Lecture 11

$$\chi \simeq \frac{N(g\mu_B)^2}{k T}\frac{1}{3}J(J+1) \sim \frac{C}{T}$$

$$C = \text{Curie constant} = \frac{N_0 (g\mu_B)^2}{3k} J(J+1)$$

$\chi \sim \frac{C}{T}$ is Curie's law

In reality there is usually a cut-off $\chi \sim \frac{1}{T-\theta}$ ← Curie-Weiss Temperature

as $T \to 0$, our expansion in $\frac{B}{T}$ breaks down at some point.

It is instructive to also make a classical treatment:

$$\epsilon_i = -\mu_i \cdot B = \mu B \cos\theta_i$$

$$\therefore \mathcal{H} = -\mu B_z \sum_i^N \cos\theta_i = \sum_i \mathcal{H}(\theta_i)$$

$$\therefore Z_{classical} = \prod_{i=1}^{N} \sum_{\{\theta_i\}} e^{-\beta \mathcal{H}(\theta_i)}$$

$$Z = \prod_i \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \; e^{-\mu\beta B_z \cos\theta} \; ; \; u = \cos\theta, \; du = -\sin\theta d\theta$$

$$Z = \prod_i \frac{2\pi}{\beta\mu B_z}\left(e^{\beta\mu B_z} - e^{-\beta\mu B_z}\right)$$

$$\therefore \quad Z_{classical} = \left(\frac{4\pi}{\beta \mu B_z} \sinh \beta \mu B_z \right)^N$$

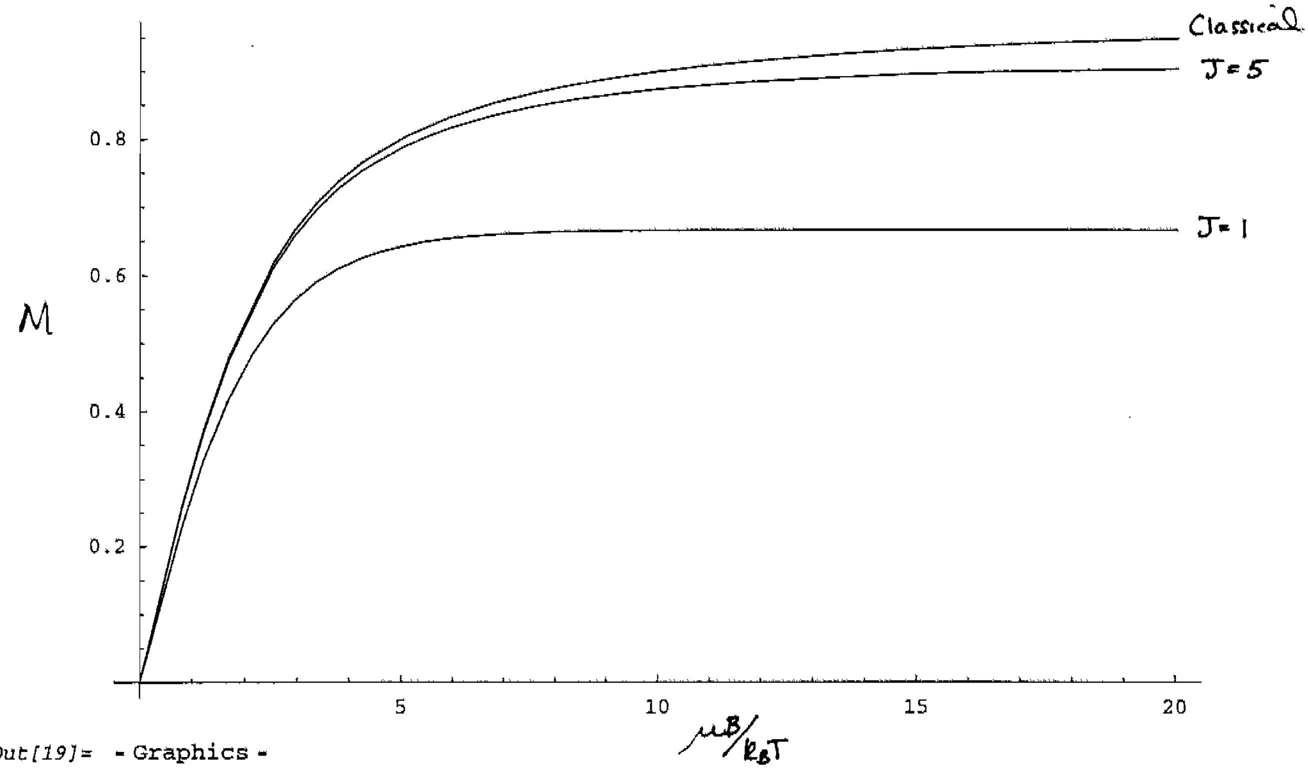
whereas $$Z_{quant} = \left(\frac{\sinh \left[\beta \left(\frac{2J+1}{2}\right) g \mu_B B_z\right]}{\sinh \left[\frac{\beta g \mu_B B_z}{2}\right]} \right)^N$$

