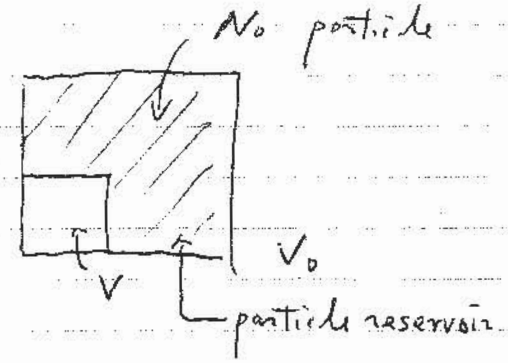
VI. Thermal fluctuations

① Thermal fluctuations of number of particle



Number of particle in V: $N = \sum_{i=1}^{N_0} x_i$

$$x_i = 1 \quad \text{if } i^{th} \text{ particle is in } V$$
$$= 0 \quad \text{otherwise}$$

$P(1)$ = probability for $x = 1$ $\qquad P(1) = \frac{V}{V_0}$

$P(0)$ = " " $x = 0$

$$\langle N \rangle = \sum_i \langle x_i \rangle = \sum_i P(1) = N_0 P(1)$$

$$\langle N^2 \rangle = \sum_i \langle x_i \rangle^2 + \sum_{i \neq j} \langle x_i x_j \rangle$$

$$= N_0 P(1) + (N_0^2 - N_0) \cdot P(1)^2 = \langle N \rangle + \langle N \rangle^2 - \langle N \rangle P(1)$$

$$\sqrt{\langle (N - \langle N \rangle)^2 \rangle} \equiv \overline{\Delta N} = \sqrt{\langle N^2 \rangle - \langle N \rangle^2}$$

$$= \sqrt{\langle N \rangle (1 - P(1))} \rightarrow \sqrt{\langle N \rangle} \quad \text{as } \frac{V}{V_0} \rightarrow 0$$

$$\boxed{\frac{\overline{\Delta N}}{\langle N \rangle} = \frac{1}{\sqrt{N}}}$$

* How to calculate the fluctuation of N for a generic system?

General ideas:

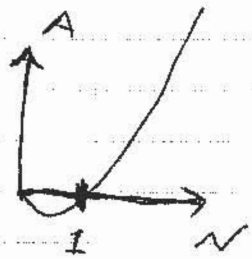
Thermal dynamical function S, A, Ω, G (Gibbs potential)

$\Rightarrow$ Probability:

$P \propto e^{S/k_B}$ ← # of state $\quad P \propto e^{-\beta A}$ ← total prob.

$P \propto e^{-\beta\Omega} \quad P \propto e^{-\beta G}$

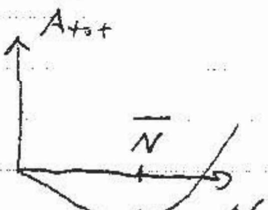
For ideal gas:



$$A(T,V,N) = Nk_BT[\ln(n\lambda^3)-1]$$
$$= Nk_BT\ln N + \text{const}$$

$P(N) = e^{-\beta A}$ is peaked at $N \sim \frac{1}{2}$

with particle reservior: $P(N) = e^{-\beta A_{tot}}$



$$A_{tot}(T,V,N) = A - \mu N$$
$$= \text{const} + \frac{1}{2}\left.\frac{\partial^2 A}{\partial N^2}\right|_{\bar{N}}(N-\bar{N})^2$$

$\bar{N}$ minimize A_{tot}

$$\frac{\partial A}{\partial N} = k_BT\ln N + k_BT, \quad \frac{\partial^2 A}{\partial N^2} = \frac{k_BT}{N}$$

$$P \propto e^{-\frac{\beta}{2}\frac{\partial^2 A}{\partial N^2}(N-\bar{N})^2} \Rightarrow \boxed{\langle (N-\bar{N})^2\rangle = \frac{k_BT}{\frac{\partial^2 A}{\partial N^2}} = \bar{N}}$$

