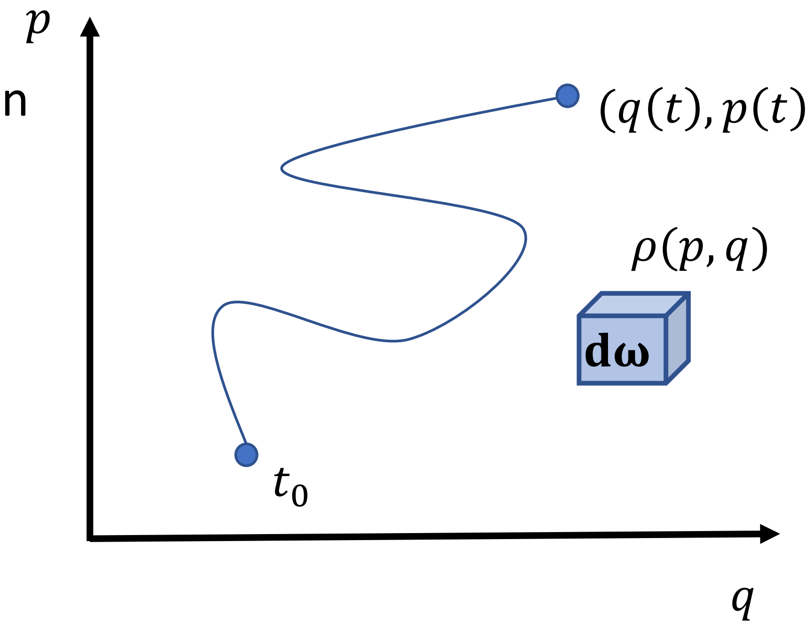
Lecture 4
23.01.2019

Canonical ensemble

Phase space and ensemble density

$(6N) - dimensional\ in\ 3D$

- $(p,q)_{2dN} = (p_1, \dots, p_{dN}, q_1, \cdots, q_{dN})$
- 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)
  - ➢ Ensemble density $\rho(p,q)$ is the probability density of finding the system in state (p,q)



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

Number of systems which occupy the microstates between (p,q) and $(p+dp, q+dq)$ is

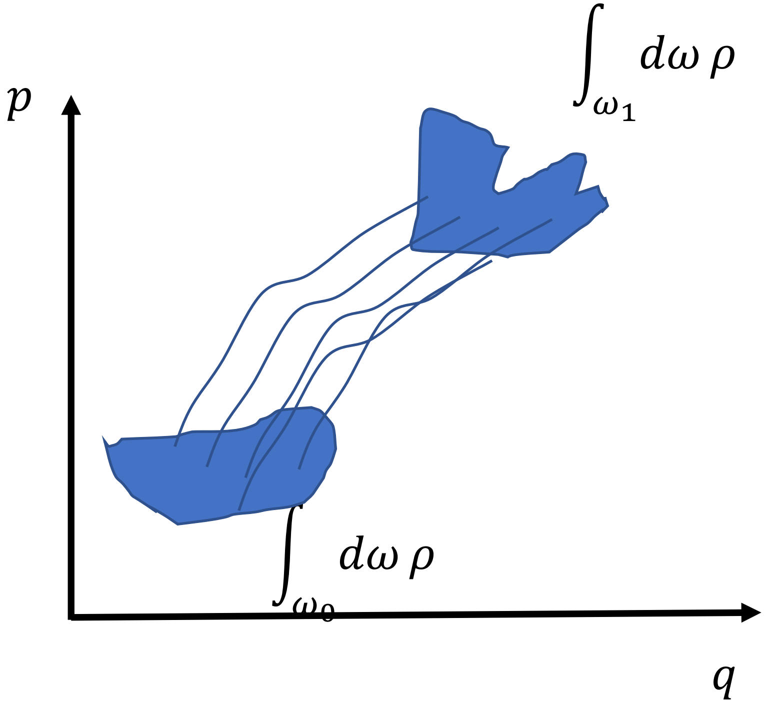
$$\rho(p,q)d\omega$$

  - ➢ Macroscopic thermodynamic variables are determined as averages over $\rho(p,q)$