Since $\langle \vec{J}^2 \rangle = J(J+1) \Leftrightarrow \mu = \sqrt{J(J+1)}\, g \mu_B$

If we take $J \to \infty \Rightarrow J g \mu_B = \mu$ is constant, then

$$Z_q \to \left[\frac{\sinh [\beta \mu B_z]}{\beta g \mu B_z / 2} \right]^N = \left(\frac{2J \sinh \beta \mu B_z}{\beta \mu B_z} \right)^N$$

so $M_q \to M_{cl}$ in this limit.



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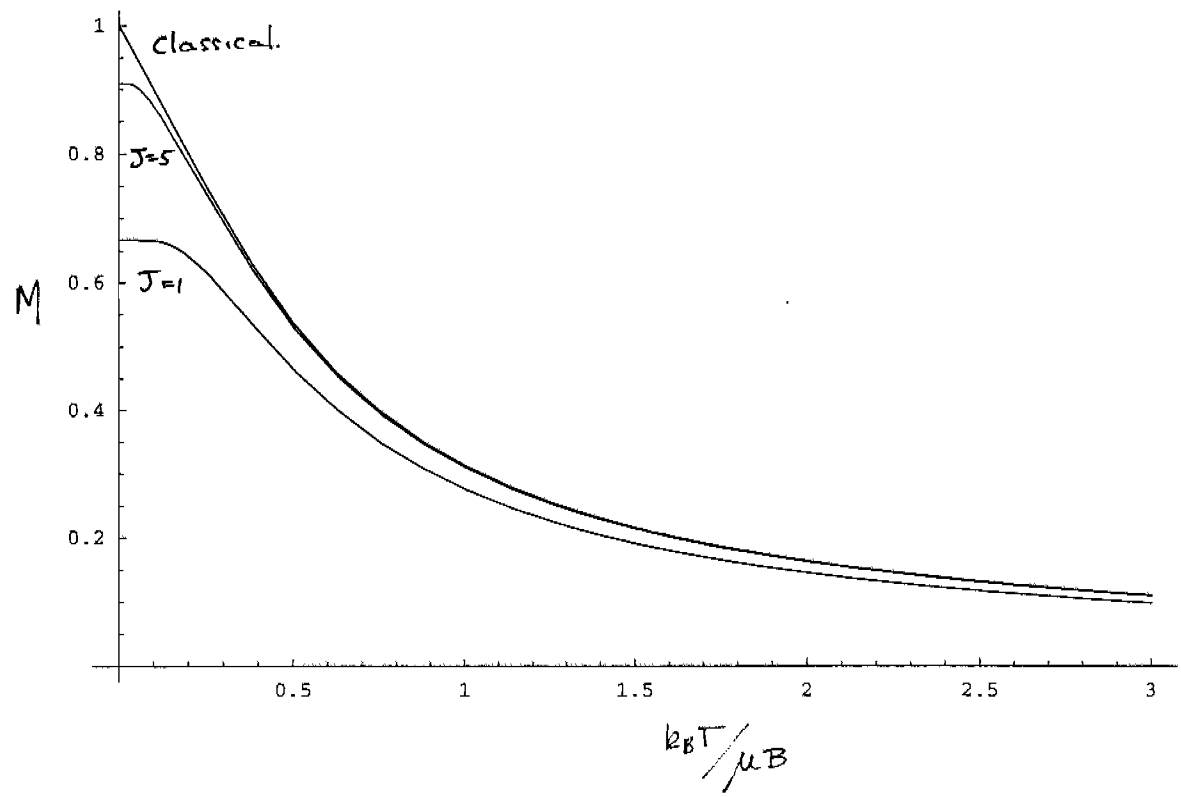

