The laws of thermodynamics

Gabriel T. Landi

References:

The calculations I am going to discuss here are not in any textbook I know of. They have been motivated by

G. Crooks, J. Stat. Phys, 90, 1481, (1998)

See also

W. L. Ribeiro, G.T. Landi and F. Semião, Arxiv 1601.01833 (To appear on Am. J. Phys. (2017)).

A nice discussion about the laws of thermodynamics may be found in

E. Fermi, Thermodynamics.

Heat and work: the first law

Consider a physical system in thermal equilibrium with a heat bath at a temperature T. Let H be the Hamiltonian and suppose that it depends on some parameter λ, that can be changed by an external agent.

Examples include

- the volume of a cylinder
- An electric or magnetic field
- the frequency ω of a harmonic trap.

etc. When the external agent changes λ he is performing work in the system. We call λ the work parameter. Thus, we may define work microscopically as

$$\boxed{\text{Work} = \text{when an external agent changes the Hamiltonian of the system}} \tag{1}$$

Now suppose that the system is in equilibrium at a temperature T and for a certain value of λ. Its state will then be given by the Gibbs probability

$$P_m(\lambda) = \sum_m \frac{e^{-\beta E_m(\lambda)}}{Z(\lambda)} \qquad (2)$$

with

$$Z(\lambda) = \sum_m e^{-\beta E_m(\lambda)} \qquad (3)$$

Everything also depends on T, but T is fixed, so we don't worry about it. [The same calculation works for classical system, in exactly the same way. Just replace sums by integrals].

The internal energy of the system is

$$U(\lambda, T) = \sum_m E_m(\lambda) P_m(\lambda, T) \qquad (4)$$

Now suppose the external agent changes λ slightly to $\lambda + d\lambda$. But after this will push the system away from equilibrium. But after some time the system and the bath will readjust and equilibrium will again be reestablished.

The change in the internal energy of the system will be

$$dU = U(\lambda + d\lambda, T) - U(\lambda, T) = \sum_m d(E_m P_m)$$

Using the product rule we get

$$\boxed{dU = \sum_m \left[(dE_m) P_m + E_m \, dP_m \right]} \qquad (5)$$

Here d() always refers to λ. The temperature is fixed

Now let us interpret these two terms. The first is the change in energy at a fixed P_m, and the 2^{nd} is the change in P_m at a fixed energy.

Since the change from λ to $\lambda + d\lambda$ is infinitesimal, we may also assume that it occurs instantaneously. The first term in (5) is therefore the cost in energy with the probabilities frozen. We may therefore attribute it to the <u>work</u> performed by the external agent.

After the change in mode, the system will have to readjust in order to reach a new equilibrium position. In the process, it will exchange some <u>heat</u> with the bath. This is the 2^{nd} term in Eq (5). It is the change in probabilities for a fixed energy.

Thus, we propose to divide Eq (5) as

$$\boxed{dU = \delta Q - \delta W} \tag{6}$$

where

$$\delta W = \sum_m (dE_m) P_m \tag{7}$$

$$\delta Q = \sum_m E_m (dP_m) \tag{8}$$

The reason why we write δW and not dW is because W and Q are not properties of the system. Rather, they are the outcomes of changes performed on the system.

Eq (6) is called the <u>first law of thermodynamics</u>

Now let us understand these two terms in more detail.
We start with δW. We may write it as

$$\delta W = \frac{1}{Z}\sum_m (dE_m)\, e^{-\beta E_m} = \frac{1}{Z}\left(-\frac{1}{\beta}\right) d\left(\sum_m e^{-\beta E_m}\right)$$

$$= -\frac{k_B T}{Z}\, dZ = -k_B T\, d(\ln Z)$$

If we now recall the definition of the free energy

$$F = -k_B T \ln Z \tag{6}$$

then we conclude that

$$\boxed{\delta W = dF} \tag{7}$$

The work performed is therefore the change of the free energy, not the internal energy. This shows why F is "free": it is the part of U that can be used to perform work. Remember that in classical mechanics we had $\delta W = dU$ (work = change in potential energy). For thermal systems this is no longer true since part of U will be consumed as heat [see Eq (6)].

We may also write (7) as

$$\boxed{\delta W = dF = \frac{\partial F}{\partial \lambda} d\lambda} \tag{8}$$

The quantity $d\lambda$ is the "stimulus" caused by the external agent. It is how much the external agent poked our system. Then $\partial F/\partial\lambda$ is the <u>response</u> of the system to this stimulus.

For instance

- If $\lambda = V$ then we have seen that the pressure was

$$p = -\frac{\partial F}{\partial V} \tag{9}$$

thus

$$\delta W = -p\, dV \tag{10}$$

$$\boxed{dU = dQ - p dV} \tag{11}$$

- If $\lambda = B$ (magnetic field) then we have seen that

$$M = -\frac{\partial F}{\partial B} \tag{12}$$

so that

$$\delta W = -M dB \tag{13}$$

$$\boxed{dU = \delta Q - M dB} \tag{14}$$

the pattern is always the same:

$$\boxed{\delta W = (\text{response}) \times d(\text{stimulus})} \tag{15}$$

We also have the following result: from (7)

$$\delta W = \sum_m (dE_m)\, P_m = \sum_m \left(\frac{\partial E_m}{\partial \lambda}\right) d\lambda\, P_m = d\lambda \sum_m \left(\frac{\partial E_m}{\partial \lambda}\right) P_m$$

comparing with (8) we conclude that

$$\boxed{\frac{\partial F}{\partial \lambda} = \left\langle \frac{\partial E_m}{\partial \lambda} \right\rangle} \tag{16}$$

But note that this is not $\partial U/\partial \lambda$. Again, it is the free energy that comes in here.

