

The laws of thermodynamics

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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

Work = when an external agent changes the Hamiltonian of the system (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

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

with

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

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

The internal energy of the system is

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

Now suppose the external agent changes λ slightly to $\lambda + d\lambda$. 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

$$dU = \sum_m \left[(dE_m) P_m + E_m dP_m \right] \quad (5)$$

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 2nd 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 work 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 heat with the bath. This is the 2nd term in Eq (5). It is the change in probabilities for a fixed energy.

Thus, we propose to divide Eq (5) as

$$\boxed{dU = \delta Q + \delta W} \quad (6)$$

where

$$\delta W = \sum_m (dE_m) P_m \quad (7)$$

$$\delta Q = \sum_m E_m (dP_m) \quad (8)$$

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 first law of thermodynamics

Now let us understand and these two terms in more detail. we start with δw . we may write it as

$$\delta w = \frac{1}{Z} \sum_n (dE_n) e^{-\beta E_n} = \frac{1}{Z} \left(-\frac{1}{\beta}\right) d \left(\sum_n e^{-\beta E_n} \right)$$

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

If we now recall the definition of the free energy

$$F = -k_B T \ln Z \quad (6)$$

then we conclude that

$$\boxed{\delta w = dF} \quad (7)$$

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

$$\boxed{\delta w = dF = \frac{\partial F}{\partial \lambda} d\lambda} \quad (8)$$

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 response of the system to this stimulus.

For instance

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

$$P = - \frac{\partial F}{\partial V} \quad (9)$$

thus

$$\delta W = - P dV \quad (10)$$

$$\boxed{dU = dQ - P dV} \quad (11)$$

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

$$M = - \frac{\partial F}{\partial B} \quad (12)$$

so that

$$\delta W = - M dB \quad (13)$$

$$\boxed{dU = dQ - M dB} \quad (14)$$

the pattern is always the same:

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

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

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

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

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

Heat and Entropy

Now let us turn to $E_f(G)$:

$$\delta Q = \sum_m E_m d(p_m)$$

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

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

Thus

$$\begin{aligned} \delta Q &= -k_B T \sum_m \ln(p_m Z) d p_m \\ &= -k_B T \left\{ \sum_m (\ln p_m) d p_m + \ln Z \sum_m d p_m \right\} \end{aligned}$$

But

$$\sum_m d p_m = d\left(\sum_m p_m\right) = d(1) = 0 \quad (19)$$

so we get

$$\delta Q = -k_B T \sum_m d p_m \ln p_m \quad (20)$$

Now let us look at

$$\begin{aligned} d\left(\sum_m p_m \ln p_m\right) &= \sum_m \left\{ d p_m \ln p_m + p_m d(\ln p_m) \right\} \\ &= \sum_m d p_m \ln p_m + \sum_m \underbrace{p_m \frac{1}{p_m} d p_m}_{=0} \end{aligned}$$

for the same reason
as above

Thus we conclude that

$$\sum_m dP_m \ln P_m = d \left(\sum_m P_m \ln P_m \right) \quad (21)$$

Eq (20) then becomes

$$\delta Q = -k_B T d \left(\sum_m P_m \ln P_m \right) \quad (22)$$

We now define a new quantity called the entropy as

$$S = -k_B \sum_m P_m \ln P_m \quad (23)$$

so that we finally arrive at

$$\delta Q = T dS \quad (24)$$

the first law (6) then becomes

$$dU = T dS - \delta W \quad (25)$$

Using the Gibbs probabilities we may write

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

so Eq (23) becomes

$$\begin{aligned} S &= -k_B (-\beta) \sum_m E_m P_m - k_B (-\ln Z) \sum_m P_m \\ &= \frac{U}{T} + \frac{k_B \ln Z}{- \frac{1}{T} (-k_B T \ln Z)} \end{aligned}$$

thus we conclude that

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

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

$$\boxed{S = -\frac{\partial F}{\partial T}} \quad (27)$$

check:

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

Comparison of thermodynamic quantities

2-state system

$$E_0 = 0, \quad E_1 = \epsilon$$

$$Z = 1 + e^{-\beta\epsilon}$$

$$U = \frac{\epsilon}{e^{\beta\epsilon} + 1}$$

$$F = -k_B T \ln(1 + e^{-\beta\epsilon})$$

$$S = \frac{\epsilon/T}{e^{\beta\epsilon} + 1} + k_B \ln(1 + e^{-\beta\epsilon})$$

$$C = k_B \left(\frac{\epsilon}{k_B T} \right)^2 \frac{e^{\beta\epsilon}}{(e^{\beta\epsilon} + 1)^2}$$

Quantum harm. oscillator

$$E_m = \hbar\omega(m + 1/2), \quad m = 0, 1, 2, \dots$$

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

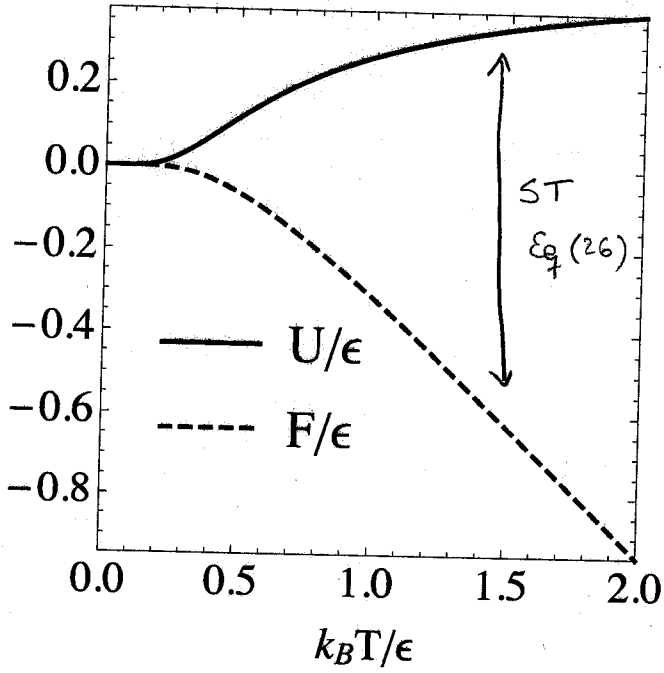
$$U = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