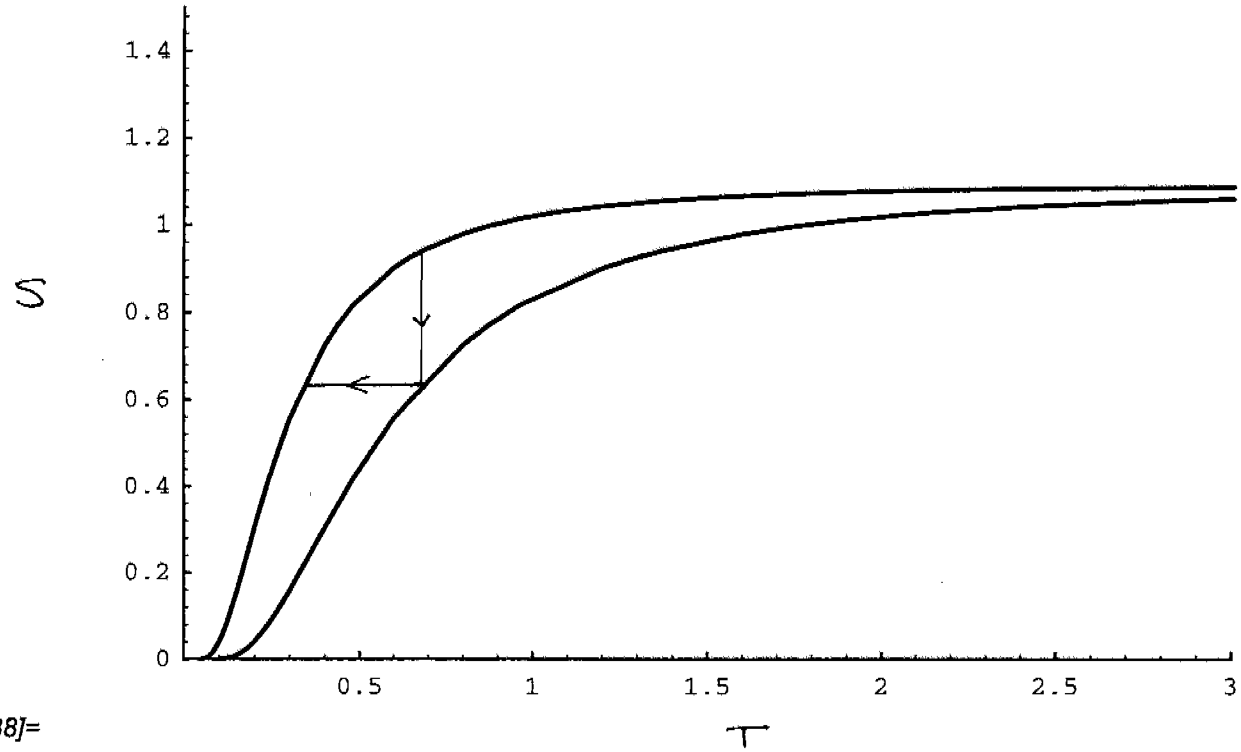

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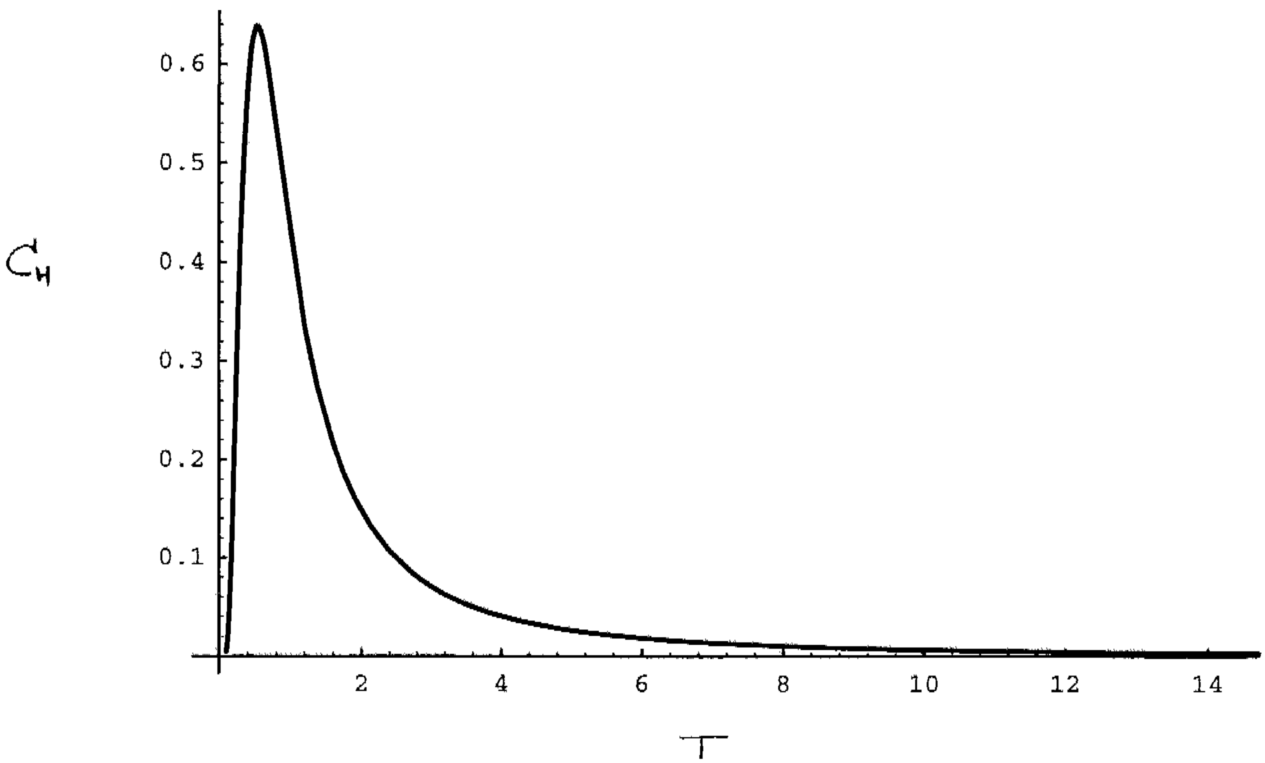
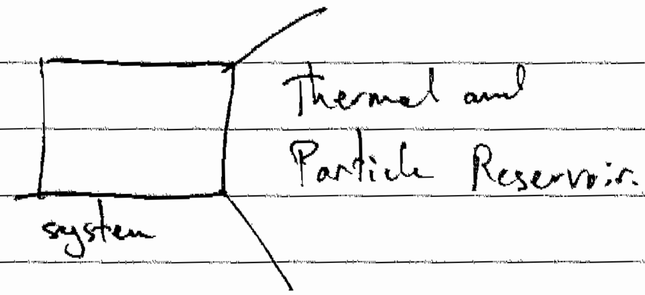


Grand Canonical Ensemble.



$E_{tot} = E_j + E_{RES}$

$N_{tot} = N_j + N_{RES}$

$$P_j = \frac{\Omega_{Res}(E_{tot} - E_j, N_{tot} - N_j)}{\Omega_{tot}(E_{tot}, N_{tot})}$$

Here we again use the principle of the micro-canonical ensemble.

