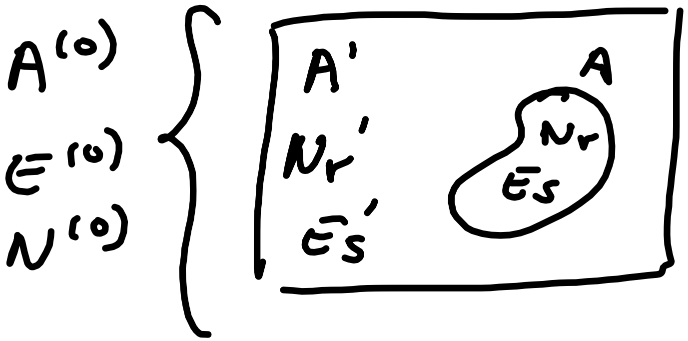
9/27

The Grand Canonical Ensemble:

Used when we know $\langle N \rangle$ but not the exact number of particles N. We also know $\langle E \rangle = U$ but not the exact E and we know T. Notice that if we do not know N we will have to know μ (chemical potential).

1) System in contact with a reservoir:



In equilibrium

$T = T'$ for A and A'

and $\mu = \mu'$ " " "

Systems can exchange energy and particles

but

$$E_s' + E_s = E^{(0)} \quad \text{and} \quad N_r' + N_r = N^{(0)}$$

Since $A' >> A \Rightarrow \dfrac{N_r}{N^{(0)}} << 1 \quad \dfrac{E_s}{E^{(0)}} << 1.$

As in the canonical we expect that

$$P_{r,s} \propto \Omega'(N_r', E_s') = \Omega'(N^{(0)} - N_r, E^{(0)} - E_s)$$

We are going to expand $\Omega'(N_r', E_s')$ about $(N^{(0)}, E^{(0)})$

$$\ln \Omega'(N^{(0)} - N_r, E^{(0)} - E_s) = \ln \Omega'(N^{(0)}, E^{(0)})$$

$$+ \underbrace{\left.\frac{\partial \ln \Omega'}{\partial N'}\right|_{N'=N^{(0)}}}_{-\mu'/kT'} \overbrace{(-N_r)}^{N_r' - N^{(0)}} + \underbrace{\left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{E'=E^{(0)}}}_{\beta'} \overbrace{(-E_s)}^{E_s' - E^{(0)}} + \dots$$

$$\simeq \ln \Omega'(N^{(0)}, E^{(0)}) + \frac{\mu'}{kT'} N_r - \frac{1}{kT'} E_s$$

In equilibrium we know that $T' = T$ and $\mu' = \mu$ then

$$P_{rs} \propto e^{-\alpha N_r - \beta E_s}$$

$$\alpha = -\frac{\mu}{kT}$$

Since $P_{r,s}$ is a probability:

$$\beta = \frac{1}{kT}$$

$$1 = \sum_{r,s} P_{r,s}$$

$$\therefore \quad P_{r,s} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}$$

Grand-canonical probability distribution.

2) Grand canonical ensemble:

$\mathcal{N}$ replicas of the system.

$\mathcal{N}\bar{N}$: number of particles in the ensemble.

$\mathcal{N}\bar{E}$: energy of the ensemble.

$\bar{E}$: average energy of the system.

$\bar{N}$: " number of particles of the system.

$n_{r,s}$: # of systems in the ensemble with N_r particles and energy E_s at a given time t.

$r: 0, 1, \ldots$

$s: 0, 1, \ldots$

Constrains:

$$(*)\begin{cases} \sum_{r,s} m_{r,s} = \mathcal{N} \\ \sum_{r,s} m_{r,s} N_r = \mathcal{N}\bar{N} \\ \sum_{r,s} m_{r,s} E_s = \mathcal{N}\bar{E} \end{cases}$$

new constrain.

All $\{n_{r,s}\}$ satisfying $(*)$ is a possible distribution for particles and energies in the ensemble. Each $\{n_{r,s}\}$ can be realized in various ways.

$$W\{n_{rs}\} = \frac{N!}{\prod_{r,s} n_{r,s}!}$$

What is the most probable distribution of $\{n_{r,s}\}$ - Following the same steps as for the canonical we obtain that

$$\frac{n^*_{r,s}}{N} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}$$

Here α and β are Lagrange multipliers.