For an infinitesimal process, we have seen that $\delta W = dF$. We can now build up a finite process as a succession of infinitesimal steps. This will work when the process is done very slowly, which is what we call a quasi-static process. In this case the total work performed will be

$$\boxed{W = \int_{\lambda_i}^{\lambda_f} dF = \Delta F = F(\lambda_f) - F(\lambda_i)} \tag{17}$$

Heat and Entropy

Now let us turn to Eq (6):

$$\delta Q = \sum_m E_m \, d(P_m)$$

I'm going to use a naughty trick: I will use the Gibbs probability formula to get rid of E_m

$$P_m = \frac{e^{-\beta E_m}}{Z} \quad \rightsquigarrow \quad E_m = -\frac{1}{\beta} \ln (P_m Z) \qquad (18)$$

Thus

$$\delta Q = -k_B T \sum_m \ln (P_m Z) \, dP_m$$

$$= -k_B T \left\{ \sum_m (\ln P_m) \, dP_m + \ln Z \sum_m dP_m \right\}$$

But

$$\sum_m dP_m = d\left(\sum_m P_m\right) = d(1) = 0 \qquad (19)$$

so we get

$$\delta Q = -k_B T \sum_m dP_m \ln P_m \qquad (20)$$

Now let us look at

$$d\left(\sum_m P_m \ln P_m\right) = \sum_m \left\{ dP_m \ln P_m + P_m \, d(\ln P_m) \right\}$$

$$= \sum_m dP_m \ln P_m + \underbrace{\sum_m P_m \frac{1}{P_m} dP_m}_{=0}$$

for the same reason as above

Thus we conclude that

$$\sum_n dP_n \ln P_n = d\left(\sum_n P_n \ln P_n\right) \tag{21}$$

Eq (20) then becomes

$$\delta Q = -k_B T\, d\left(\sum_n P_n \ln P_n\right) \tag{22}$$

We now define a new quantity called the <u>entropy</u> as

$$\boxed{S = -k_B \sum_n P_n \ln P_n} \tag{23}$$

so that we finally arrive at

$$\boxed{\delta Q = T dS} \tag{24}$$

the first law (6) then becomes

$$\boxed{dU = T dS - \delta W} \tag{25}$$

Using the Gibbs probabilities we may write

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

so Eq (23) becomes

$$S = \underbrace{-k_B(-\beta)}_{\frac{1}{T}} \underbrace{\sum_m E_m P_m}_{U} - k_B(-\ln Z) \underbrace{\sum_m P_m}_{1}$$

$$= \frac{U}{T} + \underbrace{k_B \ln Z}_{-\frac{1}{T}(-k_B T \ln Z)}$$

thus we conclude that

$$\boxed{S = \frac{U-F}{T} \quad \text{or} \quad F = U - TS} \tag{26}$$

This is a well known relation from thermodynamics. It also gives a very practical way of computing the entropy since F and U are easy to find.

Another useful formula is

$$\boxed{S = -\frac{\partial F}{\partial T}} \tag{27}$$

Check:

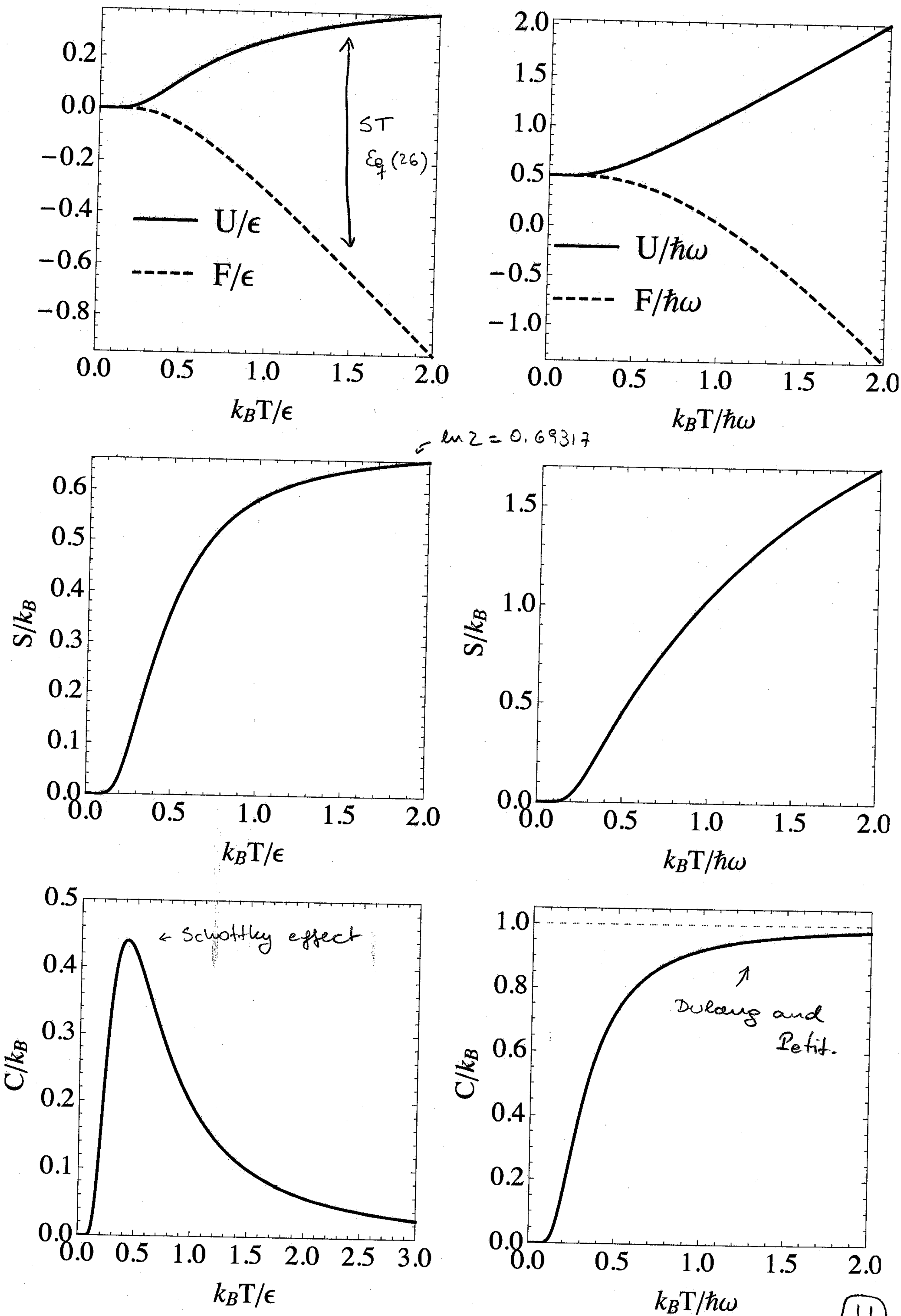
$$-\frac{\partial F}{\partial T} = -\frac{\partial}{\partial T}\left(-k_B T \ln Z\right) = \underbrace{k_B \ln Z}_{-\frac{F}{T}} + \underbrace{k_B T \frac{\partial}{\partial T} \ln Z}_{\frac{U}{T}}$$

