Lecture 5
29.01.2019
Grand-canonical ensemble

Statistical Equilibrium Ensembles

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

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

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

- Boltzmann's formula (correspondence to thermodynamics)

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

Statistical Equilibrium Ensembles

- Canonical ensemble: describes a system that is in thermal equilibrium with a heat bath at **a fixed temperature T**

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

- Canonical partition function and **Helmholtz free energy**

$$Z(T) = \int d\omega e^{-\beta H(p,q)} = e^{-\beta F(T)}$$

- Energy fluctuates around the average, equilibrium value $U = \langle E \rangle$, with a probability $P(E) = \frac{1}{Z} e^{-\beta(E-TS)}$

$$Z(T,V) = \int dE\, e^{-\beta E} \Sigma(E) = e^{-\beta F(T)}, \qquad F = U - TS(U), \qquad \langle E \rangle = U = -\frac{\partial}{\partial \beta} \ln Z(T)$$

- Energy Fluctuations

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

Fluctuations are much smaller than the average in the thermodynamic limit: $\frac{\sqrt{\langle \Delta E^2 \rangle}}{\langle E \rangle} \sim \frac{1}{\sqrt{N}} \to 0$

Statistical Equilibrium Ensembles

- Microcanonical ensemble $\boldsymbol{\rho(p,q) \sim const}$.
  - 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. $\boldsymbol{\rho(p,q) \sim e^{-\frac{H(p,q)}{kT}}}$
  - 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 $U = \langle E \rangle$
- Grand canonical ensemble $\boldsymbol{\rho(p,q,n) \sim e^{-\frac{H(p,q)}{kT}+\frac{\mu n}{kT}}}$
  - 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

Grand canonical ensemble

- 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
  - system+heat and particle reservoir = closed system

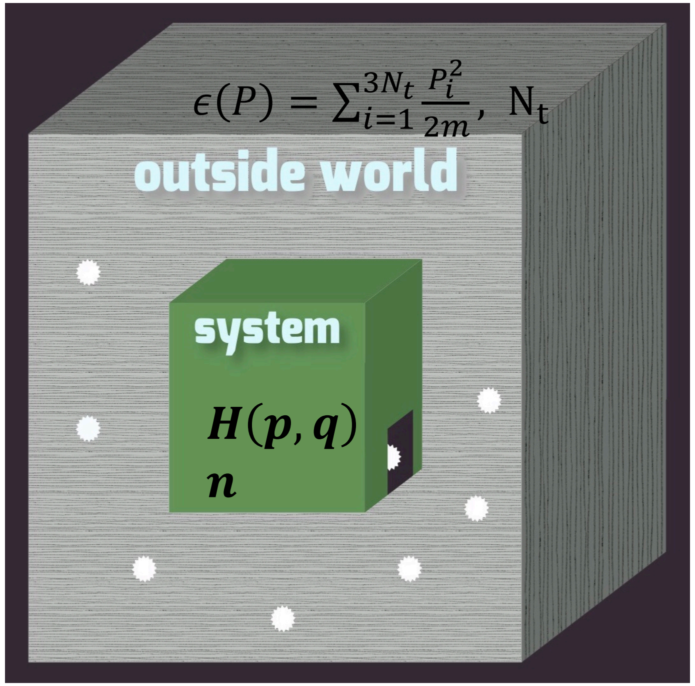
$$N_t + n = N, \qquad N_t \gg n, N_t \sim N$$

