Basic Definitions

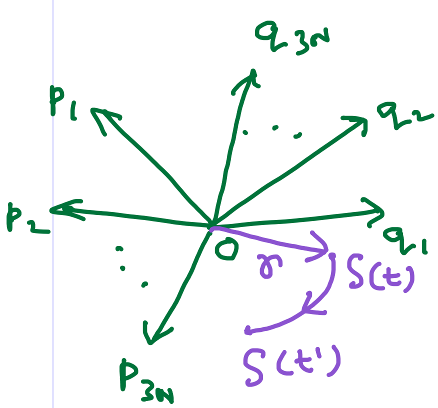
Consider an N-particle system in 3-dimensions (3N degrees of freedom) described by the canonical variables $q_1, q_2, \ldots, q_{3N}; p_1, p_2, \ldots, p_{3N}$.

These canonical variables obey Hamiltonian dynamics through:

$$\left.\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i} \end{aligned}\right\} \quad \forall\ i = 1, 2, \ldots, 3N.$$

Example: N-particles confined in a volume V enclosed by a surface that doesnot allow the flow of particles/energy.

Phase space



- We define a 6N-dimensional phase space as shown.
- The state of the system at a given instant of time t can be represented by a 6N-dimensional vector

$$r \equiv r(q_1, \ldots, q_{3N}, p_1, \ldots, p_{3N})$$

- If we specify the total energy E of the system, the evolution of the N-particle system can be conceived to be confined to a (6N−1)-dimensional surface given by $H(r) = E$. Denote this surface by $\Gamma(E)$.

- For a closed system in equilibrium, its macroscopic properties are time-independent.

For a macroscopic quantity M, we can perform an experiment over a period of time τ, s.t., $t_0 < \tau < t_0+\tau$.

During this period, the phase-point (r) traverses a part of $\Gamma(E)$.

One can construct a time average

$$\langle M \rangle_\tau = \frac{1}{\tau}\int_{t_0}^{t_0+\tau} M(r(t))\, dt$$

Ergodic Hypothesis : During any significant time interval τ, the phase space point $r(t)$ spends equal time intervals in all regions of $\Gamma(E)$.

Conceive of an average over the surface $\Gamma(E) \equiv$ Ensemble average

Ensemble: Collection of snapshots of the system at different times.

We can specify the ensemble through the probability density $\rho(r)$ for a particular member of the ensemble to occupy the phase space point r.

Thus, the ensemble average of $M(r(t))$ is

$$\langle M \rangle_{\Gamma(E)} = \int d^{6N}r \; \rho(r)\, M(r).$$

Note:

→ A microcanonical ensemble (a fixed energy E, a fixed particle number N and a chemical potential μ) for a closed classical system of energy E is given by

$$\rho(\gamma) = C\,\delta(H(\gamma) - E).$$

where, C is a normalization factor.

→ To be able to extend the formalism to quantum mechanical system, we need to consider a shell containing all γ given by

$$E < H(\gamma) < E + \delta E$$

where, each γ occur with equal apriori probability.

→ The total number of microstates (members of microcanonical ensemble) for an N-particle system is given by

$$\Omega(E, N, V) = \frac{1}{N!\,h^{3N}} \int_{E \leq H(\gamma) \leq E+\delta E} d^{6N}\gamma$$

→ Entropy S(E) is given by

$$S(E) = K_B \ln \Omega(E, N, V).$$

- $E/N < \delta E \ll E$. Else, $|\ln(\frac{\delta E}{E})| \ll N$.
- K_B is Boltzmann constant.
- h^{3N} : volume of cell in phase space.
- $N!$: factor due to indistinguishability.

Liouville's theorem

$$\rho = \rho(q_i, p_i, t)$$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i + \frac{\partial \rho}{\partial t}.$$

But $\dot{q}_i = \frac{\partial H}{\partial p_i}$ & $\dot{p}_i = -\frac{\partial H}{\partial q_i}$

$$\Rightarrow \frac{d\rho}{dt} = \frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i} + \frac{\partial \rho}{\partial t}.$$

$$= \{\rho, H\} + \frac{\partial \rho}{\partial t}. \quad \text{——— (i)}$$

As ρ represent probability density for microstates, it cannot be created or, destroyed.

