

Lecture 3

22.01.2019

Phase space, Liouville's theorem,
statistical ensembles

Statistical mechanics

- Looks at macroscopic properties of matter from a microscopic, particle-based point of view
- Contains two key elements:
 - Particle mechanics: Laws of motion of the individual particles
 - Statistical ensembles: Collections of all accessible microscopic configurations of N particles corresponding to a macroscopic (thermodynamic) equilibrium state of the system

Equilibrium statistical mechanics

- Particle mechanics: Hamiltonian particle dynamics

$$\text{Hamiltonian of one particle } H = \frac{p^2}{2m} + U(q)$$

Newton's law of motion

$$\dot{q} = \frac{\partial H}{\partial p}, \dot{p} = -\frac{\partial H}{\partial q}$$

- Statistical ensembles: Each configuration of particle is a representative point in the space of all particle coordinates, called **phase space** $(\mathbf{p}_i, \mathbf{q}_i)_{2dN-dim}$.

We define a density of states $\rho(p, q)$, such that $\rho(p, q)d^{dN}p d^{dN}q$ is the number of configurations in a volume element $d\omega \equiv d^{dN}p d^{dN}q$ around a particular point (p, q) in the phase space

Phase space example: 1d Harmonic Oscillator

- Total energy

$$H = \frac{p^2}{2m} + \frac{1}{2}m^2\omega_0^2q^2$$

$$\dot{q} = \frac{\partial H}{\partial p}, \dot{p} = -\frac{\partial H}{\partial q} \rightarrow \dot{q} = \frac{p}{m}, \dot{p} = -m\omega_0^2q$$

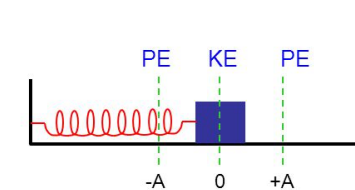
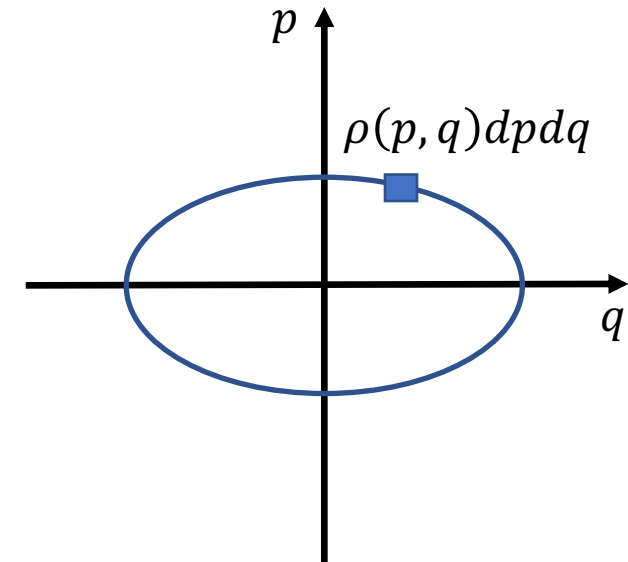
$$\ddot{q} + \omega_0^2q = 0$$

- Solution: $q(t) = A \cos(\omega_0 t + \phi)$, $p(t) = m \dot{q} = -Am\omega \sin(\omega_0 t + \phi)$

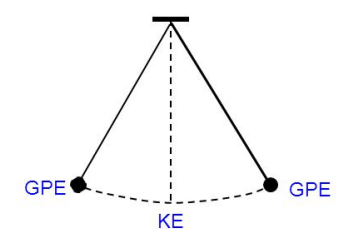
- Motion at constant total energy $H = \frac{p^2}{2m} + \frac{1}{2}m^2\omega_0^2q^2 = \text{const}$ is on an **ellipse**

$$q^2 + \frac{1}{m^2\omega_0^2}p^2 = A^2$$

- 2D-Phase space: $\rho(p, q)dpdq$ is the number of density of states around a point (p, q)



The spring has
elastic potential energy



The pendulum has
gravitational potential energy

Phase space

- System of N particles: each particle has a position coordinate q_n and a momentum coordinate p_n , where $n = 1, \dots, N$ labels each particle
- **3D**: $q_n = (x_n, y_n, z_n)$ and $p_i = (\dot{x}_n, \dot{y}_n, \dot{z}_n)$. Each particle has $2d = 6$ degrees of freedom (d.o.f.)