$$F = \frac{\hbar\omega}{2} + k_B T \ln(1 - e^{-\beta\hbar\omega})$$

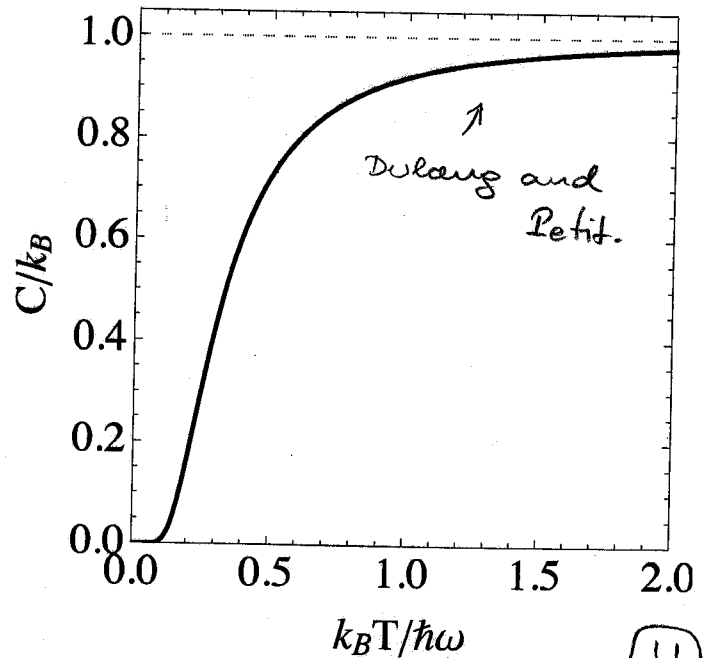
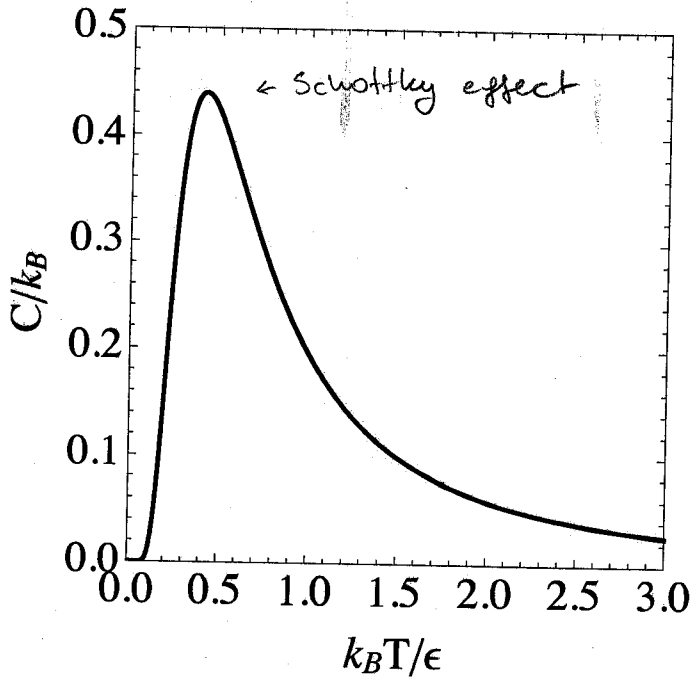
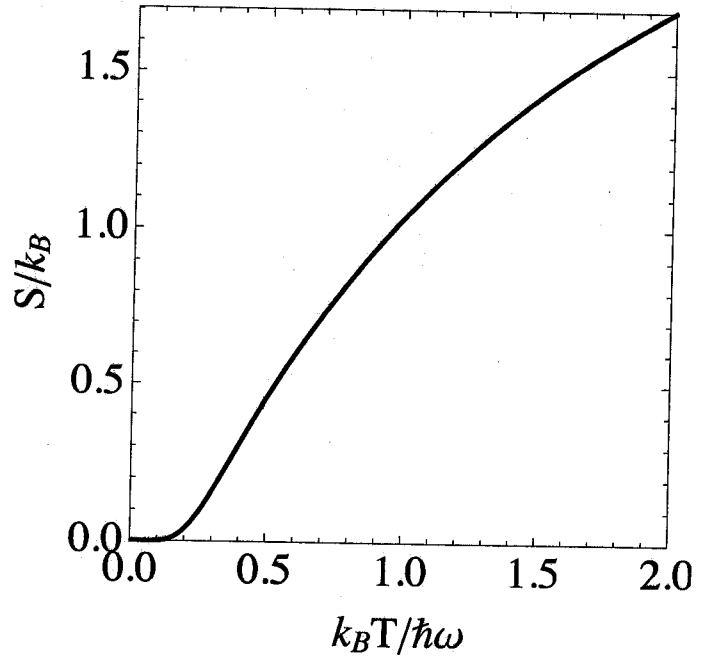