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

Liouville's theorem for equilibrium systems

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



- 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

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

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

$$\boldsymbol{\rho}=\boldsymbol{\rho}(\boldsymbol{H})$$

Statistical Equilibrium Ensembles

Microcanonical ensemble: $\rho(p,q) \sim const.\, at\ fixed\ U \rightarrow \rho(p,q) = \frac{1}{\Sigma}\delta(H(p,q) - U)$

- Microcanonical density of states: $\Sigma(U,V,N) = \int d\omega\, \delta(H(p,q) - U), \mathrm{d}\omega = \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N}}$

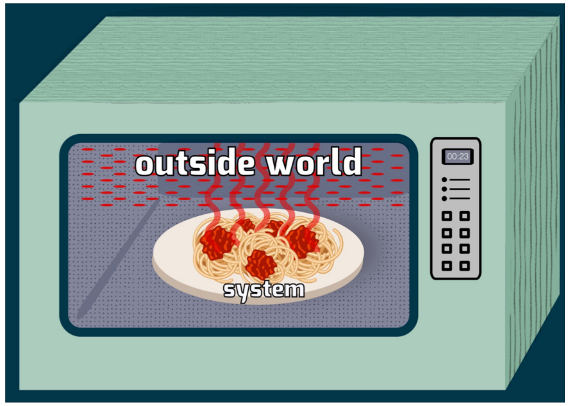
- Describes a system at a fixed energy, volume and number of particles
- **Each possible state at fixed U and N has an equal probability**

- Phase space volume: $\Omega(U,V,N) = \int_{H(p,q)\leq U} d\omega\ \ \delta(H(p,q) - U)$

- Boltzmann's formula (correspondence to thermodynamics)

Entropy: $\mathbf{S(U,V,N) = k\ ln\ [\Omega(\mathit{U,V,N})]}$

Statistical Equilibrium Ensembles



- Canonical ensemble. Derive that the equilibrium distribution of canonical ensembles

$$\rho(p,q) \sim e^{-\frac{H(p,q)}{kT}}$$

  - 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 $\rho(p,q)$
  - Internal energy U of the thermodynamic system is fixed by T and determined as an average $U = \langle E \rangle$

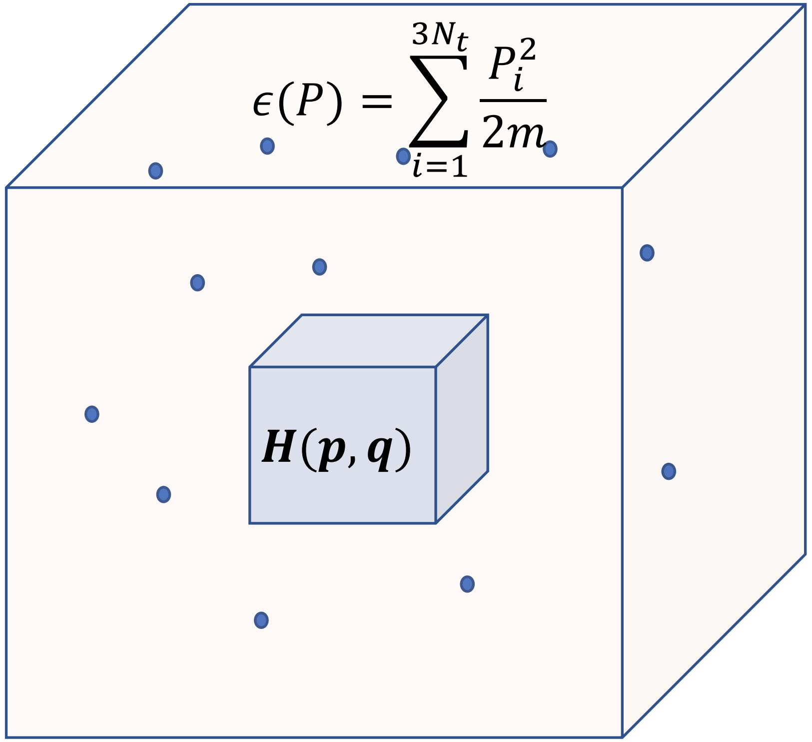
Canonical ensemble

- Describes a system that is in thermal equilibrium with a heat bath at a **fixed temperature T**
  - system+heat bath = **isolated system**
  - Heat bath≡Ideal gas (P,Q) with Hamiltonian

