Stat Mech Notes:

Extensive Parameters - a property which depends on the amount of system

Intensive Property - a property which depends on no amounts of the system

$R = N_a k_b$: Entropy Analogues - Gases Model Parameters : $\underbrace{pV = NRT}_{\text{Gas Law}}$; $\underbrace{\left(p + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_bT}_{\text{Van der Waals}}$

Program of Statistical Mechanics:

1. Assume an atomic model
2. Apply the equations of motion (Newton, Schrodinger, etc.)
3. Calculate average quantities
4. Evaluate the thermodynamic limit

Collective vs. Random Behavior $\vec{p}_i(t) = \underbrace{\vec{p}_{av}(t)}_{\text{collective components}} + \underbrace{\delta\vec{p}_i(t)}_{\text{Random components}}$

States of a System: Example - Ising Model; $\vec{\mu}_i = s_i\vec{\mu}$ $s\{-1,+1\}$ Total Magnetic Moment: $M = \sum_i s_i$

Example: How many states? Multiplicity Function: $g(N,M)$ if $N_\uparrow$ $N_\downarrow$

$= \binom{N}{N_\uparrow}$; $M = N_\uparrow - N_\downarrow$ Real Magnetic Moment: $\vec{M} = M\vec{\mu}$

$= \frac{N(N-1)\cdots(N-N_\uparrow+1)}{N_\uparrow!} = \frac{N!}{N_\uparrow!N_\downarrow!}$

$= \frac{N!}{(N-N_\uparrow)!(N_\uparrow)!}$

Binomial Expansion: $(x+y)^N = \sum_{n=0}^{N}\binom{N}{n}x^n y^{N-n}$

Thermodynamic Limit Again:

Relative Magnetization: $x = \frac{M}{N}$; $x\{-1,1\}$

Since $G(N,M)$ is maximal at $M=0$. Goal $G(N,M) \ll 1$.

If N is large, and x is small, then $N_\uparrow$ and $N_\downarrow$ are large too.

$N! \approx \sqrt{2\pi N}\cdot N^N \cdot e^{-N + \frac{1}{12N} + O(\frac{1}{N^2})}$ = Stirlings Formula; Removing terms $(\sim\frac{1}{N}) \Rightarrow \log(N!) = N\log N - N + \frac{1}{2}\log(2\pi N)$

and with $\log(g(N,x)) = \log(N!) - \log(N_\uparrow!) - \log(N_\downarrow!)$; We find that $\log(g(N,x)) = N\log N - N_\uparrow\log N_\uparrow - N_\downarrow\log N_\downarrow$

$+\frac{1}{2}(\log(2\pi N) - \log(2\pi N_\uparrow) - \log(2\pi N_\downarrow))$

$-N + N_\uparrow + N_\downarrow$;

$\approx (N_\uparrow + N_\downarrow)\log N - N_\uparrow\log(N_\uparrow) - N_\downarrow\log(N_\downarrow)$

$-\frac{1}{2}\log(2\pi N) + \cancel{\frac{1}{2}(2\log N)}\log N_\uparrow - \log N_\downarrow)$

$\approx -\frac{1}{2}\log(2\pi N) - (N_\uparrow + \frac{1}{2})\log\left(\frac{N_\uparrow}{N}\right)$

$-(N_\downarrow + \frac{1}{2})\log\left(\frac{N_\downarrow}{N}\right)$ *

* $x = \frac{N_\uparrow - N_\downarrow}{N} = \frac{2N_\uparrow - N}{N}$; $N_\uparrow = \frac{1}{2}N(1+x)$; $N_\downarrow = \frac{1}{2}N(1-x)$

$\log(g(N,x)) \approx -\frac{1}{2}\log(2\pi N)$;

$-\frac{1}{2}(N(1+x)+1)\log\left(\frac{1}{2}(1+x)\right) - \frac{1}{2}(N(1-x)+1)\log\left(\frac{1}{2}(1-x)\right)$

