Statistical Physics
Section 14: Quantum Dynamics, The Master Equation and Detailed Balance

14. 1. Quantum dynamics and the Entropy Paradox

We now look at the issues of dynamics, microscopic reversibility and macroscopic irreversibility from a quantum perspective. To discuss quantum dynamics properly, we have to keep a clear distinction between the *classical uncertainty* about which microstate a system is in, and the *quantum uncertainty* arising from the wavefunctions of individual microstates. The first is dealt with by ascribing a (classical) probability p_i to each microstate $|i\rangle$; the second enters through the time evolution of these microstates under Schrödinger's equation. Note that the weights p_i are simply probabilities and do not contain phase information etc.

The entropy paradox in quantum dynamics becomes clear when we choose as the microstates the eigenstates of the system's quantum Hamiltonian $\hat{H}$. Then, since each $|i\rangle$ evolves independently under $\hat{H}$, there is simply no mechanism, in rigorous quantum mechanics, for the system to jump from one eigenstate to another. i.e. if we write the state of the system as

$$|\Psi\rangle = \sum_i p_i |i\rangle$$

then the evolution becomes

$$i\hbar \frac{\partial |\Psi\rangle}{\partial t} = \hat{H}|\Psi\rangle = \sum_i p_i E_i |i\rangle$$

with solution

$$|\Psi(t)\rangle = \sum_i p_i \mathrm{e}^{-iE_i t/\hbar} |i\rangle$$

which doesn't affect the p_i but changes introduces a phase factor to the eigenstates. That is, Schroedinger's equation applied to energy eigenstates as microstates *cannot change* their classical weights p_i. Accordingly, the entropy $S = -k \sum p_i \ln p_i$ is trivially constant: $dS/dt = 0$ just as in classical mechanics.

*14. 2. *The density matrix*

[Not covered in lectures and nonexaminable; see e.g. Plischke and Bergersen] It is possible to prove this statement formally even when the microstates are *not* chosen to be eigenstates of the Hamiltonian $\hat{H}$. The proof proceeds by defining the 'density matrix', an operator whose eigenvalues are the (observable) classical weights ρ_i. If the chosen microstates are denoted $|i\rangle$ (not necessarily now eigenstates of $\hat{H}$), a general **density matrix** is written

$$\hat{\rho}(t) = \sum_i |i(t)\rangle\, \rho_i(t)\, \langle i(t)| \tag{1}$$

which ascribes a (possibly time-dependent) statisitical weight $\rho_i(t)$ to microstate $|i\rangle$. [The discussion of 14.1 corresponds to the special case where one of the weights is unity and the others zero.] It is then possible (see textbooks) to establish the following equation of motion for $\hat{\rho}$

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}] \tag{2}$$

which is the quantum mechanical equivalent of Liouville's theorem.

When the microstates are eigenstates of $\hat{H}$, the commutator is zero and $\hat{\rho}$ does not evolve, so that each p_i is constant and entropy is conserved. This concurs with the preceding section. Otherwise, the individual weights *do* evolve but the entropy is still conserved. To see this, note that the above evolution equation for $\hat{\rho}$ is *unitary*: it is mathematically equivalent to a time-dependent transformation between bases and therefore cannot create or destroy classical uncertainty about which quantum state the system is actually in. Formally, the proof is as follows: the Gibbs entropy obeys

$$S(t) = -k \sum_i p_i(t) \ln p_i(t) = -k\mathrm{Tr}\left(\hat{p} \ln \hat{p}\right) \tag{3}$$

Where $\hat{p} = \hat{\rho}/\mathrm{Tr}\hat{\rho}$ is just the normalised version of the density matrix. But since the trace of any matrix is basis independent, the second expression for $S(t)$ is not only valid generally, but also invariant under unitary transformations, and accordingly *constant in time*. Hence we again find $dS/dt = 0$.

14. 3. Fermi's master equation

To get anything resembling the second law, we therefore again require a *coarse graining* operation, leading to nonunitary time evolution, and the discarding of information.