$$\epsilon(P) = \sum_{i=1}^{3N_t} \frac{P_i^2}{2m}, N_t\ particles\ in\ 3D$$

  - Ensemble density for the **isolated system** is in the **microcanonical ensemble at a fixed energy $\boldsymbol{U_{total}}$**

$$\rho(p,q,P,Q) \sim \delta(H(p,q) + \epsilon(P) - U_{total})$$



Canonical ensemble $Z(T,V,N)$

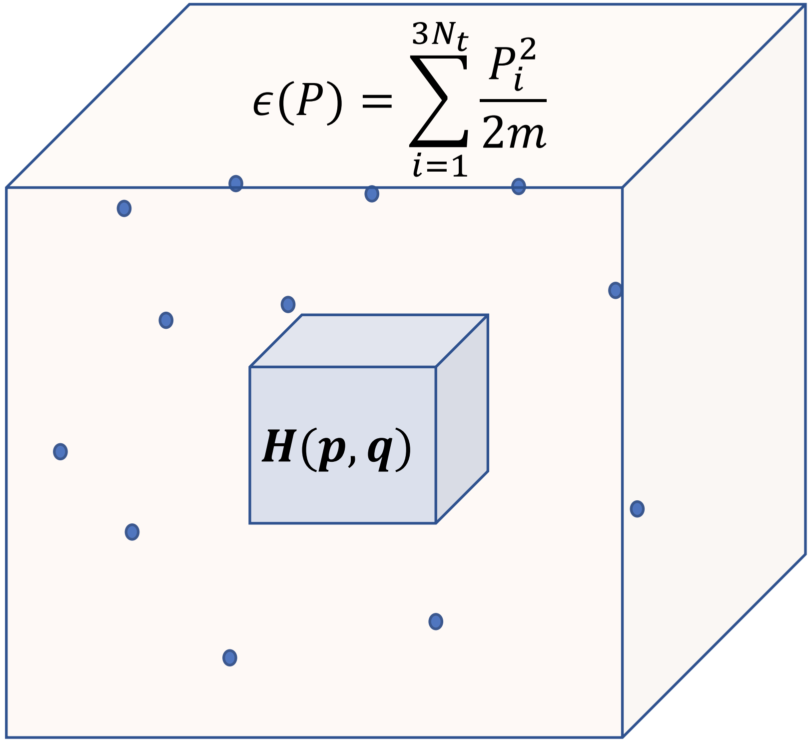
$$\rho(p,q,P,Q) \sim \delta(H(p,q) + \epsilon(P) - U_{total})$$

- Integrate out the thermal bath d.o.f. (P,Q) to find the ensemble density of the system

$$\rho(p,q) \sim \int d^{3N_t}Q\, d^{3N_t}P\, \delta(H(p,q) + \epsilon(P) - U_{total})$$

$$\rho(p,q) \sim \int d\omega_t\, \delta(H(p,q) + \epsilon(P) - U_{total})$$

- Phase space volume of **ideal gas in the** thermostate $\omega_t(\epsilon) \sim \epsilon^{\frac{3N_t}{2}}$
- Change of variables $\mathrm{d}\omega_t \sim \epsilon^{\frac{3N_t}{2}-1}d\epsilon$



Canonical ensemble $Z(T,V,N)$

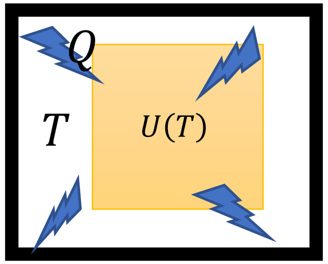
$$\rho(p,q) \sim \int d\omega_t \delta(H(p,q) + \epsilon(P) - U_{total})$$