$$\Omega = e^{S/k}$$

$$\Rightarrow P_j = \exp\left[\frac{1}{k}\left(S_{RES}(E_{tot} - E_j, N_{tot} - N_j) - S_{tot}(E_{tot}, N_{tot})\right)\right]$$

$$S_{Res}(E_{tot} - E_j + U - U, N_{tot} - N_j + N - N)$$

$\boxed{\text{Expansion}}$

$$= S_{Res}(E_{tot} - U, N - N_j) + \frac{1}{T}(U - E_j) - \frac{\mu}{T}(N - N_j)$$

we did this earlier.

$$S_{tot} = S_{Res}(E_{tot} - U, N - N_j) + S(U, N) \quad \text{(additivity of entropy)}$$

$$\therefore P_j = \exp\left[-\frac{1}{k}\left[S - \frac{1}{T}U + \frac{\mu}{T}N\right] - \frac{1}{k}\left[E_j - \mu N_j\right]\right]$$

$S - \frac{1}{T}U + \frac{\mu}{T}N$ is the Legendre transformed entropy $\frac{PV}{T} = f(T, \mu, V)$

$$P_j = e^{-\frac{1}{k}\Psi} e^{-\beta(E_j - \mu N_j)}$$

$$\sum_j P_j = 1 = e^{-\Psi/k} \sum_j e^{-\beta(E_j - \mu N_j)}$$

Define $\Xi = \sum_j e^{-\beta(E_j - \mu N_j)}$; $\Psi = k \ln \Xi$

This completes our catalogue:

$$\begin{cases} S(U,V,N) = k \ln \Omega(U,V,N) & \text{Microcanonical} \\ -\frac{F}{T}(T,V,N) = k \ln Z(T,V,N) & \text{Canonical} \\ \Psi = \frac{PV}{T}(T,V,\mu) = k \ln \Xi & \text{Grand Canonical.} \end{cases}$$

$$\therefore \quad d\Psi = -U\, d\left(\tfrac{1}{T}\right) + \frac{P}{T} dV + N\, d\left(\frac{\mu}{T}\right)$$

$$\therefore \quad U(T,V,\mu) = -\frac{\partial \Psi}{\partial\left(\frac{1}{T}\right)}\bigg|_{V,\beta\mu} = -k \frac{\partial \ln \Xi}{\partial\left(\frac{1}{T}\right)}\bigg|_{V,\beta\mu}$$

$$U(T,V,\mu) = -\frac{\partial \ln \Xi}{\partial \beta}\bigg|_{V,\beta\mu}$$

(similar to canonical relation)

$$\therefore U(T,V,\mu) = -\frac{\partial \ln \Xi}{\partial \beta}\Big|_{V,\beta\mu} = \frac{\sum_j E_j\, e^{-\beta(E_j-\mu N_j)}}{\sum_j e^{-\beta(E_j-\mu N_j)}}$$

hold $\beta\mu$ constant →

$$P_j = \exp\left[-\beta(E_j-\mu N_j)\right] \Big/ \sum_j e^{-\beta(E_j-\mu N_j)}$$

Similarly: $$N(T,V,\mu) = \frac{\partial \Psi}{\partial(\frac{\mu}{T})}\Big|_{\frac{1}{T},V} = \frac{\partial \ln \Xi}{\partial(\beta\mu)}\Big|_{\beta,V}$$

$$N(T,V,\mu) = \sum_j N_j\, e^{-\beta(E_j-\mu N_j)} \Big/ \sum_j e^{-\beta(E_j-\mu N_j)}$$

$$\Psi = \frac{PV}{T} = k \ln \Xi \Rightarrow PV = T \ln \Xi$$

<u>Entropy</u> $$\Psi = S - \frac{U}{T} + \frac{\mu}{T} N = \frac{PV}{T}$$

$$\therefore d(-PV) = -S\,dT - P\,dV - N\,d\mu$$

$$\therefore S = \frac{\partial}{\partial T}(PV)\Big|_{V,\mu} = \frac{\partial}{\partial T}\left[kT \ln \Xi\right]$$

<u>or</u> we could just calculate U, and N, + then find

$$S = \frac{1}{T} U - \frac{\mu}{T} N - \Psi$$

Grand Canonical Partition Function

$$\Xi = \sum_j e^{-\beta(E_j - \mu N_j)}$$

We can break the sum over j into 2 parts.