ρ follows a continuity equation

$$\nabla\cdot\vec{J} = -\frac{\partial \rho}{\partial t} \quad \text{——— (ii)}$$

where, $\vec{J} = \rho\vec{v}$

s.t., $\vec{v} = (\dot{q}_i, \dot{p}_i)$.

$$\Rightarrow \nabla\cdot\vec{J} = \frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i}$$

$$= \left(\frac{\partial \rho}{\partial q_i}\right)\dot{q}_i + \left(\frac{\partial \rho}{\partial p_i}\right)\dot{p}_i + \rho\left[\frac{\partial}{\partial q_i}\left(\frac{\partial H}{\partial p_i}\right) - \frac{\partial}{\partial p_i}\left(\frac{\partial H}{\partial q_i}\right)\right]$$

$$= \{\rho, H\} + 0 \Rightarrow \frac{\partial \rho}{\partial t} = -\nabla\cdot\vec{J} = -\{\rho, H\} \quad \text{(iii)}$$

$\therefore \boxed{\frac{d\rho}{dt} = 0}$ (using (i) to (iii)).

$\Rightarrow \rho = $ constant

In equilibrium (stationary condition), $\frac{\partial \rho}{\partial t} = 0. \Rightarrow \{\rho, H\} = 0.$

Volume of a Euclidean ball of radius R in n-dimensional Euclidean space

$$V_n(R) \propto R^n$$

Proportionality constant is the volume of the "unit ball".

i.e., $$V(kR) = \int_{kR} dx_1\, dx_2 \ldots dx_n$$

$$= R^n \int_{k} dy_1\, dy_2 \ldots dy_n .$$

$$= R^n\, V(k).$$

i.e., $$V(R) = V(1)\, R^n .$$

Consider the n-variable function
$$f(x_1, x_2, \ldots, x_n) = \exp\left(-\frac{1}{2}\sum_{i=1}^{n} x_i^2\right).$$

- Rotationally invariant
- product of functions of one variable each.

$$\therefore \int_{\mathbb{R}^n} f\, dV = \prod_{i=1}^{n}\left(\int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}x_i^2\right) dx_i\right)$$

$$= (2\pi)^{n/2}.$$

Implement the integral in a suitable spherical polar coordinate system:

$$\int_{\mathbb{R}^n} f\, dV = \int_0^{\infty}\int_{S^{n-1}(r)} \exp\left(-\frac{1}{2}r^2\right) dA\, dr. \quad \text{---(a.)}$$

Here, $S^{n-1}(r)$ is a $(n-1)$ sphere of radius r.

dA = area element $\equiv$ $(n-1)$ dimensional volume element.

$$\therefore \int_{R^n} f\, dV = \int_0^\infty \exp\left(-\frac{r^2}{2}\right) A_{n-1}(r)\, dr.$$

But, $A_{n-1}(r) = r^{n-1} A_{n-1}(1)$.

$$\Rightarrow \int_{R^n} f\, dV = A_{n-1}(1) \int_0^\infty \exp\left(-\frac{r^2}{2}\right) r^{n-1}\, dr.$$

$$= A_{n-1}(1) \int_0^\infty \exp(-t)\, 2^{\frac{n-2}{2}}\, t^{\frac{n-2}{2}}\, dt$$

$$\left\{ \begin{array}{l} \frac{r^2}{2} = t \Rightarrow r^2 = 2t. \\ \Rightarrow r^{n-1} = 2^{\frac{n-1}{2}} t^{\frac{n-1}{2}}. \\ r\,dr = dt \Rightarrow dr = \frac{dt}{\sqrt{2}\, t}. \end{array} \right.$$

$$= A_{n-1}(1)\, 2^{\frac{n-2}{2}} \int_0^\infty dt\, t^{\frac{n}{2}-1} e^{-t}$$

$$= A_{n-1}(1)\, 2^{\frac{n-2}{2}}\, \Gamma\left(\frac{n}{2}\right). \quad \text{—— (b.)}.$$

Comparing (a.) & (b.),

$$\Rightarrow A_{n-1}(1)\, 2^{\frac{n}{2}-1}\, \Gamma\left(\frac{n}{2}\right) = (2\pi)^{n/2}$$

$$\Rightarrow A_{n-1}(1) = \frac{2\pi^{n/2}}{\Gamma\left(\frac{n}{2}\right)}.$$

$$\therefore A_{n-1}(r) = \frac{2\pi^{n/2}}{\Gamma\left(\frac{n}{2}\right)} r^{n-1}.$$