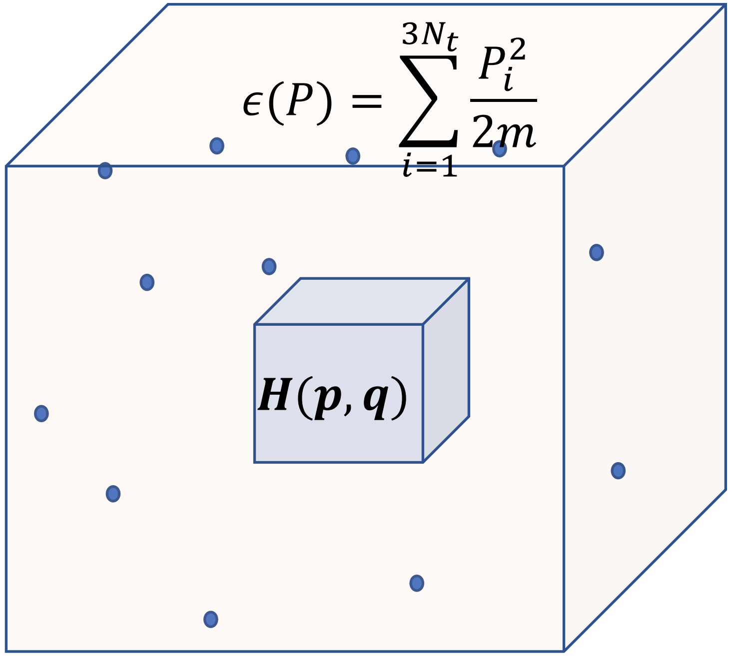
- Phase space volume of ideal gas thermostate $\omega_t(\epsilon) \sim \epsilon^{\frac{3N_t}{2}}$
- Change of variables $\mathrm{d}\omega_t \sim \epsilon^{\frac{3N_t}{2} - 1} d\epsilon$

- $\rho(p,q) \sim \int d\epsilon \; \epsilon^{\frac{3N_t}{2} - 1} \delta(H(p,q) - U_{total} + \epsilon)$

- $\rho(p,q) \sim \left(U_{total} - H(p,q)\right)^{\frac{3N_t}{2} - 1} \sim \left(1 - \frac{H(p,q)}{U_{total}}\right)^{\frac{3N_t}{2} - 1}$

(keep onlyt the $p, q - dependent$ terms)





Canonical ensemble

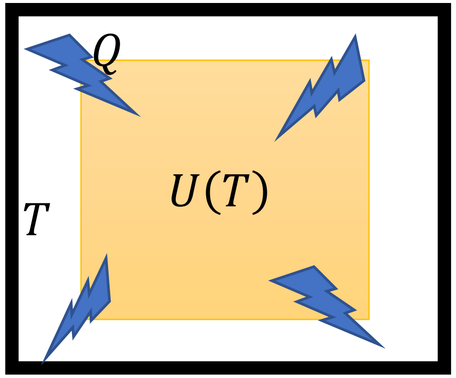
- The total energy U_{total} is dominated by the energy of the thermostate, hence it depends on the temperature and the number of particles in the thermostat as

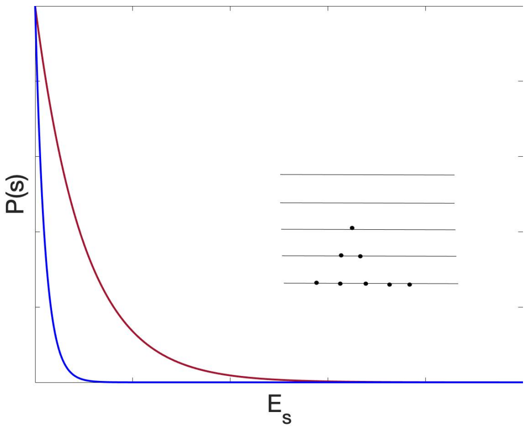
$$U_{total} \approx \epsilon = \frac{3}{2} N_t kT$$

- Substitute this in the expression for the ensemble density

$$\rho(p,q) \sim \left(1 - \frac{H(p,q)}{U}\right)^{\frac{3N_t}{2}-1} \sim \left(1 - \frac{H(p,q)}{kT}\frac{1}{\frac{3N_t}{2}}\right)^{\frac{3N_t}{2}}, for\ N_t \rightarrow \infty \text{ approaches}$$

$$\boldsymbol{\rho(p,q) \sim e^{-\frac{H(p,q)}{kT}}}$$





System+Thermal bath (R) = isolated system

The probability that the system is in a given <u>microstate</u> is proportional to the probability that the thermal bath is in *any state that accomodate the particular microstate of the system (hence the probability to be in a <u>macrostate</u>)*

