Elements of Ensemble Theory

N-particles:

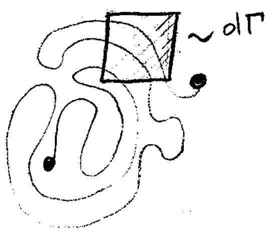
Classical System $\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i=1}^{3N} U(q_i) + \frac{1}{2}\sum_{i \neq j} \phi(q_i - q_j) + \dots$

$d=3$

$q_i : i = 1,2,\dots,3N \qquad p_i : i = 1,2,\dots,3N$

6N degrees of freedom

Phase Space: 6N-dimensional space (q_i, p_i)



$\sim d\Gamma$

(Newton II: trajectories cannot intersect)

for conservative system: $\mathcal{H}(q_i, p_i) = E = \text{const.}$

$\Downarrow$

q_i, p_i bounded

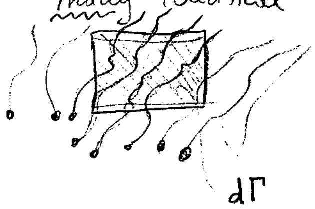
small region in phase space: T : total observation time

Δt : time spent in $d\Gamma \propto d^{3N}p\, d^{3N}q$

$\lim_{T \to \infty} \frac{\Delta t}{T} = dW$ probability that the system is in the chosen cell. (if stationary behavior is approached)

stationary time behavior. $\boxed{\bar{f} = \lim_{T \to \infty} \frac{1}{T} \int_0^T f(t)\, dt}$

many identical "virtual" copies of the system with different initial cond.



$d\Gamma$

$dW = \rho(t, p, q)\, d\Gamma$

$\boxed{d\Gamma = \frac{d^{3N}p\, d^{3N}q}{h^{3N} N!}}$

will be discussed later

$\Delta q\, \Delta p \gtrsim h$

$\rho(t,p,q)\, d\Gamma = \frac{\text{number of points in } d\Gamma \text{ around } (p,q) \text{ at time } t}{\text{total number of systems in ensemble}}$

1X

$$\int \rho(t,p,q)\, d\Gamma = 1 \qquad \rho(t,p,q): \text{probability density}$$

$t \to \infty$ $\quad \rho$ becomes t independent

ensemble ave. $\bar{f} = \int f(p,q)\, \rho(p,q)\, d\Gamma$

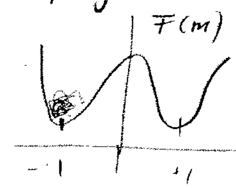
time ave. $\bar{f} = \lim_{T\to\infty} \frac{1}{T} \int_0^T f(t)\, dt$ (along the trajectory)

} ergodic hypothesis: the two method yields the same

! but in real system time-average may be hard to realize.

<u>ordering: ergodicity breaking</u>

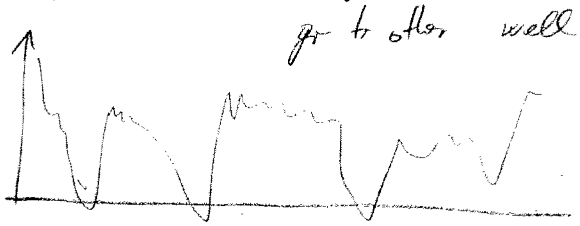
(as $N \to \infty$) e.g. magnetic system



symmetric potential
m: magnetization

typical time to spontaneously go to other well: $\sim e^{\alpha N}$ grows exponentially

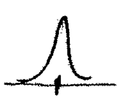
spin glasses



many local minima in high dimensional configuration landscapes

Macroscopic observables, e.g., E (energy), M (magnetization), etc., :

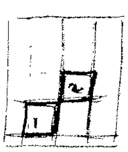
important property : $P(E), P(M)$, etc. are very sharp for large N



$\bar{f} \approx f_{\text{most probable}}$, $\frac{\Delta f}{f} \ll 1$ $\quad$ small relative standard deviation

↖ for any microscopic observable f

equilibrium: $\frac{\partial \rho}{\partial t} = 0$



$\rho_{12}\, d\Gamma_{12} = \rho_1\, d\Gamma_1\, \rho_2\, d\Gamma_2 \qquad \rho_{12} = \rho_1 \rho_2$

independent statistical subsystems

$$\left.\begin{aligned} \bar{f} &= \sum_i \bar{f_i} \sim N \\ (\Delta f)^2 &= \sum_i \overline{(f_i - \bar{f_i})^2} \sim N \end{aligned}\right\} \quad \frac{\sqrt{\overline{(\Delta f)^2}}}{\bar{f}} \sim \frac{1}{\sqrt{N}}$$

