

# Summary Chapter 3 "Statistical Mechanics"

8-3b

microcanonical ensemble: fixed energy  $U$ , volume  $V$ , and  $N$   
 $\hat{=}$  isolated system

partition function  $\hat{=}$  volume in phase space (for gas)

$$W(U, V, N) = \int_{H(p, q) = U} d^{3N}q \int d^{3N}p \quad S(\vec{q}, \vec{p}, t) = \int d^{3N}q \int d^{3N}p \quad 1$$

$S(\vec{q}, \vec{p}, t) = 1 \hat{=}$  equal a-priori probability  
density of states:  $\omega(U, V, N)$

- entropy  $S(U, V, N) = k_B \ln W(U, V, N) \sim N$  extensive
- entropy is maximal at equilibrium  $\hat{=}$  2. law of Th.O.
- $\frac{\partial S(U, V, N)}{\partial U} = \frac{1}{T}$  where  $T$  is absolute temperature
- Systems in heat contact have identical  $T \hat{=}$  0. law of Th.O.

Canonical ensemble: fixed  $T$ ,  $V$ ,  $N \hat{=}$  closed system

partition function  $Z(T, V, N) = \sum_i e^{-\beta \mathcal{H}_i}$  discrete system  
 $= \int_V d^{3N}q \int d^{3N}p e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}$   $\boxed{\beta = 1/k_B T}$

$$U = \langle \mathcal{H} \rangle = - \frac{\partial}{\partial \beta} \ln Z = U(T, V, N) \quad \text{caloric equation of state}$$

$$\text{energy variance } \Delta U^2 = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = k_B T^2 \left. \frac{\partial U}{\partial T} \right|_{V, N}$$

$$\left. \frac{\partial U}{\partial T} \right|_{V, N} = C_V \quad \text{heat capacity at const. } V \quad C_V \sim N \text{ extensive}$$

$$\rightarrow \text{relative energy fluctuations } \frac{\Delta U}{U} \sim \frac{N^{1/2}}{N} \sim N^{-1/2} \rightarrow 0 \text{ as } N \rightarrow \infty$$

for  $N \rightarrow \infty$  energy fluctuations  $\rightarrow$  microcanonical = canonical!

$$\text{free energy } F(T, V, N) = -k_B T \ln Z(T, V, N)$$

at fixed  $T, V, N$  the equilibrium state is given by minimal  $F$ !

$$S(T, V, N) = - \frac{\partial F(T, V, N)}{\partial T} \quad \text{and} \quad \boxed{F = U - TS}$$



total differential of  $U$ :  $dU = dF + TdS + SdT$  [8-3c]

$$dF(T, V, N) = \left. \frac{\partial F}{\partial T} \right|_{V, N} dT + \left. \frac{\partial F}{\partial V} \right|_{T, N} dV + \left. \frac{\partial F}{\partial N} \right|_{T, V} dN$$

$$\left. \frac{\partial F}{\partial T} \right|_{V, N} = -S(T, V, N), \quad \left. \frac{\partial F}{\partial N} \right|_{T, V} \equiv \mu(T, V, N) \quad \begin{matrix} \text{(as will see)} \\ \text{later} \\ \text{chemical potential} \end{matrix}$$

$$\rightarrow dU = \left. \frac{\partial F}{\partial V} \right|_{T, N} dV + TdS + \mu dN$$

$$\boxed{dU = -P dV + TdS + \mu dN} \rightarrow \left. \frac{\partial F}{\partial V} \right|_{T, N} = -P(T, V, N)$$

$$\boxed{dU = -\Delta W + \Delta Q + \mu dN} \quad \begin{matrix} \text{1. law of Th.O.} \\ \text{mechanical work} \quad \text{heat transfer} \quad \text{"chemical work"} \end{matrix}$$

$\Delta W$  is not an exact differential, the work  $W$  is not a state function

grand-canonical ensemble  $\mu, T, V$  fixed,  $N, U$  fluctuating  
 $\hat{=}$  open system

$$\tilde{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta N \mu} Z(N, V, T) \quad \text{grand-can. part. function}$$

$$\text{grand potential } \Omega(\mu, V, T) = -k_B T \ln \tilde{Z}(\mu, V, T) = -PV$$

$$\langle N \rangle = \frac{\partial \ln \tilde{Z}(\mu, V, T)}{\beta \partial \mu} = - \frac{\partial \Omega(\mu, V, T)}{\partial \mu}$$

$$\text{particle-number variance } \langle N^2 \rangle - \langle N \rangle^2 = \frac{\partial}{\beta \partial \mu} \frac{\partial}{\beta \partial \mu} \ln \tilde{Z}(\mu, V, T)$$

$$\rightarrow \langle N^2 \rangle - \langle N \rangle^2 = k_B T V \left. \frac{\partial^2 P}{\partial \mu^2} \right|_{T, V} = k_B T N \frac{N}{V} \kappa_T(P, T) \sim N!$$

$$\rightarrow \frac{\sqrt{\langle N^2 \rangle - \langle N \rangle^2}}{\langle N \rangle} \sim \frac{N^{1/2}}{N} \sim N^{-1/2}$$

relative particle number fluctuations vanish for  $N \rightarrow \infty$

$\rightarrow$  grand-canonical and canonical ensembles are equivalent!

