# Liouville's Theorem

$\rho(\{p,q\})$ behaves like an incompressible fluid.

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial p_i}\frac{dp_i}{dt} + \frac{\partial \rho}{\partial q_i}\frac{dq_i}{dt} \right) = 0$$

Using Hamilton's equations this becomes

$$\frac{\partial \rho}{\partial t} = \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i} - \frac{\partial \rho}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} \right)$$

If the density in phase space depends only on the energy at that point,

$$\rho(\{p,q\}) = \rho(\mathcal{H}\{p,q\}),$$

carrying out the indicated derivatives shows that

$$\frac{\partial \rho}{\partial t} = 0.$$

This proves that $\rho = \rho(\mathcal{H}\{p,q\})$ is a sufficient condition for an equilibrium probability density in phase space.

## 1. The System

$E <$ energy $< E+\Delta$

$\Delta \ll E$

Fixed:

$E$

$V$

$N$

$\vec{M}$ or $\vec{H}$

$\vec{\mathcal{P}}$ or $\vec{\mathcal{E}}$

A complete set of independent thermodynamic variables is fixed.

Many micro-states satisfy the conditions.

## 2. Probability Density

All accessible microscopic states are equally probable.

Classical

$$
\begin{aligned}
p(\{p,q\}) &= 1/\Omega \qquad && E < \mathcal{H}(\{p,q\}) \leq E+\Delta \\
&= 0 && \text{elsewhere}
\end{aligned}
$$

$$\Omega \equiv \int_{\text{accessible}} \{dp, dq\} = \Omega(E,V,N)$$

Quantum

$$
\begin{aligned}
p(k) &= 1/\Omega \qquad && E < \langle k|\mathcal{H}|k\rangle \leq E + \Delta \\
&= 0 && \text{elsewhere}
\end{aligned}
$$

$$\Omega \equiv \sum_{k,\ \text{accessible}} (1) = \Omega(E, V, N)$$

Let $X$ be a state of the system specified by a subset { p'' ,q'' } of { p,q}

$$p(X) = \int_{\text{except } \{p'',q''\}} p(\{p,q\}) \{dp, dq\}$$

$$= \frac{1}{\Omega} \int_{\text{except } \{p'',q''\}} \{dp, dq\}$$

$$= \frac{\Omega'(\text{consistent with } X)}{\Omega}$$

$$= \frac{\text{volume consistent with } X}{\text{total volume of accessible phase space}}$$

## 3. Quantities Related to $\Omega$

$$\begin{aligned}\Phi(E,V,N) &\equiv \int_{\mathcal{H}(\{p,q\})<E} \{dp,dq\} \\ &= \text{cumulative volume in phase space}\end{aligned}$$

$$\begin{aligned}\omega(E,V,N) &\equiv \frac{\partial \Phi(E,V,N)}{\partial E} \\ &= \text{density of states as a function of energy}\end{aligned}$$

$$\Rightarrow \Omega(E,V,N) = \omega(E,V,N)\Delta$$

Example Ideal Monatomic Gas

$q_i = x, y, z$ in a box $V = L_x L_y L_z$

$p_i = m\dot{x}, m\dot{y}, m\dot{z}$ $-\infty < p_i < \infty$

$N$ atoms $\mathcal{H}(\{p,q\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$

$$
\begin{aligned}
\Omega &= \int \{dp, dq\} = \int \{dq\} \int \{dp\} \\
&= \left[\int_0^{L_x} dx\right]^N \left[\int_0^{L_y} dy\right]^N \left[\int_0^{L_z} dz\right]^N \int \{dp\} \\
&= V^N \int_{E<\mathcal{H}<E+\Delta} \{dp\}
\end{aligned}
$$

$$
\Phi(E, V, N) = V^N \int_{\mathcal{H}<E} \{dp\}
$$

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \quad \Rightarrow \quad 2mE = \sum_{i=1}^{3N} p_i^2$$

This describes a $3N$ dimensional spherical surface in the $p$ part of phase space with a radius $R = \sqrt{2mE}$.