One way of doing this is to acknowledge that we cannot write down the true Hamiltonian, containing all the microscopic detail, of a physical many particle system, rather we generally use an approximate Hamiltonian $\hat{H}_0$ as our model and describe the system in terms of in terms of a set of eigenstates, $|i\rangle$, of $\hat{H}_0$. The true Hamiltonian is given by $\hat{H}_0$ plus a small perturbation $\hat{h}$ (say):

$$\hat{H} = \hat{H}_o + \hat{h} \tag{4}$$

We do not specify the perturbation $\hat{h}$ because we do no know the true Hamiltonian, but we can work out the consequences of its presence. In terms of the true Hamiltonian, the states $|i\rangle$ are *approximate* energy eigenstates. The matrix elements of $\hat{h}$ in this basis are:

$$h_{ij} = \langle i|\hat{h}|j\rangle = h^*_{ji} \tag{5}$$

where * denotes complex conjugate. This perturbation induces quantum jumps between the approximate states $|i\rangle$. These states are treated in an explicitly nonunitary way: we assign to them *changing classical probabilities* p_i, instead of keeping track of their quantum amplitudes. This can be viewed as a form of coarse graining in which the quantum coherence between these different states is wiped out.

Fermi assumed that the system could jump from a state $|i\rangle$ of energy E_i into some narrow band of final states $|f\rangle$ having energy within δE of E_i. He showed, using time-dependent perturbation theory, that the probability per unit time of a jump from state $|i\rangle$ to the band of states $|f\rangle$, given that the system is in state $|i\rangle$ to begin with, is

$$\lambda_{if} = \frac{2\pi}{\hbar} |h_{if}|^2 \rho_f \tag{6}$$

where ρ_f is the density of final states, which is *Fermi's golden rule* for the one to many state transition rate. [For details, see Quantum Physics 4.] If we convert this formula into a one to one state transition rate from a state i to a state j we should divide by the number of final states $\rho_f \delta E$ to obtain:

$$\nu_{ij} = \frac{2\pi}{\hbar\,\delta E}\,|h_{ij}|^2 \tag{7}$$

Note that, according to the golden rule, the jump rates ν_{ij} cannot be negative. Note also that because $h_{ij} = h^*_{ji}$, the jump rates obey

$$\nu_{ij} = \nu_{ji} \tag{8}$$

This is the *principle of jump rate symmetry.*

In a small enough time interval $\mathrm{d}t$

$$\boxed{\text{The probability of an event occuring in time } t \to t + \mathrm{d}t \text{ is } \textit{rate} \times \mathrm{d}t}$$

i.e. for small enough $\mathrm{d}t$, multiple jumps can safely be neglected.

Thus, in a small time interval $\mathrm{d}t$ the probabilities p_i change according to:

$$dp_i = \left[-p_i \sum_j \nu_{ij} + \sum_j \nu_{ji}\, p_j \right] dt \tag{9}$$

where the first term is the probability that the system is in state $|i\rangle$ initially but jumps out of it into some other state, and the second is the probability that the system is initially elsewhere but jumps into state $|i\rangle$. Using the principle of jump rate symmetry, we have

$$\boxed{\dot{p}_i = \sum_j \nu_{ij}(p_j - p_i)} \tag{10}$$

This is called **the master equation**. The master equation is *first order in time* and clearly does not have time reversal symmetry.

14. 4. Second law

Consider a particular pair of states, $|1\rangle$ and $|2\rangle$. Then, if we imagine holding all the other p's fixed and consider transitions only between $|1\rangle$ and $|2\rangle$, $p_1 + p_2 =$ constant and in a small interval $\mathrm{d}t$, $\mathrm{d}p_1 = -\mathrm{d}p_2$. Now

$$\mathrm{d}p_1 = -\nu_{12}(p_1 - p_2)dt \tag{11}$$

thus

$$\mathrm{d}(p_1 - p_2) = -\nu_{12}(p_1 - p_2)dt \tag{12}$$

Inspecting this equation we see that, since ν_{ij} is always positive, $|p_1 - p_2|$ always decreases.

