Quantum thermodynamics

Thermodynamics has always been a macroscopic theory, aimed at describing a large number of particles. thus, for many years it was thought that it made no sense to talk about thermodynamics of just a few particles. Around 20 years ago we learned that this is not true. It *does* make sense and, even more than that, extending thermodynamics to the microworld can give us incredible insight on fundamental aspects of physics, such as the emergence of irreversibility and the second law of thermodynamics. the purpose of these notes is to give you an idea of the exciting developments that have taken place in the last 20 years.

Heat and work

Consider a system S coupled to a large bath so that the system can be taken to be in thermal equilibrium at the bath's temperature T:

$$\rho_S = \frac{e^{-\beta H}}{Z} \qquad \beta = 1/T \qquad (1)$$

Now uncouple the system from this bath and put it in contact with another bath at a different temperature T'

What will happen is that the system will exchange some energy with the new bath until it reaches thermal equilibrium at the temperature T'. So initially it had energy

$$U(T) = \frac{\mathrm{tr}\left(H e^{-H/T}\right)}{\mathrm{tr}\left(e^{-H/T}\right)} \tag{2}$$

and afterwards it will will have energy

$$U(T') = \frac{\mathrm{tr}\left(H e^{-H/T'}\right)}{\mathrm{tr}\left(e^{-H/T'}\right)} \tag{3}$$

this change in energy is the heat which flowed to the new bath

$$\boxed{\delta Q = U(T') - U(T)} \tag{4}$$

In the particular case where $T' = T + \Delta T$, we can expand (4) in a Taylor series to find

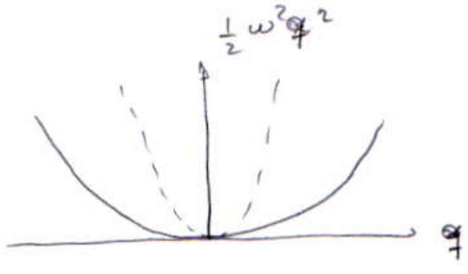
$$\delta Q = U(T+\Delta T) - U(T) \simeq \frac{\partial U}{\partial T}\Delta T = C\Delta T \tag{5}$$

this gives another interpretation to the heat capacity C. We also see that, since $C > 0$ always, δQ will have the same sign as ΔT. So if $T' > 0$ then energy will enter the system, $\delta Q > 0$ and if $T' < T$, energy will leave the system, $\delta Q < 0$.

Next we talk about work. Here we will adopt the convention that work is when an external agent changes a parameter in the Hamiltonian. For instance, suppose we have a harmonic oscillator

$$H = \frac{p^2}{2} + \frac{\omega^2}{2} q^2 \tag{6}$$

work could be, for instance, changing the frequency ω



this is actually done in the lab quite frequently nowadays. the frequency is usually determined by an optical trap, so by pressing buttons an external agent can change the trap. this is the modern version of compressing a piston. Imagine that you have some particles trapped in this potential

If you increase the frequency, you compress the gas

Thus, by pressing buttons, an external agent performs work.

We will therefore adopt from now on this notion of a <u>work parameter</u> λ, this means any parameter which enters in the Hamiltonian $H(\lambda)$ and which an external agent has control over. Examples include

- the frequency ω of a harmonic oscillator
- the volume of a gas in a piston
- the magnetic field h in a spin system

Let's talk a little bit about work in a general context and then we will specialize it to thermal problems.

The idea is that work is performed by applying a <u>work protocol</u>. that is, by specifying how $\lambda(t)$ changes in time. So it could be something like $\lambda(t)$ being linear in time, or it could be a sinusoidal function, and so on.

For an isolated system, this means working with the time dependent Schrödinger equation

$$\partial_t |\psi\rangle = -i H(t) |\psi\rangle \tag{7}$$

where $H(t) = H(\lambda(t))$. I probably forgot to teach this to you before, but in the case of mixed states, we have instead von Neumann's equation

$$\boxed{\frac{d\rho}{dt} = -i\left[H(t), \rho\right]} \tag{8}$$

<u>See appendix</u>

Solving a time-dependent equation like (8) is in general not easy. So for simplicity, let us consider instead a situation where we change λ just once and very quickly. That is, initially we had $H(\lambda)$ and then all of a sudden we change $\lambda \to \lambda'$, so the Hamiltonian becomes $H(\lambda')$. This is what we call a quantum quench.

In fact, let's imagine the following idea. Suppose we first thermalize our system by putting it in contact with a bath. That way initially the system is in a thermal state

$$\rho(0) = \frac{e^{-\beta H(\lambda)}}{Z(\lambda)} \tag{9}$$

But now we uncouple it from the bath. Describing the dynamics of the system when in contact with the bath is not very easy. That is why we use this trick of first thermalizing and then considering the dynamics of the system completely isolated (unitary dynamics).