Math:

- Volume of an $\alpha$ dimensional sphere of radius $R$ is

$$\frac{\pi^{\alpha/2}}{(\alpha/2)!}R^{\alpha}$$

- Sterling's approximation for large $M$

$$\ln(M!) \approx M \ln M - M$$

$$\rightarrow M! \approx \left(\frac{M}{e}\right)^{M}$$

$$
\begin{aligned}
\Phi(E,N,V) \;&=\; V^N \,\frac{\pi^{3N/2}}{(3N/2)!}\,(2mE)^{3N/2} \\
&\approx\; \left\{ V^N \,\left(\frac{4\pi e m E}{3N}\right)^{3N/2} \right\} \\
\omega(E,N,V) \;&=\; \left(\frac{3N}{2}\,\frac{1}{E}\right)\{\quad\} \\
\Omega(E,N,V) \;&=\; \left(\frac{3N}{2}\,\frac{\Delta}{E}\right)\{\quad\}
\end{aligned}
$$

$$p(x_i) = \frac{\Omega'}{\Omega} = \frac{V^{N-1} L_y L_z}{V^N} = \frac{1}{L_x} \qquad 0 \le x < L_x$$

$$p(x_i, y_j) = \frac{\Omega'}{\Omega} = \frac{V^{N-2} L_y L_z L_x L_z}{V^N} = \frac{1}{L_x L_y} = p(x_i)p(y_j) \Rightarrow \text{S.I.}$$

$$p(p_{x_i}) = \int \underbrace{p(\{p, q\})}_{1/\Omega} \{ \underbrace{dp}_{p \neq p_{x_i}}, dq\} = \frac{\Omega'}{\Omega}$$

Note that $\Omega'$ differs on each of the three lines, being a generic symbol for the reduced phase volume consistent with some constraint.

$\epsilon \equiv p_x^2/2m$ $\quad$ $E{-}\epsilon$ distributed over other variables

$$\Omega' = \left(\frac{3N-1}{2}\,\frac{\Delta}{E-\epsilon}\right) V^N \left(\frac{4\pi e m(E-\epsilon)}{3N-1}\right)^{(3N-1)/2}$$

$$\frac{\Omega'}{\Omega} = \underbrace{\left(\frac{3N-1}{3N}\right)}_{\approx 1}\underbrace{\left(\frac{E}{E-\epsilon}\right)}_{\approx 1}\left(\frac{4\pi e m}{3}\right)^{-1/2}$$

$$\times \quad \underbrace{\left(\frac{(N-\frac{1}{3})^{-\frac{3N}{2}+\frac{1}{2}}}{N^{-\frac{3N}{2}}}\right)}_{A} \quad \underbrace{\left(\frac{(E-\epsilon)^{\frac{3N}{2}-\frac{1}{2}}}{E^{\frac{3N}{2}}}\right)}_{B}$$

$$A = \sqrt{N - \frac{1}{3}} \; \left(1 - \frac{1}{3N}\right)^{-\frac{3N}{2}} = \sqrt{N - \frac{1}{3}} \; \left(1 + \frac{1/2}{-3N/2}\right)^{-\frac{3N}{2}}$$

but $\quad \lim_{\zeta \to \infty} \left(1 + \frac{x}{\zeta}\right)^{\zeta} = e^{x}$

so $A \approx \sqrt{N} \; e^{1/2}$

$$B = \frac{1}{\sqrt{E-\epsilon}} \left(1 - \frac{\epsilon}{E}\right)^{\frac{3N}{2}} = \frac{1}{\sqrt{E-\epsilon}} \left(1 - \frac{\frac{1}{2}\epsilon / < \epsilon >}{3N/2}\right)^{\frac{3N}{2}}$$

where we have used $< \epsilon > \equiv E/3N$ and $E = 3N < \epsilon >$.

so $B \approx \frac{1}{\sqrt{3N{<}\epsilon{>}}}\, e^{-\epsilon/2<\epsilon>}$

$$p(p_x) \;=\; \left(\frac{\sqrt{3}}{\sqrt{4\pi m}}\; e^{-1/2}\right)\left(\sqrt{N}\; e^{1/2}\right)\frac{1}{\sqrt{3N < \epsilon >}}\; e^{-\epsilon/2<\epsilon>}$$

$$= \frac{1}{\sqrt{4\pi m < \epsilon >}}\; e^{-\epsilon/2<\epsilon>}$$

Now use $\epsilon = p_x^2/2m$ and $< \epsilon > = < p_x^2 > /2m$.

$$p(p_x) = \frac{1}{\sqrt{2\pi < p_x^2 >}}\; e^{-p_x^2/2<p_x^2>}$$