7. Canonical and grand canonical ensembles

thermodynamic functions

systems with more than one component

CANONICAL and GRAND CANONICAL ENSEMBLES

A. ISOLATED SYSTEMS:

Constraints: N and E are conserved for the one system.

Molecular partition function

$$q = \sum_i g_i e^{-\epsilon_i/kT}$$

Can calculate thermodynamic quantities and averages for any ideal gas (i.e., non-interacting particles)

Microcanonical ensemble of replicas each one with N and E and each one in a given SYSTEM QUANTUM STATE. At any instant of time there is a DISTRIBUTION, i.e., there are some number of replicas that are in the j^{th} SYSTEM QUANTUM STATE with energy E

B. CANONICAL ENSEMBLE

Make replicas of the system of interest. Consider an ensemble of replicas, each one in an identical container (and fields) and with the same number of particles. Place replicas in contact — they exchange energy but NOT particles. Entire ensemble of replicas has a fixed energy, that is, the ensemble is isolated. At any instant of time there are some number of replicas that are in the j^{th} SYSTEM QUANTUM STATE with energy $E_j(V)$

C. GRAND CANONICAL ENSEMBLE

Ensemble of replicas, which can exchange energy with each other and exchange particles with each other. Each replica has the same volume V. The TOTAL number of particles is fixed at $n\bar{N}$

number of replicas (n)

average number of particles in each replica ($\bar{N}$)

$E_{jN}(V)$ is the energy in the j^{th} SYSTEM QUANTUM STATE, is a function of the volume of the system and the number of particles (interacting!) in the system. At any instant of time there is a distribution, i.e., there are

n_{Nj} replicas which have N particles and are in the SYSTEM QUANTUM STATE j for N particles.

Note that the system quantum states for N' particles are different than for N particles.

	Microcanonical	Canonical	Grand Canonical
system of interest	N particles energy E volume V	N particles energy E (var.) volume V	N particles (var.) energy E (var.) volume V
quantum states of each particle	$\epsilon_i = \underline{\epsilon_{transl} + \epsilon_{internal}}$ quantum nos. characterizes each $\psi_{\epsilon_i}(V) = \theta_{\epsilon_{transl}}(V) \cdot \phi_{\epsilon_{internal}}$	same	same
jth SYSTEM QUANTUM STATE	$E(V)$ same for each j $\left(= \sum_i \epsilon_i \text{ if non-interacting}\right)$ Ψ_E $\left(= \psi(1)\psi(2)\psi(3)\cdots\psi(N) \text{ if non-interacting}\right)$	$E_j(V)$	$E_{jN}(V)$
number of replicas (very large)	n	n	n
distribution	N_i particles in molecular energy level ϵ_i	n_j replicas in the jth system quantum state with energy E_j	n_{jN} replicas in jth system quantum state for N particles
energy of system	E (constant)	E (var.), average $= \bar{E}$	E (var.), average $= \bar{E}$
energy of ensemble	$E_{ens} = nE$	$E_{ens} = n\bar{E}$	$E_{ens} = n\bar{E}$

	Microcanonical	Canonical	Grand Canonical
no. of particles in system	N (constant)	N (constant)	N (var.), ave $= \bar{N}$
no. of particles in ensemble	$N_{ens} = nN$	$N_{ens} = nN$	$N_{ens} = n\bar{N}$
constraints and Lagrange multipliers	$\sum_{k}^{\text{particles}} \epsilon_k = E \quad -\beta$ or $\sum_i N_i \epsilon_i = E$ $\sum_i N_i = N \quad \alpha$	$\sum_{j=1}^{n \text{ replicas}} n_j E_j = n\bar{E} \quad -\beta$ $\sum_j n_j = n_{\text{replicas}} \quad \alpha$	$\sum_N \sum_j n_{jN} E_j = n\bar{E} \quad -\beta$ $\sum_N \sum_j n_{jN} = n \quad \alpha$ $\sum_N \sum_j n_{jN} N = n\bar{N} \quad \ln\lambda$
no. of configurations	$t = \frac{N!}{\prod N_i!} \prod_i g_i^{N_i}$ divide this by $N!$ to correct for indistinguishability	$t = \frac{n!}{n_1! n_2! \cdots} = \frac{n!}{\prod_j n_j!}$	$t = \prod_N \prod_j \frac{n!}{n_{jN}!}$
probability	of finding a molecule in the ith level $= \frac{N_i}{N}$	of finding a system in the jth system quantum state $\frac{n_j}{n}$	of finding a system in the jth system quantum state with N particles $\frac{n_{jN}}{n}$
conditions for most probable distribution	$\frac{\partial \ln t}{\partial N_i} + \alpha \frac{\partial N}{\partial N_i} - \beta \frac{\partial E}{\partial N_i} = 0$	$\frac{\partial \ln t}{\partial n_j} + \alpha \frac{\partial n}{\partial n_j} - \beta \frac{\partial (n\bar{E})}{\partial n_j} = 0$	$\frac{\partial \ln t}{\partial n_{jN}} + \alpha \frac{\partial n}{\partial n_{jN}} + \ln\lambda \frac{\partial (n\bar{N})}{\partial n_{jN}} - \beta \frac{\partial (n\bar{E})}{\partial n_{jN}} = 0$