Also

$$\langle n_{rs} \rangle = \frac{\sum'_{\{n_{r,s}\}} n_{r,s} W\{n_{rs}\}}{\sum'_{\{n_{rs}\}} W\{n_{rs}\}}$$

Using steepest descent the asymptotic value of $\langle n_{rs} \rangle$ for $N \to \infty$ is given by

$$\lim_{N\to\infty} \frac{\langle n_{rs} \rangle}{N} \simeq \frac{n^*_{rs}}{N} = \frac{e^{-\alpha N_r - \beta \epsilon_s}}{\sum_{r,s} e^{-\alpha N_r - \beta \epsilon_s}}$$

Now α and β can be obtained in terms of $\bar{N}$ and $\bar{E}$ since

$$\bar{N} = \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = -\frac{\partial}{\partial \alpha}\left\{\ln \underbrace{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}_{\mathcal{Z}}\right\}$$

$$\bar{E} = \frac{\sum_{r,s} E_s e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = -\frac{\partial}{\partial \beta}\left\{\ln \underbrace{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}_{\mathcal{Z}}\right\}$$

Grand Partition Function:

We will define the grand potential or Landau potential Ω:

$$\Omega = -kT\mathcal{q} = -kT \ln \sum_{r,s} e^{-\alpha N_r - \beta \epsilon_s}$$

$$\mathcal{q} = \ln \sum_{r,s} e^{-\alpha N_r - \beta \epsilon_s}$$

$\mathcal{q}$-potential (in the book)

Notice that

$$\mathcal{q} = \mathcal{q}(\alpha, \beta, \epsilon_s)$$

$$dq = \frac{\partial q}{\partial \alpha}\, d\alpha + \frac{\partial q}{\partial \beta}\, d\beta + \sum_s \frac{\partial q}{\partial \varepsilon_s}\, d\varepsilon_s =$$

$$= -\bar{N}\, d\alpha - \bar{E}\, d\beta + \frac{\sum_{r,s} (-\beta)\, e^{-\alpha N_r - \beta \varepsilon_s}\, d\varepsilon_s}{\sum_{r,s} e^{-\alpha N_r - \beta \varepsilon_s}}$$

$$\frac{\langle n_{rs} \rangle}{N}$$

$$= -\underbrace{\bar{N}\, d\alpha}_{d(\bar{N}\alpha) - \alpha\, d\bar{N}} - \overbrace{\bar{E}\, d\beta}^{d(\bar{E}\beta) - \beta\, d\bar{E}} - \frac{\beta}{N} \sum_{r,s} \langle n_{rs} \rangle\, d\varepsilon_s$$

Notice that

$$d(\bar{N}\alpha) = \bar{N}\, d\alpha + \alpha\, d\bar{N}$$

$$d(\bar{E}\beta) = \bar{E}\, d\beta + \beta\, d\bar{E}$$

$$d(q + \bar{N}\alpha + \bar{E}\beta) = \alpha\, d\bar{N} + \beta\, d\bar{E} - \frac{\beta}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle d\bar{E}_s$$

$$= \beta\left(\frac{\alpha}{\beta} d\bar{N} + d\bar{E} - \frac{1}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle d\bar{E}_s\right)$$

$$kT\, d(q + \bar{N}\alpha + \bar{E}\beta) = \frac{\alpha}{\beta} d\bar{N} + d\bar{E} - \frac{1}{\mathcal{N}} \sum_{r,s} \langle n_{rs} \rangle d\bar{E}_s \quad (1)$$

According to the first law: $d\bar{E} = \delta Q - \delta W + \mu\, dN$

then $\delta Q = d\bar{E} + \delta W - \mu\, d\bar{N}$ (2)

Comparing (1) with (2) we see that

$$\frac{\alpha}{\beta} = -\mu \qquad \delta W = -\frac{1}{\mathcal{N}} \sum_{r,s} \langle n_{rs} \rangle d\bar{E}_s$$

$$\therefore kT\, d(q + \bar{N}\alpha + \bar{E}\beta) = \delta Q$$

Then

$$d(q+\bar{N}\alpha+\bar{\epsilon}\beta) = \frac{\delta Q}{kT} = \frac{dS}{k} = d\left(\frac{S}{k}\right)$$

$\therefore \quad \beta = \frac{1}{kT}$ and $\mu = -\frac{\alpha}{\beta} = -\alpha kT$ or

$$\alpha = -\mu/kT$$

$$\therefore \boxed{q} = \frac{S}{k} - \bar{N}\alpha - \bar{\epsilon}\beta = \frac{S}{k} + \frac{\bar{N}\mu}{kT} - \frac{\bar{\epsilon}}{kT} =$$

$G = \epsilon - TS + PV$

$$= \frac{ST + \bar{N}\mu - \bar{\epsilon}}{kT} = \boxed{\frac{PV}{kT}}$$

Notice that $q = \frac{PV}{kT}$

$$\boxed{\Omega} = -kTq = -\boxed{PV}$$

Define $z = e^{-\alpha} = e^{\mu/kT}$ fugacity

Now

$$q = \ln\left\{\sum_{rs} z^{N_r} e^{-\beta \varepsilon_s}\right\} =$$

$$= \ln\left\{\sum_{N_r=0}^{\infty} z^{N_r} \underbrace{\sum_s e^{-\beta \varepsilon_s}}_{Z_{N_r}(V,T)}\right\} =$$

canonical partition function with N_r particles.

then

$$q = \ln \Big\{ \underbrace{\sum_{N_r=0}^{\infty} z^{N_r} Z_{N_r}(V,T)}_{\mathcal{Z}(z,V,T)} \Big\} = \qquad Z_0 = 1$$

$$= \ln \mathcal{Z}(z,V,T)$$

$\mathcal{Z}$: grand-canonical partition function
(Q in the book).