Note that $\rho(0)$ commutes with $H(\lambda)$, so if we don't change λ, the system will remain in $\rho(0)$

$$[H(\lambda), e^{-\beta H(\lambda)}] = 0 \rightsquigarrow \frac{d\rho}{dt} = 0 \tag{10}$$

But now we do a quench: splash! All of a sudden the Hamiltonian will be $H(\lambda')$. If

$$[H(\lambda'), H(\lambda)] \neq 0 \tag{11}$$

then things will start happening. the system will start to change in time:

$$\frac{d\rho}{dt} = -i[H', \rho] \tag{12}$$

where $H' = H(\lambda')$. The solution of this equation is

$$\rho(t) = e^{-iH't} \rho(0) e^{iH't} \tag{13}$$

The energy of the system will then be diffent from the energy before the quench

$$\begin{aligned} U(t) &= \mathrm{tr}\{H' \rho(t)\} \\ &= \mathrm{tr}\{H' e^{-iH't} \rho(0) e^{iH't}\} \\ &= \mathrm{tr}\{\underbrace{e^{iH't} H' e^{-iH't}}_{H'} \rho(0)\} \\ &= \mathrm{tr}\{H' \rho(0)\} \end{aligned}$$

we see that the energy doesn't depend on time. that's because H is not changing with time. It only changed once at the quench.

The change in energy due to quench was therefore

$$\boxed{\Delta U = \mathrm{tr}\{H(\lambda')\rho(0)\} - \mathrm{tr}\{H(\lambda)\rho(0)\}} \qquad (14)$$

Since the quench is really fast, ΔU is simply the average of $H' - H$ in the initial state $\rho(0)$, because the system didn't even have time to adapt.

Moreover, in this case there is no heat because the system is isolated. Thus, this ΔU <u>must</u> be associated with work $\delta W = \Delta U$,

$$\boxed{\delta W = \langle H(\lambda') - H(\lambda)\rangle_0} \qquad (15)$$

We therefore arrive here with two complementary situations. In one we put the system in contact with a bath at a different temperature. And in this case all change in energy will be <u>heat</u> that flows to the bath.

In the other case there is no bath. The system is isolated. But we do a quantum quench by abruptly changing λ. As a consequence, all the change in energy must be attributed to the <u>work</u> performed by an external agent

The next natural question is then how to consider a situation in which there is both heat and work. This would mean executing a work protocol with the system coupled to a bath at all times.

Unfortunately, in this case a general description is quite hard, as it would require detailed knowledge of the system + environment dynamics.

Instead, a situation which can be treated analytically is when the work protocol is quasi-static. That is, when $\lambda(t)$ changes so slowly that the system can be assumed to be in equilibrium at all times.

We can describe this situation theoretically as follows. We assume that $\lambda(t)$ changes in infinitesimal steps $d\lambda$. Each step is assumed to occur instantaneously, as in the quantum quench scenario. Then after each small change in λ, we allow the system to relax toward equilibrium once again. In the quench part the state is fixed and only the Hamiltonian changes, so we can attribute this only to work performed. In the second part, no work is done because λ is fixed, so all change in energy can be attributed to heat.

In symbols, for one change of λ to $\lambda + d\lambda$,

$$\boxed{\delta W = \mathrm{tr}\{H(\lambda+d\lambda)\rho(\lambda)\} - \mathrm{tr}\{H(\lambda)\rho(\lambda)\}} \qquad (16)$$

where

$$\rho(\lambda) = \frac{e^{-\beta H(\lambda)}}{Z(\lambda)} \qquad (17)$$

Then the system will relax from $\rho(\lambda)$ to $\rho(\lambda+d\lambda)$, exchanging with the bath a heat

$$\boxed{\delta Q = \mathrm{tr}\{H(\lambda+d\lambda)\rho(\lambda+d\lambda)\} - \mathrm{tr}\{H(\lambda+d\lambda)\rho(\lambda)\}} \qquad (17)$$

If we add δW and δQ we get the total change in energy of the system

$$\delta W + \delta Q = \mathrm{tr}\{H(\lambda+d\lambda)\rho(\lambda+d\lambda)\} - \mathrm{tr}\{H(\lambda)\rho(\lambda)\}$$

$$= U(\lambda+d\lambda) - U(\lambda) \qquad (18)$$

this is the first law of thermodynamics

$$\boxed{dU = \delta Q + \delta W} \qquad (19)$$

Now let's explore in more detail the formulas for δW and δQ. First, for δW we expand $H(\lambda+d\lambda)$ in a Taylor series to find

$$\delta W = d\lambda \, \mathrm{tr}\left\{\frac{\partial H}{\partial \lambda}\rho(\lambda)\right\} = d\lambda \left\langle \frac{\partial H}{\partial \lambda} \right\rangle \qquad (20)$$