	Microcanonical	Canonical	Grand Canonical
leads to this equation for most probable distribution	CB: $\ln \frac{g_i}{N_i} + \alpha - \beta \epsilon_i = 0$	$-\ln n_j + \alpha - \beta E_j = 0$	$-\ln n_{jN} + \alpha - \beta E_{jN} + N \ln \lambda = 0$
define the partition function	molecular $q = \sum_i g_i e^{-\frac{\epsilon_i}{kT}}$	canonical $Q = \sum_j e^{-E_j/kT}$	grand canonical $\Xi = \sum_N \sum_j \lambda^N e^{-\frac{E_{jN}}{kT}}$ $\Xi = \sum_N Q_N(T,V) e^{\frac{N\mu}{kT}}$
Lagrange multipliers	$\beta = 1/kT$ $e^\alpha = \frac{N}{q}$ we will find: $\alpha = \frac{\mu}{kT}$	$\beta = 1/kT$ $e^\alpha = \frac{n}{Q}$	$\beta = 1/kT$ $e^\alpha = \frac{n}{\Xi}$ λ = absolute activity $(\mu = kT \ln \lambda)$ i.e. we will find $\ln \lambda = \mu/kT$
probability of being in a state	$P_i = \frac{N_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{q}$	$P_j = \frac{n_j}{n} = \frac{e^{-E_i/kT}}{Q}$	$P_{jN} = \frac{n_{jN}}{n} = \frac{e^{\frac{\mu N}{kT}} e^{-E_{jN}/kT}}{\Xi}$ $P_N = \frac{Q_N e^{\mu N/kT}}{\Xi}$
normalized probability density			$\Xi = \sum_N \sum_j e^{\frac{\mu N}{kT}} e^{-\frac{E_{jN}}{kT}}$

	Microcanonical	Canonical	Grand Canonical
nature of the distribution law	large no. of molecular energy levels which are populated	distribution is sharply peaked around $\bar{E}$, all other states nil	distribution is sharply peaked around $\bar{N}$ and $\bar{E}$
model for	isolated system	closed system in a thermostat (one is the system of interest, the rest constitutes the heat bath)	open system in a thermostat (used for treating statistical mechanical problems of systems of INTERACTING particles)
thermodynamic functions of the system (ensemble averages)	$E = -N\left[\frac{\partial \ln q}{\partial \beta}\right]_V$ $\bar{\epsilon} = \frac{E}{N} = -\left(\frac{\partial \ln q}{\partial \beta}\right)_V$ $S = k \ln t_{mp}$ most probable $S = \frac{E}{T} + kN \ln \frac{q}{N} + kN$ $\boxed{\mu = -kT \ln \frac{q}{N}}$ fundamental equation	$E = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V$ N is understood $nS = k \ln t \simeq k \ln t_{mp}$ total no. of states ensemble can exist $S = \frac{E}{T} + k \ln Q$ $\boxed{A \equiv E - TS = -kT \ln Q}$ fundamental eqn. $\mu = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}$ $P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$	$\bar{E} = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{V,\lambda}$ $\bar{N} = \left(\frac{\partial \ln Z}{\partial \ln \lambda}\right)_{\beta,V}$ $n\bar{S} = k \ln t$ $\bar{S} = \frac{\bar{E}}{T} + k \ln Z - k\bar{N} \ln \lambda$ $A = k\bar{N}T \ln \lambda - kT \ln Z$ ~~fundamental eqn~~ $\boxed{PV = kT \ln Z}$ $\mu = kT \ln \lambda$