ρ ~ sharp function

Liouville's Theorem

evolution of ensembles:  ~ fluid flow
(in phase space)

$$d\Gamma \propto d^{3N}p\, d^{3N}q$$

no source/sink in phase space (number of "virtual" systems is the same in the ensemble)

conservation of points in any closed volume in phase-space

$$\boxed{\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \bar{v}) = 0}$$

$\rho(t, p, q)$

$\bar{v} = (\dot{p}, \dot{q})$ "velocity" in phase space

$$\operatorname{div}(\rho \bar{v}) = \rho \sum_i \left(\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} \right) + \sum_i \left(\frac{\partial \rho}{\partial p_i} \dot{p}_i + \frac{\partial \rho}{\partial q_i} \dot{q}_i \right) =$$

$$\left[\text{Hamilton's equation:} \quad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i} \qquad \dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i} \right]$$

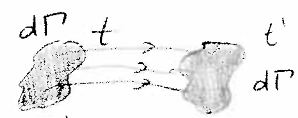
$$= \rho \underbrace{\sum_i \left(-\frac{\partial^2 \mathcal{H}}{\partial p_i \partial q_i} + \frac{\partial^2 \mathcal{H}}{\partial q_i \partial p_i} \right)}_{\emptyset} + \sum_i \left(\frac{\partial \rho}{\partial p_i} \dot{p}_i + \frac{\partial \rho}{\partial q_i} \dot{q}_i \right)$$

$$\frac{\partial \rho}{\partial t} + \sum_i \left[\frac{\partial \rho}{\partial p_i} \dot{p}_i + \frac{\partial \rho}{\partial q_i} \dot{q}_i \right] = 0 \longrightarrow \{\rho, \mathcal{H}\} = \sum_i \left(\frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right)$$

"Poisson bracket"

$$\boxed{\frac{d\rho}{dt} = 0}$$

(does not imply $\frac{\partial \rho}{\partial t} = 0$!)

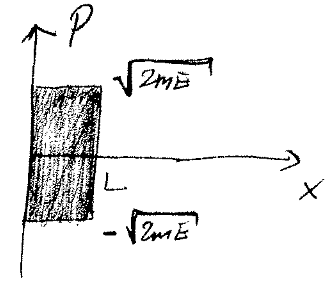
since the # of points conserved: 

$$\rho(t, p(t), q(t))\, d\Gamma = \rho(t', p(t'), q(t'))\, d\Gamma' \Rightarrow \boxed{d\Gamma = d\Gamma'}$$

37) ρ can only depend on conserved combinations of (p, q) $\quad \rho_{12} \approx \rho_1 \rho_2 \quad$ $\ln \rho$ can only depend on additive

Matching Quantum and Classical limits

"number" of states with energy less than E $\qquad 0 \le x \le L$



classically: $\quad E = \dfrac{p^2}{2m}$

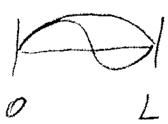
elementary phase cell:

$\Delta p \, \Delta x = h'$ "action" dimension

$\Delta p \, \Delta x \gtrsim \hbar$

\# of states with energy $< E$ $\qquad \boxed{\Omega_<^{\text{class.}}(E) = \dfrac{2\sqrt{2mE}\,L}{h'}}$

Quantum calculation (exact enumeration of states are possible



$\dfrac{\lambda}{2} n = L \qquad p\lambda = h$ (de-Broglie)

$p = \dfrac{h}{\lambda} = \dfrac{nh}{2L} \qquad E = \dfrac{p^2}{2m} = \dfrac{1}{2m}\dfrac{n^2 h^2}{(2L)^2}$

$n = \dfrac{2L\sqrt{2mE}}{h} \quad \Rightarrow \quad \Omega_<^{\text{quant.}}(E) = \dfrac{2L\sqrt{2mE}}{h}$

$\boxed{\Rightarrow \Delta p \, \Delta x = h' = h}$

$d\Gamma = \dfrac{dp\,dq}{h}$ $\qquad$ for one particle

Microcanonical Ensemble

Closed System : E, V, N are constant $\qquad \rho(E,V,N)$

$\mathcal{H}(p,q) = E$ fixed $\qquad$ $\delta E \sim$ uncertainty principle limits it

hypersurface 

$E < \mathcal{H}(p,q) \leq E + \delta E \longrightarrow$ hyper shell 

$\delta E \ll E$

$$d\Gamma = \frac{dp^{3N}\, dq^{3N}}{h^{3N} N!} \quad \text{if particles are indistinguishable}$$

$$\Omega(E, \delta E) = \int_{E<\mathcal{H}(p,q)\leq E+\delta E} d\Gamma$$

number of microscopic states satisfying the "fixed E"

$$\Omega(E, \delta E) = g_N(E)\, \delta E$$

density of states

$$\boxed{\Omega_<(E) : \int_{\mathcal{H}(p,q)\leq E} d\Gamma}$$

E = const.

volume in phase-space

volume (E) - area (E) δE

$$\Omega(E, \delta E) = \underbrace{\frac{d\Omega_<(E)}{dE}}_{\text{"area"}} \delta E \qquad \left(g_N(E) = \frac{d\Omega_<(E)}{dE} \right)$$

Examples: ① Ideal Gas (monoatomic) $\qquad \mathcal{H}(p,q) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} = E$