But now notice that

$$\frac{\partial Z}{\partial \lambda} = \frac{\partial}{\partial \lambda}\mathrm{tr}\{e^{-\beta H(\lambda)}\} = -\beta\, \mathrm{tr}\left\{\frac{\partial H}{\partial \lambda} e^{-\beta H(\lambda)}\right\}$$

which is almost what we have in (20)

Thus

$$\delta W = d\lambda \left[-T \frac{1}{Z} \frac{\partial Z}{\partial \lambda} \right]$$

$$= d\lambda \frac{\partial}{\partial \lambda} \left[-T \ln Z \right]$$

we now see here the free energy

$$F = -T \ln Z \qquad (21)$$

Thus

$$\delta W = d\lambda \frac{\partial F}{\partial \lambda} \qquad (22)$$

which we can also write as

$$\boxed{\delta W = dF} \qquad (23)$$

this is a very important result and it explains why F is called a "free" energy. We see that, when the system is coupled to a bath, the work is not the change in energy because part of ΔU will be related to heat. Instead, work is related to the change in <u>free</u> <u>energy</u>. Or, putting it differently, not all ΔU can be used to perform work, the part of the energy available to perform work is the <u>free</u> energy

As a biproduct, if we compare (20) with (22) we also learn that

$$\boxed{\frac{\partial F}{\partial \lambda} = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle} \qquad (24)$$

Now let's talk about δQ in Eq (17). We again expand in a Taylor series to get

$$\delta Q = d\lambda \, \mathrm{tr}\left\{ H(\lambda + d\lambda) \frac{\partial \rho}{\partial \lambda} \right\} \tag{25}$$

Notice that if we expand

$$H(\lambda + d\lambda) \simeq H(\lambda) + d\lambda \frac{\partial H}{\partial \lambda} \tag{26}$$

the term with $\partial H / \partial \lambda$ will be of order $d\lambda^2$, so we may neglect it. thus, it suffices to write

$$\delta Q = d\lambda \, \mathrm{tr}\left\{ H(\lambda) \frac{\partial \rho}{\partial \lambda} \right\} \tag{27}$$

We now do a naughty trick: we invert Eq (17) to get

$$H(\lambda) = - T \ln \rho(\lambda) - T \ln Z(\lambda) \tag{28}$$

Plugging this in (27) we get

$$\delta Q = - T d\lambda \, \mathrm{tr}\left\{ \frac{\partial \rho}{\partial \lambda} \ln \rho \right\} - T d\lambda \ln Z \, \mathrm{tr}\left\{ \frac{\partial \rho}{\partial \lambda} \right\} \tag{29}$$

But

$$\mathrm{tr}\left\{ \frac{\partial \rho}{\partial \lambda} \right\} = \frac{\partial}{\partial \lambda} \mathrm{tr}(\rho) = \frac{\partial}{\partial \lambda} (1) = 0 \tag{30}$$

As for the first, it is now starting to look like an entropy. But that really appear, we first need to establish something called the Hellmann-Feynman theorem. Let us define the eigenstuff of $\rho(\lambda)$ as

$$\rho(\lambda)|k(\lambda)\rangle = p_k(\lambda)|k(\lambda)\rangle \tag{31}$$

where I emphasize that both the eigenvalues and eigenvectors are functions of λ. We now write

$$p_k(\lambda) = \langle k(\lambda)|\rho(\lambda)|k(\lambda)\rangle \tag{32}$$

and compute

$$\begin{aligned}
\frac{\partial p_k}{\partial\lambda} &= \left\langle \frac{\partial k(\lambda)}{\partial\lambda}\right|\rho(\lambda)|k(\lambda)\rangle + \langle k(\lambda)|\frac{\partial\rho}{\partial\lambda}|k(\lambda)\rangle \\
&\quad + \langle k(\lambda)|\rho(\lambda)\left|\frac{\partial k}{\partial\lambda}\right\rangle \\
&= p_k(\lambda)\left\{\left\langle\frac{\partial k}{\partial\lambda}\right|k\rangle + \langle k\left|\frac{\partial k}{\partial\lambda}\right\rangle\right\} + \langle k|\frac{\partial\rho}{\partial\lambda}|k\rangle \\
&= p_k(\lambda)\underbrace{\frac{\partial}{\partial\lambda}\underbrace{\langle k(\lambda)|k(\lambda)\rangle}_{1}}_{0} + \langle k|\frac{\partial\rho}{\partial\lambda}|k\rangle
\end{aligned}$$

Thus, we arrive at the Hellmann-Feynman theorem

$$\boxed{\frac{\partial p_k}{\partial\lambda} = \langle k(\lambda)|\frac{\partial\rho}{\partial\lambda}|k(\lambda)\rangle} \tag{33}$$