Also notice that

$$\Omega = -kT q = -kT \ln \mathcal{Z}(z,V,T)$$

analogous of $F = -kT \ln Z$ in canonical

Despite the formal form of $\mathcal{Z}$ in terms of Z_{N_r} many times it is possible to obtain $\mathcal{Z}$ without having to explicitly calculate Z_{N_r}.

Relationship of $\mathfrak{z}$, Ω and $\mathcal{Z}$ to thermodynamic quantities:

Since $\mathfrak{z} = \frac{PV}{kT} \Rightarrow P = \frac{kT\mathfrak{z}}{V} = \frac{kT}{V}\underbrace{\ln \mathcal{Z}(\mathfrak{z}, V, T)}_{-\Omega}$ (3)

$$\equiv -\frac{\Omega}{V}$$

Let's use $\bar{N} \equiv N$ and $\bar{E} \equiv U$

$$\mathcal{Z} = \sum_{N_r=0}^{\infty} z^{N_r} Z_{N_r}(V,T) = \sum_{N_r=0}^{\infty} e^{-\alpha N_r} \sum_s e^{-\beta \epsilon_s}$$

$$N(z,V,T) = -\frac{\partial}{\partial \alpha}\left\{ \ln \sum_{r,s} e^{-\alpha N_r - \beta \epsilon_s} \right\} =$$

$$= z \frac{\partial}{\partial z} q(z,V,T)\Big|_{V,T} = z \frac{\sum_{N_r=0}^{\infty} N_r z^{N_r-1} Z_{N_r}(V,T)}{\mathcal{Z}} =$$

$$= \frac{\sum_{N_r=0}^{\infty} N_r z^{N_r} Z_{N_r}}{\mathcal{Z}} \underset{4}{=} kT \frac{\partial q(\mu,V,T)}{\partial \mu}\Big|_{V,T}$$

$$z = e^{-\alpha}$$

$$\frac{\partial}{\partial \alpha} = \frac{\partial}{\partial z}\frac{\partial z}{\partial \alpha} = -e^{-\alpha}\frac{\partial}{\partial z} = -z\frac{\partial}{\partial z}$$

Notice that

$$\alpha = -\frac{\mu}{kT}$$

$$\partial\alpha = -\frac{\partial\mu}{kT}$$

$$\frac{1}{\partial\alpha} = -kT\frac{\partial}{\partial\mu} \quad (4)$$

Also $N = kT \left.\frac{\partial q}{\partial\mu}\right|_{V,T} = -\left.\frac{\partial\Omega}{\partial\mu}\right|_{V,T}$ (5)

Notice that

$\Omega = F - \mu N$ because $\Omega = \Omega(V, T, \mu)$

$$U(z,V,T) = -\frac{\partial}{\partial \beta}\left\{\ln \sum_{r,s} e^{-\alpha N_r - \beta E_s}\right\} =$$

$$= -\frac{\partial}{\partial \beta} q(z,V,T)\Big|_{z,V} \overset{\circledast}{=} kT^2 \frac{\partial}{\partial T} q(z,V,T)\Big|_{z,V}$$

⑥

$$\beta = \frac{1}{kT}$$

$$\frac{\partial}{\partial \beta} = \frac{\partial}{\partial T}\frac{\partial T}{\partial \beta} =$$

$$= -\frac{1}{k\beta^2}\frac{\partial}{\partial T} =$$

$$= -kT^2 \frac{\partial}{\partial T} \quad \circledast$$

Notice that ③ and ⑤ provide the equation of state if we solve for z in each of them.

From ⑤ and ⑥ we can get $U = U(N,V,T)$ solving for z in each equation. From U we get $c_V = \frac{\partial U}{\partial T}\Big|_{N,V}$.

$$E - TS = TS - PV + N\mu - TS$$

Helmholz:

$$F = N\mu - PV = NkT\ln z \underbrace{- kTq}_{-\Omega} =$$

$$z = e^{\mu/kT}$$

$$= NkT\ln z - kT\ln \mathcal{Z} =$$

$$= -kT\ln \mathcal{Z}/z^N$$