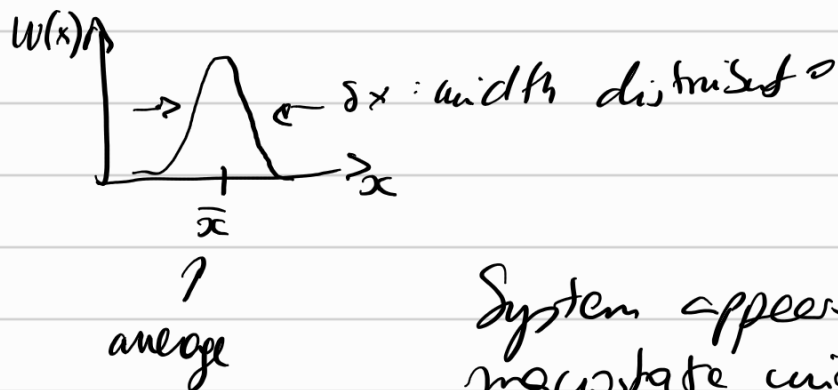


Part 1: "Thermodynamic limit"

Part 2: The closed system

degree of freedom

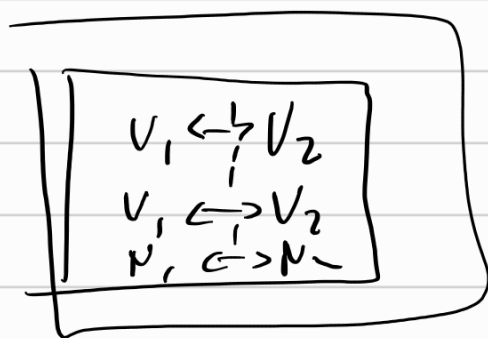


As $N \rightarrow \infty$, $\frac{\delta x}{x} \rightarrow 0$

(std deviat^o) / average $\rightarrow 0$

System appears to choose macrostate with greatest stat weight

The closed system



internal eqs:

$U_0 = U_1 + U_2$

$V_0 = V_1 + V_2$

$N_0 = N_1 + N_2$

(particle n^o)

} fixed

Allow the exchange of energy, volume, p^oles
btw n sub systems (heats)

Entropy

\rightarrow Thermodynamics:

$$dS = \frac{\delta Q}{T}$$

\rightarrow Stat Mech

consider stat weight

$W, (U, V, P)$

microstates

extensive depends
quantity: size system

$$W_2 (U_2, V_2, N_2)$$

$$S = S_1 + S_2 \quad \text{sum subsystems}$$

stat weight of size syst
but not \sum subsystems

$\downarrow \uparrow$ they multiply

MDT extensive

$$W_0 = W_1 \times W_2$$

$$\ln(W_0) = \ln(W_1) + \ln(W_2)$$

Intensive

we look at this
extensive quantity

\wedge we need to work
with extensive quant

Boltzmann eqn

$$S = k_B \ln(W)$$

$$\begin{cases} S = S_1 + S_2 \\ \ln(W_0) = \ln(W_1) + \ln(W_2) \end{cases}$$

entropy & stat weight
 S W

$\rightarrow \ln W$ is extensive
 $\rightarrow \ln W$ is maximized for closed system in eq^{to}
($\frac{\partial W}{\partial x} = 0 \Rightarrow \frac{\partial \ln W}{\partial x} = \frac{1}{W} \frac{\partial W}{\partial x} = 0$)

Thermodynamic principles:

$$\frac{\partial \ln(W_0)}{\partial x} = 0$$

$x = U_2, V_2, N_2$ (for subsystem 2)

$$(1) x = U_2 \quad \left(\frac{\partial \ln(W_0)}{\partial U_2} \right)_{V_2, W_2} = 0$$

$$\ln(W_0) = \ln(W_1) + \ln(W_2)$$

$$0 = \frac{\partial \ln(W_1)}{\partial (V_2)} + \frac{\partial \ln(W_2)}{\partial (V_2)}$$

$$= \frac{\partial \ln(W_1)}{\partial V_1} = - \frac{\partial \ln(W_1)}{\partial V_1}$$

$$U_0 = U_1 + U_2 \Rightarrow 0 = dU_1 + dU_2$$

$$\frac{dU_1}{dU_2} = -1$$

$$0 = - \frac{\partial \ln W_1}{\partial V_1} + \frac{\partial \ln W_2}{\partial V_2}$$

①

$$\frac{\partial \ln W_1}{\partial V_1} = \frac{\partial \ln W_2}{\partial V_2}$$

← only works under the assumption of equilibrium

$$\beta = \frac{1}{k_B T} = \frac{\partial \ln(W)}{\partial U}$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial k_B \ln W}{\partial U}$$

$\left(T = \left(\frac{\partial U}{\partial S} \right)_{V, N} \right)$: 0th law of thermodynamics (temperature exists)

②

$$\frac{\partial \ln W_0}{\partial V_2} = 0, \quad x = V_2$$

$$\frac{\partial \ln W}{\partial V_2} = \frac{\partial \ln W_1}{\partial V_1} \quad (\text{same as before})$$

$$= k_B T \left(\frac{\partial \ln W}{\partial V} \right)_{V, N}$$

← 2 sys + = pressure → no exchange Vol

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

If $P_1 = P_2 \Rightarrow$ mechanical equilibrium

$$\textcircled{3} \quad x = N_2 \quad \frac{\partial \ln(W)}{\partial N_2} = 0$$

$$\frac{\partial \ln(W_2)}{\partial N_2} = \frac{\partial \ln(W_1)}{\partial N_1}$$

Chemical potential

$$= \frac{1}{T} \left(\frac{\partial \ln W}{\partial N} \right)$$

$$\mu = -T \left(\frac{\partial \tilde{S}}{\partial N} \right)_{U, V} = -k_B T \left(\frac{\partial \ln \Omega}{\partial N} \right)_{U, V}$$

If $\mu_1 = \mu_2 \Rightarrow$ diffusive eqⁿ