We now use this to take the trace of (29) in the basis $|k(\lambda)\rangle$

$$\mathrm{tr}\left\{\frac{\partial\rho}{\partial\lambda}\ln\rho\right\} = \sum_k \langle k(\lambda)|\frac{\partial\rho}{\partial\lambda}|k(\lambda)\rangle \ln p_k(\lambda)$$

$$= \sum_k \frac{\partial p_k}{\partial\lambda}\ln p_k$$

Thus

$$\delta Q = -T\,d\lambda \sum_k \frac{\partial p_k}{\partial\lambda}\ln p_k \tag{34}$$

We now connect this with the van Neumann entropy

$$S(\rho) = -\mathrm{tr}(\rho\ln\rho) = -\sum_k p_k\ln p_k \tag{35}$$

Note that

$$\frac{\partial S}{\partial\lambda} = -\sum_k \frac{\partial p_k}{\partial\lambda}\ln p_k - \sum_k p_k\frac{1}{p_k}\frac{\partial p_k}{\partial\lambda}$$

$$= -\sum_k \frac{\partial p_k}{\partial\lambda}\ln p_k - \underbrace{\frac{\partial}{\partial\lambda}\sum_k p_k}_{0}$$

Thus

$$\frac{\partial S}{\partial\lambda} = -\sum_k \frac{\partial p_k}{\partial\lambda}\ln p_k \tag{36}$$

which is precisely what we see in (34). Thus

$$\delta Q = T\,d\lambda\,\frac{\partial S}{\partial\lambda} \tag{37}$$

We may now finally write this as

$$\boxed{\delta Q = T dS} \tag{38}$$

this is the clausius equality.

Thus, to summarize, in the case of a quasi-static work protocol, we have

$$\boxed{\begin{aligned} dU &= \delta W + \delta Q \\ \delta W &= dF \\ \delta Q &= T dS \end{aligned}} \tag{39}$$

this all holds for a single infinitesimal quench $\lambda \to \lambda + d\lambda$. But now it is straightforward to generalize this to finite protocols. we simply assume λ varies from λ_i to λ_f in infinitesimal steps. the total work performed in the process will then be

$$W = \int_{\lambda_i}^{\lambda_f} dF = F(\lambda_f) - F(\lambda_i) = \Delta F \tag{40}$$

and the total heat exchanged will be

$$Q = \int_{\lambda_i}^{\lambda_f} T dS = T \Delta S \tag{41}$$

The Jarzynski - Wójcik fluctuation theorem

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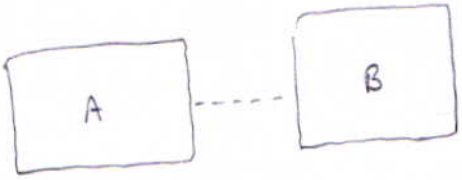
Now I want to tell you about one of my favourite papers of all time. The paper deals with heat exchange. We have two systems, A and B, each in equilibrium at temperatures T_A and T_B. We then put them in contact and allow them to evolve.



If A and B are huge macroscopic systems, we all know what will happen: they will exchange energy, with heat flowing from hot to cold. And this will continue until they are both at the same temperature.

But what if A and B are not macroscopic? Maybe they are just 2 qubits, or two harmonic oscillators. In this case fluctuations become important.

Imagine that A and B are oscillators. Since they are thermalized, their state is random. So there is a chance that when we put them together, the cold guy actually has more energy than the hot guy. Of course, the average energy of the cold guy is smaller. But the stochastic (random) energy at that given time could be higher.

thus, we see that there is a possibility that heat may flow from cold to hot. the point is that when fluctuations matter, the experiment becomes random. Every time we repeat it, we will get a different answer. And it is possible that in certain experimental runs, heat flows from cold to hot, instead of from hot to cold.

We therefore see that heat itself, is a random variable. this simple idea has led to a complete change in paradigm in the last 20 years. Before that, it was thought that trying to define thermodynamics for small systems was pointless. But now we learned that this can be done, provided we pay proper attention to the fluctuations and randomness present in microscopic systems. And, as we will now see, this leads to incredible new insights, which are still revolutionizing this field of research.