	Microcanonical	Canonical	Grand Canonical
For N independent particles (perfect gas)	q $S = \frac{E}{T} + Nk\left[\ln\left(\frac{q}{N}\right) + 1\right]$ $A = -NkT\left[\ln\left(\frac{q}{N}\right) + 1\right]$ $G = -NkT \ln\left(\frac{q}{N}\right)$	$Q = \frac{q^N}{N!}$ $S = \frac{E}{T} + Nk\left[\ln\left(\frac{q}{N}\right) + 1\right]$ $A = -NkT\left[\ln\left(\frac{q}{N}\right) + 1\right]$ $G = -NkT \ln\left(\frac{q}{N}\right)$ i.e., <u>same</u> as microcanonical ensemble	$Z = \sum_N \frac{\lambda q^N}{N!}$ Z depends on the laws of interactions between particles
For a two-component system	N' non-interacting N'' $S = \frac{E'}{T} + N'k\left[\ln\frac{q'}{N'} + 1\right] + \frac{E''}{T} + N''k\left[\ln\frac{q''}{N''} + 1\right]$ $A = E - TS$ $= E' - TS' + E'' - TS''$	N_A $E_j(N_A, N_B)$ N_B $Q = \sum_j e^{-E_j(N_A, N_B)/kT}$	$\bar{N}_A = kT\left(\frac{\partial \ln Z}{\partial \mu_A}\right)_{T,V,\mu_B}$ $\bar{N}_B = kT\left(\frac{\partial \ln Z}{\partial \mu_B}\right)_{T,V,\mu_A}$ $\bar{S} = \frac{\bar{E}}{T} + k\ln Z - \frac{(N_A\mu_A + N_B\mu_B)}{T}$ $A = \bar{E} - T\bar{S}$ $= N_A\mu_A + N_B\mu_B - kT\ln Z$

Mixtures of Particles:

As before, get each kind of particle obeying its own distribution law but with a common β. still non-interacting particles, so each type retains its own energy levels (unchanged by presence of other types of particles)

$$t' \quad t'' \quad t''' \qquad \sum_i N_i' = N' \qquad t = t' \cdot t'' \cdot t'''$$

$$N' \quad N'' \quad N''' \qquad \sum_j N_j'' = N''$$

$$\epsilon_i' \quad \epsilon_j'' \quad \epsilon_k''' \qquad \sum_k N_k''' = N'''$$

$$\underbrace{\sum_i N_i' \epsilon_i'}_{E'} + \underbrace{\sum_j N_j'' \epsilon_j''}_{E''} + \underbrace{\sum_k N_k''' \epsilon_k'''}_{E'''} = E$$

$$S \equiv k \ln t = \underbrace{k \ln t'}_{S'} + \underbrace{k \ln t''}_{S''} + \underbrace{k \ln t'''}_{S'''}$$

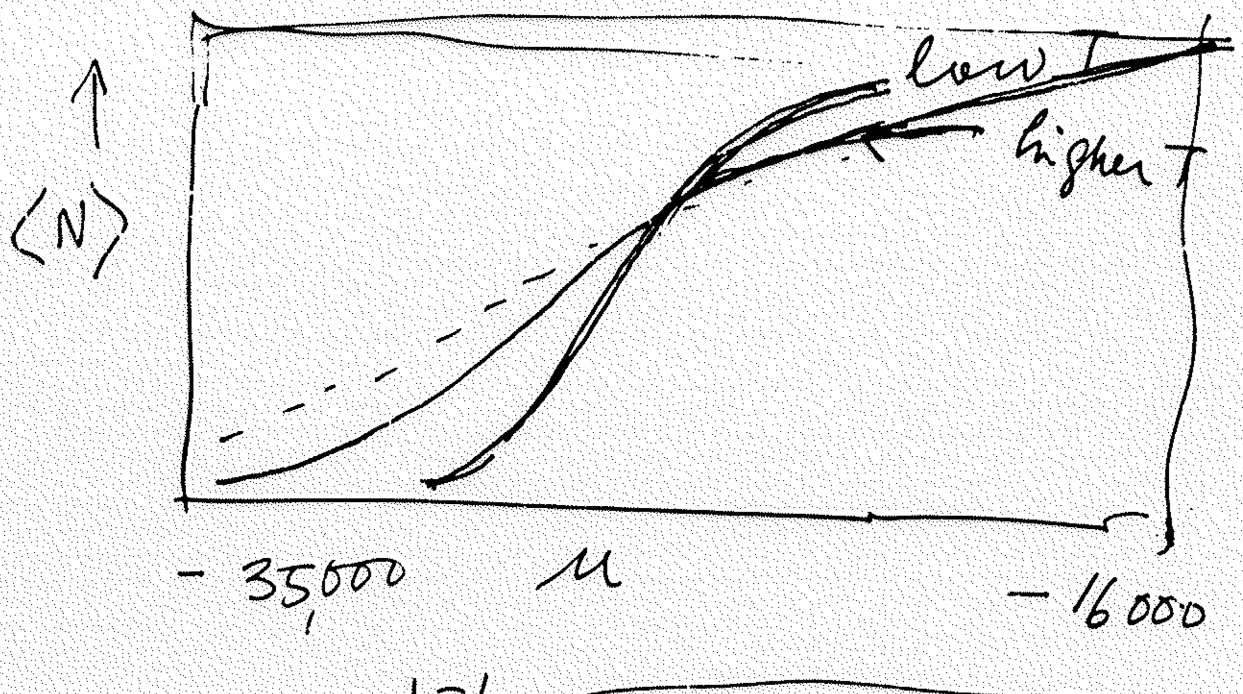
$$A = E - TS = A' + A'' + A'''$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \mu' + \mu'' + \mu'''$$

