R. Shankar Principles of QM 2nd ed. Springer

Ch. 4, 4

Postulates

Classical	Quantum
1 State of a system at any time t is specified by its position $x(t)$ and momentum $p(t)$, i.e. a point in phase space $\Gamma(t)$;	State of a system is a vector $\|\psi(t)\rangle$ in a Hilbert space;
2 Every dynamical variable ω is a function of x and p: $\omega = \omega(x, p)$ Every observable is a function of x, p;	Every observable is an Hermitian operator $\hat{\Omega}$;
3 If the system is in a state x, p, the measurement of the observable ω will yield a value $\omega(x, p)$; the state of the system will not be affected;	If the system is in a state $\|\psi\rangle$, the measurement of the observable $\hat{\Omega}$ will yield one of the eigenvalues of $\hat{\Omega}$, ω, with probability $P(\omega) \propto \|\langle\omega\|\psi\rangle\|^2$. The state will change from $\|\psi\rangle$ to $\|\omega\rangle$;
4 The state changes in time according to (H is the Hamiltonian) $\dot{x} = \frac{\partial H}{\partial p}$ $\dot{p} = -\frac{\partial H}{\partial x}$	The state changes in time according to $i\hbar \frac{d}{dt}\|\psi(t)\rangle = \hat{H}\|\psi(t)\rangle$

Classical : from microscopic to macroscopic observables

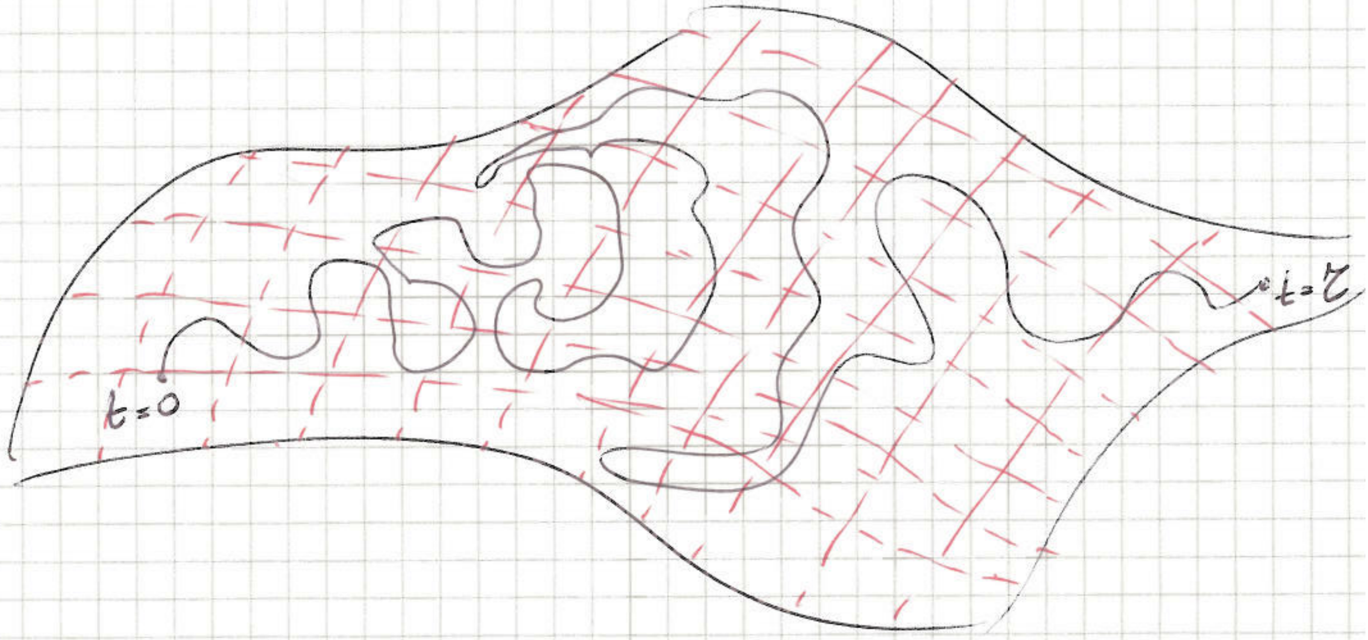
Typical atomistic time and lengthscales are of the order of the fs → ps (i.e. $10^{-15} \to 10^{-12}$ s) and Å → nm ($10^{-15} \to 10^{-9}$ m)

Typical human times ~1 s, 1 mm : orders of magnitudes of difference

Standard observations do not capture the instantaneous state of the system but rather its average behaviour.
(This is not always true today, and indeed we'll see how later) ⟹ Statistical mechanics

Boltzmann : macroscopic observables (e.g. Temperature, pressure, ..., diffusion, stress) are averages of microscopic observables over time

$$\bar{A} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} dt \; a(x(t), p(t)) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} dt \; a(\Gamma(t))$$



Γ space

$$\lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt\, a(\Gamma(t)) \simeq \lim_{N dt \to \infty} \frac{1}{N dt} \sum_{n=0}^{N} dt\, a(\Gamma(t_n))$$

$$t_n = n\, dt \quad \text{and} \quad dt = \frac{\tau}{N}$$

N number of steps but also number of observations.

Divide Γ in ~~cells~~ of volume ~~$d\Gamma$~~ and mul~~tiply and~~ divide by ~~number of cells N_s~~

Now assume the $a(\Gamma)$ is smooth enough that it does not change much within a cell and associate the value $a(\Gamma_s)$ to cell "s" in Γ. Then reorganize the counting by summing over the cells and grouping the number of times that the system was found in each cell, n_s,

$$\lim_{N \to \infty} \frac{1}{N} \sum_{s=1}^{N_s} n_s\, a(\Gamma_s) = \lim_{N \to \infty} \sum_{s=1}^{N_s} \frac{n_s}{N}\, a(\Gamma_s)$$

$$\lim_{N \to \infty} \frac{n_s}{N} = p(\Gamma_s) = \rho(\Gamma_s)\, d\Gamma$$

$$\cong \sum_{s=1}^{N_s} p(\Gamma_s)\, a(\Gamma_s) = \sum_{s=1}^{N_s} \rho(\Gamma_s)\, d\Gamma\, a(\Gamma_s)$$

$$\simeq \int d\Gamma\, \rho(\Gamma)\, a(\Gamma)$$

i.e. average over a probability density over the microscopic states of the system $\Longrightarrow$ Gibbs.