The system can exchange energy with the thermal bath $\Delta\epsilon = -\Delta \mathrm{E}$
Probability ratio between two microstates ($(p_1, q_1) \equiv s_1, (p_2, q_2) \equiv s_2$)

$$\frac{\rho(p_1, q_1)}{\rho(p_1, q_1)} = \frac{\Omega_R(s_1)}{\Omega_R(s_2)} = e^{\frac{\Delta S_R}{k}} = e^{\frac{\Delta\epsilon}{kT}} = e^{-\frac{\Delta E}{kT}} \rightarrow \rho_s \sim e^{-\frac{E_s}{kT}}$$

$$E(s) \equiv H(p, q)$$

Probability of the system in a specific configuration at fixed temperature T

$$\boldsymbol{\rho(p, q) = \frac{1}{Z(T)} e^{-\frac{H(p,q)}{kT}}}$$

Canonical ensemble $Z(T,V,N)$

- **Boltzmann's distribution** $\boldsymbol{\rho(p,q) = \frac{1}{Z} e^{-\frac{H(p,q)}{kT}}}$
- From the normalization condition $\int d\omega \rho(p,q) = 1 \rightarrow$

$$\boldsymbol{Z = \int d\omega e^{-\frac{H(p,q)}{kT}}}$$

- **Canonical Partition function**

$$\mathbf{Z(T,V,N) \equiv \text{sum over all states weighted by Boltzmann factor } e^{-\frac{H(p,q)}{kT}}}$$

- $Z(T,V,N)$ does not depend on the nature of the thermostat

Canonical ensemble: Energy fluctuations

- Number of systems in a **macrostate** with energy between E and $E + dE$ equals the number of systems that occupy the corresponding microstates between (p, q) and $(p + dp, q + dq)$

$$P(E)dE = \rho(p,q)d\Omega$$

- Using the canonical distribution of the density of states

$$P(E) = \rho(p,q)\left|\frac{d\Omega}{dE}\right| \rightarrow P(E) = \frac{1}{Z}e^{-\frac{E}{kT}}\left|\frac{d\Omega}{dE}\right|$$

$$\underset{\text{macrostate}}{P(E)} = \frac{\Sigma(E)}{Z(T)}\underset{\text{microstate}}{e^{-\frac{E}{kT}}}$$

Ensemble equivalence

- Correspondence between microcanonical and canonical ensembles
- **Laplace transform** of the microcanonical density of states $\boldsymbol{\Sigma(E)}$

$$Z(T,V) = \int d\omega \, e^{-\beta H(p,q)}, \;\; \beta = \frac{1}{kT}$$

$$Z(T,V) = \int d\omega \left[\int dE e^{-\beta E} \delta(H(p,q) - E)\right]$$

$$Z(T,V) = \int dE \, e^{-\beta E}\left[\int d\omega \delta(H(p,q) - E)\right]$$

$$\boldsymbol{Z(T,V) = \int dE \, e^{-\beta E}\Sigma(E)}$$

- Normalization condition for $P(E) = \frac{\Sigma(E)}{Z} \, e^{-\beta E}$: $\int dE \, P(E) = 1 \rightarrow Z(T,V) = \int dE \, e^{-\beta E}\Sigma(E)$

Thermodynamic correspondence

- Correspondence between different thermodynamic constraints:

Legendre transform: $F(T,V) = U(S,T) - TS$

- Correspondence between different statistical ensembles:

Laplace transform:

$$\boldsymbol{Z(T) = \int dE\, e^{-\beta E}\, \Sigma(E), where\, \Sigma(\mathrm{E}) \approx \Omega(\mathrm{E}) = \mathrm{e}^{\frac{S}{k}}}$$

$$\boldsymbol{Z(T) = \int dE\, e^{-\beta(E-TS)} \approx e^{-\beta(\langle E\rangle - TS(\langle E\rangle))}}$$

- $\boldsymbol{Z(T) = e^{-\beta F(T)}}$, $\quad F(T) = \langle E\rangle(T) - TS(\langle E\rangle)$
- $\boldsymbol{F(T) = -kT\, ln\, [Z(T)]}$

Canonical ensemble: average energy

The average energy corresponds to the internal energy U of the thermodynamic system and is fixed by T

- Average energy

$$\langle E\rangle = \frac{1}{Z}\int d\omega\, H(p,q)\, e^{-\beta H(p,q)}$$

$$\langle E\rangle = -\frac{1}{Z(T)}\frac{\partial}{\partial\beta}\int d\omega\, e^{-\beta H(p,q)}$$

$$\boldsymbol{\langle E\rangle = -\frac{1}{Z(T)}\frac{\partial}{\partial\beta}Z(T) = -\frac{\partial}{\partial\beta}\, ln\, Z(T)}$$