- General coordinate for the N -collection of Hamiltonian particles

$$(p, q) = (p_1, \dots, p_{3N}, q_1, \dots, q_{3N})$$

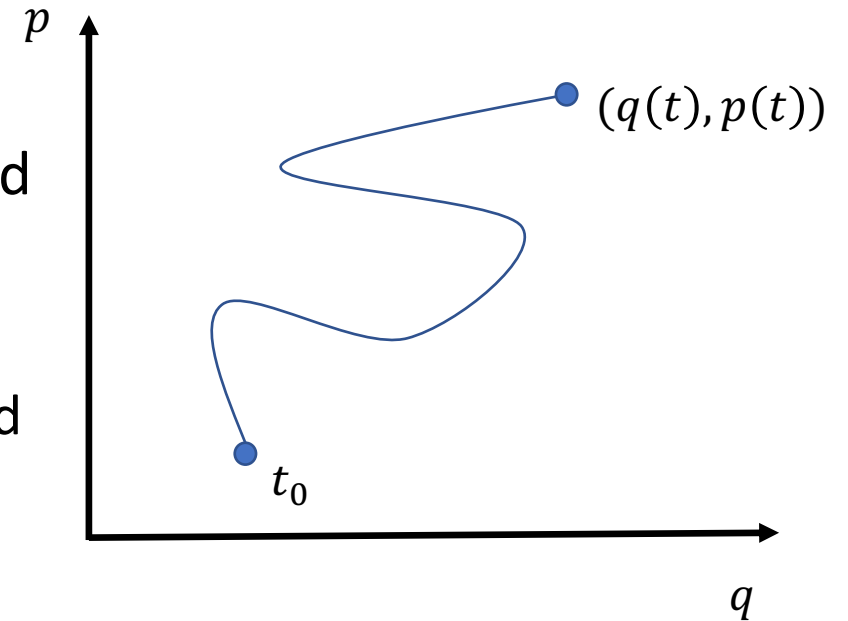
- The system is described by a collection of particles with Hamiltonian dynamics

$$H = \sum_{i=1}^{3N} \frac{p^2}{2m} + U(q_1, \dots, q_{3N})$$

Phase space

- $(p, q) = (p_1, \dots, p_{dN}, q_1, \dots, q_{dN})$
- (p, q) has $N \times 2d$ coordinates
- A state of the N particles that specify the position and momentum of each particles is given by a representative point in the phase space (p, q)
 - **Macroscopic properties** of the system are determined as **ensemble averages** over the density of state
 - The **macroscopic evolution** of the system is described by the **"flow"** of the **density of states** in the phase space

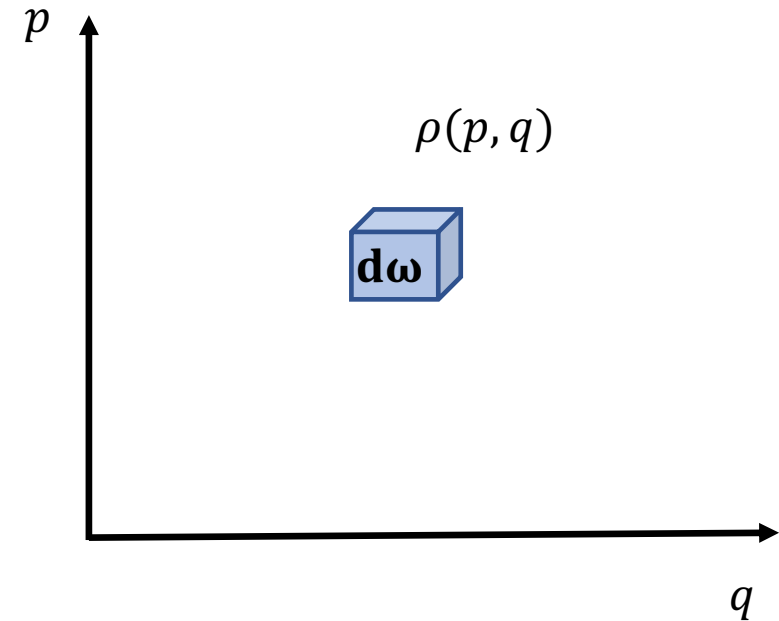
$(6N) - \text{dimensional}$



Ensemble density of states

- Imagine that the phase space is filled with accessible microstates in analogy to how a container is filled with a fluid
- The "fluid" is the large collection of identical systems that are in the same macroscopic state are in different possible microstates
- This ensemble is described by a density of systems occupying a point in the phase space ("fluid density") $\rho(p, q)$
- Number of systems which occupy the microstates between (p, q) and $(p + dp, q + dq)$ is

$$\rho(p, q)d\omega$$



Ensemble density of states

- Ensemble density $\rho(p, q)$ is the probability density of finding the system in state (p, q)