$\therefore$ Volume of the n-ball is,

$$\equiv \int_0^R A_{n-1}(r)\, dr$$

$$= \frac{2\pi^{n/2}}{\Gamma\left(\frac{n}{2}\right)} \frac{R^n}{n} = \frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2}+1\right)} R^n.$$

$$\Rightarrow \boxed{V_n(R) = \frac{\pi^{n/2}}{\Gamma(\frac{n}{2}+1)} R^n .}$$

Check : $n=1$, $V_1 = 2R$

$n=2$, $V_2 = \pi R^2$

$n=3$, $V_3 = \frac{4}{3}\pi R^3$.

$\therefore$ For ideal gas with N particles,

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} .$$

$$\therefore \Omega(E,N,V) = \frac{1}{h^{3N} N!} \int dq_1 \dots dq_{3N} \underbrace{\int_{\sum_{i=1}^{3N} p_i^2 = 2mE} dp_1 \dots dp_{3N}}_{\text{Note: Need to be careful (see next page)}}$$

$$= \frac{V^N}{h^{3N} N!} V_n(R) \text{ with } R = \sqrt{2mE} .$$

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

$$= \frac{V^N}{h^{3N} N!} \frac{(2\pi m E)^{3N/2}}{\Gamma(\frac{3N}{2}+1)} .$$

The equation $\sum_i p_i^2 = 2mE$ defines the surface of a $3N$-dimensional sphere of radius $\sqrt{2mE}$.

Alternately (for $\delta E \ll E$),

$$\Omega(E,N,V) = \frac{V^N}{h^{3N} N!} \underbrace{A_{3N}(\sqrt{2mE})}_{\text{Area of 3N-dimensional sphere of radius } \sqrt{2mE}} \frac{m\,\delta E}{\sqrt{2mE}} .$$

Also, $2p\,dp = 2m\,\delta E$ $(\because p^2 = 2mE)$

$$\Rightarrow dp = \frac{m\,\delta E}{\sqrt{2mE}} .$$

$$= \frac{V^N}{h^{3N} N!} \frac{(2m\pi E)^{3N/2}}{(\frac{3N}{2}-1)!} \frac{\delta E}{E} .$$

This leads to identical results for $|\ln(\delta E/E)| \ll N$.

$$S(E,N,V) = k_B \ln \Omega(E,N,V).$$

$$= k_B \Big[N\ln V - 3N\ln h - N\ln N + N - \frac{3N}{2}\ln\left(\frac{3N}{2}\right) + \frac{3N}{2} + \frac{3N}{2}\ln(2\pi m) + \frac{3N}{2}\ln E \Big].$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = k_B \frac{3N}{2E} \Rightarrow \boxed{E = \frac{3}{2} N k_B T.}$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{N k_B}{V} \Rightarrow \boxed{pV = N k_B T}$$

$$\boxed{S = N k_B \ln\left(\frac{V}{N}\right) + \frac{3N k_B}{2} \ln\left(\frac{4\pi m E}{3N h^2}\right) + \frac{5}{2} N k_B}$$

Sackur-Tetrode formula

Extensivity of Entropy

Note: $S \propto N$ in the limit $N \to \infty$ & $\frac{N}{V} \to$ constant with $E \propto N$.

In general, $dS = \frac{dE}{T} + \frac{p\,dV}{T} - \frac{\mu\,dN}{T}$.

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

$\frac{3}{2}\ln(k_B T)$

$$\Rightarrow \mu = -k_B T\Big(\ln V - 3\ln h - 1 + 1 - \ln N - \frac{3}{2}\ln\left(\frac{3N}{2}\right) - \frac{3}{2} + \frac{3}{2} + \frac{3}{2}\ln(2\pi m) + \frac{3}{2}\ln E\Big).$$

$$\therefore \boxed{\mu = k_B T \ln\left(\frac{N\lambda^3}{V}\right)}.$$

where, $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$

(thermal de Broglie wavelength)

T, p and μ are intensive quantities (independent of N).