Comparison of thermodynamic quantities

2-state system	Quantum harm. oscillator
$E_0 = 0, \quad E_1 = \epsilon$	$E_n = \hbar\omega(n+1/2), \quad n=0,1,2,\dots$
$Z = 1 + e^{-\beta\epsilon}$	$Z = \dfrac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$
$U = \dfrac{\epsilon}{e^{\beta\epsilon}+1}$	$U = \dfrac{\hbar\omega}{2} + \dfrac{\hbar\omega}{e^{\beta\hbar\omega}-1}$
$F = -k_BT\ln(1+e^{-\beta\epsilon})$	$F = \dfrac{\hbar\omega}{2} + k_BT\ln(1-e^{-\beta\hbar\omega})$
$S = \dfrac{\epsilon/T}{e^{\beta\epsilon}+1} + k_B\ln(1+e^{-\beta\epsilon})$	$S = \dfrac{\hbar\omega/T}{e^{\beta\hbar\omega}-1} - k_B\ln(1-e^{-\beta\hbar\omega})$
$C = k_B\left(\dfrac{\epsilon}{k_BT}\right)^2\dfrac{e^{\beta\epsilon}}{(e^{\beta\epsilon}+1)^2}$	$C = k_B\left(\dfrac{\hbar\omega}{k_BT}\right)^2\dfrac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$

2−state system

Q harm. oscillator



Understanding the entropy

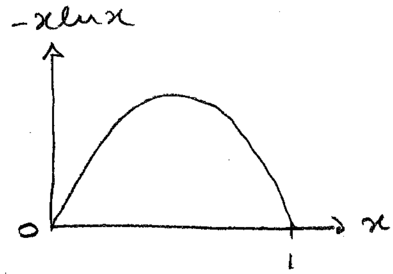
The entropy is given by

$$S = -k_B \sum_m P_m \ln P_m \tag{28}$$

It is a sum of terms of the form

$$-x \ln x \, , \qquad x \in [0,1]$$

This function looks like this



It is zero when $x=0$ and when $x=1$. Thus, any state that has $P_m = 0$ or $P_m = 1$ will not contribute to the entropy. This is why we say entropy is related to disorder. Its main contributions come from states with moderate probabilities.

Now let's see what happens when $T \to 0$. In this case we know that the system will tend to the ground state. If the ground state is unique then $P_0 = 1$ and all other P_n are zero. In this case we therefore see that S will be zero.

But if the ground state is degenerate, then we will have several states with the same energy. Let $P_{0,i}$ be the probabilities of these states and let g denote the degeneracy of the ground state (so $i = 1, \dots, g$). Then all ground states will have the same probabilities which, by normalization, must be

$$P_{0,i} = 1/g \quad , \quad P_n = 0 \quad n > 0 \tag{29}$$

Thus, the entropy in this case will be

$$S = - \sum_{i=1}^{g} P_{0,i} \ln P_{0,i} = - \sum_{i=1}^{g} \frac{1}{g} \ln (1/g) = - \frac{g}{g} \ln g$$

Or

$$\boxed{\lim_{T \to 0} S = \ln g = \ln (\text{deg. of the GS})} \tag{30}$$

This is known as the third law of thermodynamics, or Nernst's postulate

Entropy and heat capacity

Consider now a different experiment; a system is in equilibrium at a temperature T. Then we get it and place it in contact with another bath, at a temperature $T+dT$ [This is like taking a hot sword from the oven and dipping it in a bucket of water].

The change in the energy of the system will be

$$dU = \sum_m E_m \, dP_m \tag{31}$$

where, now,

$$dP_m = P_m(T+dT) - P_m(T)$$

[there is no work parameter in this problem].

Eq (31) is the same formula we had before for δQ:

$$dU = \delta Q \tag{32}$$

which makes sense since in this case no work is performed in the system. Thus, we conclude that in this case

$$dU = T\,dS \tag{33}$$

But we may also write

$$dU = \frac{\partial U}{\partial T} dT = C\,dT$$

comparing the two we then conclude that

$$\boxed{C = \frac{\delta Q}{dT} = T \frac{\partial S}{\partial T}} \tag{34}$$

This formula puts on more concrete grounds the connection between <u>heat capacity</u> and <u>heat</u> and <u>entropy</u>.

This is also how one computes the entropy experimentally. No one can measure entropy directly. What they do is they measure C and then integrate:

$$\frac{\partial S}{\partial T} = \frac{C}{T} \rightsquigarrow S = \int \frac{C}{T} dT \tag{35}$$

<u>Note</u>:

If you want to do a process in which no heat is exchanged between your system and the bath ($\delta Q = 0$) then you should keep S constant, since $\delta Q = T dS$. This is called an <u>adiabatic process</u>

Example : magnetic cooling

Samples may be cooled to around 3K by liquefying Helium. If you want to go beyond that you will need more sophisticated tricks. Magnetic cooling is one of those tricks, which can usually take you to around a few mK.

To use it you must glue your sample to some paramagnetic material. I will assume for simplicity that this material is spin 1/2, but that is not at all restrictive.

we have seen that in this case

$$E_\sigma = -\mu_B B \sigma \tag{36}$$

and

$$z = 2\cosh\left(\frac{\mu_B B}{k_B T}\right) \tag{37}$$

the magnetization was

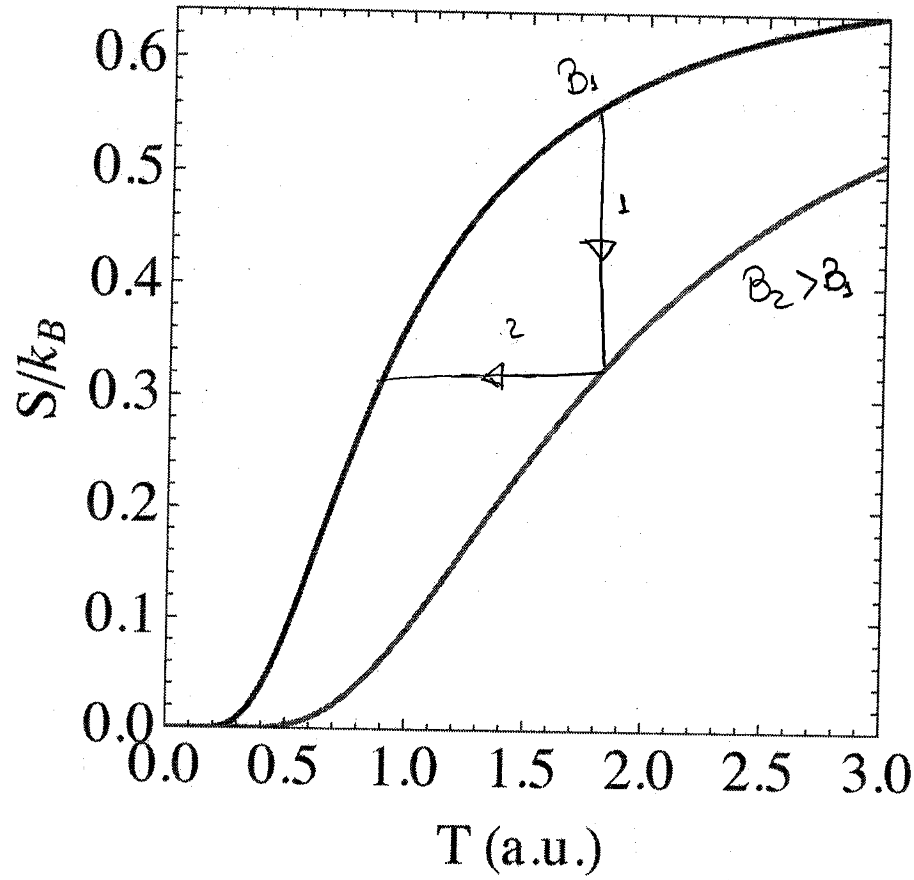
$$\langle \sigma \rangle = \tanh\left(\frac{\mu_B B}{k_B T}\right) \tag{38}$$