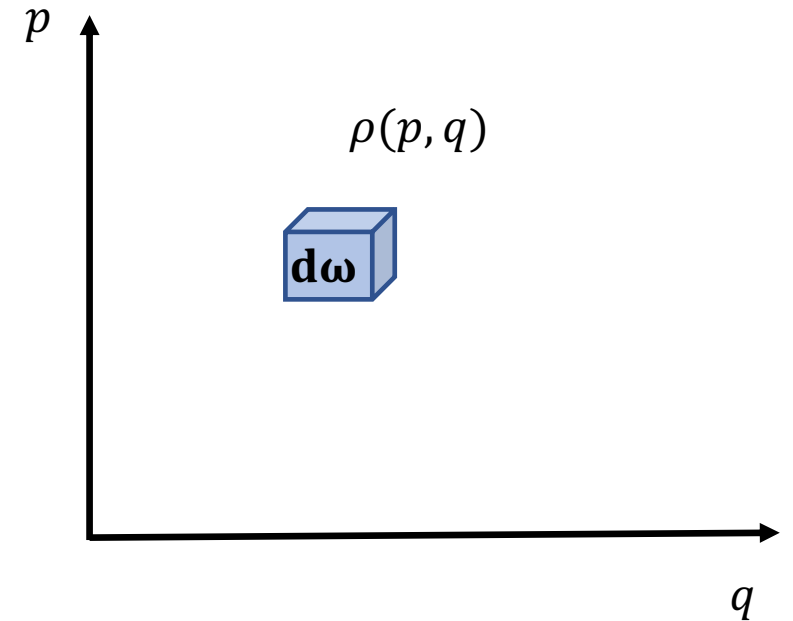
$$\int \rho(p, q) d\omega = 1$$

- Macroscopic thermodynamic variables are determined as averages over $\rho(p, q)$
 - E.g. internal energy

$$U = \langle H(p, q) \rangle = \int \rho(p, q) H(p, q) d\omega$$

In general

$$\langle F \rangle(t) = \int \rho(p, q, t) F(p, q) d\omega$$



Liouville's theorem

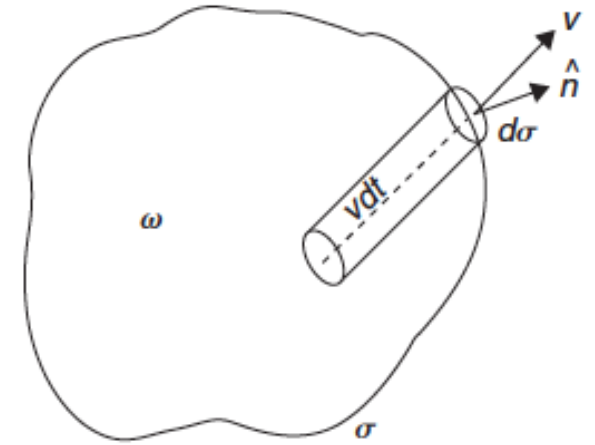
- Arbitrary volume ω with the enclosing surface σ . The rate at which the number of systems (representative points) increases with time is

$$\frac{\partial}{\partial t} \int_{\omega} d\omega \rho$$

- The net rate at which the representative points flow across the boundary σ

$$\int_{\sigma} d\sigma \rho \mathbf{v} \cdot \mathbf{n} = \int_{\omega} d\omega \nabla \cdot (\rho \mathbf{v})$$

- Conservation of the number of representative points (no sinks or sources): $\frac{\partial}{\partial t} \int_{\omega} d\omega \rho = - \int_{\omega} d\omega \nabla \cdot (\rho \mathbf{v})$



