Consider a system in thermodynamic and diffusive equilibrium with a reservoir, at constant volume.

In general, $\sigma(U, V, N)$, so from the total derivative

constant volume

$$d\sigma = \left(\frac{\partial \sigma}{\partial U}\right)_{\cancel{V},N} dU + \left(\frac{\partial \sigma}{\partial V}\right)_{U,N} \overset{0}{\cancel{dV}} + \left(\frac{\partial \sigma}{\partial N}\right)_{U,\cancel{V}} dN$$ KK Eq. 5.31

if ~~all~~ the system is in thermal equilibrium, $d\tau = 0$, we can write this as $(\delta\sigma)_\tau$ ← constant temp $\Rightarrow d\tau = 0$

small change

$(\delta U)_\tau$

$$\frac{(\delta\sigma)_\tau}{(\delta N)_\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N \frac{(\delta U)_\tau}{(\delta N)_\tau} + \left(\frac{\partial \sigma}{\partial N}\right)_U \frac{(\delta N)_\tau}{(\delta N)_\tau}$$ KK Eq. 5.32

Compare with derivation on page 39 of my notes.

$$\left(\frac{\partial \sigma}{\partial N}\right)_\tau = \underbrace{\left(\frac{\partial \sigma}{\partial U}\right)_N}_{1/\tau} \left(\frac{\partial U}{\partial N}\right)_\tau + \left(\frac{\partial \sigma}{\partial N}\right)_U$$

$$\left(\frac{\partial \sigma}{\partial N}\right)_\tau = \frac{1}{\tau}\left(\frac{\partial U}{\partial N}\right)_\tau + \left(\frac{\partial \sigma}{\partial N}\right)_U$$

$$\Rightarrow \left(\frac{\partial \sigma}{\partial N}\right)_U = \left(\frac{\partial \sigma}{\partial N}\right)_\tau - \frac{1}{\tau}\left(\frac{\partial U}{\partial N}\right)_\tau$$

$$\Rightarrow \tau \left(\frac{\partial \sigma}{\partial N}\right)_{\tau,V} = \left(\frac{\partial U}{\partial N}\right)_{\tau,V} + \tau\left(\frac{\partial \sigma}{\partial N}\right)_{U,V}$$

Remember that $F = U - \tau\sigma$, so

$$\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \left(\frac{\partial U}{\partial N}\right)_{\tau,V} - \tau\left(\frac{\partial \sigma}{\partial N}\right)_{\tau,V}$$ KK Eq. 5.34

$$\Rightarrow + \tau\left(\frac{\partial \sigma}{\partial N}\right)_{\tau,V} = -\mu + \left(\frac{\partial U}{\partial N}\right)_{\tau,V}$$

so

$$-\mu + \cancel{\left(\frac{\partial U}{\partial N}\right)_{\tau,V}} = \cancel{\left(\frac{\partial U}{\partial N}\right)_{\tau,V}} + \tau\left(\frac{\partial \sigma}{\partial N}\right)_{U,V}$$

$$\boxed{\mu = -\tau\left(\frac{\partial \sigma}{\partial N}\right)_{U,V}}$$ KK Eq. 5.35

Temperature is inversely proportional to the rate of change of the entropy with respect to the energy, the chemical potential is proportional to the rate of change of the entropy with respect to the number of particles.

KK Eq. 5.31 can be rewritten as

$$d\sigma = \underbrace{\left(\frac{\partial \sigma}{\partial U}\right)_{V,N}}_{1/\tau} dU + \underbrace{\left(\frac{\partial \sigma}{\partial V}\right)_{U,N}}_{p/\tau} dV + \underbrace{\left(\frac{\partial \sigma}{\partial N}\right)_{U,V}}_{-\mu/\tau} dN$$ KK Eq 5.37

← see my notes pg. 40

$$\tau\, d\sigma = dU + p\,dV - \mu\, dN$$ KK Eq. 5.38

$$\Rightarrow \boxed{dU = \tau d\sigma - p dV + \mu dN}$$ KK Eq. 5.39

Thermodynamic identity like we saw before, but with an additional term for the chemical potential and number of particles. Chemical potential is the intensive variable and number of particles the extensive variable.