★ What is $\left.\frac{\partial^2 A}{\partial N^2}\right|_{V,T} = \left.\frac{\partial \mu}{\partial N}\right|_{V,T}$? $\Rightarrow$ compressibility

$$A(V,T,N) = N a(T, \tfrac{V}{N}) = \frac{V}{v} a(T, v)$$

$$v = \frac{V}{N}$$

Change variable $(V,T,N) \Rightarrow (V,T,v)$

$$\left.\frac{\partial}{\partial N}\right|_{V,T} = \left.\frac{\partial v}{\partial N}\right|_{V,T} \left.\frac{\partial}{\partial v}\right|_{V,T}$$

$$= -\frac{V}{N^2}\left.\frac{\partial}{\partial v}\right|_{V,T} = -\frac{v^2}{V}\left.\frac{\partial}{\partial v}\right|_{V,T}$$

$$\frac{\partial A}{\partial N} = -\frac{v^2}{V}\frac{\partial}{\partial v}\left(\frac{V}{v} a(v,T)\right)\Big|_{V,T} \qquad \boxed{\left.\frac{\partial a}{\partial v}\right|_T = \left.\frac{\partial A}{\partial V}\right|_{T,N} = P}$$

$$= a(v,T) - v\left.\frac{\partial a}{\partial v}\right|_T = a(v,T) - v P(v,T)$$

$$\frac{\partial^2 A}{\partial N^2} = -\frac{v^2}{V}\frac{\partial}{\partial v}\left[a(v,T) - vP(v,T)\right]\Big|_{V,T}$$

$$= -\frac{v^2}{V}\left[\left.\frac{\partial a}{\partial v}\right|_T - P - v\left.\frac{\partial P}{\partial v}\right|_T\right]$$

$$= \frac{v^3}{V}\frac{\partial P}{\partial v} = -\frac{v^2}{V}\frac{1}{K_T}$$

isothermal compressibility

$$\boxed{K_T \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)\Big|_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T}$$

$$\Rightarrow \boxed{\langle (N-\bar{N})^2\rangle = k_B T\,\frac{V K_T}{v^2}}$$

$\langle (N-\bar{N})^2\rangle \Rightarrow$ fluctuation

$K_T = -\frac{1}{V}\frac{\partial V}{\partial P} \Rightarrow$ response

closely related.

$\Leftrightarrow \frac{\partial^2 A}{\partial N^2}$

δN has large fluctuations near the critical point

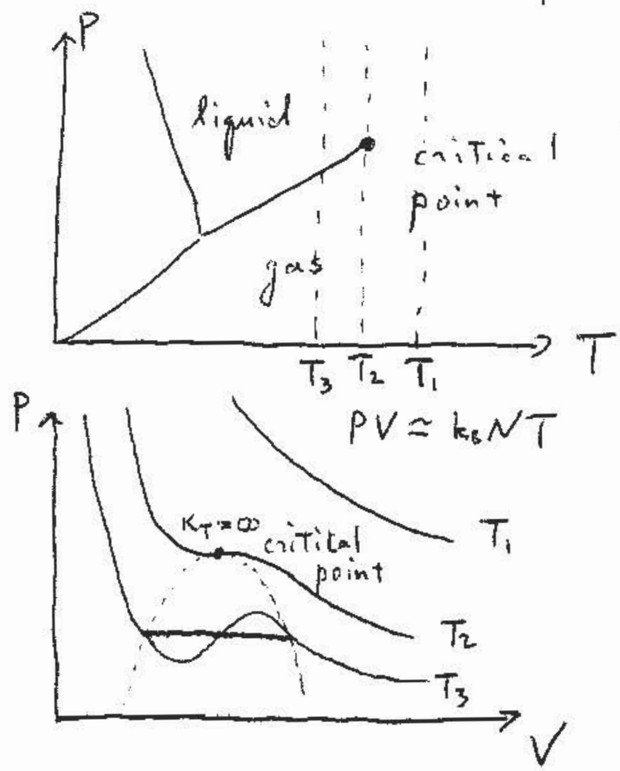
$$\frac{\delta n}{n} = \frac{\sqrt{\langle (N-\bar{N})^2 \rangle}}{N}$$