So here is the setup. Let H_A and H_B denote the Hamiltonians of A and B. Initially we assume they are thermalized so

$$\rho(0) = \rho_{th}^{A} \rho_{th}^{B} = \frac{e^{-\beta_A H_A}}{Z_A} \frac{e^{-\beta H_B}}{Z_B} \tag{42}$$

we then put them in contact, by introducing an interaction potential V, so that the total system is now governed by the Hamiltonian

$$H = H_A + H_B + V \tag{43}$$

And we allow them to evolve, so that the global density matrix $\rho = \rho_{AB}$ will obey the von Neumann equation

$$\frac{d\rho}{dt} = -i [H, \rho] \tag{44}$$

subject to the inial condition (42). The solution is then

$$\rho(t) = e^{-iHt} \rho_0 \, e^{iHt} \tag{45}$$

We will then be interested in the energy exchanged between A and B:

$$\langle H_A \rangle_t = tr\{H_A \rho(t)\} \tag{46}$$

$$\langle H_B \rangle_t = tr\{H_B \rho(t)\}$$

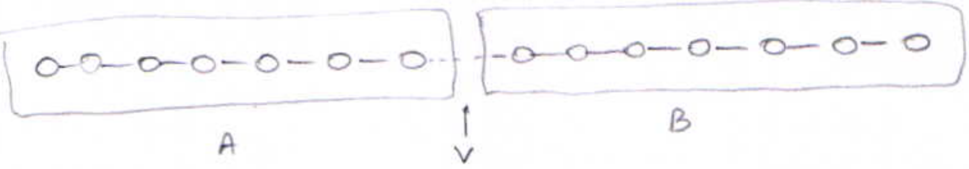
But now comes a subtle point, which is quite relevant for microscopic systems. Namely, the total energy is not $H_A + H_B$, but rather $H_A + H_B + V$. But who does V belong to? A or B?

When A and B interact, there will be some energy going back and forth between $\langle H_A \rangle$ and $\langle H_B \rangle$, but there will also be some energy that will be trapped in the interaction $\langle V \rangle$

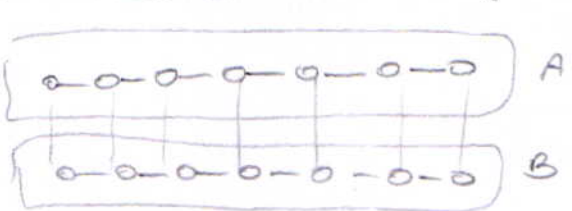
This is a fundamental property of microscopic systems. In the macroworld we are taught to think about energy as a local concept. But interactions are inherently non-local.

This leads us to the concepts of weak-coupling and strong-coupling. When $\langle V \rangle$ is significant compared to $\langle H_A + H_B \rangle$, we say A and B are strongly coupled.

Hamiltonians usually depend on the number of particles. And quite often, the number of particles participating in V is much smaller than those contained in H_A and H_B. In this case weak coupling would naturally emerge. So, for instance, if we have something like



In this case, if the number of particles is large, the coupling will naturally become weak. Instead if we have something like



then weak vs. strong will really depend on what is in V.

In what follows I will assume weak coupling. Even more that, I will *impose* weak-coupling as an *assumption*. The way to do this is quite simple actually. All we need is to assume that

$$[H_A + H_B, V] = 0 \tag{47}$$

This is called a *thermal operation*. Assuming this may seem a bit artificial, but we will see in the end that it is not really.

To give an example, suppose we have 2 QHO's with

$$H_A = \omega a^\dagger a \qquad H_B = \omega b^\dagger b \tag{48}$$

then a choice for V satisfying (47) would be

$$V = g\,(a^\dagger b + b^\dagger a) \tag{49}$$

We see that this V annihilates an energy quanta from A and puts it on B. But since $\omega_a = \omega_b = \omega$, this will conserve energy. We simply take it from one system and put it in the other. Nothing gets retained in V.

We can actually see more formally why (47) represents energy conservation. From (46) we have

$$\langle H_A \rangle_t = \mathrm{tr}\left\{ H_A \, e^{-i(H_A + H_B + V)t} \rho_0 \, e^{i(H_A + H_B + V)t} \right\}$$

But because of (47),

$$e^{-i(H_A + H_B + V)t} = e^{-i(H_A + H_B)t} e^{-iVt}$$

Thus

$$\langle H_A \rangle_t = \mathrm{tr}\left\{ e^{iVt} \underbrace{e^{i(H_A + H_B)t} H_A \, e^{-i(H_A + H_B)t}}_{H_A} e^{-iVt} \rho_0 \right\}$$

$$\therefore \quad \langle H_A \rangle_t = \langle e^{iVt} H_A \, e^{-iVt} \rangle_0 \tag{50}$$

Similarly

$$\langle H_B \rangle_t = \langle e^{iVt} H_B \, e^{-iVt} \rangle_0 \tag{51}$$

But now note that V does not commute with H_A and H_B individually. But it commutes with $H_A + H_B$. Thus

$$\langle H_A \rangle_t + \langle H_B \rangle_t = \langle e^{iVt} (H_A + H_B) e^{-iVt} \rangle_0$$

$$= \langle H_A \rangle_0 + \langle H_B \rangle_0 \tag{52}$$

or

$$\langle H_A \rangle_t - \langle H_A \rangle_0 = -\left(\langle H_B \rangle_t - \langle H_B \rangle_0 \right) \tag{53}$$

Hence, all energy that leaves A enters B. Nothing gets stuck on V.