$$\mu dN = dU - \tau d\sigma + p dV$$

$$\mu = \frac{\partial U}{\partial N} - \tau\left(\frac{\partial \sigma}{\partial N}\right) + p\left(\frac{\partial V}{\partial N}\right)$$

Variables: U, σ, V

Let σ, V constant, then

$$\boxed{\mu = \left(\frac{\partial U}{\partial N}\right)_{\sigma,V}} - \cancel{\tau\left(\frac{\partial \sigma}{\partial N}\right)_{\sigma,V}} + \cancel{p\left(\frac{\partial V}{\partial N}\right)_{\sigma,V}}$$

Let U, V constant, then

$$\mu = \cancel{\left(\frac{\partial U}{\partial N}\right)_{U,V}} \boxed{- \tau\left(\frac{\partial \sigma}{\partial N}\right)_{U,V}} + \cancel{p\left(\frac{\partial V}{\partial N}\right)_{U,V}}$$

Let U, σ constan, then

$$\mu = \cancel{\left(\frac{\partial U}{\partial N}\right)_{U,\sigma}} - \cancel{\tau\left(\frac{\partial \sigma}{\partial N}\right)_{U,\sigma}} \boxed{+ p\left(\frac{\partial V}{\partial N}\right)_{U,\sigma}}$$

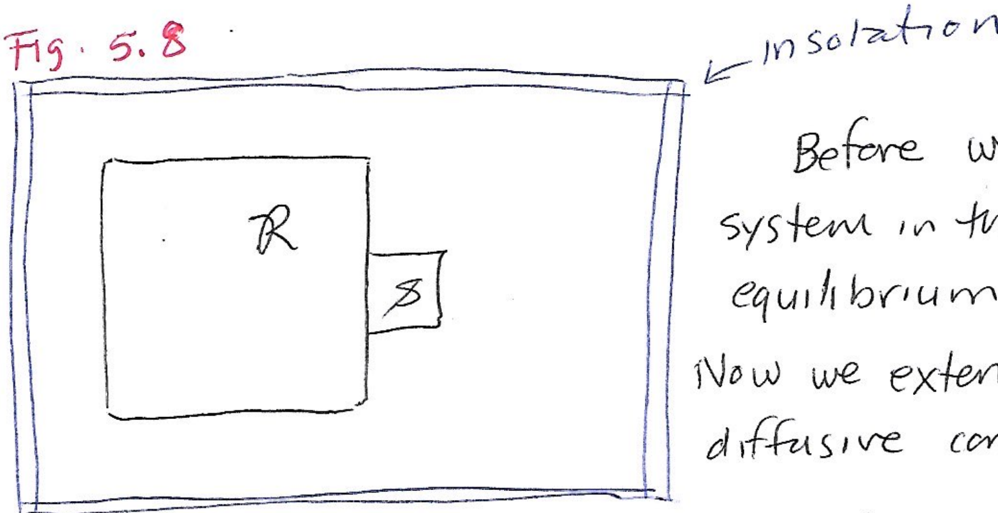
	$\sigma(U,V,N)$	$U(\sigma,V,N)$	$F(\tau,V,N)$
τ:	$1/\tau = \left(\frac{\partial \sigma}{\partial U}\right)_{V,N}$	$\tau = \left(\frac{\partial U}{\partial \sigma}\right)_{V,N}$	
p:	$p/\tau = \left(\frac{\partial \sigma}{\partial V}\right)_{U,N}$	$-p = \left(\frac{\partial U}{\partial V}\right)_{\sigma,N}$	$-p = \left(\frac{\partial F}{\partial V}\right)_{\tau,N}$
μ:	$-\mu/\tau = \left(\frac{\partial \sigma}{\partial N}\right)_{U,V}$	$\mu = \left(\frac{\partial U}{\partial N}\right)_{\sigma,V}$	$\mu = \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$

Compare to derivations on page 40 of my notes

Table ~~Fig~~ 5.1 KK

Gibbs Factor and Gibbs Sum

KK Fig. 5.8



Before we considered a system in thermodynamic equilibrium with a reservoir. Now we extend the idea to diffusive contact/equilibrium.