Canonical ensemble: average energy

The average energy corresponds to the internal energy U of the thermodynamic system and it is fixed by T

- Average energy

$$\langle E\rangle = \int dE\ E\ P(E)$$

$$\langle E\rangle = \frac{1}{Z(T)}\int dE\ E\ e^{-\beta E}\Sigma(E)$$

$$\langle E\rangle = -\frac{1}{Z(T)}\frac{\partial}{\partial\beta}\int dE\ e^{-\beta E}\Sigma(E)$$

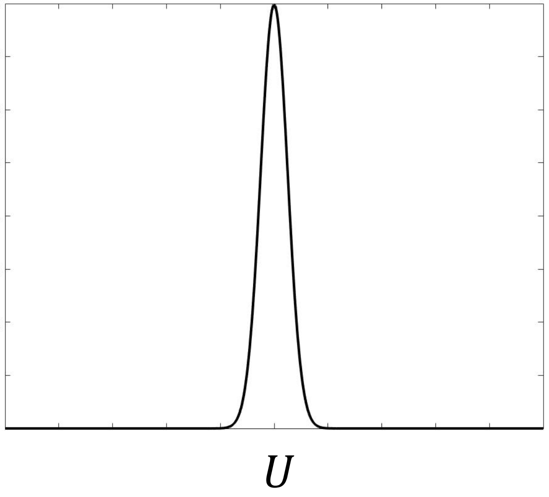
$$\boldsymbol{\langle E\rangle = -\frac{1}{Z(T)}\frac{\partial}{\partial\beta}Z(T) = -\frac{\partial}{\partial\beta}\ ln\ Z(T)}$$

Canonical ensemble: average energy

- Average energy

$$\mathrm{U} = \langle \boldsymbol{E} \rangle = -\frac{\boldsymbol{\partial}}{\boldsymbol{\partial\beta}} \boldsymbol{log\, Z(T)}$$

- **The system has the highest probability to have an energy given by the average U**



  - $P(E) = \frac{1}{Z}\, e^{\beta(E-TS(E))}$
  - Let us look at the distribution of energy around the mean: $E = U + \delta E$
    - $S(E) = S(U) + \frac{\partial S}{\partial E}|_{E=U}\delta E + \frac{1}{2}\frac{\partial^2 S}{\partial E^2}|_{E=U}\delta E^2 + \cdots$

$$= S(U) + \frac{1}{T}\delta E + \frac{1}{2}\frac{\partial}{\partial U}\left(\frac{1}{T}\right)\,\delta E^2 + \cdots$$

$$= S(U) + \frac{1}{T}\delta E - \frac{1}{2C_V T^2}\delta E^2 + \cdots$$

$$P(E) \approx \frac{1}{Z}\, e^{\beta(U-TS(U))} e^{-\frac{1}{2C_V k T^2}(E-U)^2}$$

$$\sigma_E = \sqrt{C_V k T^2}, \qquad \mathrm{P(E)} \sim e^{\frac{\delta E^2}{2\sigma_E^2}}$$

$$\frac{\sigma_E}{U} = \frac{\sqrt{C_V k}\,T}{U} \sim \frac{1}{\sqrt{C_V}} \sim \frac{1}{\sqrt{N}} \to 0$$

Canonical ensemble: energy fluctuations

- Fluctuations around the average energy

$$\sigma_E^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle \Delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

  - $\langle E^2 \rangle = \frac{1}{Z(T)} \int dE\, E^2\, e^{-\beta E} \Sigma(E)$
  - $\langle E^2 \rangle = \frac{1}{Z(T)} \frac{\partial^2}{\partial \beta^2} Z(T)$

- $\boldsymbol{\langle \Delta E^2 \rangle = \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z - \left(\frac{1}{Z} \frac{\partial}{\partial \beta} Z \right)^2 = \frac{\partial^2}{\partial \beta^2} \log Z}$