Equation of continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad \mathbf{v} = (\dot{q}, \dot{p}) = (\dot{q}_1, \dot{q}_2, \dots, \dot{q}_{3N}, \dot{p}_1, \dot{p}_2, \dots, \dot{p}_{3N})$$

- Use the Hamiltonian eq. of motion

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] = 0$$

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right] = 0 \rightarrow \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \quad \text{Liouville's theorem}$$

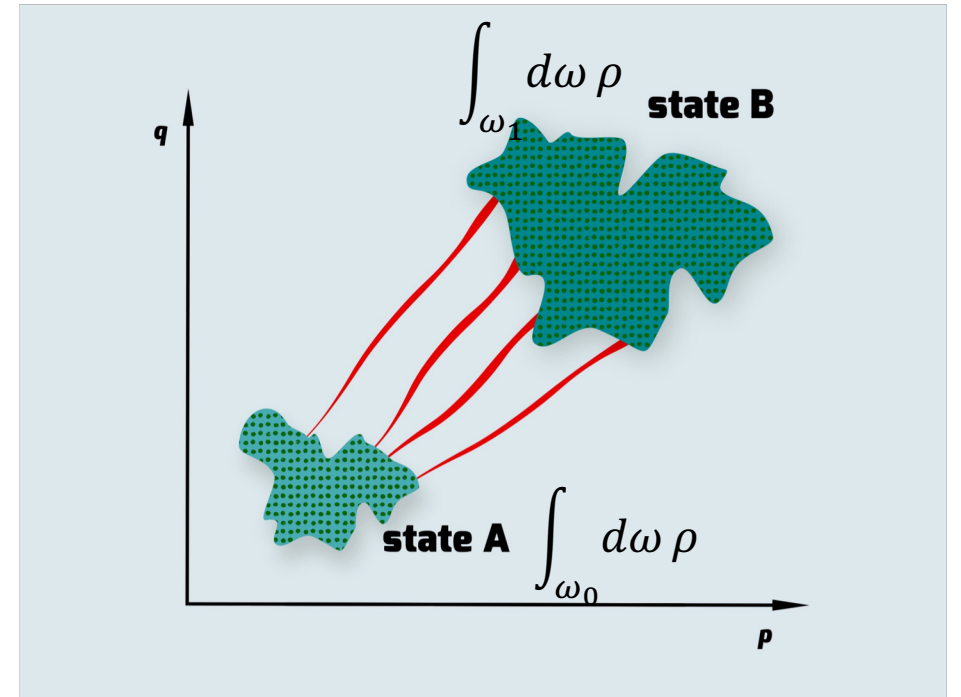
Liouville's theorem for equilibrium systems

- For systems in thermodynamic equilibrium, all the averages are time-independent, hence the density of states is time-independent
- Liouville's equation implies then that

