

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 :

$$P_S = \frac{e^{-\beta H}}{Z}$$

$$\beta = 1/T$$

(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

$$U(T) = \frac{\text{tr}(H e^{-H/T})}{\text{tr}(e^{-H/T})} \quad (2)$$

and afterwards it will have energy

$$U(T') = \frac{\text{tr}(H e^{-H/T'})}{\text{tr}(e^{-H/T'})} \quad (3)$$

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

$$\delta Q = U(T') - U(T) \quad (4)$$

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

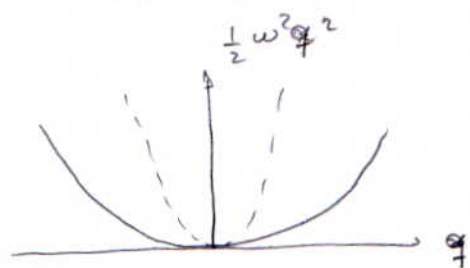
$$\delta Q = U(T + \Delta T) - U(T) \approx \frac{\partial U}{\partial T} \Delta T = C \Delta T \quad (5)$$

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 $T' > T$ 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

$$H = \frac{p^2}{2} + \frac{\omega^2}{2} q^2 \quad (6)$$

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 work parameter 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 work protocol, 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

$$\partial_t |\psi\rangle = -i H(t) |\psi\rangle \quad (7)$$

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 van Neumann's equation

$$\frac{d\rho}{dt} = -i [H(t), \rho] \quad (8)$$

See appendix

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 $\lambda \rightarrow \lambda'$, 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

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

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 $\rho(0)$

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

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

$$[H(\lambda'), H(\lambda)] \neq 0 \quad (11)$$

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

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

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

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

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

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

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

$$\Delta U = \text{tr}\{H(\lambda')\rho(0)\} - \text{tr}\{H(\lambda)\rho(0)\} \quad (14)$$

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 must be associated with work $\delta W = \Delta U$,

$$\delta W = \langle H(\lambda') - H(\lambda) \rangle_0 \quad (15)$$

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 heat 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 work 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 $\lambda + d\lambda$,

$$\delta w = \text{tr} \{ H(\lambda + d\lambda) \rho(\lambda) \} - \text{tr} \{ H(\lambda) \rho(\lambda) \} \quad (16)$$

where

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

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

$$\delta Q = \text{tr} \{ H(\lambda+d\lambda) \rho(\lambda+d\lambda) \} - \text{tr} \{ H(\lambda+d\lambda) \rho(\lambda) \} \quad (17)$$

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

$$\begin{aligned} \delta W + \delta Q &= \text{tr} \{ H(\lambda+d\lambda) \rho(\lambda+d\lambda) \} - \text{tr} \{ H(\lambda) \rho(\lambda) \} \\ &= U(\lambda+d\lambda) - U(\lambda) \end{aligned} \quad (18)$$

This is the first law of thermodynamics

$$dU = \delta Q + \delta W \quad (19)$$

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

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

But now notice that

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

which is almost what we have in (20)