Now let's talk about fluctuations. Recall that we started this discussion by saying that heat exchange is random and would change every time we repeat the experiment. So far all we talked about are average quantities.

To obtain a stochastic formulation we use a 2-point measurement protototocol: we measure A and B before and after they interact

It goes like this. First we take A and B prepared in ρ_{th}^A and ρ_{th}^B. Now let

$$H_A | m\rangle = E_m^A | m\rangle \tag{54}$$

$$H_B | \nu\rangle = E_\nu^B | \nu\rangle$$

We then measure A and B in these energy bases. Then with prob.

$$P_{m,\nu} = P_m P_\nu = \frac{e^{-\beta_A E_m^A}}{Z_A} \frac{e^{-\beta_B E_\nu^B}}{Z_B} \tag{55}$$

we will find the state $|m,\nu\rangle$

We then allow them to interact and evolve. The state at a time t will then be

$$\rho(t|m,\nu) = e^{-iHt} |m,\nu\rangle\langle m,\nu| e^{iHt} \tag{56}$$

I write this as $\rho(t|m,\nu)$ to emphasize that this is the state conditioned on the fact that the first measurement gave outcomes $|m,\nu)$

At a certain time τ (of our choice) we then measure A and B again. We will find them in the state $|m,\nu\rangle$ with probability

$$p(m,\nu|n,\mu) = \langle m,\nu|\rho(\tau)|m,\nu\rangle \tag{57}$$

This therefore represents a <u>transition</u> <u>probability</u>. It is the probability that at time τ A and B have jumped from (n,μ) to (m,ν).

Using (56) we get

$$p(m,\nu|n,\mu) = |\langle m,\nu|e^{-iHt}|n,\mu\rangle|^2 \tag{58}$$

This sequence of measurement outcomes describe a <u>quantum trajectory</u>

$$x = \{n,\mu,m,\nu\} \tag{59}$$

The probability of this trajectory is

$$\mathcal{P}[x] = p(m\nu|n\mu)\, p_n\, p_\mu \tag{60}$$

because the trajectory involves both the initial outcomes [Eq (55)] and the jumps. We therefore see that we have both <u>thermal fluctuations</u>, from the initial thermal states, and <u>quantum fluctuations</u> from the time evolution jumps

We now ask how much heat was exchange in this process. Well, initially A and B were found in $|m,\nu\rangle$, so their energies were E_m^A and E_ν^B. Then, in the end, they were in $|m,v\rangle$ so their energies were E_m^A and E_v^B. The change in energy of A was then $E_m^A - E_m^A$ and that of B was $E_v^B - E_\nu^B$.

If the process was not weak-coupling / thermal operation, some heat would be contained in the interaction. But if we assume a thermal operation then

$$E_m^A - E_m^A = -(E_v^B - E_\nu^B) \equiv Q_{m,m} \tag{61}$$

Thus, we may unambiguously define the heat by looking only at the change in energy of one of the system. Here we opted to look at A, so $Q_{m,m} > 0$ means energy entered A.

What is now the probability that we observe a heat exchange Q? Well,

$$\boxed{P(Q) = \sum_{m,m,\nu,v} \delta(Q - Q_{m,m})\ P(m v|m\nu)\ p_m p_\nu} \tag{62}$$

We simply sum over all possible quantum trajectories and select those for which the heat exchanged was Q. This is the prob. of Q.

Now I want to use this distribution to make 2 calculations which I think are really really cool. First, although it may seem a bit crazy let's compute

$$\langle e^{-\Delta\beta Q}\rangle = \int dQ\, P(Q)\, e^{-\Delta\beta Q} \qquad (63)$$

where $\Delta\beta = \beta_A - \beta_B$. Using (62) we get

$$\langle e^{-\Delta\beta Q}\rangle = \int dQ \sum_{\substack{n,m \\ \mu,\nu}} e^{-\Delta\beta Q}\, \delta(Q-(E_m^A - E_n^A))\, p(m\nu|n\mu)\, p_n p_\mu$$

$$= \sum_{\substack{n,m \\ \mu,\nu}} e^{-\Delta\beta(E_m^A - E_n^A)}\, p(m\nu|n\mu)\, \frac{e^{-\beta_A E_n^A}}{Z_A}\, \frac{e^{-\beta_B E_\mu^B}}{Z_B}$$

$$= \frac{1}{Z_A Z_B} \sum_{\substack{n,m \\ \mu,\nu}} p(m\nu|n\mu)\, e^{-\beta_A E_m^A} e^{\beta_B E_m^A} e^{\beta_A E_n^A} e^{-\beta_B E_n^A} \cdot e^{-\beta_A E_n^A} e^{-\beta_B E_\mu^B}$$

$$= \frac{1}{Z_A Z_B} \sum_{\substack{n,m \\ \mu,\nu}} p(m\nu|n\mu)\, e^{-\beta_A E_m^A} e^{\beta_B E_m^A} e^{-\beta_B (E_n^A + E_\mu^B)}$$