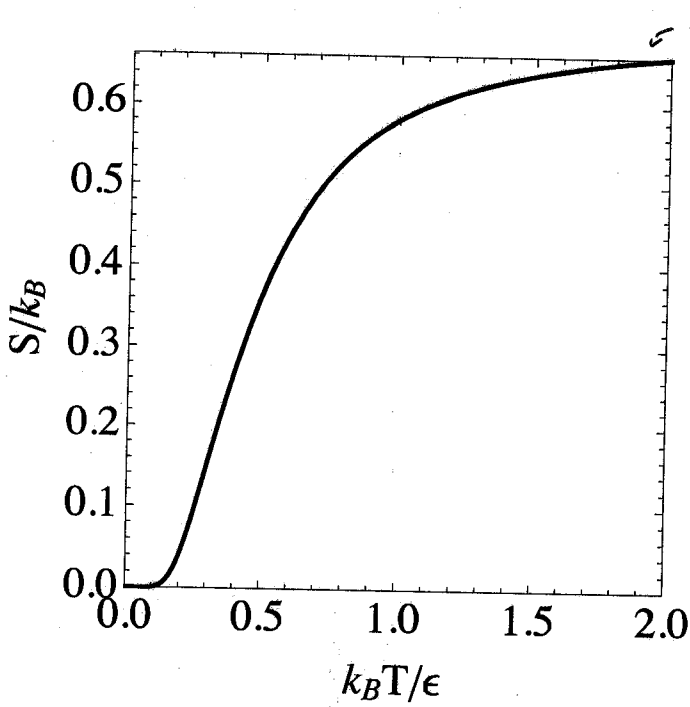
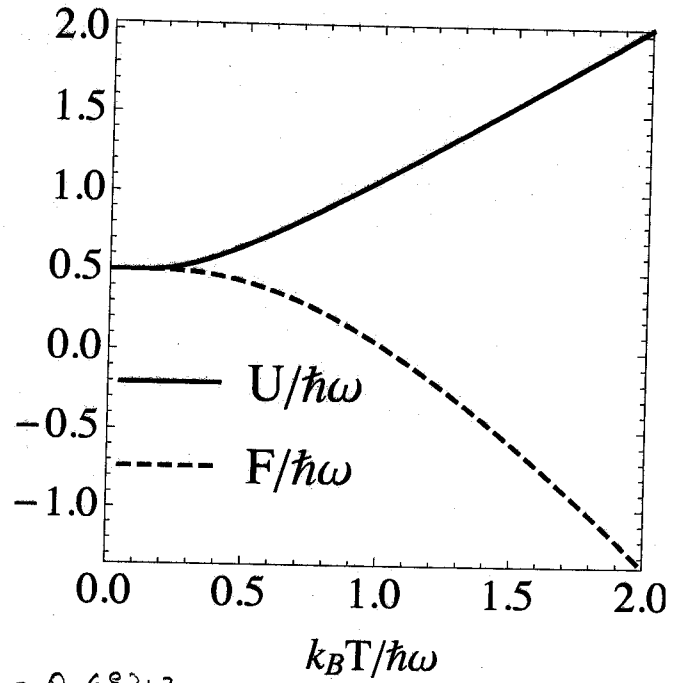
$$S = \frac{\hbar\omega/T}{e^{\beta\hbar\omega} - 1} - k_B \ln(1 - e^{-\beta\hbar\omega})$$