The entropy change which results from this is always positive. The proof is again based on the *concavity* of the function $s(p) = -kp \ln p$. Let us call $p_1(t + \mathrm{d}t) = p'_1$ and $p_2(t + \mathrm{d}t) = p'_2$ Taking for example $p_1 < p_2$ we have $p'_1 > p_1$ and $p'_2 < p_2$ we see from a sketch of the concave function $s(p)$ that

$$\frac{s(p_1) + s(p_2)}{2} \le \frac{s(p'_1) + s(p'_2)}{2} \tag{13}$$

Figure 1: Due to concavity the entropy always increases under the master equation with symmetric rates

thus the constribution to the enropy from these two states always increases. Since the master equation describes the overall effect of many pairwise contributions of this kind, each of which can only increase the entropy, it follows that

$$\frac{dS}{dt} \geq 0 \tag{14}$$

which is the second law. As in the classical case, there are some much more elaborate proofs of this "quantum H-theorem"; but in the end they all boil down to the same argument about the concavity of the function $s(p)$.

The coarse graining implicit in the master equation succeeds in reconciling microscopic quantum dynamics with the observed thermodynamic properties of large systems. But the actual nature of the coarse graining is less clear than in the classical case; it involves discarding quantum (phase), as well as classical, information. Hence there is an unresolved issue as to whether *wavepacket collapse* (implicit in the concept of a quantum jump) is somehow required to fix the arrow of time, as needed for the second law. A competing view is the opposite, namely that the wavepacket collapse is a *result* of the second law. There are many other issues concerning the arrow of time, quantum mechanics, determinism and the like which exercise the minds both of philosophers and physicists.

14. 5. Applications of the master equation: Random walk and diffusion

The basic structure of the master equation underlies most irreversible processes in physics, whether quantum or classical.

As a ubiquitous example, we consider the case of diffusion on a lattice in one dimension, i.e. a continuous time random walk. This could be the motion of a vacancy (or of an impurity atom) in a crystal that moves by swapping places with (other) atoms.

We label the lattice sites of the system by positive and negative integers $i = -L \ldots + L$ where L is very large (effectively infinite so that we avoid discussion of boundary conditions). The state of the system is then given by i the spatial position of the particle.

In small time interval dt there is probability νdt for our particle to move to the right in time interval dt and the same to the left. Then

$$\nu_{ij} = \nu \quad \text{if} \;\; j = i + 1 \;\; \text{or} \;\; j = i - 1 \tag{15}$$

$$\nu_{ij} = 0 \quad \text{otherwise} \tag{16}$$

so that

$$\dot{p}_i = \sum_j \nu_{ij}(p_j - p_i) = \nu\,(p_{i-1} - p_i) + \nu\,(p_{i+1} - p_i) \tag{17}$$

This is the master equation for a random walk – specifically, for a *continuous time* random walk on a *discrete* lattice. You should have already met the case when the time variable is also discrete, which yields the binomial distribution for p_i if we start at the origin (say). The continuous time case is a bit messier (the solution for $p_i(t)$ involves modified Bessel functions rather than Binomial coefficients). However things simplify if we assume that p_i varies smoothly with i. (In fact this will always be true eventually even if not to begin with.)

In that case we can rewrite the master equation as continuous also in space by introducing the probability density $p(x,t)dx$ of finding our particle (or defect, or whatever) in a small region centred on $x = ia$. Here we introduce a as the lattice spacing. Then the idea is to replace $p_i(t)$ by $p(x,t)$ and expand $p_{i\pm1} = p(x \pm a)$ for a small. i.e.

$$p_{i+1} = p(x,t) + a\frac{\partial p(x,t)}{\partial x} + \frac{a^2}{2}\frac{\partial^2 p(x,t)}{\partial x^2}\dots \tag{18}$$

$$p_{i-1} = p(x,t) - a\frac{\partial p(x,t)}{\partial x} + \frac{a^2}{2}\frac{\partial^2 p(x,t)}{\partial x^2}\dots \tag{19}$$

Then keeping terms up to $O(a^2)$ in (17) we obtain

$$\frac{\partial p}{\partial t} \simeq \nu a^2 \frac{\partial^2 p}{\partial x^2} \tag{20}$$

which is the diffusion equation for the probability density of a particle with diffusion constant (sometimes called diffusivity) $D = \nu a^2$. The dimensions of D are $[length]^2/[time]$. Often, once we have expanded, we set the lattice spacing a to 1. Also we can use the diffusion equation to describe many non-interacting particles diffusing. We then replace p by ρ the density or concentration of particles. The normalisation is $\int \mathrm{d}x\rho = M$ where M is the number of particles.

