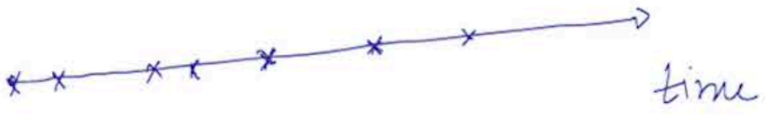
Poisson distribution:

Random in time/space

Independent of each other

Mean rate of events:



Mean rate

$$\alpha = \frac{\text{No. of events in } T}{T}$$

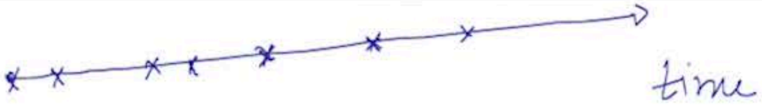
Factory with manufacturing dolls.

$$\alpha = \frac{120 \text{ dolls}}{60 \text{ min}} = 2 \text{ dolls/minute}$$

Question: What is the probability of observing 4 dolls in 2 minutes?

Subjectively: $P(4)$

$\alpha T = 4$



Mean rate

$$\alpha = \frac{\text{No. of events in } T}{T}$$

2 minutes?

Subjectively: $$P_{\alpha T}(m) = \frac{(\alpha T)^m \cdot e^{-\alpha T}}{m!}$$

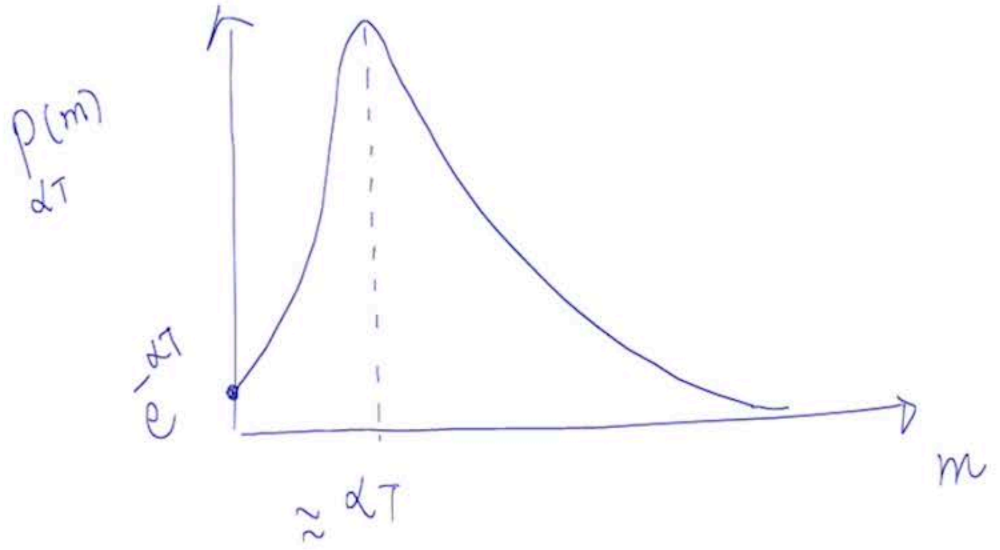
$$\alpha T = (2/\text{min})\, 2 \text{ min} = 4$$

$$P_{\alpha T = 4}(4) = \frac{4^4 \cdot e^{-4}}{4!} = \frac{\cancel{4}\cdot\cancel{4}^{2}\cdot 4\cdot 4}{\cancel{4}\cdot 3\cdot\cancel{2}\cdot 1}\, e^{-4}$$

$$= (32/3)\, e^{-4}$$

$$P(4)\Big|_{\alpha T = 4} = \frac{4^4 \cdot e^{-4}}{4!} = \frac{\cancel{4}\cdot\cancel{4}^{2}\cdot 4\cdot 4}{\cancel{4}\cdot 3\cdot\cancel{2}\cdot 1}\, e^{-4}$$

$$= \left(32/3\right) e^{-4}$$



What is the probability of observing less than 4 dolls in $\underset{\substack{\downarrow \\ 2\,\text{doll/min}}}{\alpha}\ \underset{\substack{\downarrow \\ 2\,\text{min}}}{T} = 4$

$$\underset{\alpha T = 4}{P(m<4)} = \sum_{m=0}^{3} P(m)$$

Probability of getting more than 4 dolls when $\underbrace{\alpha}_{2\,\text{doll}/\text{min}}\ \underbrace{T}_{2\,\text{min}} = 4$?