Identity: $\log(1+x) \approx x - \frac{1}{2}x^2$

$\log(g(N,x)) \approx -\frac{1}{2}\log(2\pi N) - \frac{1}{2}(N(1+x)+1)\left[\log\left(\frac{1}{2}\right) + x - \frac{1}{2}x^2\right]$

$-\frac{1}{2}(N(1-x)+1)\left(\log\left(\frac{1}{2}\right) - x - \frac{1}{2}x^2\right)$

$\approx -\frac{1}{2}\log(2\pi N) - (N+1)\log\left(\frac{1}{2}\right) - \frac{1}{2}((N+1) + Nx)(x - \frac{1}{2}x^2)$

$-\frac{1}{2}((N+1) - Nx)(-x - \frac{1}{2}x^2) = -\frac{1}{2}\log(2\pi N) + (N+1)\log 2 - \frac{1}{2}(N-1)x^2$

The multiplicity function is a Gaussian $x_0 = \sqrt{\frac{2}{N-1}}$ and has a maximum at

$g(N,x) \approx \sqrt{\frac{2}{\pi N}}\cdot 2^N \cdot e^{-\frac{1}{2}x^2(N-1)}$

States of a System: Replace N by $N-1$: $g(N,x) \approx \sqrt{\frac{2}{\pi N}}\,2^N e^{-\frac{1}{2}x^2 N}$

$\sum_x g(N,x) = 2^N$; Step size: $\frac{2}{N}$; $2^N \cdot \frac{2}{N} = \sum g(N,x)\cdot\Delta x \to \int_{-1}^{1} g(N,x)\,dx$; $\int_{-1}^{1}\sqrt{\frac{2}{\pi N}}\,2^N e^{-\frac{1}{2}x^2 N}\,dx = \int_{-\sqrt{\frac{N}{2}}}^{\sqrt{\frac{N}{2}}}\sqrt{\frac{2}{\pi N}}\cdot 2^N \cdot e^{-t^2}\cdot dt\sqrt{\frac{N}{2}}$

$\approx \int_{-\infty}^{\infty}\sqrt{\frac{2}{\pi N}}\cdot 2^N \cdot e^{-t^2}\,dt\sqrt{\frac{2}{N}} = 2^N\left(\frac{2}{N}\right)$

How to use the Multiplicity Function?

$\langle f \rangle = \frac{\sum_{\text{states}} f(\text{state})}{\sum_{\text{states}} 1} = \int f(x)g(N,x)\,dx\,\frac{N}{2}\cdot 2^{-N}$

For Ising Model using Gaussian: $\langle x\rangle = 0$; $\langle x^2\rangle = \frac{1}{N}$

Averages: All accessible quantum states are equally probable

Ensemble: $\langle f\rangle_{ensemble} = \frac{\sum_{states} f(state)}{\sum_{states} 1}$ Example Ising Model $\langle f\rangle = 2^{-N}\sum_M g(N,M) f(M)$

$= \frac{1}{l}\sum_s f(system) = \frac{1}{L}\sum_M L\, g(N,M) f(M) 2^{-N}$; L = Identical Systems

Ensemble of time: $\langle f\rangle_{time} = \frac{1}{T}\int_0^T f(t)\,dt$; Ergodic Theorem: $\langle f\rangle_{ensemble} = \langle f\rangle_{time}$

Spatial Averages:

$\langle f\rangle_{space} = \frac{1}{V}\int f(\vec{r})\,d^3r$ ★ All accessible states of the total system are equally probable ★

Thermal Equilibrium: What determines energy flow between A and B

Ising Model Example: $U = -\sum_i s_i \vec{\mu}\cdot\vec{B} = -M\vec{\mu}\cdot\vec{B} = -xN\vec{\mu}\cdot\vec{B}$

Multiplicity

A: $\boxed{U_A = -x_A N_A \vec{\mu}\cdot\vec{B}}$ B: $\boxed{U_B = -x_B N_B \vec{\mu}\cdot\vec{B}}$

