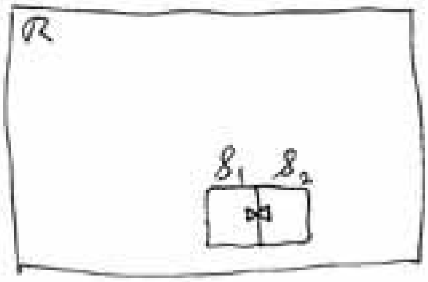
Previously



Exchange U, N between S_1 and S_2

Minimize $\mathbf{F}$ @ constant T, V

$\Rightarrow$ chemical potential $\mu = \left(\frac{\partial \mathbf{F}}{\partial \mathbf{N}}\right)_{V, T, \ldots}$

and $\boxed{\begin{array}{l} \mu_1 = \mu_2 \\ T_1 = T_2 \end{array}}$ @ equilibrium

we also found that

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

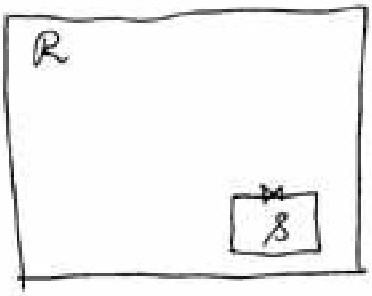
and we had the thermodynamic relation

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

And before we introduced μ, we had the Boltzmann factor

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{e^{-\varepsilon_1/\tau}}{e^{-\varepsilon_2/\tau}}$$

Today we will derive the generalization of this formula for systems which can exchange N, not just U.



Total energy fixed

$$U_R + U_S = U_0$$

Total particle # fixed

$$N_R + N_S = N_0$$

System has $(U,N) \Rightarrow$ reservoir has $(U_0-U,\ N_0-N)$

* To find bulk thermodynamics, ask as before about S in particular quantum states and calculate relative probabilities.

Let probability of system being in state with energy ε_s and particle # N be

$$P(N, \varepsilon_s).$$

Since the state of S is specified, we are interested in

$$g(R+S) = g(R)\, g(S)$$
$$= g(R) \qquad \leftarrow \text{multiplicity function}$$

The states here have $(N_0-N,\ U_0-\varepsilon_s)$
(of the reservoir)

So the relative probability

$$\frac{P(N_1, \varepsilon_1)}{P(N_2, \varepsilon_2)} \cong \frac{g_R(U_0-\varepsilon_1,\ N_0-N_1)}{g_R(U_0-\varepsilon_2,\ N_0-N_2)}$$

but $\qquad g = \exp(\sigma) \qquad$ because $\qquad \sigma = \log(g)$

thus

$$\frac{P(N_1, \varepsilon_1)}{P(N_2, \varepsilon_2)} = \frac{\exp[\sigma_R(U_0-\varepsilon_1, N_0-N_1)]}{\exp[\sigma_R(U_0-\varepsilon_2, N_0-N_2)]} \equiv \exp[\Delta\sigma_R]$$

Now we use the Math Taylor expansion story

$$\sigma_R(U_0-\varepsilon, N_0-N) = \sigma_R(U_0, N_0) - N\left(\frac{\partial\sigma_R}{\partial N_0}\right)_{U_0} - \varepsilon\left(\frac{\partial\sigma_R}{\partial U_0}\right)_{N_0} + \dots$$

So

$$\Delta\sigma_R = \sigma_R(U_0, N_0) - N_1\left(\frac{\partial\sigma_R}{\partial N_0}\right)_{U_0} - \varepsilon_1\left(\frac{\partial\sigma_R}{\partial U_0}\right)_{N_0} + O(\varepsilon_i^2, N_i^2)$$

$$-\sigma_R(U_0, N_0) + N_2\left(\frac{\partial\sigma_R}{\partial N_0}\right)_{U_0} + \varepsilon_2\left(\frac{\partial\sigma_R}{\partial U_0}\right)_{N_0}$$

$$= (N_2 - N_1)\left(\frac{-\mu}{\tau}\right) + (\varepsilon_2-\varepsilon_1)\left(\frac{1}{\tau}\right)$$

i.e. $\Delta\sigma = \dfrac{(N_1-N_2)\mu}{\tau} + \dfrac{-(\varepsilon_1-\varepsilon_2)}{\tau}$

$$\Rightarrow \boxed{\frac{P(N_1, \varepsilon_1)}{P(N_2, \varepsilon_2)} = \frac{\exp((N_1\mu-\varepsilon_1)/\tau)}{\exp((N_2\mu-\varepsilon_2)/\tau)}}$$ ← Gibbs Factor

Now, previously we defined the canonical partition function Z by

$$Z = \sum_s e^{-\varepsilon_s/\tau}$$

Now we want to define the grand canonical analogue

So, sum

Gibbs factor $e^{-(\varepsilon_s - \mu N)/\tau}$

Sum over all energies $\varepsilon_{s(N)}$

and sum over all particle #s:

$$\boxed{\mathcal{Z}(\mu,\tau) = \underbrace{\sum_{N=0}^{\infty} \sum_{s(N)}}_{} e^{-(\varepsilon_{s(N)} - N\mu)/\tau}}$$

grand partition function

KK call this $\sum_{ASN}$

"sum over all states and numbers..."