$$C = k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

2-state system



Q harm. oscillator



Understanding the entropy

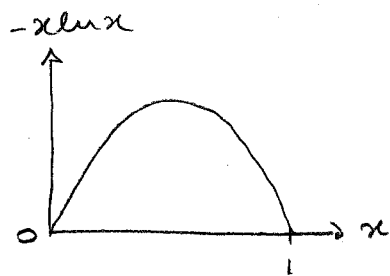
The entropy is given by

$$S = -k_B \sum_m P_m \ln P_m \quad (28)$$

It is a sum of terms of the form

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

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 $T \rightarrow 0$. 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_m 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

$$P_{0,i} = 1/g, \quad P_m = 0 \quad m > 0 \quad (29)$$

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

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

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

$$dU = \sum_n E_n dP_n \quad (31)$$

where, now,

$$dP_n = P_n(T+dT) - P_n(T)$$

[there is no work parameter in this problem].

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

$$dU = \delta Q \quad (32)$$

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

$$dU = T dS \quad (33)$$

But we may also write

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

comparing the two we then conclude that

$$C = \frac{\delta Q}{dT} = T \frac{\partial S}{\partial T} \quad (34)$$

This formula puts on more concrete grounds the connection between heat capacity and heat and entropy.

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:

$$\frac{\partial S}{\partial T} = \frac{C}{T} \implies S = \int \frac{C}{T} dT \quad (35)$$

note:

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 adiabatic process.

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 give 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

$$E_{\sigma} = -\mu_B B \sigma \quad (36)$$

and

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

the magnetization was

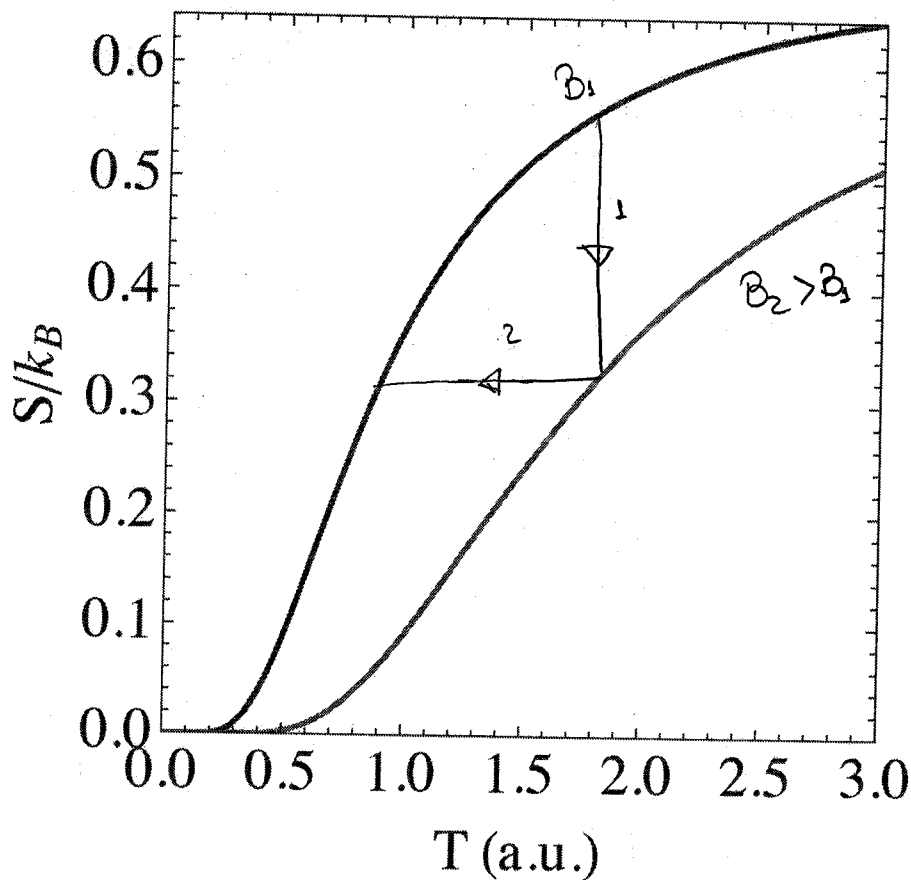
$$\langle \sigma \rangle = \tanh\left(\frac{\mu_B B}{k_B T}\right) \quad (38)$$

so the internal energy is

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

Finally, the entropy is

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



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.

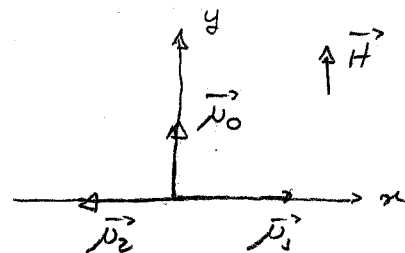
In the first step the system is always at the same T (because you apply B slowly). Since T is fixed and B goes up, U goes down [Eq (39)]. So in the end of (1) the temperature remained the same, but U went down.