$xN = x_A N_A + x_B N_B$

Assume A and B are not correlated: Multiplicity $g(N,x)$

Shorthand $t(x_A) = g(N_A, x_A)\, g(N_B, x_B)$ ‖ $= \sum_{x_A} g(N_A, x_A)\, g(N_B, x_B)$

Model Multiplicity $g(x) = \sqrt{\frac{2}{\pi N}}\, 2^N e^{-\frac{1}{2}x^2 N}$

Therefore $t(x_A) = \ldots e^{-\frac{1}{2}(x_A^2 N_A + x_B^2 N_B)} = t_0 e^{-\frac{1}{2}(x_A^2 N_A + x_B^2 N_B)}$

$\log(t(x_A)) = \log(t_0) - \frac{1}{2}(x_A^2 N_A + x_B^2 N_B) = \log(t_0) - \frac{1}{2}x_A^2 N_A - \frac{1}{2N_B}(xN - x_A N_A)^2$

$\left(\frac{\partial \log(t)}{\partial x_A}\right) = -x_A N_A - \frac{N_A}{N_B}(x_A N_A - xN)$; $\left(\frac{\partial^2 \log(t)}{\partial x_A^2}\right) = -N_A - \frac{N_A^2}{N_B^2} = -\frac{N N_A}{N_B}$

negative = maximum

$0 = -x_A N_B - (x_A N_A - xN)$; $x_A = x_B = x$

$t(x_A) \approx t(x)\, e^{-\frac{N_A N}{2N_B}(x_A - x)^2}$; $g(N,x) = \sum t(x_A) \approx t(x)\sum_{x_A} e^{-\frac{N_A N}{2N_B}(x_A - x)^2}$

$g(N,x) \approx t(x)\int dx_A \frac{N_A}{2} e^{-\frac{N_A N}{2N_B}(x_A - x)^2} = t(x)\,\frac{1}{2}\sqrt{\frac{\pi N_A N_B}{N}}$

$\log(g(N,x)) \approx \log(t(x)) + \log\left(\frac{1}{2}\sqrt{\frac{\pi N_A N_B}{N}}\right)$

Entropy & Temperature: $t(U_A) = g_A(N_A, U_A)\, g_B(N_B, U - U_A)$

Condition for Equilibrium: $0 = \frac{dt}{dU_A} = \left(\frac{\partial g_A}{\partial U}\right)(N_A, U_A)\, g_B(N_B, U - U_A)$

$+ g_A(N_A, U_A)\left(\frac{\partial g_B}{\partial U}\right)(N_B, U - U_A)(-1)$

$\frac{1}{g_A(N_A, U_A)}\left(\frac{\partial g_A}{\partial U}\right)_N (N_A, U_A) = \frac{1}{g_B(N_B, U - U_B)}\left(\frac{\partial g_B}{\partial U}\right)(N_B, U - U_A)$

This leads to define the entropy: $S(U,N,V) = k_B \log g(U,N,V)$

Temperature of the system is defined by: $\frac{1}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,V}$; $T_A = T_B$ @ Equilibrium

Multiplicity Function g_{TOT} is found by $\log(g_{TOT})(U) = \log(g_A(\hat{U}_A)) + \log(g_B(U-\hat{U}_A))$

Hence, the total entropy is $S = S_A + S_B$; Statistical Mechanics Temperature: $\frac{1}{T^{SM}} = \left(\frac{\partial S^{SM}}{\partial U}\right)_{N,V}$

The construction of the real temperature $T^{SM} = f(T)$; Therefore, the differential entropy $dQ = TdS = f(T)\,dS^{SM}$; $T^{SM} = \kappa T$; $S^{SM} = \frac{1}{\kappa} S$; $N_A \cdot k_B = R$

Laws of Thermodynamics: Zeroth Law: $T_A = T_B \cup T_B = T_C$; $T_A = T_C$.