so the internal energy is

$$U = -\mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right) \tag{39}$$

Finally, the entropy is

$$S = \frac{U-F}{T} = -\frac{\mu_B B}{T}\tanh\left(\frac{\mu_B B}{k_B T}\right) + k_B \ln\left[2\cosh\left(\frac{\mu_B B}{k_B T}\right)\right] \tag{40}$$



Magnetic cooling works by repeating the following 2 steps

1) Apply a mag field B very slowly from B_1 to B_2

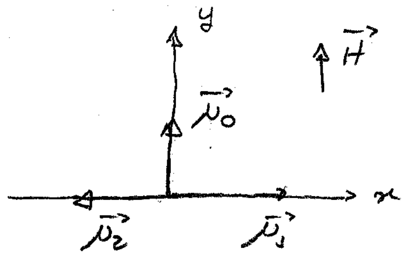
2) Turn off the field very quickly.

In the first step the system is always at the same T (because you apply B slowly). Since T is fixed and B goes up, U goes down [Eq (39)]. So in the end of (1) the temperature remained the same, but U went down.

In step 2 you turn off B very quickly, so there is no time to exchange heat. Thus, S remains constant (adiabatic; see figure). But if you look at S in Eq (40) you will see that it depends only on B/T. Hence, if S is constant but B goes down, then so must T, hence cooling down your sample.

Example : EUF 2014-1

Consider a system of N non-interacting magnetic atoms, whose magnetic moments $\vec{\mu}$ can point in only 3 directions. The energies in the 3 directions are



$$E_0 = -\mu H \qquad\qquad (41)$$

$$E_1 = E_2 = 0$$

The ground state will depend on the sign of H

- If $H > 0$: $gs = 0$
- If $H < 0$: $gs = 1, 2 \Rightarrow$ 2-fold degenerate.

The partition function is

$$Z_1 = \sum_m e^{-\beta E_m} = 2 + e^{\beta \mu H} \rightsquigarrow Z = Z_1^N \qquad (42)$$

So

$$F = -k_B T \ln Z = -N k_B T \ln (2 + e^{\beta\mu H}) \qquad (43)$$

and

$$U = -\frac{\partial}{\partial \beta} \ln Z = -N \frac{\mu H e^{\beta \mu H}}{2 + e^{\beta\mu H}} \qquad (44)$$

The entropy will then be

$$S = \frac{U - F}{T} = -N \frac{\mu H}{T} \frac{e^{\beta\mu H}}{2 + e^{\beta\mu H}} + N k_B \ln (2 + e^{\beta\mu H})$$

The entropy has units of k_B so it is convenient to write

$$\frac{S}{N k_B} = -\beta\mu H \frac{e^{\beta\mu H}}{2 + e^{\beta\mu H}} + \ln(2 + e^{\beta\mu H}) \qquad (45)$$

Now let us understand what happens at very low temperatures. To do that we need to distinguish the cases of $H>0$ and $H<0$. We

$\underline{H>0}$: $\beta\mu H >> 1$ at low T.

So we may approximate $2+e^{\beta\mu H} \approx e^{\beta\mu H}$. We then get

$$\frac{F}{N} \approx -k_B T \ln e^{\beta\mu H} = -\mu H \tag{46a}$$

$$\frac{U}{N} \approx -\mu H \frac{e^{\beta\mu H}}{e^{\beta\mu H}} = -\mu H \tag{46b}$$

$$\frac{S}{Nk_B} \approx -\beta\mu H \frac{e^{\beta\mu H}}{e^{\beta\mu H}} + \ln e^{\beta\mu H} = 0 \tag{46c}$$

When $H>0$ the ground state has energy $E_0 = -\mu H$ and is non-degenerate. Thus $S \to 0$ and U and F tend to E_0.

$H<0$: $\beta\mu H << -1$ so we may approximate $e^{\beta\mu H} \approx 0$

We then get

$$\frac{F}{N} \approx -N k_B T \ln 2 \approx 0 \quad (\text{because } T\to 0) \tag{47a}$$

$$\frac{U}{N} = -\mu H \frac{e^{\beta\mu H}}{2+e^{\beta\mu H}} \approx 0 \tag{47b}$$

$$\frac{S}{Nk_B} \approx \ln 2 \tag{47c}$$

Thus, in this limit both U and F tend to $E_{1,2}=0$, which is the GS when $H<0$. Moreover, $\frac{S}{N}$ tends to $k_B \ln 2$, because this GS is two-fold degenerate.

Now let's see what happens in the opposite limit, $T \to \infty$. In this case we may approximate $e^{\beta \mu H} \approx 1$, for both $H > 0$ and $H < 0$.

The Gibbs probabilities become

$$P_0 = \frac{e^{\beta \mu H}}{2 + e^{\beta \mu H}} \approx \frac{1}{3} \qquad (48a)$$

$$P_{1,2} = \frac{1}{2 + e^{\beta \mu H}} \approx \frac{1}{3} \qquad (48b)$$

Thus, the 3 states become <u>equally likely</u>; at $T = \infty$ all states become equally populated.

As for the thermodynamic quantities, we get

$$F \approx -N k_B T \ln 3 \to -\infty \qquad (49a)$$

$$U \approx -\frac{N \mu H}{3} \qquad (49b)$$

$$S \approx k_B \ln 3 \qquad (49c)$$

The energy U tends to the arithmetic average of all energies, since all states are equally likely

$$U = \sum_m E_m P_m = E_0 P_0 + E_1 P_1 + E_2 P_2$$

$$= -\frac{\mu H}{3} + 0 + 0$$

The entropy tends to $k_B \ln 3$. Since all states are equally accessible, what enters here is the ln of the total number of states. Finally, $F = U - TS$. Since U and S are finite, but $T \to \infty$, F will tend to $-\infty$.