$$= \sqrt{k_B T \frac{K_T}{v}} \; \frac{1}{\sqrt{N}}$$

$$= \sqrt{k_B T \, K_T} \; \frac{1}{\sqrt{V}}$$

$$= \sqrt{\frac{V_c}{V}}$$

$$V_c = k_B T \, K_T$$



$\Rightarrow$ Water density in a smaller volume has a stronger fluctuation

The fluctuations become of order 1 when $V \sim V_c$

Usually $V_c \sim (1 \text{Å})^3$

$V_c \to \infty$ at the critical point

When $V_c \sim (5000 \text{Å})^3$, the water turn milky

(2) Fluctuations of V:

$$\star\quad e^{-\beta(A(V,T)+VP)} = \# \, e^{-\frac{1}{2}\beta \frac{\partial^2 A}{\partial V^2}(V-\bar{V})^2}$$

$$\left.\frac{\partial^2 A}{\partial V^2}\right|_T = -\left.\frac{\partial P}{\partial V}\right|_T = -\frac{1}{\left.\frac{\partial V}{\partial p}\right|_T} = \frac{1}{VK_T}$$

$$\boxed{K_T\text{: compressibility} = \frac{-1}{V}\left.\frac{\partial V}{\partial p}\right|_T}$$

For ideal gas:

$$V = \frac{Nk_BT}{P}, \quad VK_T = +\frac{Nk_BT}{P^2} = \frac{V}{P} = \frac{V^2}{Nk_BT}$$

$$\boxed{\langle (V-\bar{V})\rangle^2 = \frac{k_BT}{\partial^2 A/\partial V^2} = k_BTK_TV \underset{\text{ideal gas}}{=} \frac{V^2}{N}} \Rightarrow \boxed{\delta V = \sqrt{\langle (V-\bar{V})^2\rangle} = \frac{V}{\sqrt{N}}}$$

ideal gas

$\star$ Second way:

$$\frac{\partial}{\partial p} G = -k_BT \frac{\int dV\, (-\beta)V\, e^{-\beta[A(V,T)+VP]}}{\int dV\, e^{-\beta[A(V,T)+VP]}}$$

$$= +\langle V\rangle$$

$$\boxed{\frac{\partial G(P,T)}{\partial P} = V}$$

$$\boxed{P = -\frac{\partial A}{\partial V} \quad V = \frac{\partial G}{\partial P} \quad V \leftrightarrow P \text{ conjugate}}$$

$$\frac{\partial^2 G}{\partial p^2} = -\beta \frac{\int dV\, V^2 e^{-\beta(A+VP)}}{\int dV\, e^{-\beta(A+VP)}} - \frac{-\beta\left(\int dV\, V e^{-\beta(A+VP)}\right)^2}{\left(\int dV\, e^{-\beta(A+VP)}\right)^2}$$

$$= \left[\langle V^2\rangle - (\langle V\rangle)^2\right](-\beta)$$

$$\boxed{\langle (V-\bar{V})^2\rangle = \frac{k_BT}{\partial^2 A/\partial V^2} = -k_BT\frac{\partial^2 G}{\partial p^2}} \quad \begin{matrix} A(V,T) \\ G(P,V) \end{matrix}$$

$$\boxed{\langle (V-\bar{V})^2\rangle = -k_BT\frac{\partial^2 G}{\partial p^2}} = k_BT\,VK_T$$

Total entropy $\boxed{S_{tot} = S(E) - \frac{E}{T}}$ entropy of heat bath

$\boxed{\text{sys}} \leftrightarrow \boxed{\text{heat bath}}$

③ Fluctuation of energies

$$\text{Prob.} \propto e^{\frac{1}{2}\left[\frac{d^2}{dE^2}\frac{1}{k_B}\left[S(E) - \frac{E}{T}\right]\right](E-\bar{E})^2}$$

$$= e^{+\frac{1}{2}k_B^{-1}\frac{d^2S(E)}{dE^2}(E-\bar{E})^2}$$

$$\boxed{\begin{aligned} -\frac{\partial^2 S}{\partial E^2} &= \frac{1}{T^2}\frac{\partial T}{\partial E} \\ &= \frac{1}{T^2 C_V} \end{aligned}}$$