First Law: Heat is a form of energy. and is exchanged between ...
Work is a form of energy.

Second Law: Entropy always increases: Also, trivial, U_A^0 and U_B^0

$$g_A(U_A^0)g_B(U_B^0) \leq g_A(U_A)g_B(U_B); S_A^{init} + S_B^{init} \leq S_A^{final} + S_B^{final}$$

Third Law: $S(0) = k_B \cdot \ln(g) = k_B\, p\, \frac{\log N}{N}$; $\left(\frac{\partial^2 S}{\partial U^2}\right)_{N,V} \leq 0$

Problems for Chapter 1:

1) $\vec{\mu}_v = s_i \vec{\mu}$; $s_i = \pm 1$; N; $x = \frac{1}{N}\sum s_i$; $g(N,x) \approx \sqrt{\frac{2}{\pi N}}\, 2^N e^{-\frac{1}{2}Nx^2}$

a) Calculate $U(x) = -\sum s_i \vec{\mu} \circ \vec{B} = -M\vec{\mu}\circ\vec{B} = xN\vec{\mu}\circ\vec{B} = \frac{1}{N}\cancel{4}(-1)\vec{\mu}\circ\vec{B}$; $= 0$

b) Calculate $S(N,U) = k_B \log(N,U) = k_B$ $\quad \log\frac{1}{Nx} = \frac{1}{2}Nx^2 \quad \frac{1}{Nx^{1/2}} = e^{\sqrt{\frac{1}{2}N}x} \quad -Nx = 0$

c) Calculate $U(T,N) = \int T\,dS = (S_2 - S_1)\cdot T$

2)

$N_j = 10^{24}$ $x_j = \frac{1}{N_j}\sum s_{ij}$	

a) Most Probable: $\hat{x}_1 = \frac{2}{\sum s_{ij}} x_j$; $\hat{x}_2 = \frac{2}{\sum s_{ij}}$; $= -xN\vec{\mu}\cdot\vec{B}$

b) $g_{TOT}(N,\delta_1) = g(N_1, \hat{x}_1 + \delta_1)\, g(N_2, \hat{x}_2 + \delta_2)$

$$= \sqrt{\frac{2}{\pi N_1}}\, 2^N e^{-\frac{1}{2}N_1(\hat{x}_1+\delta_1)^2} \cdot \sqrt{\frac{2}{\pi N_2}}\, 2^N e^{-\frac{1}{2}N_2(\hat{x}_2+\delta_2)^2}$$

$$= \frac{2}{\pi N_j} \cdot 2^{2N_j} \cdot e^{-\frac{1}{2}\left[N_j\left[(\hat{x}_1+\delta_1)^2 + (\hat{x}_2+\delta_2)^2\right]\right]}$$

c)

$N_j = 10^2(+1)$ $N_j = 10^2(-1)$ $x_j = \frac{1}{N_j}\sum s_{ij}$	

$$g_{TOT}(N,\delta) = \frac{2}{\pi \cdot N_j}\, 2^{2N_j} \cdot e^{-\frac{1}{2}\left[N_j\left[(\hat{x}_1+\delta_1)^2 + \frac{1}{2}(\hat{x}_2+\delta_2)^2\right]\right]}$$

$$= \frac{N_0}{N_j} \cdot 2^{2(N_i - N_j)} \cdot e^{-\frac{1}{2}\left[N_i - N_j\left[(\hat{x}_1+\delta_1)^2 + (\hat{x}_2+\delta_2)^2\right]\right] + \frac{1}{2}\left(\frac{1}{2}\left[(\hat{x}_1+\delta_1)^2 + (\hat{x}_2+\delta_2)^2\right]\right)}$$