Canonical ensemble: Ideal gas

- $Z(T,V,N) = \frac{1}{(2\pi\hbar)^{3N}} \int d^{3N}q d^{3N}p \ \prod_i \ e^{-\beta \frac{p_i^2}{2m}} = \frac{V^N}{(2\pi\hbar)^{3N}} \int d^{3N}p \ \prod_i \ e^{-\beta \frac{p_i^2}{2m}}$

- $Z(T,V,N) = \frac{V^N}{(2\pi\hbar)^{3N}} \left(\int dp \ e^{-\frac{p^2}{2mkT}} \right)^{3N}$, $\qquad \int_{-\infty}^{+\infty} dp \ e^{-\frac{p^2}{2mkT}} = \sqrt{2\pi mkT}$

- $Z(T,V,N) = \frac{V^N}{(2\pi\hbar)^{3N}} (2m\pi kT)^{\frac{3N}{2}}$

$\boldsymbol{Z = \frac{V^N}{\Lambda^{3N}(T)}}$, where $\Lambda(\mathrm{T}) = \frac{1}{\sqrt{2m\pi kT}}$ is the thermal wavelength of a particle

Canonical ensemble: Ideal gas

- $Z(T, V, N) = \frac{V^N}{\Lambda^{3N}} = Z_1^N$

- Particles are indistinguishable, thus we must divide the N-particle partition function by $N!$

$$Z(T, V, N) = \frac{V^N}{\mathrm{N!}\,\Lambda^{3N}} = \frac{Z_1^N}{N!} = e^{-\beta F(T,V,N)}$$

Thermodynamic correspondence

$$\boldsymbol{Z(T, V, N) = \frac{Z_1^N}{N!} = e^{-\beta F(T,V,N)}}$$

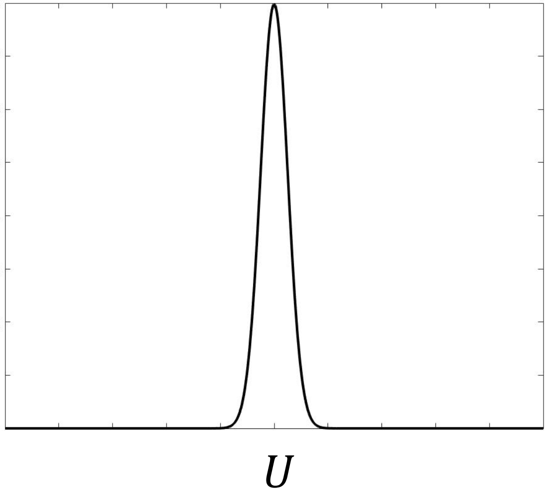
Ideal gas: Thermodynamics

$$F(T,V,N) = -kT\left[\ln\left(\frac{V^N}{\Lambda^{3N}}\right) - \ln N!\right], \qquad \ln N! \approx N\ln N - N$$

$$F(T,V,N) = -NkT\left[\ln\left(\frac{V}{N\Lambda^3(T)}\right) + 1\right]$$

- Thermodynamic identity: $dF = -SdT - PdV + \mu dN$
- $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk[\ln\left(\frac{V}{N\Lambda^3(T)} + 1\right) + \frac{3N}{2}k = \frac{-F+U}{T}$
- $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V}$
- $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\left[\log\left(\frac{V}{N\Lambda^3(T)}\right) + 1\right] + NkT\frac{1}{N} = -kT\ln\left(\frac{V}{N\Lambda^3(T)}\right) \rightarrow \frac{V}{N\Lambda^3(T)} = e^{-\beta\mu}$

Ideal gas: energy fluctuations



- Average energy and fluctuations:
- $Z(T,V,N) = \frac{V^N}{\mathrm{N!}\Lambda^{3N}} = \frac{V^N}{N!}(2\pi mkT)^{\frac{3N}{2}}$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\log Z = -\frac{3N}{2}\frac{\partial}{\partial\beta}\log\frac{2\pi m}{\beta} = \frac{3N}{2}kT \sim N$$

$$\langle\Delta E^2\rangle = \frac{\partial^2}{\partial\beta^2}\log Z = -\frac{3N}{2}\frac{\partial}{\partial\beta}\frac{1}{\beta} = \frac{3N}{2}k^2T^2 \sim N$$

- $\frac{\sqrt{\langle\Delta E^2\rangle}}{\langle E\rangle} \sim \frac{1}{\sqrt{N}} \to 0$