$$\Rightarrow \langle (E-\bar{E})^2 \rangle = -\frac{k_B}{d^2S(E)/dE^2}$$

$$= -N\frac{k_B}{d^2s/d\epsilon^2} = k_B T^2 C_V \qquad s = S/N \text{ or } S/V, \quad \epsilon = E/N \text{ or } E/V$$

$$\Rightarrow \delta E = \sqrt{\langle (E-\bar{E})^2 \rangle} \simeq \sqrt{k_B T^2 C_V} \sim \sqrt{N}$$

$$\bar{E} \sim N \quad \Rightarrow \quad \bar{E} \gg \sqrt{\langle (E-\bar{E})^2 \rangle}$$

small fluctuation

$$\boxed{\frac{\delta E}{\bar{E}} \sim \frac{1}{\sqrt{N}}}$$

✶ For ideal gas $\quad S = k_B \ln \frac{v(2m\epsilon)^{3/2}}{h^3}$

$$\frac{d^2s}{d\epsilon^2} = k_B \frac{3}{2}\frac{1}{\epsilon^2}$$

$$\boxed{\delta E = \sqrt{N}\sqrt{\frac{2}{3}}\,\epsilon = \sqrt{\frac{2}{3}}\frac{E}{\sqrt{N}}}$$

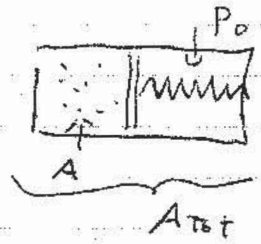
(4) Fluctuation and response

In general $\quad A(x)$

$\uparrow$ some parameter which can fluctuate

$$P \propto e^{-\beta A(x)} \qquad A = \text{const} + \frac{1}{2}\frac{\partial^2 A}{\partial x^2}(x-\bar{x})^2$$

$$\Rightarrow \boxed{\langle (x-\bar{x})^2 \rangle = \frac{k_B T}{\left.\frac{\partial^2 A}{\partial x^2}\right|_{\bar{x}}}}$$



$$A_{Tot} = A + P_o V$$

$$\langle (V-\bar{V})^2 \rangle = \frac{k_B T}{\frac{\partial^2 A_{Tot}}{\partial V^2}}$$

$$= k_B T \Big/ \frac{\partial^2 A}{\partial V^2} = k_B T \Big/ \left(-\frac{\partial P}{\partial V}\right)_T$$

Ideal gas $\quad PV = k_B T N \qquad -\frac{\partial P}{\partial V} = \frac{k_B T N}{V^2}$

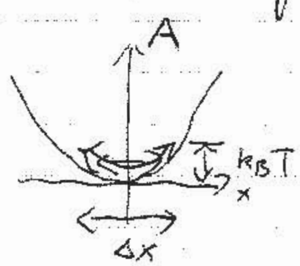
$$\Rightarrow \langle (V-\bar{V})^2 \rangle = \frac{\bar{V}^2}{N} = \Delta V^2 \Rightarrow \boxed{\Delta V = \frac{V}{\sqrt{N}}}$$

$$\boxed{\frac{\Delta V}{V} = \frac{1}{\sqrt{N}}}$$

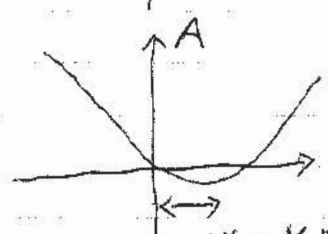
$$\langle (V-\bar{V})^2 \rangle = \frac{k_B T}{\left(-\frac{\partial P}{\partial V}\right)_T} = k_B T\left(-\frac{\partial V}{\partial P}\right)$$

$\uparrow$ fluctuation $\qquad \uparrow$ response $\frac{\partial V}{\partial P} \qquad P \leftrightarrow$ "force"

Thermal fluctuations — response



fluctuation



$x = K F$ $\quad$ "Force" $\quad A - xF$

response $\qquad K = 1 \Big/ \frac{\partial^2 A}{\partial x^2}$

$$\boxed{\langle \Delta x^2 \rangle = k_B T K}$$