$$\{\rho, H\} = 0$$

- *General solution of ensemble density commutes with the Hamiltonian*

$$\rho = \rho(H)$$



Liouville's theorem and ergodicity

- Ensemble density is time-independent

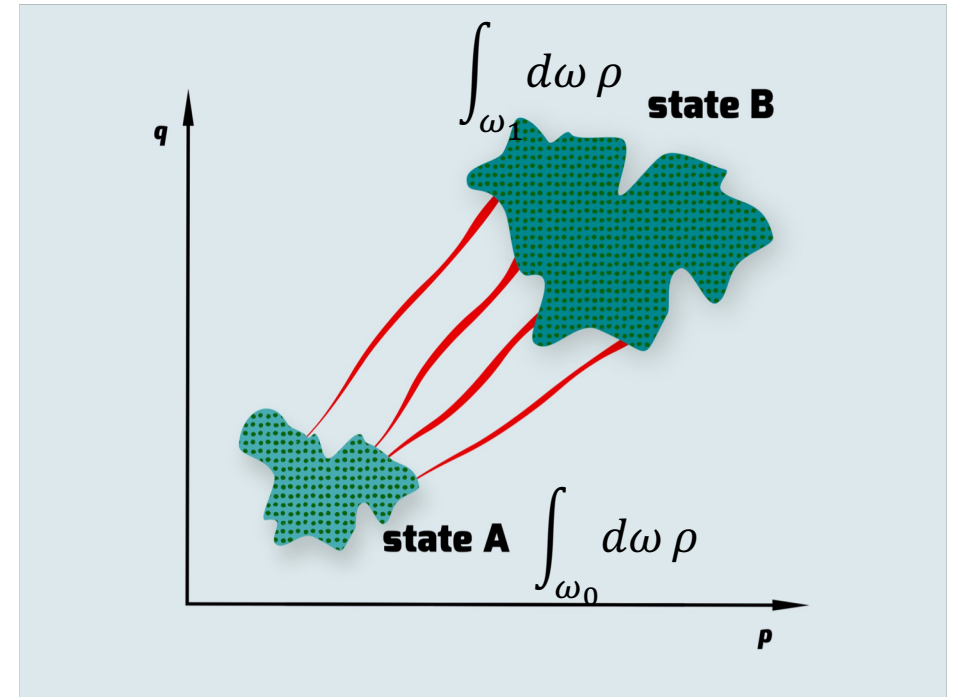
$$\{\rho, H\} = 0$$

- *Particular solution*

$$\rho = \text{const.}$$

- It means that all the available states in the phase space are equally probably for the systems in the ensemble
- This ensemble is called microcanonical ensemble and the states are called microstates
- Systems in the microcanonical ensemble are ergodic

$$\begin{aligned}\langle F(p, q) \rangle &= \int \rho(p, q) F(p, q) d\omega \text{ (ensemble average)} \\ &= \text{time-average of } F\end{aligned}$$



Statistical Equilibrium Ensembles

- Microcanonical ensemble $\rho(\mathbf{p}, \mathbf{q}) \sim \text{const.}$
 - Describes a system at a fixed energy, volume and number of particles
 - Each possible state at fixed U and N has an equal probability
- Canonical ensemble. $\rho(\mathbf{p}, \mathbf{q}) \sim e^{-\frac{H(\mathbf{p}, \mathbf{q})}{kT}}$
 - describes a system at a fixed volume and number of particles, and that is thermal equilibrium with a heat bath at a fixed temperature T
 - The energy fluctuates according to a probability distribution function (PDF) $P(E)$ determined by $\rho(\mathbf{p}, \mathbf{q})$
 - Internal energy U of the thermodynamic system is fixed by T and determined as an average $U = \langle E \rangle$
- Grand canonical ensemble $\rho(\mathbf{p}, \mathbf{q}, \mathbf{n}) \sim e^{-\frac{H(\mathbf{p}, \mathbf{q})}{kT} + \frac{\mu n}{kT}}$
 - describes a system with varying number of particles and that is in thermal and chemical equilibrium with a thermodynamic reservoir, i.e. fixed T and μ
 - Particle number and energy are fluctuating variables drawn from corresponding PDFs $P(E)$, $P(n)$
 - The average energy and number of particles are fixed by the temperature and chemical potential

Microcanonical ensemble $\rho(p, q) \sim \text{const}$

- Describes a system at a fixed energy U , volume V and number of particles N
- Each possible state at fixed U and N has an equal probability

$$\rho(p, q) = \frac{1}{\Sigma} \delta(H(p, q) - U),$$

with the proportionality constant fixed by the normalization condition of the ensemble density $\int \rho(p, q) d\omega = 1$

Microcanonical density of states $\Sigma(U, V, N)$

$$\Sigma(U) = \int d\omega \delta(H(p, q) - U)$$

Microcanonical ensemble

- Microcanonical density of states $\Sigma(U, V, N)$

$$\Sigma(U) = \int d\omega \delta(H(p, q) - U)$$

- *Phase space volume with energy less than or equal to U,*

$$\Omega(U) = \int_{H(p,q) \leq U} d\omega$$

$$\Sigma(U) = \frac{\partial}{\partial U} \Omega(U) \text{ and } \Omega(U) = \int_0^U dE \Sigma(E)$$

Correspondence to the thermodynamics

Phase space volume with energy less than or equal to U ,

$$\Omega(U) = \int_{H(p,q) \leq U} d\omega$$

$\Omega(E) \sim$ multiplicity of a microstate, except is dimensional.