The diffusion equation, like the master equation from which it was derived, explicitly violates time reversal symmetry and allows entropy to increase.

The solution of the diffusion equation for an initial condition in which the particle is initially localised at the origin (formally, $p(x,0) = \delta(x)$) is the Gaussian:

$$p(x,t) = (4\pi Dt)^{-1/2}\exp[-x^2/4Dt] \tag{21}$$

Exercise: Check this result. Confirm that $\langle x^2\rangle = 2Dt$. This formula may be checked directly but is most conveniently derived (on an infinite system) by using the Fourier transform of the diffusion equation (20) (See *Methods of Mathematical Physics*).

If you are unhappy that this solution violates our assumption of a smooth p initially, we can start the clock ticking instead from some finite time t_0 with a smooth initial condition $p(x,t_0) = \sqrt{4\pi/Dt_0}\exp[-x^2/4Dt_0]$. This gives the same expression as above for $p(x,t)$ at all later times (check if unsure).

We can explicitly see the arrow of time by sketching (21) for different t. As t increases the gaussian 'bell-shaped' curve spreads out. The width grows $\langle x^2\rangle^{1/2} \sim t^{1/2}$. This is 'diffusive scaling' and implies that after time t a particle will typically be found a distance $t^{1/2}$ from its starting point. Conversely a particle will take time $O(L^2)$ to explore a region of size L.

Figure 2: The solution of the diffusion equation (gaussian distribution (21)) as t increases

14. 6. Detailed balance

As we have seen, by introducing a type of coarse-graining, the master equation violates time reversal symmetry and leads to the second law. Remarkably, however, the fact that the underlying microphysics *is actually time reversal-symmetric* has several deep consequences which survive the coarse-graining procedure. These results are some of the cornerstones of nonequilibrium thermodynamics. Here we discuss detailed balance and we shall return to other consequences in the next section

In equilibrium for an isolated system (i.e. microcanonical ensemble) the Principle of equal a priori probabilities (PEAPP) holds ($p_i^{eq} = p$) and we have transition rate symmetry, therefore trivially

$$\boxed{\nu_{ij} p_i^{eq} = \nu_{ji} p_j^{eq}} \tag{22}$$

This is the condition of **detailed balance**. On average, the actual rate of quantum jumps from i to j (which is the left hand side) is the same as from j to i. In the other words the probability flux from i to j is exactly balanced by the probability flux from j to i.

This is a stronger statement than the master equation (10), which only states that to have a stationary distribution ($\dot{p}_i = 0$) there should be *overall* balance between rate of jumping into and out of state i. What the *principle of detailed balance* states is that in equilibrium there is balance between any two pairs of states

The result is very powerful, because it applies not only to individual states but any grouping of them: consider two groups of states A and B. Summing (22) over i a member of group A and j a member of group B yields

$$\sum_{i \in A} \sum_{j \in B} \nu_{ij} p_i^{eq} = \sum_{i \in A} \sum_{j \in B} \nu_{ji} p_j^{eq} \tag{23}$$