But $E_n^A + E_\mu^B = E_m^A + E_\nu^B$ so we get

$$\langle e^{-\Delta\beta Q}\rangle = \frac{1}{Z_A Z_B} \sum_{\substack{n,m \\ \mu,\nu}} p(m\nu|n\mu)\, e^{-\beta_A E_m^A} e^{\beta_B E_m^A} e^{-\beta_B E_m^A} e^{-\beta_B E_\nu^B}$$

$$= \frac{1}{Z_A Z_B} \sum_{\substack{n,m \\ \mu\,\nu}} p(m\nu|n\mu)\, e^{-\beta_A E_m^A} e^{-\beta_B E_\nu^B}$$

But now we can carry out the sum over n and μ:

$$\sum_{n,\mu} p(m,\nu|n,\mu) = \sum_{n,\mu} \langle m\nu| e^{-iHt} |n\mu\rangle\langle n\mu| e^{iHt} |m\nu\rangle$$

$$= \sum_{n\mu} \langle n\mu| e^{iHt} |m\nu\rangle\langle m\nu| e^{-iHt} |n\mu\rangle$$

$$= \mathrm{tr}\left\{ e^{iHt} |m\nu\rangle\langle m\nu| e^{-iHt} \right\}$$

$$= \mathrm{tr}\left\{ |m\nu\rangle\langle m\nu| \right\}$$

$$= 1$$

thus we are left with

$$\langle e^{-\Delta\beta Q}\rangle = \frac{1}{Z_A Z_B} \sum_{m\nu} e^{-\beta_A E_m^A} e^{-\beta_B E_\nu^B}$$

$$= \frac{1}{Z_A Z_B} Z_A Z_B$$

We therefore finally reach the absolutely incredible result

$$\boxed{\langle e^{-\Delta\beta Q}\rangle = 1} \qquad (64)$$

this is called the Jarzynski equality

This result is incredible for many reasons. But the most important is, perhaps, because it is an equality and holds for situations which are arbitrarily far from equilibrium. In thermodynamics it is usually impossible to write down equalities for processes which are not quasi-static, so one has to settle for inequalities.

Another cool thing we can do is to use Jensen's inequality which states that for any concave function (like e^{-x})

$$\langle e^{-\Delta\beta Q} \rangle \geq e^{-\Delta\beta \langle Q \rangle} \tag{65}$$

Thus, we get

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

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

Now suppose

$$T_B > T_A \quad \rightsquigarrow \quad \beta_B < \beta_A$$

so that

$$\Delta\beta = \beta_A - \beta_B > 0$$

Then we find that

$$\boxed{\langle Q \rangle \geq 0} \tag{66}$$

In thermodynamics we say heat flows from hot to cold. In the microworld heat fluctuates so sometimes we may see heat flowing from cold to hot. However, according to this result, on average, heat flows from hot to cold

This can be viewed as a generalization of the 2nd law of thermodynamics to the case where fluctuations are important.

Now I want to derive another cool result from the distribution (62). But to do that I need to introduce a property of quantum systems which you may not have seen before: time-reversal invariance. Essentially what it says is that

$$\boxed{p(m\nu|n\mu) = p(n\mu|m\nu)} \qquad (67)$$

The prob. of jumping in one way is always equal to the prob. of jumping backwards.

Let's then introduce this in (62) and, moreover, let us use the fact that $E_m^A + E_\mu^B = E_{\mathfrak{m}}^A + E_\nu^B$. We then get

$$\mathcal{P}(Q) = \sum_{\substack{m\,\mathfrak{m}\\ \mu,\nu}} \delta\left[Q - (E_{\mathfrak{m}}^A - E_m^A)\right] p(m\mu|\mathfrak{m}\nu) \frac{e^{-\beta_A E_m^A}}{Z_A} \frac{e^{-\beta_B E_{\mathfrak{m}}^B}}{Z_B}$$

We now play with the exponentials as follows.