$$\underset{\alpha T = 4}{P(m>4)} = \sum_{m=5}^{\infty} P(m)$$

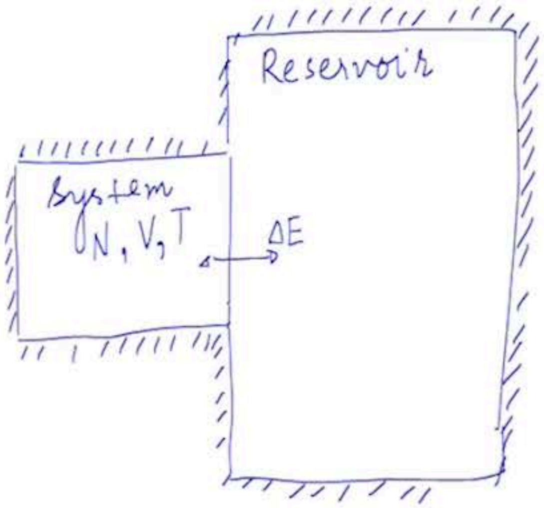
$$\sum_{m=0}^{\infty} P(m) = 1$$

"Normalized"

$$= 1 - P(m \leq 4)$$

$$= 1 - \left[P(0) + P(1) + P(2) + P(3) + P(4)\right]$$

Q: Canonical Ensemble:



Partition function $Z(N, V, T) = \sum_{\nu} p(\nu)$

$$= \int d\Gamma \, p(\Gamma) g(\Gamma)$$

$$p(\nu) = e^{-\beta \mathcal{H}(\nu)}$$

$$\mathcal{H}(\nu) = \sum_{i=1}^{N} p_i^2/2m$$

$$Z(N, V, T) = \frac{1}{h} \frac{1}{N!} \int \cdots \int e^{-\beta \sum_{i=1}^{N} p_i^2/2m} \prod_{i=1}^{N} d^3\vec{r}_i \, d^3\vec{p}_i$$

$\vec{r}_i \in V$,

$-\infty < \vec{p}_i < \infty$

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$$Z(N, V, T) = \frac{1}{h^3} \cdot \frac{V^N}{N!} \cdot \left(\frac{2\pi m}{\beta}\right)^{\frac{1}{2} \cdot 3N}$$

$$\int_{p_x=-\infty} e^{-\beta p_x^2/2m} \, dp_x = \sqrt{\frac{2\pi m}{\beta}}$$

$$= \frac{1}{N!} \cdot V^N \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}$$

$$\left(\int_{\vec{r}_i} d^3\vec{r}_i\right)^N = V^N$$

$$Z(1 \quad = \frac{1}{N!} \frac{V^N}{\Lambda(T)^{3N}}$$

$\Lambda(T)$ = De-Broglie's Thermal length scale

$$= \frac{h}{\sqrt{2\pi m k_B T}}.$$

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Connection to thermodynamics:

$$F = -k_B T \ln Z(N,V,T)$$

length scale

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

$$F = -k_B T \cdot \left[N \ln V - N \ln N + N - 3N \ln \Lambda(T) \right]$$

Stirling approximation:

$$\ln N! = N \ln N - N + \frac{1}{2} \cancel{\ln(2\pi N)}^{\,0}$$

6 / 6

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$$F = -k_B T \cdot \left[N \ln V - N \ln N + N - 3N \ln \Lambda(T) \right]$$

stirling approximation:

$$\ln N! = N \ln N - N + \cancel{\frac{1}{2} \ln(2\pi N)}^{\,0}$$

$$= -N k_B T \ln \left[\frac{eV}{N \Lambda(T)^3} \right]$$

$$= -N k_B T \ln \left[\frac{e}{n \Lambda(T)^3} \right]$$

$N/V = n$ "No. density"

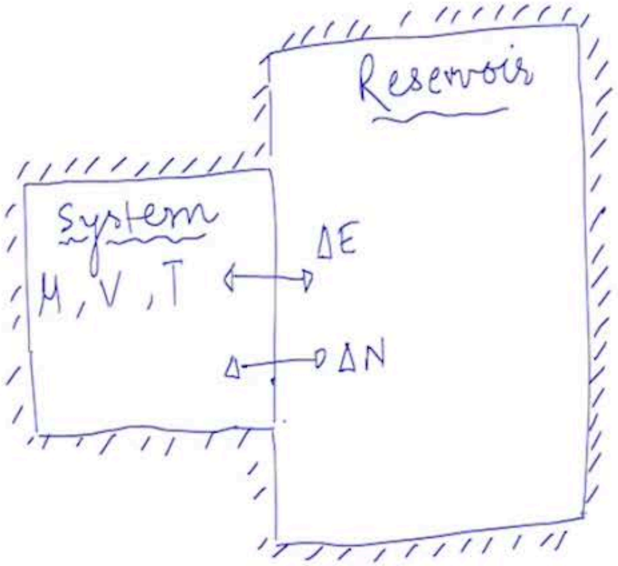
Classical limit: $n \Lambda(T)^3 << 1.$

n is low

T is high : $\Lambda(T) \sim \frac{1}{\sqrt{T}}$ low

Ideal gas in Grand Canonical Ensemble

$(\mu, V, T) \equiv$ Macrostate



$$\nu = \{\vec{r}_i, \vec{p}_i\}, \quad N(\nu)$$

$$p(\nu) = \frac{e^{-\beta H(\nu)}}{\sum_{\nu} e^{-\beta H(\nu)}} = \frac{e^{-\beta H(\nu)}}{\mathcal{Z}\,(}$$

