= -\hat{Q}(y_0)$$

Thus

$$\hat{Q}(\bar{y}_0) = -\hat{Q}(y_0) \qquad (39)$$

For every trajectory which exchanges a heat $\hat{Q}(y_0)$, we have a time-reversed trajectory, which exchanges the opposite amount of heat.

we also have the following result: by definition

$$P(\bar{y}_0) = \frac{e^{-\beta_A H_A(\bar{y}_{A,0})}}{Z_A} \frac{e^{-\beta_B H_B(\bar{y}_{B,0})}}{Z_B} \qquad (40)$$

comparing with (32) we get

$$\frac{P(y_0)}{P(\bar{y}_0)} = \exp\Big\{-\beta_A\left[H_A(y_{A,0}) - H_A(\bar{y}_{A,0})\right] \\ - \beta\left[H_B(y_{B,0}) - H_B(\bar{y}_{B,0})\right]\Big\}$$

$$= \exp\Big\{-\beta_A\left[H_A(y_{A,0}) - H_A(y_{A,\tau})\right] \\ - \beta_B\left[H_B(y_{B,0}) - H_B(y_{B,\tau})\right]\Big\}$$

$$= e^{\beta_A \Delta E_A + \beta_B \Delta E_B}$$

$$= e^{(\beta_B - \beta_A) Q}$$

Thus

$$\frac{P(y_0)}{P(\bar{y}_0)} = e^{\Delta\beta Q} \qquad \Delta\beta = \beta_B - \beta_A \qquad (41)$$

To finish the job we go back to $P_\tau(Q)$ in (36) and use (41) to get

$$P_\tau(Q) = \int dy_0 \, P(y_0) \, \delta\left[Q - \hat{Q}(y_0)\right]$$

$$= \int dy_0 \, P(\bar{y}_0) \, e^{\Delta\beta Q} \, \delta\left[Q + \hat{Q}(\bar{y}_0)\right]$$

$$= e^{\Delta\beta Q} \int dy_0 \, P(\bar{y}_0) \, \delta\left[Q + \hat{Q}(\bar{y}_0)\right]$$

$$= P_\tau(-Q)$$

Thus, we finally arrive at the Jarzynski- Wojcik fluctuation theorem

$$\boxed{\frac{P_\tau(Q)}{P_\tau(-Q)} = e^{\Delta\beta Q}} \qquad \Delta\beta = \beta_B - \beta_A \qquad (42)$$

This relates the prob. of observing a positive and a negative heat after a certain time τ.

If $T_A > T_B$ (left side hotter) than $\Delta\beta > 0$. Thus

$$P_\tau(+Q) > P_\tau(-Q)$$

this means it is more likely to observe heat flowing from hot to cold.

For macroscopic systems Q will be an extensive quantity so $e^{\Delta\beta Q}$ will be enormous, making it overwhelmingly more likely to observe a positive heat. This is why, in our daily lives, we always observe the heat from hot to cold, which is the 2nd law.

If we want to observe violations of the 2nd law we must look at microscopic systems.

Another thing we can do is this. Let us compute

$$\langle e^{-\Delta\beta Q}\rangle = \int dQ\, e^{-\Delta\beta Q} P_\tau(Q) = \int dQ\, e^{-\Delta\beta Q} e^{\Delta\beta Q} P_\tau(-Q)$$

$$= \int dQ\, P_\tau(Q)$$

$$= 1$$

whence

$$\boxed{\langle e^{-\Delta\beta Q}\rangle = 1} \tag{43}$$

This is called a <u>Jarzynski equality</u>, or a <u>non-equilibrium equality</u>.

we may combine this result with Jensen's inequality

$$\langle e^{-\Delta\beta Q} \rangle \geqslant e^{-\Delta\beta \langle Q \rangle}$$

this is an inequality valid for concave functions.

we then get

$$e^{-\Delta\beta\langle Q \rangle} \leqslant 1$$

$$-\Delta\beta \langle Q \rangle \leqslant 0$$

or

$$\boxed{\langle Q \rangle \geqslant 0} \qquad (44)$$

This can be stated as "on average, heat flows from hot to cold". For macroscopic systems realizations Q become arbitrarily close from the average $\langle Q \rangle$, so there is no need to distinguish the two.