  - Reservior $\equiv$ Ideal gas (P, Q, N_t)
  - Distribution of particles between the system and the reservoir

$$\frac{N!}{n!\,N_t!}$$

  - Ensemble density for the closed system is in the microcanonical ensemble

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



Grand canonical ensemble

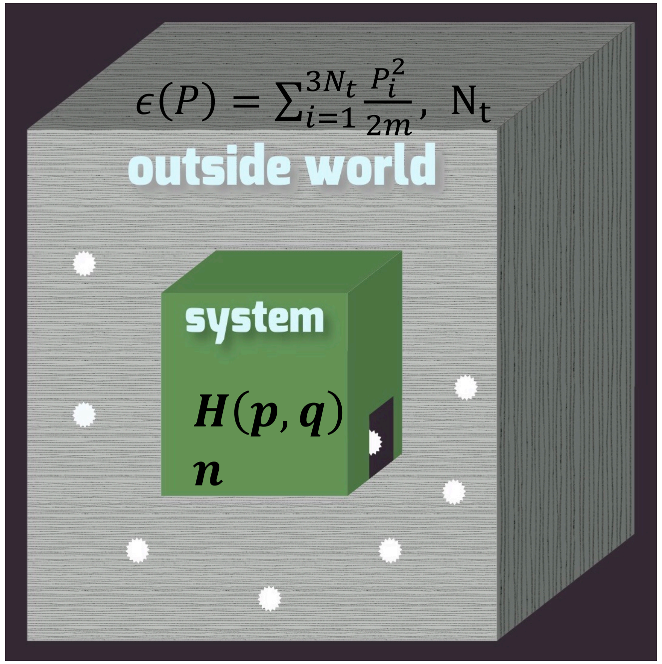
- Integrate out the d.o.f of the reservoir to find the density of state of the system

$$\rho(p,q,n) \sim \frac{N!}{n!N_t!}\frac{1}{(2\pi\hbar)^{3N_t}}\int d^{3N_t}P d^{3N_t}Q\delta(H(p,q)+\epsilon(P)-U_{total})$$

- *Integral over reservoir's d.o.f. = ideal gas microcanonical density of states*

$$\frac{1}{(2\pi\hbar)^{3N_t}}\int d^{3N_t}P d^{3N_t}Q\delta(H(p,q)+\epsilon(P)-U_{total}) = \Sigma_t(U_{total}-H)$$

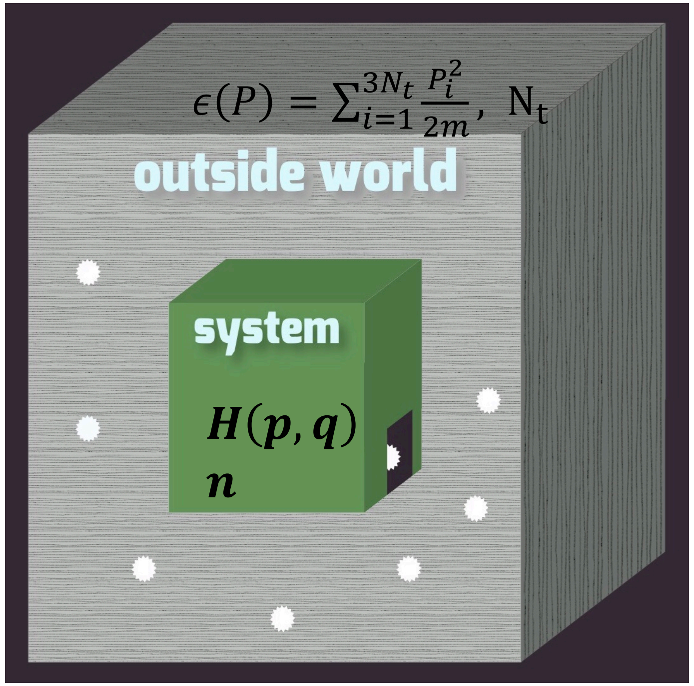
$$\Sigma_t^{ideal\ gas}(E-H) = \frac{V^{N_t}}{h^{3N_t}}\frac{\pi^{\frac{3N_t}{2}}}{\left(\frac{3N_t}{2}\right)!}(2m)^{\frac{3N_t}{2}}\frac{3N_t}{2}(E-H)^{\frac{3N_t}{2}-1}$$



$$\rho(p,q,n) \sim \frac{(N_t+n)!}{n!\,N_t!}\frac{V^{N_t}}{h^{3N_t}}\frac{\pi^{\frac{3N_t}{2}}}{\left(\frac{3N_t}{2}-1\right)!}\frac{(2mU_{total})^{\frac{3N_t}{2}}}{U_{total}}\left(1-\frac{H(p,q)}{U_{total}}\right)^{\frac{3N_t}{2}-1}$$