If we rescale $d\omega \equiv \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^N}$

$$\Omega(U) := \frac{1}{(2\pi\hbar)^N} \int_{H(p,q) \leq U} d^{3N}p d^{3N}q$$

- *Boltzmann Entropy*

$$S(U) = k \ln \Omega(U)$$

Thermodynamics in the microcanonical ensemble

Boltzmann Entropy

$$S(U, V, N) = k \ln \Omega (U, V, N)$$

Temperature $\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N}$

Pressure $\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{U, N}$

Chemical potential $\frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{U, V}$

Helmholtz free energy $F = U - TS = U - kT \ln \Omega$

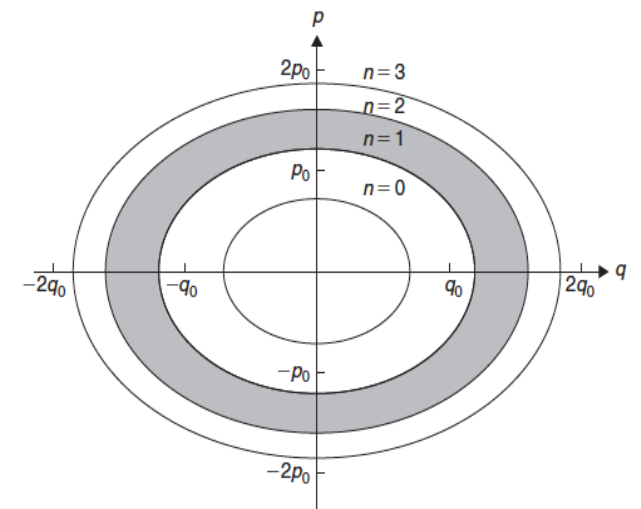
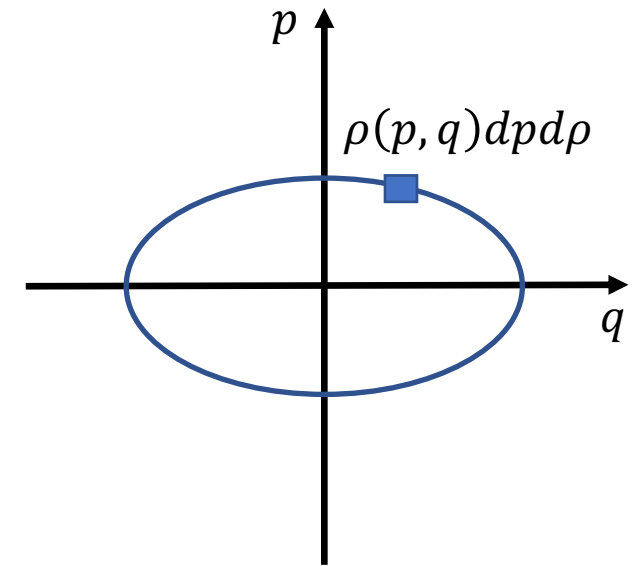
Microcanonical ensemble examples: 1D harmonic oscillator

$$\ddot{q} + \omega_0^2 q = 0$$

- Solution: $q(t) = A \cos(\omega_0 t + \phi)$, $p(t) = m \dot{q} = -Am\omega_0 \sin(\omega_0 t + \phi)$
- Motion at constant total energy $\frac{p^2}{2mU} + \frac{q^2}{2U/m\omega_0^2} = 1$ is on an **ellipse**
- Phase space volume of a shell corresponding to an energy gap Δ :

$$\frac{1}{h} \int_{(U-\frac{1}{2}\Delta) \leq H(p,q) \leq (U+\frac{1}{2}\Delta)} dp dq = \frac{2\pi \left(U + \frac{1}{2}\Delta \right)}{h\omega_0} - \frac{2\pi \left(U - \frac{1}{2}\Delta \right)}{h\omega_0} = \frac{2\pi\Delta}{h\omega_0} = \frac{\Delta}{\hbar\omega_0}$$

- « h » is the minimum phase space shell volume between two consecutive trajectories of a quantum harmonic oscillator with energy levels $\epsilon_n = \left(\frac{1}{2} + n \right) \hbar\omega_0$



1D harmonic oscillator: thermodynamics

- Phase space volume :

$$\Omega(U) = \frac{1}{2\pi\hbar} \int_{H(p,q) \leq U} dp dq = \frac{\text{Area}}{2\pi\hbar} = \frac{U}{\hbar\omega_0}$$

- Entropy:

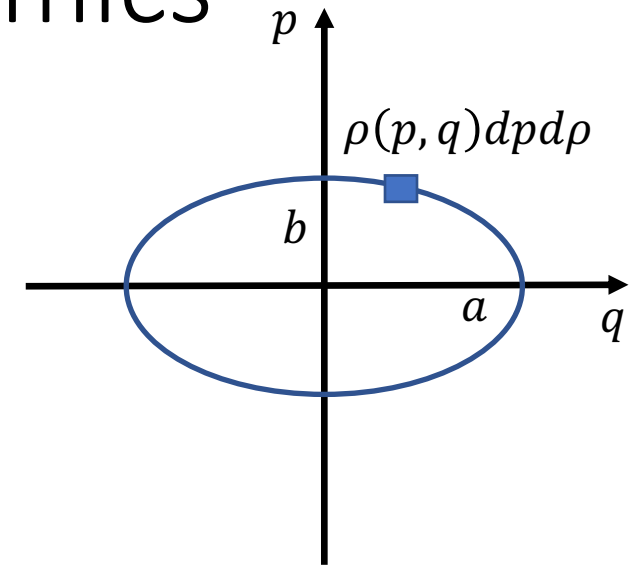
$$S = k \ln(\Omega) \rightarrow S(U) = k \ln\left(\frac{U}{\hbar\omega_0}\right)$$

- Temperature:

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{k}{U} \rightarrow U = kT$$

Equipartition of energy: an oscillator in 1D has 2 degrees of freedom (1 translational and 1 vibrational),

$$\text{hence } U(T) = 2 \cdot \left(\frac{1}{2} kT\right) = kT$$



$$\frac{p^2}{2mU} + \frac{q^2}{2U/m\omega_0^2} = 1$$

$$A = \pi ab$$

$$A = \pi \sqrt{2mU} \sqrt{\frac{2U}{m\omega_0^2}} = \frac{2\pi U}{\omega_0}$$

Microcanonical ensemble of free particle

Hamiltonian of N non-interacting particles in 3D

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

- Microcanonical density of states

$$\Sigma(U) = \frac{1}{(2\pi\hbar)^{3N}} \int d^{3N}p d^{3N}q \delta\left(\sum_{i=1}^{3N} \frac{p_i^2}{2m} - U\right)$$

$$\Sigma(U) = \frac{V^N}{(2\pi\hbar)^{3N}} \int d^{3N}p \delta\left(\sum_{i=1}^{3N} \frac{p_i^2}{2m} - U\right)$$

Microcanonical ensemble of free particle

- Equation of a **hyper-sphere** in a $3N$ –dimensional momentum space

$$p_1^2 + p_2^2 + \dots + p_{3N}^2 = R^2, \quad R = \sqrt{2mU}$$

- Surface integral over the momentum space

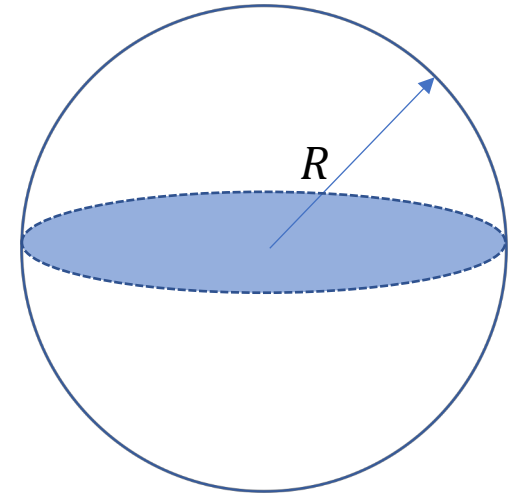
$\int d^{3N}p \delta\left(\sum_{i=1}^{3N} \frac{p_i^2}{2m} - U\right)$ can be evaluated from the volume of the hypersphere V_{3N}

$$V_{3N} = \int_{H(p) \leq U} d^{3N}p$$

- Volume of the hyper-sphere scales with its radius $V_{3N} = C_{3N}R^{3N}$
- Area of the hyper-sphere is related to the volume by

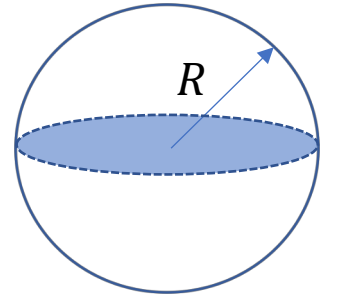
$$S_{3N-1} = \frac{dV_{3N}}{dR} = 3NC_{3N}R^{3N-1}$$