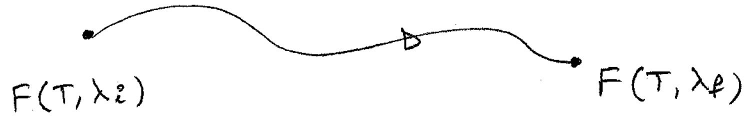
The 2^{nd} law of thermodynamics.

The 2^{nd} law of thermodynamics is perhaps one of the deepest laws of physics. It's statement, according to Lord Kelvin, is

> 2^{nd} law: "A transformation whose only final result is to transform into work, heat from a source which is at the same temperature throughout, is impossible"

The part you need to remember in the statement "whose only final result." For instance, we can heat up a gas and let it expand a piston. In this process you have extracted work from a reservoir at a fixed temperature. But that was not the "only final result" because in the end the volume of the gas is larger. Extracting work without changing anything else is impossible.

Now suppose you perform some work and take the system from a point λ_i to a point λ_f.



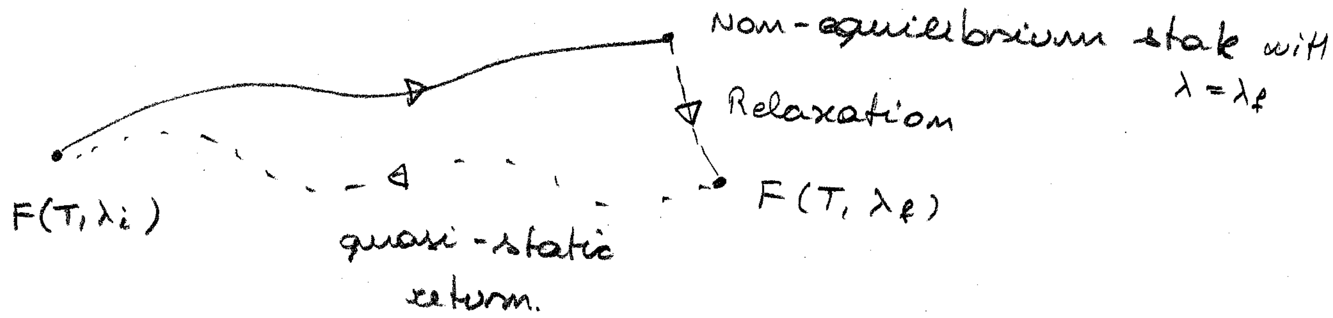
If you do this quasi-statically then we have seen in Eq (17) that $W = \Delta F = F_f - F_i$

If we now go back, also quasi-statically, the work in the return journey will be $W_R = -\Delta F$. So overall, the total work performed was

$$W_{tot} = W + W_R = 0$$

In the end you came back to exactly the same stage, but you also did not perform any work. Thus the 2^{nd} law is not violated.

Now consider a process divided in 3 steps



The steps are

1) You change λ from λ_i to λ_f in an arbitrary way (not necessarily quasi-static). This will take the system toward a non-equilibrium state

2) You allow the system to relax (no work) until it again establishes an equilibrium with the bath. λ remains fixed at λ_f

3) You return from λ_f to λ_i quasistatically.

Let W_1 be the work done in the first part. It will depend on the particular choice of protocol. The work on step 2 is 0 and the work on step 3 is $-\Delta F$ since the process is quasi-static.

Thus, the total work will be

$$W_{tot} = W_1 + W_2 + W_3 = W_1 - \Delta F$$

But in the end we are back where we started. So we must have $W_{tot} \geq 0$ because, otherwise work would have been extracted from the reservoir without any other change (extract work $= W_{tot} < 0$). Thus we conclude that $W_1 \geq \Delta F$. Dropping the suffix 1, we conclude that <u>for any non-equilibrium process</u>

$$\boxed{W \geq \Delta F} \qquad (49')$$

This is the mathematical statement of the 2nd law. It says that the <u>minimum work</u> that must be done in taking the system from λ_i to λ_f is ΔF and this occurs in a quasi-static process. For any other process, the work will always be larger than ΔF.

The 2nd law of thermodynamics : derivation

We now reach the climax of these notes: the 2nd law. The 2nd law deals with systems away from equilibrium, so it is not embedded in the Gibbs formalism. We will therefore need extra assumptions. I will show you that we actually only need one: detailed balance.

I will demonstrate the 2nd law using a very modern approach, that began with

G. Crooks, J. Stat Phys. 90, 1481 (1998)

C. Jarzynski, Phys. Rev. Lett. 78, 2690 (1997)

Their idea is quite awesome: treat work as a random variable. Suppose you perform some work on a system. If the system is connected to a heat bath its microstate will be constantly fluctuating. So the work you will end up performing will be a random variable.

This randomness is imperceptible in macroscopically large systems, but can be detected in small systems. In fact we can study the distribution of work $P(W)$ that you obtain if you repeat the process several times, always starting at the same initial condition.

This has actually been done experimentally! (see next page).

I must say: I love the century we live in.