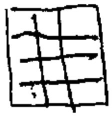
$$= \frac{1}{2} \cdot \frac{1}{2} \cdot e$$

d) $\log(t(x_i)) = \log\left(\frac{2}{\pi N_j} 2^{2N}\right) - \frac{1}{2}N_j\left[(\hat{x}_1+\delta_1)^2 + (\hat{x}_2+\delta_2)^2\right]$: $\frac{\partial \log(t(x_1))}{\partial x_1} = -N_j(\hat{x}_1 + \delta_1)$

$\frac{\partial^2 \log(t(x_2))}{\partial x_2} = -N_j$ Negative

$x_1 = \delta_1$; $x_2 = \delta_2$; $\delta_1 = \hat{x} = \frac{2}{\sum s_{ij}}$; $\delta_2 = \hat{x}_2 = \frac{2}{\sum s_{ij}}$

Problem 3



N sites
$\xi =$ filled / Total

a) Find $P(M,N,\xi)$ that M out of N are occupied

$$P(M) = \frac{N!}{(N-r)!\,r!} p^{x} q^{n-x}$$

$N = \#$ of sites
$M =$ spots to fill
$p = x$ trials successful
$q = x$ trials unsuccessful

$$\boxed{= \frac{(N-\xi)!}{(N-\xi-M)!\,M!}}$$

b) $P(M,A) = \dfrac{(N-A)!}{(N-A-M)!\,M!}$ A = Average $\lim p(M,A) = (+)$

Remember:
$$(a+b)^n = \sum_{k=0}^{n} \binom{n}{k} a^{n-k} \cdot b^k$$

c) Prove $\sum_{m=0}^{\infty} P(M,A) = \sum_{M=0}^{1} \binom{1}{M} A^{m} (1-A)^{n-M} = \binom{1}{0} A^{0} (1-A)^{1-0} + \binom{1}{1} A^{1} (1-A)^{1-1}$

$$= \frac{1!}{(1-0)!\,0!} A^0 (1-A)^{1-0} + \frac{1!}{(1-1)!\,1!} A^1 (1-A)^{1-1} = A^0(1-A) + A = 1$$

$$\boxed{= \binom{n}{M} A^{M} (1-A)^{n-M} = (A + (1-A))^{n} = 1}$$

$$\langle M \rangle = \sum_{M=0}^{\infty} M p(M,A) = A = \sum_{M=0}^{\infty} M \binom{\infty}{M} A^{M} (1-A)^{\infty - M} = \sum M \frac{\infty!}{(\infty-M)!\,M!} A^{M} (1-A)^{\infty-M}$$

$$= \sum_{M=0}^{\infty} \frac{\infty!}{(\infty-M)!\,(M-1)!} A^{M} (1-A)^{\infty-M}$$

$$= A.$$

$$= \sum_{M=0}^{n} M C^{n}_{M} A^{M} (1-A)^{n-M}$$

$$= \sum_{M=1}^{n} \frac{Mn}{M} C^{n-1}_{M-1} A^{M} (1-A)^{n-M}$$

$$= A \sum_{M=1}^{n} n C^{n-1}_{M-1} A^{M-1} (1-A)^{n-M}$$

$$= nA \sum_{M=1}^{n} C^{n-1}_{M-1} A^{M-1} (1-A)^{[N-1]-[M-1]} = nA\,(A + (1-A))^{n-1} = \boxed{nA}$$

$$\langle M^2 \rangle = \sum_{M=0}^{n} M^2 p(M,A) = \sum_{M=0}^{n} M^2 C^{n}_{M} A^{M} (1-A)^{n-m} = \sum_{M=0}^{n} (M^2 - M + M) \left[C^{n}_{m} A^{M} (1-A)^{n-m} \right]$$

$$= \sum_{M=0}^{n} (M^2 - M) \left[C^{n}_{M} A^{M} (1-A)^{n-M} \right] + \sum_{n=0}^{N} M C^{N}_{M} A^{M} (1-A)^{N-M} = \sum_{M=0}^{n} M(M-1) C^{N}_{M} A^{M} (1-A)^{N-M} + nA$$

$$= A^2 n(n-1) \sum_{M=2}^{N} C^{n-2}_{M-2} A^{M-2} \cdot (1-A)^{[N-2]-[M-2]} + nA = \boxed{n(n-1)A^2 + nA}$$

d) $f(x) = \dfrac{1}{\sqrt{2\pi\sigma}} e^{-\frac{1}{2\sigma}(x-\bar{x})^2} = \dfrac{1}{\sqrt{2\pi [nA^2 + nA - n^2A^2]}} e^{-\frac{1}{2(An(1-A))}(x-nA)^2}$ $= x^2 - nAx \cdot 2 + nA^2$