▷ the energy $\varepsilon_{s(N)}$ is the exact eigenstate of the N-particle Hamiltonian(!)

Only if the particles are noninteracting would this be expressable in terms of $N \cdot \varepsilon_s$

# of particles ↑ ↖ energy of 1-particle $\hat{H}$

Now, we can compute the correctly normalized probability

$$\boxed{P(N_1, \varepsilon_1) = \frac{e^{-(\varepsilon_1 - \mu N_1)/\tau}}{\mathcal{Z}(\mu,\tau)}}$$

equilibrium

This is normalized: $\sum_{N=0}^{\infty} \sum_{s(N)} P(N, \varepsilon_s) = 1$

Average values

Previously we derived an expression for U by differentiating Z. Let's do the analogue here.

For any quantity X
let the notation be that its value in the state $s(N)$ with N particles is $X(N, s)$

Then
$$\langle X \rangle = \sum_{N,s} X(N,s)\, P(N, \varepsilon_s)$$
$$= \sum_{N,s} X(N,s) \frac{e^{-(\varepsilon_s - \mu N)/\tau}}{\mathcal{Z}(\mu,\tau)}$$

This computes the thermal average.

Particle

This is an important quantity to know!

$$\langle N \rangle = \sum_{N,s} \frac{N e^{-(\varepsilon_s - \mu N)/\tau}}{\mathcal{Z}(\mu,\tau)}$$

Recall the definition of the grand partition function

$$\mathcal{Z}(\mu,\tau) = \sum_{N,s} e^{-(\varepsilon_s - \mu N)/\tau}$$

So
$$\frac{\partial \mathcal{Z}}{\partial \mu} = \sum_{N,s} \frac{N}{\tau} e^{-(\varepsilon_s - \mu N)/\tau}$$

can pull out of the sum

Hence

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

or

$$\boxed{\langle N \rangle = \tau \frac{\partial \log \mathcal{Z}}{\partial \mu}.}$$

Shorthand notation - (absolute) activity $\boxed{\lambda \equiv e^{\mu/\tau}}$

Then

$$\mathcal{Z}(\mu,\tau) = \sum_{N=0}^{\infty} \sum_{S(N)} \lambda^N e^{-\varepsilon_s/\tau}$$

and (algebra)

$$\boxed{\langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \log \mathcal{Z}}$$

This is especially useful if we know N for a problem but need to find $\mu = \tau \log \lambda$.

$\boxed{\text{Energy}}$

$$\langle \varepsilon \rangle \equiv U = \sum_{N,s} \varepsilon_s \frac{e^{-(\varepsilon_s - \mu N)/\tau}}{\mathcal{Z}(\mu,\tau)}$$

More shorthand: $\boxed{\beta \equiv \frac{1}{\tau}}$

so

$$P(N,\varepsilon_s) = \frac{e^{-\beta(\varepsilon_s - \mu N)}}{\mathcal{Z}(\mu,\tau)}$$

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So, notice what happens when we $\frac{\partial}{\partial \beta}$ to $\mathcal{Z}$:

$$\mathcal{Z} = \sum_{N,s} e^{-\beta(\varepsilon_s - \mu N)}$$

$$\Rightarrow \frac{\partial}{\partial \beta}\mathcal{Z} = \sum_{N,s} -(\varepsilon_s - \mu N)\, e^{-\beta(\varepsilon_s - \mu N)}$$

$$= \Big[-\langle \varepsilon_s \rangle + \mu \langle N \rangle\Big]\mathcal{Z}$$

this is what we want

So $\langle \varepsilon_s \rangle = U = \mu \langle N \rangle + -\frac{\partial \mathcal{Z}}{\partial \beta} \cdot \frac{1}{\mathcal{Z}}$

but $\langle N \rangle = \tau \frac{\partial \log \mathcal{Z}}{\partial \mu} = \frac{1}{\beta}\frac{\partial}{\partial \mu} \log \mathcal{Z}$

so

$$\boxed{U = \left(\frac{\mu}{\beta}\frac{\partial}{\partial \mu} - \frac{\partial}{\partial \beta}\right)\log \mathcal{Z}}$$