Grand canonical ensemble $\Xi(T, V, \mu)$

$$\rho(p,q,n) \sim \frac{(N_t+n)!}{n!\,N_t!}\frac{V^{N_t}}{h^{3N_t}}\frac{\pi^{\frac{3N_t}{2}}}{\left(\frac{3N_t}{2}-1\right)!}\frac{(2mU_{total})^{\frac{3N_t}{2}}}{U_{total}}\left(1-\frac{H}{U_{total}}\right)^{\frac{3N_t}{2}-1}$$



- Total energy is determined by the energy of ideal gas

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

$$Hence\ \left(1-\frac{H}{U_{total}}\right)^{\frac{3N_t}{2}-1} = \left(1-\frac{H}{\frac{3N_t}{2}kT}\right)^{\frac{3N_t}{2}-1} \to e^{-\frac{H}{kT}}$$

$$\rho(p,q,n) \sim \frac{(N_t+n)!}{n!\,N_t!}\frac{V^{N_t}}{h^{3N_t}}\frac{\pi^{\frac{3N_t}{2}}}{\left(\frac{3N_t}{2}-1\right)!}\frac{(2mU_{total})^{\frac{3N_t}{2}}}{U_{total}}\,e^{-\beta H(p,q)}$$

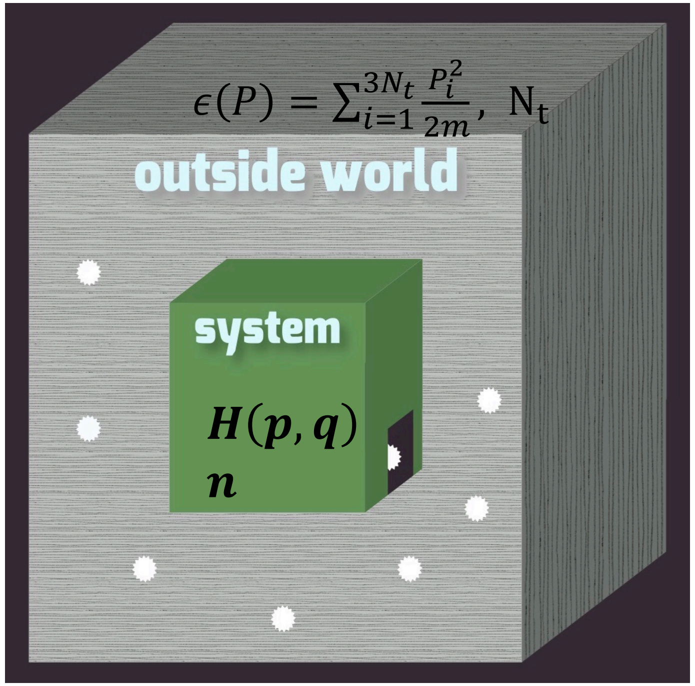
Grand canonical ensemble

$$\rho(p,q,n) \sim \frac{(N_t+n)!}{n!\,N_t!} \frac{V^{N_t}}{h^{3N_t}} \frac{\pi^{\frac{3N_t}{2}}}{\left(\frac{3N_t}{2}-1\right)!} \frac{(2mU_{total})^{\frac{3N_t}{2}}}{U_{total}} e^{-\beta H(p,q)}$$