$$\left. \frac{\partial^2 P}{\partial \mu^2} \right|_{T, V} = \frac{N^2}{V^2} \kappa_T(P, T), \quad \kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_{T, N} \geq 0$$

isothermal compressibility



## The ideal gas

### A) Canonical ensemble

$$Z(N, V, T) = \int d\vec{p}_1 \dots d\vec{p}_N \int d\vec{q}_1 \dots \int d\vec{q}_N e^{-\beta \mathcal{H}(\vec{q}, \vec{p})} \frac{1}{N! h^{3N}}$$

$$\mathcal{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$$

$$\rightarrow Z = \left[ \int d^3 p e^{-\vec{p}^2 \beta / 2m} \int d^3 q \cdot 1 \right]^N \frac{1}{N! h^{3N}} = \frac{1}{N!} \left( \frac{V}{\lambda_T^3} \right)^N$$

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \quad \text{thermal wavelength}$$

$$F(N, V, T) = -k_B T \ln Z(N, V, T) = k_B T N \left[ \ln \left( \frac{N \lambda_T^3}{V} \right) - 1 \right]$$

$$\rightarrow S = - \frac{\partial F}{\partial T} \Big|_{N, V} = - \frac{F}{T} + \frac{3}{2} k_B N = -k_B N \left[ \ln \left( \frac{N \lambda_T^3}{V} \right) - \frac{5}{2} \right]$$

$$\rightarrow S(N, V, T) !$$

$$P(N, V, T) = - \frac{\partial F}{\partial V} \Big|_{N, T} = \frac{k_B T N}{V} \quad \text{ideal equation of state}$$

from  $U = F + TS \rightarrow U(N, V, T) = \frac{3}{2} N k_B T$  Caloric eq. of state

for ideal gas,  $U(N, V, T)$  is independent of  $V$ !

$$C_V = \frac{\partial U(N, V, T)}{\partial T} = \frac{3}{2} N k_B$$

example of equipartition theorem: per degree of freedom  
(= quadratic term in Hamiltonian)  $\rightarrow U = \frac{1}{2} k_B T$  and  $C_V = \frac{k_B}{2}$

### B) Microcanonical ensemble: $\omega(N, V, U) = \frac{(V [2mU\pi]^{3/2} / h^3)^N}{N! (3N/2 - 1)!}$

$$\rightarrow S(N, V, U) = -k_B N \left[ \ln \left( \frac{N h^3}{V} \left( \frac{3N}{4mU\pi} \right)^{3/2} \right) - \frac{5}{2} \right]$$

### C) Grand canonical ensemble: $\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta N \mu} Z(N, V, T)$

$$\mathcal{Z}(\mu, V, T) = \exp \left\{ \frac{V}{\lambda_T^3} e^{\beta \mu} \right\} \rightarrow \Omega(\mu, V, T) = -k_B T \ln \mathcal{Z} = -\frac{k_B T V}{\lambda_T^3} e^{\beta \mu}$$



~~The Foundations~~ Foundations

grand potential explicitly given by  $\Omega = -PV$

we also derived  $F = \Omega + \mu N = -PV + \mu N$   
Free energy

we also derived  $U = F + TS = TS - PV + \mu N$   
internal energy : fundamental equation  
of thermodynamics

Gibbs free energy  $G = F + PV = \mu N$   
enthalpy  $H = U + PV$

$\Omega, F, U, G, H$  are the thermodynamic potentials which are extensive ( $\sim N$ ) and consist of bilinear terms that are products of intensive variables ( $T, P, \mu$ ) and their conjugate extensive state variables ( $S, V, N$ ).

In principle, other potentials exist, but are not common! They can all be derived from the fund. eq. for  $U$ !

we know that  $dU = -PdV + TdS + \mu dN$

so if we have  $U(V, S, N)$  in terms of its canonical variables  $V, S, N$  we can derive  $P(V, S, N), T(V, S, N), \mu(V, S, N)$  and from that all other th.d. potentials!

as an example:  $dF = d(U - TS) = dU - TdS - SdT$   
 $dF = -PdV - SdT + \mu dN$

so if we have  $F(V, T, N)$  we get  $S(V, T, N) = -\frac{\partial F(V, T, N)}{\partial T}$   
and similarly  $P(V, T, N), \mu(V, T, N) \Rightarrow$  complete information!

canonical forms of th.d. potentials:

$U(V, S, N), \Omega(V, T, \mu), F(V, T, N), G(P, T, N)$

$H(P, S, N) \dots$  in different ensembles different th.d. potentials are extremal and therefore useful!



making use of extensive/intensive properties:

of the th.d. potentials  $U, \Omega, F, G, H$  two depend on one extensive variable and two intensive ones:

$$\Omega(V, T, \mu) = V f_{\Omega}(T, \mu)$$

$$G(P, T, N) = N f_G(P, T)$$

from  $\frac{\partial \Omega(V, T, \mu)}{\partial V} = -P \rightarrow f_{\Omega} = -P(T, \mu) \rightarrow \Omega = -VP$

$$\frac{\partial G(P, T, N)}{\partial N} = \mu \rightarrow f_G = \mu(P, T) \rightarrow G = \mu N$$

in agreement with our explicit derivation for  $\Omega$ !