$H(\nu) =$ Enthalpy of microstate $= \mathcal{H}(\nu) - \mu N(\nu)$

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Grand partition function : $\mathcal{Z}(\mu, V, T) = \sum_{\nu} e^{-\beta[\mathcal{H}(\nu) - \mu N(\nu)]}$

$$= \sum_{\nu} e^{\beta \mu N(\nu)} \cdot e^{-\beta \mathcal{H}(\nu)}$$

"Unrestricted" sum

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{\nu | N} e^{-\beta \mathcal{H}(\nu)}$$

"Constrained sum"

"Constrained sum

$$\mathcal{Z}(N, V, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(N, V, T)$$

Q. Get an expression for pressure P

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microstate

Grand partition function : $\mathcal{Z}(\mu, V, T) = \sum_{\nu} e^{-\beta[\mathcal{H}(\nu) - \mu N(\nu)]}$

$= \sum_{\nu} e^{\beta\mu N(\nu)} \cdot e^{-\beta\mathcal{H}(\nu)}$ "Unrestricted" sum

$p(N) = \dfrac{e^{\beta\mu N} Z(N, V, T)}{\mathcal{Z}(N, V, T)}$

$= \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\nu|N} e^{-\beta\mathcal{H}(\nu)}$

"Constrained sum"

$\mathcal{Z}(N, V, T) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N, V, T)$

Grand Potential $\mathcal{G} = -k_B T \ln \mathcal{Z}(N,V,T) = E - TS - \mu N$

using stat mech

$$\langle N \rangle = \sum_{N=0}^{\infty} N \, p(N)$$

$$= \frac{1}{\mathcal{Z}} \frac{\partial}{\partial(\beta\mu)} \mathcal{Z}(N,V,T)$$

$$= \frac{\partial}{\partial(\beta\mu)} \ln \mathcal{Z}$$

$\langle N \rangle$ from thermodynamics

$$H = E - \mu N$$

$$dH = dE - \mu dN - N d\mu$$

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$\because \quad TdS = dE + PdV - \mu dN$

$$\left.\frac{\partial \mathcal{G}}{\partial V}\right|_{T,\mu} = -P \quad \text{——} \quad (1)$$

$$dH = d(TS) - SdT - PdV - Nd\mu$$

$$d(H - TS) = -SdT - PdV - Nd\mu$$

$$d\left[E - \mu N - TS\right] = -SdT - PdV - Nd\mu$$

$$d\mathcal{G} = -SdT - PdV - Nd\mu$$

$$N = -\left.\frac{\partial \mathcal{G}}{\partial \mu}\right|_{T,V}$$

Partition function:

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} \cdot Z(N, V, T)$$

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$$= \sum_{N=0}^{\infty} \left(\frac{e^{\beta\mu} V}{\Lambda(T)^3} \right)^N \cdot \frac{1}{N!}$$

$$Z(\mu, V, T) = \exp\left(\frac{e^{\beta\mu} V}{\Lambda(T)^3} \right)$$

$$G = -k_B T \ln Z = -k_B T \cdot \frac{e^{\beta\mu} V}{\Lambda(T)^3}$$

$$\mathcal{G} = -k_B T \ln \mathcal{Z} = -k_B T \cdot \frac{e^{\beta\mu} V}{\Lambda(T)^3} \quad \text{--- (2)}$$

$$\left.\frac{\partial \mathcal{G}}{\partial V}\right|_{T,\mu} = -P$$

$$-P = -k_B T \cdot \frac{e^{\beta\mu}}{\Lambda(T)^3} \quad \text{--- (3)}$$

Comparing (2) & (3)

$$\boxed{\mathcal{G} = -PV}$$

$$\left.\frac{\partial \mathcal{G}}{\partial V}\right|_{T,\mu} = -P$$

$$dH = d(TS) - S\,dT - P\,dV - N\,d\mu$$

$$d(H - TS) = -S\,dT - P\,dV - N\,d\mu$$

$$d[E - \mu N - TS] = -S\,dT - P\,dV - N\,d\mu$$

$$d\mathcal{G} = -S\,dT - P\,dV - N\,d\mu$$

$$N = -\left.\frac{\partial \mathcal{G}}{\partial \mu}\right|_{T,V}$$

$$S = -\left.\frac{\partial \mathcal{G}}{\partial T}\right|_{V,\mu}$$

Partitition function:

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta\mu N} \cdot Z(N, V, T)$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} \left(\frac{V^N}{N!\,\Lambda(T)^{3N}} \right)$$

$\infty \quad \Big(\beta\mu \quad \Big)^N$