- $\boldsymbol{N_t \sim N \gg n}$

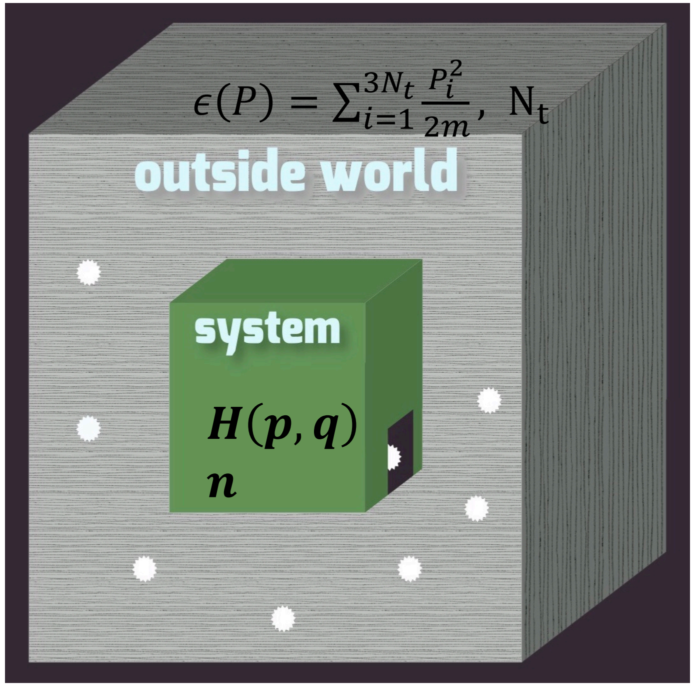
$$\frac{(N_t+n)!}{n!\,N_t!} = \frac{(N_t+1)(N_t+2)\cdots(N_t+n)}{n!} \sim \frac{N_t^n}{n!} \sim \frac{N^n}{n!}$$

$$\rho(p,q,n) \sim \frac{N^n}{n!} \left(\frac{V(2\pi m U_{total})^{\frac{3}{2}}}{h^3}\right)^{N_t} \frac{1}{U_{total}} \frac{1}{\left(\frac{3N_t}{2}-1\right)!} e^{-\beta H(p,q)}$$



Grand canonical ensemble

$$\rho(p,q,n) \sim \frac{N^n}{n!}\left(\frac{V(2\pi m U_{total})^{\frac{3}{2}}}{h^3}\right)^{N-n} \frac{1}{U_{total}} \frac{1}{\left(\frac{3N}{2}-1-\frac{3n}{2}\right)!} e^{-\frac{H}{kT}}$$



- Keep only the terms dependent on n, q, and p (all the rest can be taken care of by the normalization condition)

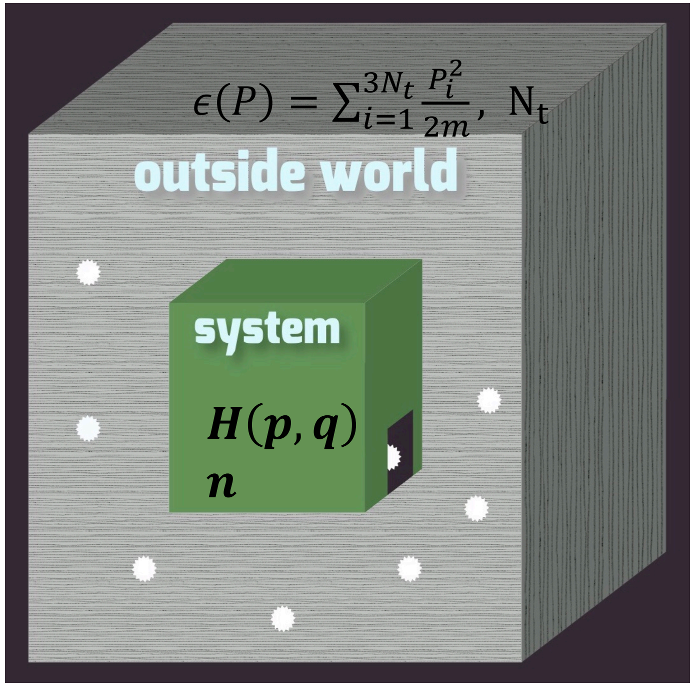
$$\frac{1}{\left(\frac{3N}{2}-1-\frac{3n}{2}\right)!} \approx \frac{1}{\left(\frac{3N}{2}-1\right)!}$$