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nature

LETTERS

Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies

D. Collin[1*], F. Ritort[2*], C. Jarzynski[3], S. B. Smith[4], I. Tinoco Jr[5] & C. Bustamante[4,6]

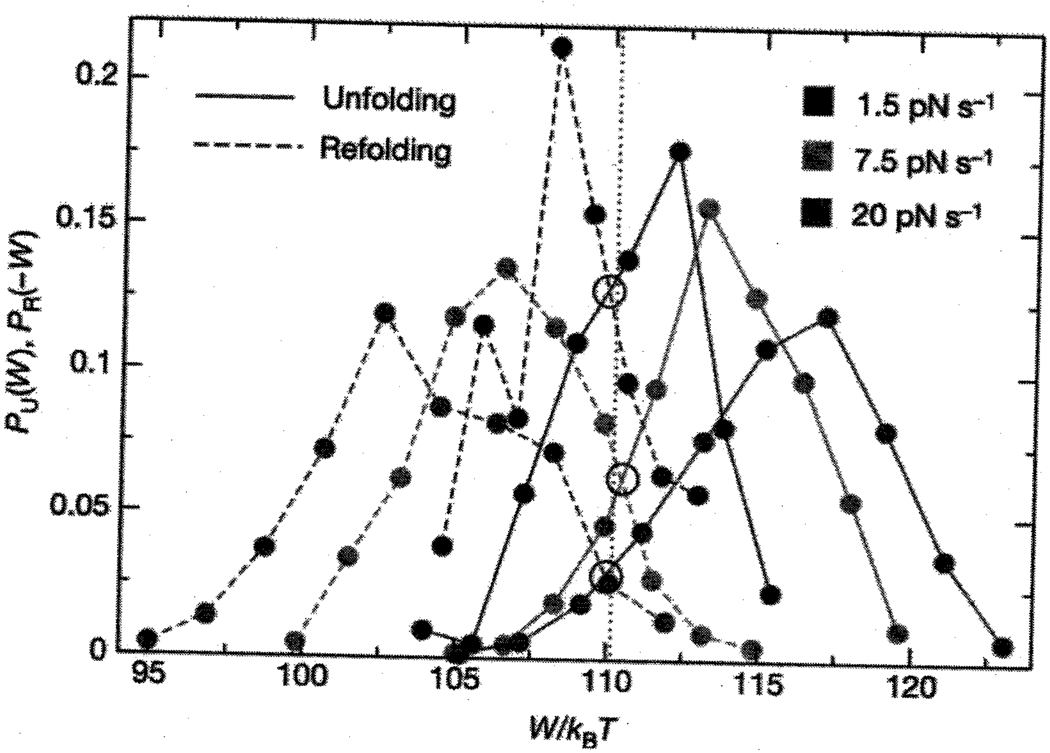

Figure 2 | Test of the CFT using an RNA hairpin. Work distributions for RNA unfolding (continuous lines) and refolding (dashed lines). We plot negative work, $P_R(-W)$, for refolding. Statistics: 130 pulls and three molecules ($r = 1.5\,\mathrm{pN\,s^{-1}}$), 380 pulls and four molecules ($r = 7.5\,\mathrm{pN\,s^{-1}}$), 700 pulls and three molecules ($r = 20.0\,\mathrm{pN\,s^{-1}}$), for a total of ten separate experiments. Good reproducibility was obtained among molecules (see Supplementary Fig. S2). Work values were binned into about ten equally spaced intervals. Unfolding and refolding distributions at different speeds show a common crossing around $\Delta G = 110.3\,k_BT$.

they do work by folding and unfolding individual RNA molecules using an optical tweezer.

I will repeat here the calculations exactly as was done in Crooks' paper. We assume we have a system that may be modeled by a Markov Chain (discrete states, discrete time). Let X_t be the state of the system at time t, where X_t can take on a discrete set of levels m.

Also, let $E(m, \lambda)$ be the energy of the system for a given state m and a given work parameter λ.

We assume that initially the system was in thermal equilibrium at a temperature T and a work parameter λ_0. The state of the system will then be drawn from the Gibbs distribution

$$X_0 \sim P_m^{eq}(\lambda_0) = \frac{e^{-\beta E(m, \lambda_0)}}{Z(\lambda_0)} \tag{50}$$

Then an external agent begins to change λ (ie, perform work). We will assume that λ changes also in discrete steps and instantaneously. So at $t=0$ we change $\lambda_0 \to \lambda_1$ and then allow the system to evolve up to time $t=1$. Then at $t=1$ we change (instantaneously) $\lambda_1 \to \lambda_2$ and then let the system evolve up to $t=2$. We assume this continues up to a time τ. We will then have a Markov chain

$$X_0 \xrightarrow{\lambda_1} X_1 \xrightarrow{\lambda_2} X_2 \longrightarrow \cdots X_{\tau-1} \xrightarrow{\lambda_\tau} X_\tau \tag{51}$$

This process may be modeled by a Markov Chain as

$$p_n(t+1) = \sum_m{}' Q_{nm}(\lambda_t)\, p_m(t) \tag{52}$$

the difference is that now the transition probabilities will depend on time because they may depend on λ. We don't know what the Q_{nm} are. All we impose is that they obey detailed balance for each value of λ

$$Q_{nm}(\lambda)\, p_m^{eq}(\lambda) = Q_{mn}(\lambda)\, p_n^{eq}(\lambda) \tag{53}$$

so

$$\boxed{\frac{Q_{nm}(\lambda)}{Q_{mn}(\lambda)} = \frac{e^{-\beta E(n,\lambda)}}{e^{-\beta E(m,\lambda)}}} \tag{54}$$

If the λ's change very little and very slowly, the system will always remain close to equilibrium at all times. This is what we call a quasi-static process. But if λ changes quickly the probabilities $p_n(t)$ will differ substantially from $p_n^{eq}(\lambda_t)$.

At each step, when we change λ abruptly from λ_t to λ_{t+1}, we perform some work. Since the change is instantaneous the state of the system has not yet changed, so the work performed in this step will be

$$\delta W_t = E(x_t, \lambda_{t+1}) - E(x_t, \lambda_t) \tag{55}$$

After this change the system will evolve to x_{t+1}. In this second step no work is performed so any change in the energy must be attributed to heat:

$$\delta Q_t = E(x_{t+1}, \lambda_{t+1}) - E(x_t, \lambda_{t+1}) \tag{56}$$

Summing these contributions for the entire process, we then find that the total work performed was

$$\boxed{W = \sum_{t=0}^{6-1} \left[E(x_t, \lambda_{t+1}) - E(x_t, \lambda_t)\right]} \tag{57}$$

whereas the total heat exchanged was

$$\boxed{Q = \sum_{t=0}^{6-1} \left[E(x_{t+1}, \lambda_{t+1}) - E(x_t, \lambda_{t+1})\right]} \tag{58}$$

If we add the two we see that most terms will cancel out. We will only be left with

$$\boxed{\Delta U = Q + W = E(x_6, \lambda_6) - E(x_0, \lambda_0)} \tag{59}$$

this shows clearly why U is a function of state and Q, W are not.

The quantity W in Eq (57) is a random variable because the X_t are random variables. What I want to compute is $P(w)$, the distribution of work. We see that it will depend on all the X_t so what we need is the joint distribution

$$P(X_0 = n_0, X_1 = n_1, \ldots, X_\tau = n_\tau)$$

This is the distribution of the full stochastic path. For systems satisfying the Markov property this probability is easy to find

$$\boxed{P(X_0 = n_0, \ldots, X_\tau = n_\tau) = Q_{n_\tau, n_{\tau-1}}(\lambda_\tau) \ldots Q_{n_1, n_0}(\lambda_1)\, P^{eq}_{n_0}(\lambda_0)} \qquad (60)$$

The full distribution of work may then be computed using the formulas we studied for transformation of variables:

$$\boxed{P(w) = \sum_{n_0, \ldots, n_\tau} P(X_0 = n_0, \ldots, X_\tau = n_\tau)\, \delta[w - W(n_0, \ldots, n_\tau)]} \qquad (61)$$

where $W(X_0, \ldots, X_\tau)$ is given in Eq (57).