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

$$\begin{aligned} E_0 &= -\mu H \\ E_1 &= E_2 = 0 \end{aligned} \quad (41)$$



The ground state will depend on the sign of H

• If $H > 0$: $g_S = 0$

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

The partition function is

$$z_1 = \sum_m e^{-\beta E_m} = 2 + e^{\beta\mu H} \Rightarrow z = z_1^N \quad (42)$$

So

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

and

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

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

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

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

$H > 0$: $\beta\mu H \gg 1$ at low T .

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

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

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

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

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

$H < 0$: $\beta\mu H \ll -1$ so we may approximate $e^{\beta\mu H} \approx 0$. We then get

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

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

$$\frac{S}{Nk_B} \approx \ln 2 \quad (47c)$$

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, $T \rightarrow \infty$.
 In this case we may approximate $e^{\beta \mu H} \approx 1$, for both
 $H > 0$ and $H < 0$.

The Gibbs probabilities become

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

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

Thus, the 3 states became equally likely; at $T = \infty$ all states
 become equally populated.

As for the thermodynamic quantities, we get

$$F \approx -Nk_B T \ln 3 \rightarrow -\infty \quad (49a)$$

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

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

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

$$\begin{aligned} U &= \sum_m E_m P_m = E_0 P_0 + E_1 P_1 + E_2 P_2 \\ &= -\frac{\mu H}{3} + 0 + 0 \end{aligned}$$

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
 $T \rightarrow \infty$, F will tend to $-\infty$.

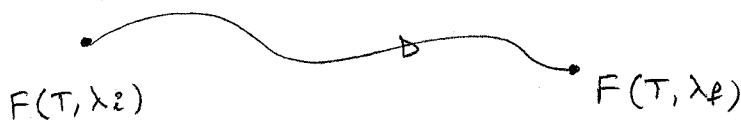
The 2nd law of thermodynamics.

The 2nd law of thermodynamics is perhaps one of the deepest laws of physics. Its statement, according to Lord Kelvin, is

2nd 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)

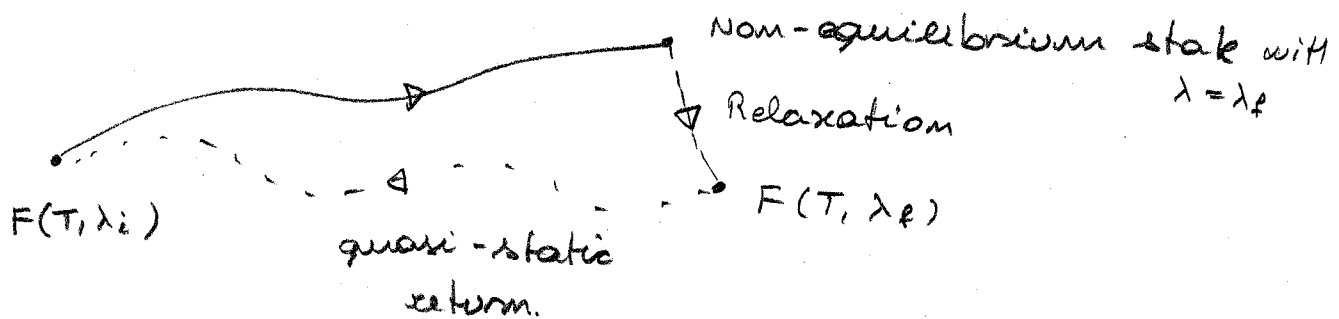
$$\text{that } W = \Delta F = F_f - F_i$$

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

$$w_{\text{tot}} = w + w_R = 0$$

In the end you came back to exactly the same state, but you also did not perform any work. Thus the 2nd 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

$$w_{\text{tot}} = w_1 + w_2 + w_3 = w_1 - \Delta F$$

But in the end we are back where we started. So we must have $w_{\text{tot}} \geq 0$ because, otherwise work would have been extracted from the reservoir without any other change

(extract work = $w_{\text{tot}} < 0$). Thus we conclude that $w_1 \geq \Delta F$.