Now consider the mean rate of transition from group A to group B:

$$p_A \nu_{AB} = \sum_{i \in A} p_i^{eq} \sum_{j \in B} \nu_{ij} \tag{24}$$

The right hand side is the total probability of being in group A

$$p_A = \sum_{i \in A} p_i^{eq} \tag{25}$$

mutiplied by the mean rate from group A to group B *given* that the system is in group A. To understand the left hand side note that we must start in some state i in group A. Thus we consider the total rate from state i into group B given by $\sum_{j\in B}\nu_{ij}$ then average over the states i in group A each with their equilibrium probability p_i^{eq}. Then (24) becomes

$$\nu_{AB}\, p_A^{eq} = \nu_{BA}\, p_B^{eq} \tag{26}$$

i.e. the transitions from A to B are exactly balanced by the transitions from B to A and we have detailed balance between the two groups. It is important here to note since $p_A \neq p_B$ for different size groups the transitions rates between the two groups are generally not symmetric

$$\nu_{AB} \neq \nu_{BA} \tag{27}$$

Now we can use this result to describe dynamics in the *Canonical ensemble*: recall the set up used to derive the Canonical ensemble in Physics 3. A microstate of the 'composite' of

Figure 3: In the Canonical ensemble the 'composite' of the assembly and the heat bath forms an isolated system.

assembly + bath specifies the state of both. However if we just specify the microstate of the assembly this corresponds to many possible states (with the allowed energy) of the bath and thus a group of states of the composite. Therefore, by (26) transitions between states (say α and γ) of the assembly in the canonical ensemble are between groups of states in the composite and obey detailed balance

$$\nu_{\alpha\gamma}\, p_\alpha^{eq} = \nu_{\gamma\alpha}\, p_\gamma^{eq} \tag{28}$$

Further since we know in the canonical ensemble that $p_\alpha^{eq} \propto \mathrm{e}^{-\beta E_\alpha}$ we find

$$\frac{\nu_{\alpha\gamma}}{\nu_{\gamma\alpha}} = \mathrm{e}^{\beta(E_\alpha - E_\gamma)} \tag{29}$$

Thus the transition rates are asymmetric and the ratio is a function of the energy difference between the states.

One general consequence of detailed balance is that there are no probability currents or, more generally, currents of physical quantities in equilibrium.

As an illustrative example let us write the one-dimensional diffusion equation in the form

$$\frac{\partial \rho}{\partial t} + \frac{\partial J}{\partial x} = 0 \tag{30}$$

where

$$J = -D\frac{\partial \rho}{\partial x} \tag{31}$$

is the diffusive particle current (recall we have diffusion down a concentration gradient). The current is of the globally conserved particle concentration ρ. A stationary solution $\frac{\partial \rho}{\partial t} = 0$ requires $J = constant$. An equilibrium solution goes further and fixes

$$J^{eq} = 0 \tag{32}$$

implying ρ^{eq} is spatially constant.

A nonequilibrium stationary solution would have $J \neq 0$ thus implying from (31)

$$\rho(x) = Const - \frac{Jx}{D} \tag{33}$$

Such a linear density profile would have to be maintained in a stationary state by forcing particles through the system from an external reservoir for example. The system is then held out of equilibrium in a nonequilibrium steady state.

Computer simulation: In computer simulation, good results should be obtained if one follows (as accurately as possible) the microscopic equations of motion (this is the *molecular dynamics* method). However this restricts the size of simulations to at most a few million particles (fewer if interactions are long range).

To obtain the equilibrium properties of the system, it may be much faster to use a dynamics which does not look anything like the actual equations of motion. However, if one can prove that *in the required equilibrium distribution, the artifical dynamics obey the principle of detailed balance*, then it is (almost) guaranteed that the steady state found by simulation is the true equilibrium state.

The best known example is the *Monte Carlo method*, in which the dynamical algorithm consists of random jumps. The jump rates ν_{AB} for all pairs of states (A, B) take the form

$$\nu_{AB} = \nu_o \quad \text{if } E_B \leq E_A \tag{34}$$

$$\nu_{AB} = \nu_o e^{-\beta(E_B - E_A)} \quad \text{if } E_B \geq E_A \tag{35}$$

where ν_o is a constant.

Note that the *Monte Carlo method* is a stochastic algorithm i.e. is non-deterministic. It thus represents a form of coarse-graining over the deterministic microscopic dynamics. (The epithet Monte Carlo was inspired by the spinning of wheels in a Casino.)

Exercise: Show that this gives the canonical distribution in steady state using condition (29)