Computing $P(w)$ is a difficult task, and is also problem specific. Luckly, to demonstrate the second law we will not have to compute it what we need to demonstrate the 2nd law is to look at the <u>reversed process</u>, that is, to look at what happens when we start at $X_{\mathcal{T}}$ and then let time evolve backwards up to $t=0$. The stochastic path in this case is

$$X_0 \xleftarrow{\lambda_1} X_1 \xleftarrow{\lambda_2} X_2 \;\; \cdots \;\; \longleftarrow X_{\mathcal{T}-1} \xleftarrow{\lambda_{\mathcal{T}}} X_{\mathcal{T}}$$

So the path probability will be

$$\mathbb{P}\,(X_{\mathcal{T}} = m_{\mathcal{T}}, \ldots, X_0 = m_0) = Q_{m_0, m_1}(\lambda_1) \ldots Q_{m_{\mathcal{T}-1}, m_{\mathcal{T}}}(\lambda_{\mathcal{T}})\, P^{eq}_{m_{\mathcal{T}}}(\lambda_{\mathcal{T}}) \qquad (62)$$

and the work performed in this process is simply minus the work of the forward process, Eq (57). Thus, the distribution of work in the reversed process will be

$$P_R(w) = \sum_{m_0, \ldots, m_{\mathcal{T}}} P_R\,(X_{\mathcal{T}} = m_{\mathcal{T}}, \ldots, X_0 = m_0)\, \delta\left[w + W(m_0, \ldots, m_{\mathcal{T}})\right] \qquad (63)$$

Now I will show you that the forward probability $P(w)$ and the reversed prob. $P_R(w)$ are actually related to each other

To see that we look at the ratio of the two path probabilities, Eq (60) and Eq (62), together with the det. bal. cond. (54), we get

$$\frac{P(X_0 = m_0, \ldots, X_\tau = m_\tau)}{P_R(X_\tau = m_\tau, \ldots, X_0 = m_0)} = \frac{Q_{m_\tau, m_{\tau-1}}(\lambda_\tau) \ldots Q_{m_1, m_0}(\lambda_1)\, P^{eq}_{m_0}(\lambda_0)}{Q_{m_0, m_1}(\lambda_1) \ldots Q_{m_\tau, m_{\tau-1}}(\lambda_\tau)\, P^{eq}_{m_\tau}(\lambda_\tau)}$$

$$= \left[\frac{Q_{m_\tau, m_{\tau-1}}(\lambda_\tau)}{Q_{m_{\tau-1}, m_\tau}(\lambda_\tau)}\right] \cdots \left[\frac{Q_{m_1, m_0}(\lambda_1)}{Q_{m_0, m_1}(\lambda_1)}\right] \frac{P^{eq}_{m_0}(\lambda_0)}{P^{eq}_{m_\tau}(\lambda_\tau)}$$

$$= \left[\frac{e^{-\beta E(m_\tau, \lambda_\tau)}}{e^{-\beta E(m_{\tau-1}, \lambda_\tau)}}\right] \cdots \left[\frac{e^{-\beta E(m_1, \lambda_1)}}{e^{-\beta E(m_0, \lambda_1)}}\right] \frac{e^{-\beta E(m_0, \lambda_0)}/Z(\lambda_0)}{e^{-\beta E(m_\tau, \lambda_\tau)}/Z(\lambda_\tau)}$$

$$= \exp\left\{ \beta\left[E(m_{\tau-1}, \lambda_\tau) - E(m_{\tau-1}, \lambda_{\tau-1})\right] + \ldots \right.$$

$$\left. + \beta\left[E(m_0, \lambda_1) - E(m_0, \lambda_0)\right]\right\} \frac{Z(\lambda_\tau)}{Z(\lambda_0)} \tag{64}$$

The quantity inside the exponential is, looking back at Eq (57), $\beta W(m_0, \ldots, m_\tau)$. Moreover

$$F = -k_B T \ln Z \rightsquigarrow Z = e^{-\beta F}$$

Thus

$$\frac{Z(\lambda_\tau)}{Z(\lambda_0)} = \frac{e^{-\beta F(\lambda_\tau)}}{e^{-\beta F(\lambda_0)}} = e^{-\beta \Delta F} \tag{65}$$

where

$$\Delta F = F(\lambda_\tau) - F(\lambda_0) \tag{66}$$

Thus we conclude that

$$\boxed{\frac{P(X_0 = m_0, \dots, X_\tau = m_\tau)}{P_R(X_\tau = m_\tau, \dots, X_0 = m_0)} = \exp\{\beta[W(m_0, \dots, m_\tau) - \Delta F]\}} \qquad (67)$$

Now we substitute this in Eq (61) for $P(w)$:

$$P(w) = \sum_{m_0, \dots, m_\tau} P(X_0 = m_0, \dots, X_\tau = m_\tau)\, \delta[w - W(m_0, \dots, m_\tau)]$$

$$= \sum_{m_0, \dots, m_\tau} P_R(X_\tau = m_\tau, \dots, X_0 = m_0)\, e^{\beta[W(m_0, \dots, m_\tau) - \Delta F]}\, \delta[w - W(m_0 .. m_\tau)]$$

because of the δ function this exponential may be taken out of the sum. We then get

$$P(w) = e^{\beta(w - \Delta F)} \sum_{m_0, \dots, m_\tau} P_R(X_\tau = m_\tau, \dots, X_0 = m_0)\, \delta[w - W(m_0, \dots, m_\tau)]$$

If we compare this with Eq (63) we see that the remaining sum is $P_R(-w)$. Thus we conclude that

$$\boxed{\frac{P(w)}{P_R(-w)} = e^{\beta(w - \Delta F)}} \qquad (68)$$

this is known as the <u>Crooks</u> <u>fluctuation</u> <u>theorem</u> (not to be confused with the fluctuation-dissipation theorem, which is something else).

Eq (68) is <u>exact</u>. It gives a relation between two probabilities for a process that is performed <u>arbitrarily far from equilibrium</u>.

We have seen in Eq (17) that for a quasistatic process, the work performed is exactly ΔF. Thus, for a quasi-static process $P(w) = P_R(-w)$; or, in words: if you go backwards the work performed is simply the original work. This is why we say that quasi-static processes are <u>reversible</u>.

But when a process is not quasi-static, the forward and backward protocols are not equivalent and the process is <u>irreversible</u>.

The Jarzynski equality

Now I want to show you a remarkable consequence of Eq (68). Since we have $P(w)$ we may compute any quantity we want. For instance

$$\langle W \rangle = \int w \, P(w) \, dw \tag{69}$$

Let us compute the characteristic function $\langle e^{isW} \rangle$. But I will not use any s; instead I will use $is = -\beta$. We then get

$$\langle e^{-\beta W} \rangle = \int e^{-\beta w} P(w) \, dw \underset{(68)}{=} \int e^{-\beta w} P_R(w) \, e^{\beta(w-\Delta F)} dw$$

$$= e^{-\beta \Delta F} \underbrace{\int P_R(w) \, dw}_{1}$$

Thus we conclude that

$$\boxed{\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}} \tag{70}$$

This is known as the Jarzynski equality. Jarzynski first found it in 1997 for Hamiltonian systems. Then 1 year later Crooks derived it for a Markov chain. They are actually more general. In fact, the only thing they require is detailed balance. It all follows from detailed balance.