The total number of particles and the total energy are conserved.

when the system has N particles, reservoir has $N_0 - N$ particles
" " " " energy ε, " " energy $U_0 - \varepsilon$

A "state" now has a specified number of particles N and its energy is $\varepsilon_{s(N)}$, typically written ε_s.

The multiplicity of the reservoir plus system is

$$g(R+S) = g(R) \times g(S)$$

if the state of $\mathcal{S}$ is specified (so ε, N), then

$$g(\mathcal{R}+\mathcal{S}) = g(\mathcal{R}) \times 1$$ KK Eq. 5.41

the multiplicity is just the multiplicity of the reservoir.

The probability that the reservoir is in state "s" is proportional to the multiplicity, so $P(N, \varepsilon_s) \propto g(N_0 - N, U_0 - \varepsilon_s)$ KK Eq. 5.42

The ratio of the probabilities that the reservoir is in state N_1, ε_1 and state N_2, ε_2 is

$$\frac{P(N_1, \varepsilon_1)}{P(N_2, \varepsilon_2)} = \frac{g(N_0 - N_1, U_0 - \varepsilon_1)}{g(N_0 - N_2, U_0 - \varepsilon_2)}$$ KK Eq. 5.43

Compare to KK Eq. 3.2 and my notes pgs. 33-34.

$$\exp\left\{ \ln\left[\frac{g_{\mathcal{R}}(N_0 - N_1, U_0 - \varepsilon_1)}{g_{\mathcal{R}}(N_0 - N_2, U_0 - \varepsilon_2)} \right] \right\}$$

$$= \exp\left\{ \ln g_{\mathcal{R}}(N_0 - N_1, U_0 - \varepsilon_1) - \ln g_{\mathcal{R}}(N_0 - N_2, U_0 - \varepsilon_2) \right\}$$

$$= \exp\left[\sigma_{\mathcal{R}}(N_0 - N_1, U_0 - \varepsilon_1) - \sigma_{\mathcal{R}}(N_0 - N_2, U_0 - \varepsilon_2) \right]$$

with $\Delta\sigma_{\mathcal{R}} \equiv \sigma_{\mathcal{R}}(N_0 - N_1, U_0 - \varepsilon_1) - \sigma_{\mathcal{R}}(N_0 - N_2, U_0 - \varepsilon_2)$ KK Eq. 5.47

so $P_1(N_1, \varepsilon_1)/P(N_2, \varepsilon_2) = \exp(\Delta\sigma_{\mathcal{R}})$ KK Eq. 5.46

Now, let's Taylor expand about $\sigma_R(N_0, U_0)$. Recall

$$f(x_0+a) = f(x_0) + a\left(\frac{df}{dx}\right)_{x=x_0} + \frac{1}{2!}a^2\left(\frac{d^2f}{dx^2}\right)_{x=x_0} + \cdots$$

KK Eq. 3.6

then

$$\sigma_R(N_0-N_1, U_0-\varepsilon_1) =$$

$$\cancel{\sigma_R(N_0,U_0)} - N_1\overset{-\mu/\tau}{\left(\frac{d\sigma_R}{dN}\right)_{N=N_0}} - \varepsilon_1\overset{1/\tau}{\left(\frac{d\sigma_R}{dU}\right)_{U=U_0}}$$

$$+ \frac{1}{2}N_1^2\left(\frac{d^2\sigma_R}{dN^2}\right)_{N=N_0} + \frac{1}{2}\varepsilon_1^2\left(\frac{d\sigma_R}{dU}\right)_{U=U_0} + \cdots$$

$$-\sigma_R(N_0-N_2, U_0-\varepsilon_2) =$$

$$-\cancel{\sigma_R(N_0,U_0)} + N_2\overset{-\mu/\tau}{\left(\frac{d\sigma_R}{dN}\right)_{N=N_0}} + \varepsilon_2\overset{1/\tau}{\left(\frac{d\sigma_R}{dU}\right)_{U=U_0}}$$

$$-\frac{1}{2}N_2^2\left(\frac{d^2\sigma_R}{dN^2}\right)_{N=N_0} - \frac{1}{2}\varepsilon_2\left(\frac{d\sigma_R}{dU}\right)_{U=U_0} + \cdots$$