$$\rho(p,q,n) \sim \frac{N^n}{n!}\left(\frac{V(2\pi m U_{total})^{\frac{3}{2}}}{h^3}\right)^{-n} e^{-\frac{H(p,q)}{kT}}$$

$$\rho(p,q,n) \sim \frac{1}{n!}\left(\frac{Nh^3}{V(2\pi m kT)^{\frac{3}{2}}}\right)^{n} e^{-\frac{H(p,q)}{kT}}$$

Grand canonical ensemble $\Xi(T, V, \mu)$

$$\rho(p, q, n) \sim \frac{1}{n!}\left(\frac{N\Lambda^3(T)}{V}\right)^n e^{-\frac{H(p,q)}{kT}}$$



- Chemical potential of the reservoir $\mu_t = \mu$

$$\frac{N\Lambda^3(T)}{V} \approx \frac{N_t\Lambda^3(T)}{V_t} = e^{\frac{\mu_t}{kT}} = e^{\frac{\mu}{kT}}$$

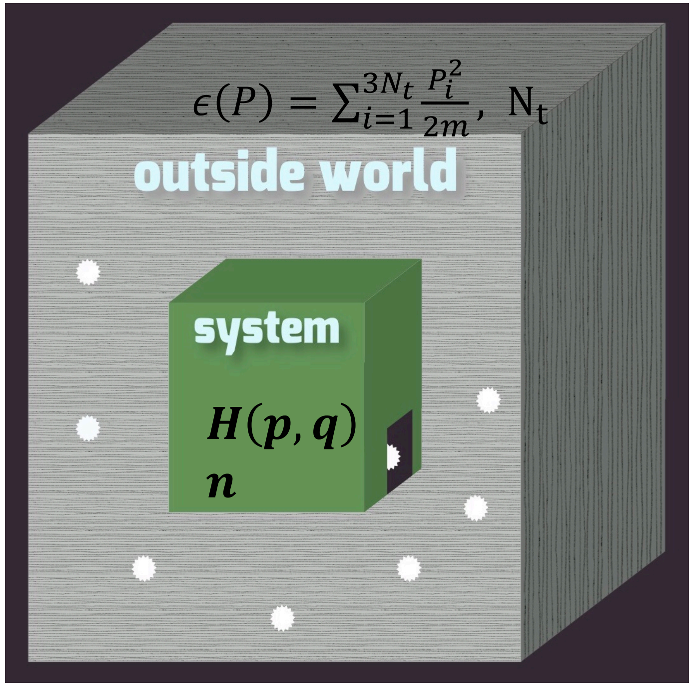
$$\rho(p, q, n) \sim \frac{1}{n!} e^{\frac{\mu n}{kT}} e^{-\frac{H}{kT}}$$

Grand canonical ensemble $\Xi(T,V,\mu)$

- $\rho(p,q,n) \sim \frac{1}{n!}\left(\frac{Nh^3}{V(2\pi mkT)^{\frac{3}{2}}}\right)^n e^{-\frac{H}{kT}}$