The 2^{nd} law of thermodynamics

Eqs (68) and (70) are exact equalities and are valid arbitrarily far from equilibrium. That is something very rare. We know very little about non-equilibrium systems and usually all we have are inequalities. An equality is much much stronger.

I now claim to you that Eqs (68) and (70) contain in them the 2^{nd} law of thermodynamics. Thus, we have just demonstrated the 2^{nd} law! Isn't all this awesome?!

Let me explain this in detail. The function e^{-x} is a concave function. For concave functions we can use Jensen's inequality (if you want to find a demonstration, search on wikipedia)

$$\boxed{\langle e^{-\beta W}\rangle \geq e^{-\beta\langle W\rangle}} \qquad \text{(Jensen)} \qquad (71)$$

Eq (70) then becomes

$$e^{-\beta\langle W\rangle} \leq \langle e^{-\beta W}\rangle = e^{-\beta\Delta F}$$

Since $\ln(x)$ is monotonically increasing, taking the $\ln$ on both sides gives

$$-\beta\langle W\rangle \leq -\beta\Delta F$$

or

$$\boxed{\langle W\rangle \geq \Delta F} \qquad (72)$$

Thus, we see that from the Jarzynski equality we recover the 2^{nd} law (49') for the average work. For macroscopic systems, due to the law of large numbers, the distinction between W and $\langle W \rangle$ is not important. Since thermodynamics is only interested in large systems, we only see W in Eq (49').

But from our calculations we find that, even for microscopic systems, the 2^{nd} law continues to hold. But it does so only on average.

Since work fluctuates, in a given experiment there is a certain probability to observe stochastic realizations where $W < \Delta F$. These would therefore constitute local violations of the second law.

The prob. of observing a violation is

$$P(W < \Delta F) = \int_{-\infty}^{\Delta F} P(w)\,dw \tag{73}$$

when a system is macroscopically large, this prob. becomes insanely small. But for microscopic systems it can be observed.

Experimental Reconstruction of Work Distribution and Study of Fluctuation Relations in a Closed Quantum System

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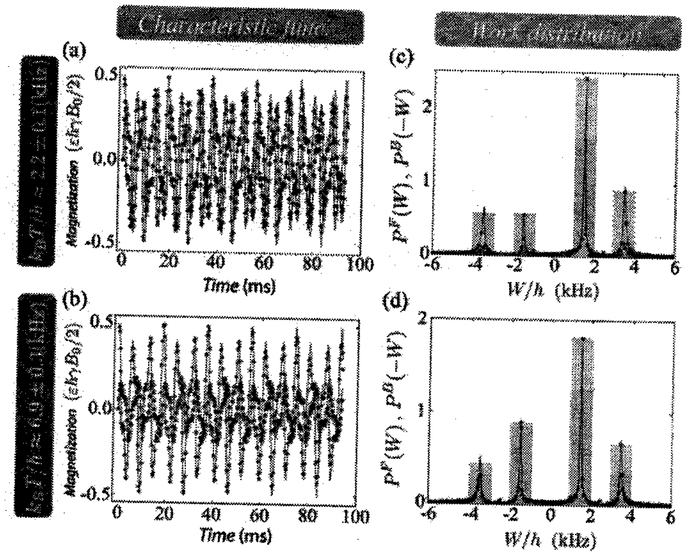
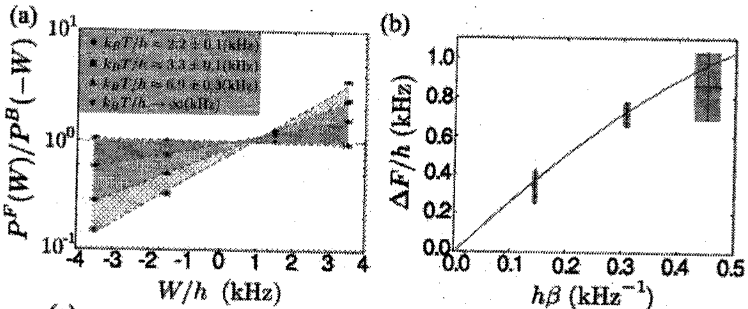


FIG. 2 (color online). (a) and (b): Experimental data for the x and y components of the ^{1}H transverse magnetization (blue circles and red squares, respectively) at two different values of the spin pseudotemperature, plotted against the time length $s = u\pi\nu_2/J$ of the controlled operations $\hat{G}_1$ and $\hat{G}_2$. The solid lines show Fourier fittings, which are in agreement with the theoretical simulation of the protocol. The error bars are smaller than the size of the symbols and are not shown (cf. Ref. [25] for the definition of ϵ, γ and B_0). (c) and (d): The experimental points for the distribution corresponding to the forward (backward) protocol are shown as red squares (blue circles).



(c)

k_BT/h (kHz)	2.2 ± 0.1	3.3 ± 0.1	6.9 ± 0.3
$\log\langle e^{-\beta W}\rangle$	0.38 ± 0.03	0.20 ± 0.02	0.06 ± 0.01
$\beta\Delta F$	0.39 ± 0.06	0.22 ± 0.02	0.05 ± 0.01
Theory	0.43 ± 0.03	0.22 ± 0.01	0.053 ± 0.003

FIG. 3 (color online). (a): The ratio $P^F(W)/P^B(-W)$ is plotted in logarithmic scale for four values of the spin pseudotemperature. The data are determined using the values of $P^F(W)$ and $P^B(-W)$ at the peaks shown in Figs. 2(c) and 2(d) and in Ref [25]. (b): Mean values and uncertainties for ΔF and β obtained using a linear fit of the data corresponding to $T > 0$ in panel (a). The full red line represents the theoretical expectation, $\Delta F = (1/\beta)\ln(\cosh(\beta\nu_1)/\cosh(\beta\nu_2))$. (c): We report the experimental values of the left- and right-hand sides of the Jarzynski identity, measured for three choices of pseudotemperature, together with the respective uncertainties. The experimental results are compared to the theoretical predictions for $\ln(Z_\tau/Z_0)$.

Their system is composed of 2 spin 1/2 particles (the nuclear spins of ^{1}H and ^{13}C in a chloroform molecule having one of the carbons as the isotope ^{13}C). Thus, the system has 4 allowed values for the work.