- How do we compute the constant C_{3N} ?*



Microcanonical ensemble of free particle

- How do we compute the constant C_{3N} ?
- Product of Gaussian integrals = volume integral of a Gaussian



$$\prod_i^{3N} \int_{-\infty}^{+\infty} dx_i e^{-x_i^2} = \pi^{\frac{3N}{2}} = \int dV_{3N} e^{-R^2} = 3N C_{3N} \int dR R^{3N-1} e^{-R^2}$$

$\Gamma(z)$ integral:

$$\int_0^{\infty} dR (R^2)^{\frac{3N-1}{2}} e^{-R^2} =_{(x=R^2)} \frac{1}{2} \int_0^{\infty} dx x^{\frac{3N}{2}-1} e^{-x} = \frac{1}{2} \Gamma\left(\frac{3N}{2}\right)$$

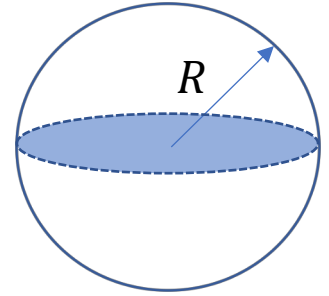
$$\pi^{\frac{3N}{2}} = \frac{3N}{2} C_{3N} \Gamma\left(\frac{3N}{2}\right) \rightarrow C_{3N} = \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2} + 1\right)} = \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}$$

$$C_2 = \frac{\pi}{(1)!} \rightarrow \Omega_{2D} = \pi R^2$$

$$C_2 = \frac{\pi^{3/2}}{\left(\frac{3}{2}\right)!} = \frac{\pi^{3/2}}{3\sqrt{\pi}/4}$$

$$\rightarrow \Omega_{3D} = \frac{4\pi}{3} R^3$$

Microcanonical ensemble of free particle



- *Microcanonical phase space volume of free particles*

$$\Omega(U) = \frac{V^N}{(2\pi\hbar)^{3N}} V_{3N}, \text{ and } V_{3N} = C_{3N} (2mU)^{\frac{3N}{2}}$$

$$\Omega(U) = \frac{V^N}{(2\pi\hbar)^{3N}} \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} (2mU)^{\frac{3N}{2}}$$

$$\Sigma(U) = \frac{\partial \Omega(U)}{\partial U}$$

Entropy of the microcanonical ensemble

- *Indistinguishable particles*: the number of microstates is reduced by $N!$

$$\Omega \rightarrow \frac{\Omega}{N!}$$

- *Boltzmann's formula*

$$S = k \ln \frac{\Omega}{N!}$$

Entropy of the free particles in the microcanonical ensemble

- Phase space volume $\Omega(U) = \frac{V^N}{(2\pi\hbar)^{3N}} \frac{1}{(3N/2)!} (2\pi mU)^{\frac{3N}{2}}$

$$\ln \Omega \sim \frac{3N}{2} \ln U \sim \frac{3N-1}{2} \ln U \sim \ln \Sigma(U) \quad (\text{In high dimensions, the volume and area scales the same!})$$

$$S = k \ln \frac{\Omega}{N!}$$

- $S = kN \ln \left[V \left(\frac{mU}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right] - k \ln \left(\frac{3N}{2} \right)! - k \ln(N!)$

Using Stirling approx $N! \sim N \log N - N$

$$S(U, V, N) = kN \left\{ \frac{5}{2} + \ln \frac{V}{N} \left(\frac{mU}{3\pi N \hbar^2} \right)^{\frac{3}{2}} \right\}$$

Thermodynamic properties of the ideal gas

- *Thermodynamic potential*

$$S(U, V, N) = kN \left\{ \frac{5}{2} + \ln \frac{V}{N} \left(\frac{mU}{3\pi N \hbar^2} \right)^{\frac{3}{2}} \right\}$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV + \mu dN$$

- *Temperature*

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N} = kN \frac{\partial}{\partial U} \ln U^{\frac{3}{2}} = \frac{3Nk}{2} \frac{1}{U} \rightarrow U = \frac{3}{2} NkT$$

- *Pressure*

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{T, N} = \frac{Nk}{V} \rightarrow PV = NkT$$

- *Sackur-Tetrode formula*

$$S = kN \left\{ \mathbf{1} + \ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{me}{2\pi \hbar^2} \right) \right\}$$