- $\boldsymbol{\rho(p,q,n) = \frac{1}{\Xi}\frac{1}{n!}e^{\beta(\mu n - H)}}$

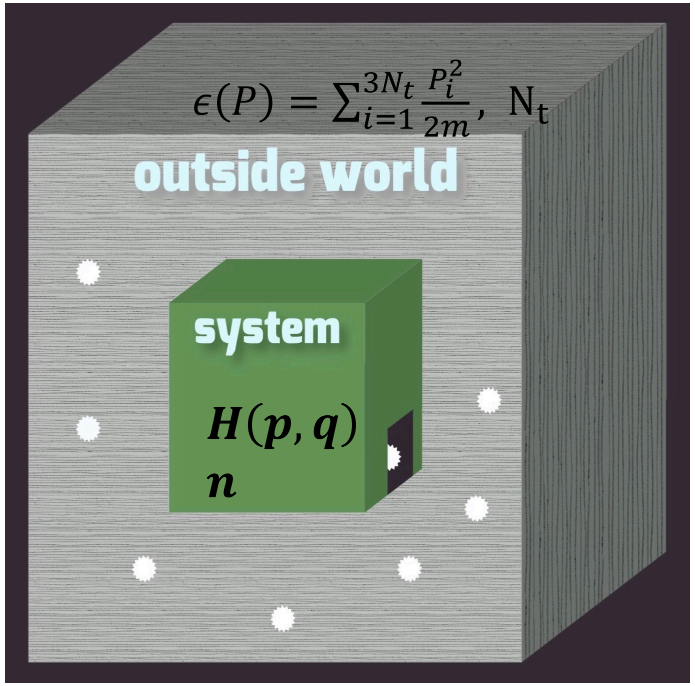
- *Grand-canonical partition function*
- $\Xi(T,\mu) = \sum_{n=0}^{\infty}\frac{e^{\beta\mu n}}{n!}\int d\omega\, e^{-\beta H(p,q)}, \beta = \frac{1}{kT}$



Grand canonical ensemble

- 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

$$\boldsymbol{\rho(p,q,N) = \frac{1}{\Xi}\frac{1}{n!}e^{\beta(\mu N - H)}}$$



- *Grand-canonical partition function and Landau potential*

$$\Xi(T,\mu) = \sum_{n=0}^{\infty}\frac{e^{\beta\mu n}}{n!}\int d\omega e^{-\beta H(p,q)}$$

$$\Xi(T,\mu) = \sum_{n=0}^{\infty}\frac{e^{\beta\mu n}}{n!}\tilde{Z}(T,n) = \sum_{n=0}^{\infty}e^{\beta\mu n}Z_n(T), \qquad Z_n(T) = e^{-\beta F}$$

$$\boldsymbol{\Xi(T,\mu) = \sum_{n=0}^{\infty}e^{-\beta(F-\mu n)} = e^{-\beta\Omega(\mathrm{T},\mu)}}, \qquad \boldsymbol{\Omega(\mathrm{T},\mu) = \mathrm{F}(\mathrm{T},\mathrm{N}) - \mathrm{N}\mu}$$

Grand-Canonical ensemble: number fluctuations

Probability $P(n)$ represents probability that the system is <u>any</u> microstates with n particles (**macrostate**)

$$P(n) = \int d\omega \, \frac{1}{\Xi(T,\mu)} \frac{1}{n!} \, e^{-\beta H(p,q)} e^{\beta\mu n} = \frac{1}{\Xi(T,\mu)} \, Z_n(T) e^{\beta\mu n}, \qquad \sum_{n=0}^{\infty} P(n) = 1$$

- *Average number N*

$$N \equiv \langle n \rangle = \sum_{n=0}^{\infty} n \, P(n)$$

$$\langle n \rangle = \frac{1}{\Xi(T,\mu)} \sum_{n=0}^{\infty} n \, Z_n(T) e^{\frac{\mu n}{kT}} = \frac{kT}{\Xi(T,\mu)} \frac{\partial}{\partial\mu} \sum_{n=0}^{\infty} Z_n(T) e^{\frac{\mu n}{kT}} = \frac{kT}{\Xi(T,\mu)} \frac{\partial}{\partial\mu} \Xi(T,\mu)$$

$$\langle n \rangle = kT \frac{\partial}{\partial\mu} \ln \Xi$$

Grand-Canonical ensemble: number fluctuations

Probability $P(n)$ follows from the transformation of probability density

$$P(n) = \frac{1}{\Xi(T,\mu)} Z_n(T) e^{\beta\mu n}, \qquad \sum_{n=0}^{\infty} P(n) = 1$$