$$e^{-\beta_A E_m^A} e^{-\beta_B E_{\mathfrak{m}}^B} = e^{-\beta_A E_m^A} e^{-\beta_B E_{\mathfrak{m}}^B} e^{\Delta\beta(E_\mu^B - E_\nu^B)} e^{-\Delta\beta(E_\mu^B - E_\nu^B)}$$

$$= e^{\Delta\beta(E_\mu^B - E_\nu^B)} e^{-\beta_A E_m^A} \cancel{e^{-\beta_B E_\mu^B}} e^{-\beta_A E_\mu^B} \cancel{e^{\beta_B E_\mu^B}} e^{\beta_A E_\nu^B} e^{-\beta_B E_\nu^B}$$

$$= e^{\Delta\beta(E_\mu^B - E_\nu^B)} \underbrace{e^{-\beta_A(E_m^A + E_\mu^B)}}_{e^{-\beta_A(E_{\mathfrak{m}}^A + E_\nu^B)}} e^{\Delta\beta E_\nu^B}$$

$$= e^{\Delta\beta \underbrace{(E_\mu^B - E_\nu^B)}_{E_{\mathfrak{m}}^A - E_m^A}} e^{-\beta_A E_{\mathfrak{m}}^A} e^{-\beta_B E_\nu^B}$$

Thus we get

$$\mathcal{P}(Q) = \sum_{\substack{m,\mathfrak{m}\\ \mu,\nu}} \delta\left[Q - (E_{\mathfrak{m}}^A - E_m^A)\right] e^{\Delta\beta \overbrace{(E_{\mathfrak{m}}^A - E_m^A)}^{Q}} p(m\mu|\mathfrak{m}\nu) \frac{e^{-\beta_A E_{\mathfrak{m}}^A}}{Z_A} \frac{e^{-\beta_B E_\nu^B}}{Z_B}$$

The term $e^{\Delta\beta Q}$ can now go outside the sum because of the δ

$$\mathcal{P}(Q) = e^{\Delta\beta Q} \sum_{\substack{m\,\mathfrak{m}\\ \mu\,\nu}} \delta\left[Q - (E_{\mathfrak{m}}^A - E_m^A)\right] p(m\mu|\mathfrak{m}\nu) \frac{e^{-\beta_A E_{\mathfrak{m}}^A}}{Z_A} \frac{e^{-\beta_B E_\nu^B}}{Z_B}$$

But we are summing over n, m, μ, ν, so we may as well exchange the indices $n \leftrightarrow m$ and $\mu \leftrightarrow \nu$. We then get

$$P(Q) = e^{\Delta\beta Q} \sum_{\substack{nm\\ \nu\mu}} \delta\left[Q + (E_m^A - E_n^A)\right] P(m\nu|n\mu)\, p_n p_\mu$$

But now we recognize the resulting sum as being simply $P(-Q)$, thus we finally arrive at

$$\boxed{P(Q) = e^{\Delta\beta Q} P(-Q)} \tag{68}$$

This is called a *fluctuation theorem* and it is awesome! What it says is that positive Q is *exponentially* more likely than negative Q. So if we are talking about macroscopic systems for which Q is a large number, then it will be extremely rare to observe a heat from cold to hot. But the Q's involved are small, then $P(-Q)$ may become of a similar order to $P(Q)$.

Appendix: von Neumann's equation (oops! Sorry!)

I forgot to tell you about von Neumann's equation. It is the equivalent of Schrödinger's equation but for mixed states. Recall that kets evolve as

$$\partial_t |\psi\rangle = -i H |\psi\rangle \tag{A.1}$$

[I will assume time-independent Hamiltonians, but the result is general] The solution is

$$|\psi(t)\rangle = e^{-iHt} |\psi(0)\rangle \tag{A.2}$$

Now recall that density matrices can always be written as

$$\rho = \sum_i q_i |\psi_i\rangle\langle\psi_i| \tag{A.3}$$

for any set of states $|\psi_i\rangle$ and weights q_i satisfying $q_i \in [0,1]$ and $\sum_i q_i = 1$.

Each $|\psi_i\rangle$ will evolve according to (A.2) so $\rho(t)$ will evolve as

$$\begin{aligned}\rho(t) &= \sum_i q_i |\psi_i(t)\rangle\langle\psi_i(t)| \\ &= \sum_i q_i e^{-iHt} |\psi_i(0)\rangle\langle\psi_i(0)| e^{iHt} \\ &= e^{-iHt}\Big[\sum_i q_i |\psi_i(0)\rangle\langle\psi_i(0)|\Big] e^{iHt}\end{aligned}$$

Thus we see that just like kets evolve according to (A.2), density matrices evolve according to

$$\boxed{\rho(t) = e^{-iHt}\,\rho(0)\,e^{iHt}} \tag{A.4}$$

Differentiating with respect to time we then get

$$\frac{d\rho}{dt} = -iH\,e^{-iHt}\rho(0)\,e^{iHt} + e^{-iHt}\rho(0)\,e^{iHt}(iH)$$

$$= -iH\rho(t) + i\rho(t)H$$

or, finally

$$\boxed{\frac{d\rho}{dt} = -i\,[H(t),\rho]} \tag{A.5}$$

which is von Neumann's equation. Here I already wrote H(t), just to emphasize that even though I assumed a time-independent Hamiltonian in the derivation, the result holds for arbitrary H(t).