N particles

$$\sum_{i=1}^{3N} p_i^2 = 2mE \quad \to \text{"radius" } \sqrt{2mE} \quad , \ 3N\text{-dim sphere}$$

$$\Omega_<(E) = \frac{V^N}{h^{3N} N!} \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} \left(\sqrt{2mE}\right)^{3N} = \frac{V^N}{h^{3N} N!} \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)} (2mE)^{\frac{3N}{2}}$$

$$\Omega(E, \delta E) = \frac{d\Omega_<(E)}{dE} \delta E = \frac{V^N}{h^{3N} N!} \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)} \frac{3N}{2} (2mE)^{\frac{3N}{2}-1}\, 2m\, \delta E$$

$\Gamma(x+1) = x\,\Gamma(x)$

$$\Omega(E,\delta E) = \frac{V^N}{h^{3N} N!} \frac{(2m\pi)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} E^{\frac{3N}{2}-1}\,\delta E$$

number of microstates between E, $E+\delta E$

$$\boxed{\Omega(E,\delta E) = \frac{V^N}{h^{3N} N!} \frac{(2m\pi)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} E^{\frac{3N}{2}} \frac{\delta E}{E}}$$

In general we can anticipate that systems with large degrees of freedom, f

$$\Omega(E,\delta E) \propto E^{\alpha f} \qquad \alpha = O(1)$$

on the above energy shell $(E < \mathcal{H}(p,q) \leq E+\delta E)$, the distribution is uniform "equal apriori probabilities" ① — in equilibrium $\frac{\partial \rho}{\partial t} \to 0$

microcanonical ensemble:

② $$\rho(p,q) = \begin{cases} \frac{1}{\Omega(E,\delta E)} & \text{if} \quad E < \mathcal{H}(p,q) \leq E+\delta E \\ 0 & \text{otherwise} \end{cases}$$

"almost" closed system

$$\int_{E \leq \mathcal{H} \leq E+\delta E} \rho \frac{d^{3N}p \, d^{3N}q}{N! \, h^{3N}} = 1$$

Consider an other macroscopic observable, $X(p,q)$

$$P(X) = \frac{1}{\Omega(E,\delta E)} \int_{X(p,q)=X} d\Gamma = \frac{\Omega(E,\delta E,X)}{\Omega(E,\delta E)}$$

Entropy: $S \propto -\sum_i p_i \ln p_i$ (Shannon)

microcanonical ensemble: $p_i = \frac{1}{\Omega}$ $\quad i = 1,2,\dots,\Omega$

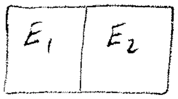
uniform distribution

$$S \propto -\sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = \ln \Omega$$

$S = k \ln \Omega$ $\quad$ k is Boltzmann constant

$$\boxed{S(E,V,N) = k \ln \Omega(E,\delta E)}$$ for microcanonical ensemble

Equilibrium Conditions ① and ② independent subsystems



$$E_1 < \mathcal{H}_1 \leq E_1 + \delta E$$
$$E_2 < \mathcal{H}_2 \leq E_2 + \delta E \qquad\qquad E \simeq E_1 + E_2 \quad \text{"fixed"}$$
$$E < \mathcal{H}_1 + \mathcal{H}_2 \leq E + 2\delta E$$

$$P(E_1) = \frac{\Omega(E, 2\delta E, E_1)}{\Omega(E, \delta E)} = \frac{\Omega_1(E_1, \delta E)\,\Omega_2(E_2, \delta E)}{\Omega(E, \delta E)}$$

$$\ln P(E_1) = \ln \Omega_1(E_1, \delta E) + \ln \Omega_2(E_2, \delta E) + \text{const.}$$

equilibrium corresponds to maximum probability : $d \ln P(E_1) = 0$

$$d \ln P(E_1) = \frac{\partial \ln \Omega_1(E_1, \delta E)}{\partial E_1} dE_1 + \frac{\partial \ln \Omega_2(E_2, \delta E)}{\partial E_2} dE_2$$

$dE_2 = -dE_1$ $\qquad$ $\tilde{E}_1$ and $\tilde{E}_2$: most probable value

$$d \ln P(E_1) = \left[\left.\frac{\partial \ln \Omega_1(E_1, \delta E)}{\partial E_1}\right|_{E_1 = \tilde{E}_1} - \left.\frac{\partial \ln \Omega_2(E_2, \delta E)}{\partial E_2}\right|_{E_2 = \tilde{E}_2} \right] dE_1 = 0$$

$$\boxed{\beta = \frac{1}{kT} = \frac{\partial \ln \Omega}{\partial E}} \text{ in equilibrium} \implies \boxed{T_1 = T_2}$$

also consistent with $\quad \dfrac{1}{T} = k \dfrac{\partial \ln \Omega}{\partial E} = \left(\dfrac{\partial S}{\partial E}\right)_{V,N}$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \qquad -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V}$$

$$\boxed{dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN} \quad \text{fundamental equation}$$