- *Number fluctuations*

$$\langle n^2 \rangle = \sum_{n=0}^{\infty} n^2 \, P(n)$$

$$\langle n^2 \rangle = \frac{1}{\Xi(T,\mu)} \sum_{n=0}^{\infty} n^2 \, Z_n(T) e^{\frac{\mu n}{kT}} = \frac{(kT)^2}{\Xi(T,\mu)} \frac{\partial^2}{\partial \mu^2} \sum_{n=0}^{\infty} Z_n(T) e^{\frac{\mu n}{kT}} = \frac{(kT)^2}{\Xi(T,\mu)} \frac{\partial^2}{\partial \mu^2} \Xi(T,\mu)$$

$$\langle \Delta n^2 \rangle = \langle n^2 \rangle - \langle n \rangle^2 = (kT)^2 \frac{\partial^2}{\partial \mu^2} \ln \Xi$$

Grand-Canonical ensemble: Ideal gas

- $Z(T,V,N) = \frac{V^N}{\mathrm{N!}\Lambda^{3N}(T)}, \quad \Lambda(T) = \sqrt{\frac{h^2}{2\pi mkT}}$

- $\Xi(T,V,\mu) = \sum_{n=0}^{\infty} e^{\beta\mu n} Z(T,V,n)$

- $\Xi(T,V,\mu) = \sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{V}{\Lambda^3} e^{\beta\mu}\right)^n = e^{z(T,\mu)V}, \ \mathrm{z} = \frac{\mathrm{e}^{\beta\mu}}{\Lambda^3(T)}$ is the **fugacity**

$$\boldsymbol{\Xi(T,V,\mu) = e^{zV} = e^{-\beta\Omega(T,V,\mu)}}$$

Grand-Canonical ensemble: Ideal gas

- Thermodynamic correspondence: Landau potential

$$\Omega(\mathrm{T},\mu) = -kT\, zV = -kTV\,\frac{e^{\beta\mu}}{\Lambda^3(T)}$$

- Thermodynamic identity: $d\Omega = -SdT - PdV - Nd\mu$

- $N = \langle \mathrm{n} \rangle = \frac{\partial \Omega}{\partial \mu} = kT\,\frac{\partial}{\partial \mu} \ln \Xi = V\,\frac{e^{\beta\mu}}{\Lambda^3(T)} = \mathrm{zV} \rightarrow \Omega = -\mathrm{kT}\langle n \rangle$

- $P = -\frac{\partial \Omega}{\partial V} = kTz \rightarrow P = \frac{\langle n \rangle kT}{V}$

Grand-Canonical ensemble: Ideal gas

- Number fluctuations

- $\langle \Delta \mathrm{n}^2 \rangle = (kT)^2 \frac{\partial^2}{\partial \mu^2} \ln \Xi = (kT)^2 \frac{\partial^2}{\partial \mu^2} \left(V \frac{e^{\beta\mu}}{\Lambda^3(T)} \right) = V \frac{e^{\beta\mu}}{\Lambda^3(T)}$

- $\frac{\sqrt{\langle \Delta \mathrm{n}^2 \rangle}}{\langle n \rangle} = \left(V \frac{e^{\beta\mu}}{\Lambda^3(T)} \right)^{-\frac{1}{2}} \to 0$

Grand-Canonical ensemble: Ideal gas

- Distribution of number fluctuations

$$P(n) = \frac{1}{\Xi(T,\mu)} Z_n(T) e^{\beta\mu n}$$

$$P(n) \sim \frac{1}{n!}\frac{V^n}{\Lambda^{3n}} e^{\beta\mu n}$$

$$P(n) \sim \frac{v^n}{n!} e^{\beta\mu n}$$