$$\Delta\sigma_R = +\frac{\mu N_1}{\tau} - \frac{\varepsilon_1}{\tau} - \frac{\mu N_2}{\tau} + \frac{\varepsilon_2}{\tau}$$

$$-\frac{1}{2}N_1^2\frac{d}{\underset{\text{extensive}}{dN}}\left(\underset{\text{intensive}}{\mu/\tau}\right) + \frac{1}{2}\varepsilon_1^2\frac{d}{\underset{\text{extensive}}{dU}}\left(\underset{\text{intensive}}{1/\tau}\right)$$

$$+\frac{1}{2}N_2^2\frac{d}{dN}(\mu/\tau) - \frac{1}{2}\varepsilon_2^2\frac{d}{dU}(1/\tau) + \cdots$$

they go to zero in the limit of an infinitely large reservoir.

$$\Delta\sigma_{R} = \frac{(N_1 - N_2)\mu}{\tau} - \frac{(\varepsilon_1 - \varepsilon_2)}{\tau}$$ KK Eq. 5.51

$$\boxed{\frac{P(N_1, \varepsilon_1)}{P(N_2, \varepsilon_2)} = \frac{\exp[(N_1\mu - \varepsilon_1)/\tau]}{\exp[(N_2\mu - \varepsilon_2)/\tau]}}$$ KK Eq. 5.52

"The central result of statistical mechanics."

$\exp[(N_1\mu - \varepsilon_1)\tau]$ is called the <u>Gibbs factor</u>, which reduces to the Boltzmann factor when $\mu = 0$. It was first derived by Willard Gibbs, who called it the "grand canonical" distribution.

Remember that the sum of all probabilities must be equal to 1 (the zeroth moment)

$$\sum_{N=0}^{\infty} \sum_{S(N)} \exp[(N\mu - \varepsilon_{S(N)})/\tau] = \mathcal{Z}(\mu, \tau)$$ KK Eq. 5.53

$$\sum_{ASN} \exp[(N\mu - \varepsilon_{S(N)})/\tau] = \mathcal{Z}(\mu, \tau)$$

all states of the system for all numbers of particles

In the case of only thermodynamic equilibrium, the sum ~~was~~ is called the partition function. Here, $\mathcal{Z}$ is called Gibbs sum, grand sum, or grand partition function.

$$P(N_1, \varepsilon_1) = \frac{\exp[(N_1\mu - \varepsilon_1)/\tau]}{\mathcal{Z}}$$ KK Eq. 5.54

$$\sum_N \sum_S P(N, \varepsilon_s) = \frac{1}{\mathcal{Z}} \sum_N \sum_S \exp[(N\mu - \varepsilon_{s(N)})/\tau] = \frac{\mathcal{Z}}{\mathcal{Z}} = 1$$ KK Eq. 5.55

Consider the thermal average of the number of particles in the system.

KK Eq. 5.57

$$\langle N \rangle = \sum_{ASN} N\, P(N, \varepsilon_{s(N)}) = \frac{\sum_{ASN} N \exp[(N\mu - \varepsilon_s)/\tau]}{\mathcal{Z}}$$

but

$$\frac{d}{d\mu}\mathcal{Z} = \frac{d}{d\mu} \sum_{ASN} e^{(N\mu - \varepsilon_s)/\tau} = \sum_{ASN} \frac{d}{d\mu} \frac{e^{N\mu/\tau}}{e^{\varepsilon_s/\tau}}$$

$$= \sum_S e^{-\varepsilon_s/\tau} \sum_N \frac{d}{d\mu} e^{N\mu/\tau}$$

Let $u = N\mu/\tau$, then $du = N/\tau$

KK Eq. 5.58

$$\frac{d}{d\mu}\mathcal{Z} = \sum_S e^{-\varepsilon_s/\tau} \sum_N \frac{N}{\tau} e^{N\mu/\tau} = \frac{1}{\tau} \sum_{ASN} N \exp[(N\mu - \varepsilon_s)/\tau]$$

KK Eq. 5.59

$$\langle N \rangle = \tau \frac{d}{d\mu}\mathcal{Z} \cdot \frac{1}{\mathcal{Z}} = \frac{\tau}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \frac{\tau\, \partial \ln \mathcal{Z}}{\partial \mu}$$