We first sum over states such that N is fixed. These states have energy $E_k(N)$. We then sum over all N.

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{k} e^{-\beta E_k(N)}$$

define $z = \exp(\beta\mu)$ as the Fugacity

$$\Xi = \sum_{N=0}^{\infty} z^N Z(T,V,N) \quad , \quad Z \text{ is canonical partition function w/ fixed } N.$$

$\therefore\ \Xi(z)$ is the generating function for the Canonical partition function

$$Z(T,V,N) = \frac{1}{N!}\frac{\partial^N}{\partial z^N}\Xi\Big|_{z=0}$$; Usually Ξ is easier to calculate

Example of application of GCE

Consider a gas in contact with a solid surface that has atomic absorption sites. Each site can be empty ($E=0$), singly occupied ($E=\epsilon_1$) or doubly occupied ($E=\epsilon_2$). The gas serves as a particle reservoir

$$\therefore \Xi = \sum_j e^{-\beta(E_j-\mu N_j)} = \sum_{\{n_i,\epsilon_i\}} e^{-\beta(\epsilon_1-\mu n_1)} \otimes e^{-\beta(\epsilon_2-\mu n_2)} \otimes \cdots$$

where ϵ_i and n_i represent the energy and # of particles at each site.

$$\Xi = \prod_{\{sites\}} \Xi_{site} = (\Xi_{site})^{N_s} \quad \text{for } N_s \text{ sites.}$$

$$\Xi_{site} = \sum_{n_i,\epsilon_i} e^{-\beta(\epsilon_i-\mu n_i)} = \underset{0 \text{ particles}}{1} + \underset{1 \text{ particles}}{e^{-\beta(\epsilon_1-\mu)}} + \underset{2 \text{ particles}}{e^{-\beta(\epsilon_2-2\mu)}}$$

$$N = \left.\frac{\partial \ln \Xi}{\partial \beta\mu}\right|_{\beta,V} = \frac{N_s}{\Xi_{site}}\left[0 + 1e^{-\beta(\epsilon_1-\mu)} + 2e^{-\beta(\epsilon_2-2\mu)}\right]$$

$\Rightarrow$ Interpret: $\dfrac{1}{\Xi_{site}}$ = prob. that a site is unoccupied.

$\dfrac{e^{-\beta(\epsilon_1-\mu)}}{\Xi_{site}}$ = prob. that 1 site is occupied

$\frac{e^{-\beta(\varepsilon_2 - 2\mu)}}{\Xi}$ is prob. that a site is doubly occupied

Similarly: $U = -\frac{\partial \ln \Xi}{\partial \beta}\Big|_{\beta\mu, V}$

$$U = \frac{N_s}{\Xi_{site}}\left[0 + \epsilon_1 e^{-\beta(\varepsilon_1 - \mu)} + \epsilon_2 e^{-\beta(\varepsilon_2 - \mu \cdot 2)}\right]$$

This is much simpler than a canonical partition function calculation.

For fixed N particles, $N = N_1 + 2N_2$

$E_j = N_1\epsilon_1 + N_2\epsilon_2$

$$Z = \sum_j e^{-\beta E_j} = \sum_{\{N_1, N_2, N_0\}} \frac{N_s!}{N_0!\,N_1!\,N_2!} e^{-\beta(\varepsilon_1 N_1 + \varepsilon_2 N_2)}$$

define $N_0 = N_s - N_1 - N_2$; define $M = N_1 + N_2$

$$Z = \sum_{\{M, N_2\}} \frac{N_s!}{(N_s - M)!\,(M - N_2)!\,N_2!} e^{-[M\varepsilon_1 + N_2(\varepsilon_2 - \varepsilon_1)]\beta}$$

sum $N_2 \in [0, M]$

Now (from before) $\Xi = \sum_{N=0}^{2N_s} e^{\beta\mu N} Z_N$, but $N = N_1 + 2N_2 = M + N_2$

gives triple sum → Math →

$$\rightarrow \Xi = \left[1 + e^{-\beta(\varepsilon_1 - \mu)} + e^{-\beta(\varepsilon_2 - 2\mu)}\right]^{N_s}$$