Dropping the suffix 1, we conclude that for any non-equilibrium process

$$w \geq \Delta F$$

(491)

This is the mathematical statement of the 2nd law. It says that the minimum work 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.

LETTERS

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

D. Collin^{1*}, F. Ritort^{2*}, C. Jarzynski³, S. B. Smith⁴, I. Tinoco Jr⁵ & C. Bustamante^{4,6}

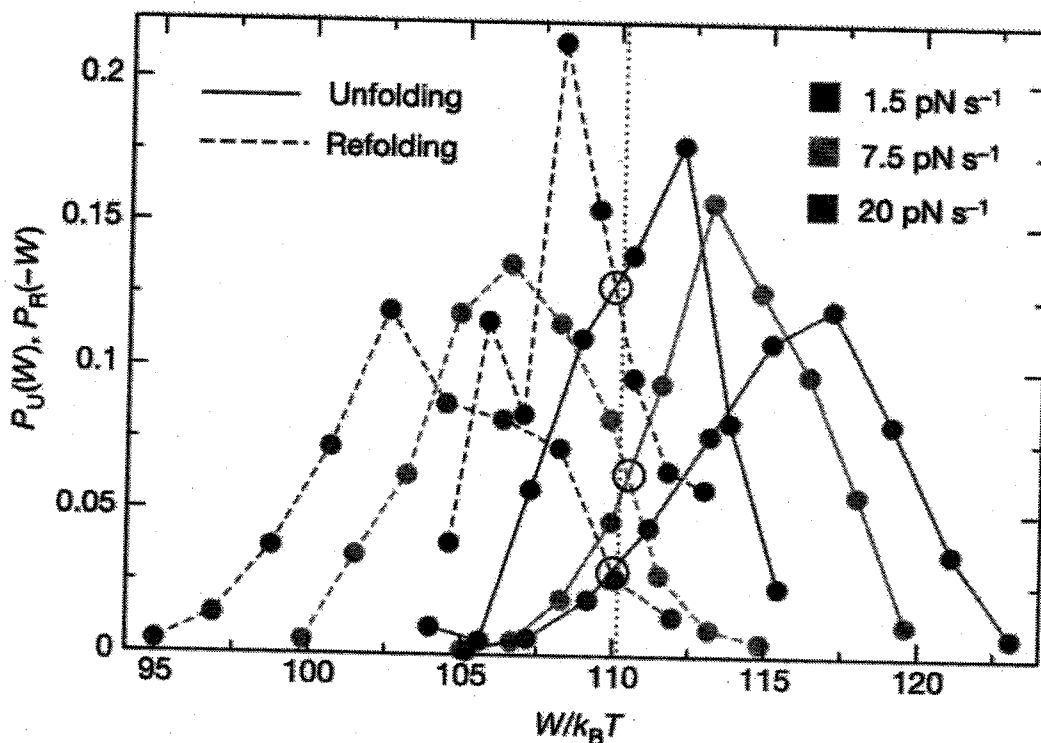


Figure 2 | Test of the CFT using an RNA hairpin. Work distributions for RNA unfolding (continuous lines) and refolding (dashed lines). We plot negative work, $P_R(-W)$, for refolding. Statistics: 130 pulls and three molecules ($r = 1.5 \text{ pN s}^{-1}$), 380 pulls and four molecules ($r = 7.5 \text{ pN s}^{-1}$), 700 pulls and three molecules ($r = 20.0 \text{ pN s}^{-1}$), 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 $\Delta G = 110.3 k_B T$.

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