$$\mu' = \left(\frac{\partial A}{\partial N'}\right)_{T,V,N'',N'''} \quad \text{etc.}$$

$$G = N\mu = G' + G'' + G'''$$

$$N'\mu' + N''\mu'' + N'''\mu'''$$



E_j

$$Q = \sum_{\{\Gamma\}} e^{-\mathcal{H}(\Gamma)/kT}$$

canonical NVT if no internal energy

$$Q_{NVT} = \frac{1}{N!} \frac{1}{h^{3N}} \int d\vec{r}\, d\vec{p}\, e^{-\frac{\mathcal{H}(\vec{r},\vec{p})}{kT}}$$

$$= \underbrace{\frac{1}{N!} \frac{1}{h^{3N}} \int d\vec{p}\, e^{-\mathcal{F}(\vec{p})/kT}}_{} \underbrace{\int d\vec{q}\, e^{-V(\vec{q})/kT}}_{}$$

$$= Q^{ideal}_{NVT} \cdot Q^{excess}_{NVT}$$

$$= \frac{V^N}{N! \left[\left(h^2 / 2\pi m k T \right)^{1/2} \right]^{3N}} \cdot \frac{1}{V^N} \underbrace{\int d\vec{r}\, e^{-\frac{V(\vec{r})}{kT}}}$$

dim is V^N

$$A = -\ln Q_{NVT}$$

NPT
Isothermal-
Isobaric
ensemble

$$\rho_j = \frac{e^{-\left(\frac{\mathcal{H} + PV}{kT}\right)}}{Q_{NPT}}$$

V variable

$$Q_{NPT} = \sum_{\Gamma} \sum_{V} e^{-\left(\frac{\mathcal{H} + PV}{kT}\right)}$$

$$= \sum_{V} \left(e^{-\frac{PV}{kT}} \cdot Q_{NVT} \right)$$

$$Q_{NPT} = \frac{1}{N!} \frac{1}{h^{3N}} \frac{1}{V^0} \int dV \int d\vec{r}\, d\vec{p}\, e^{-\frac{(\mathcal{H} + PV)}{kT}}$$

V^0 = unit of volume to make Q_{NPT} dimless

note this allows for changes in the volume

$$G = -\ln Q_{NPT}$$

Grand Canonical

μVT

N variable

probability $P_{jN} = e^{-\left(\frac{\mathcal{H}_{jN} - \mu N}{kT}\right)}$

$$Z_{\mu VT} = \sum_N \sum_j e^{\frac{\mu N}{kT}} e^{-\frac{E_{jN}}{kT}}$$

$$Z_{\mu VT} = \sum_N Q_{NVT} \, e^{\frac{\mu N}{kT}}$$

for an atomic system (no internal energy)

$$Z_{\mu VT} = \sum_N \frac{1}{N!} \frac{1}{h^{3N}} e^{\frac{\mu N}{kT}} \int d\vec{r} \, d\vec{p} \, e^{-\mathcal{H}/kT}$$