Problem 4: (1) $\log(N!) \approx N\log(N)$: Find smallest value of N relative to $N! < 1\%$

$$\boxed{1 \cong \frac{N^N}{N!}};$$

$$\frac{N! - N!}{N!} = \frac{N(1-(N-1)!)}{N(N-1)!} = \frac{1}{(N-1)!} - 1$$

Rel error: $\dfrac{|X_{ap} - X_{ex}|}{|X_{ex}|}$

$$1 \cong \frac{N^N}{\frac{100}{101} \cdot N}$$

$$\frac{1}{100} > \frac{1}{(N-1)!}$$

$$\boxed{(N-1)! = \frac{100}{101}}$$

$$\boxed{\cong \frac{101}{100} N^{N-1}};$$

Stirlings Formula: $N! = N^N e^{-N} \sqrt{2\pi N}\, e^{-\frac{1}{12}\frac{1}{N} + R(N)}$

Relative Error: $G_1 = \left| 1 - e^N \frac{1}{\sqrt{2\pi N}} e^{+\frac{1}{12}\frac{1}{N} - R(N)} \right|$

$$\lim_{N \to \infty} G_1 = \infty$$

Problem 3d) $\binom{n}{k}p^k q^{n-k} \approx \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{1}{2\sigma}(x-\mu)^2} = \frac{1}{\sqrt{2\pi np}} e^{-\frac{(k-np)^2}{2np}}$; $p+q=1$; $p,q>0$.

How? Binomial Distribution: $P(n) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n}$; $\bar{n} = np$

Poisson Limit: $p \ll 1 : N \gg 1$; $\bar{n} = Np \cong 1$

Therefore, $\frac{N!}{(N-n)!} = \underline{N}(\underline{N-1})(\underline{N-2})\cdots(\underline{N-n+2})(\underline{N-n+1}) \xrightarrow[N \gg n]{} N^n$

$\underbrace{(1-p)}_{\cong e^{-p}}^{N-\cancel{n}} \longrightarrow e^{-Np}$

Putting it together:

$P(n) \cong \frac{1}{n!}(Np)^n e^{-(Np)} = \frac{(\bar{n})^n e^{-\bar{n}}}{n!}$

Gaussian Limit: $n \gg 1$; Stirling Approximation: $n! \cong \sqrt{2\pi n}\left(\frac{n}{e}\right)^n$

$P(n) = \frac{(\bar{n})^n e^{-\bar{n}}}{n!} = \frac{(\bar{n})^n e^{-\bar{n}}}{\sqrt{2\pi n}\left(\frac{n}{e}\right)^n} = \frac{1}{\sqrt{2\pi \bar{n}}}\left(\frac{\bar{n}}{n}\right)^{n+\frac{1}{2}} e^{n - \bar{n}}$

Problem 4

(II) $\log(N!) \approx N\log N - N$

$\therefore e^N \approx \frac{N^N}{N!} = e^{\frac{N!}{\sqrt{2\pi N}}} e^{\frac{1}{12}\frac{1}{N} - R(N)}$

$\epsilon = |1 - \frac{1}{\sqrt{2\pi N}} e^{\frac{1}{12}\frac{1}{N} - R(N)}|$

$\lim_{N\to\infty} \epsilon = 1$

(III) $\log(N!) \approx N\log(N) - N + \frac{1}{2}\log(N)$; $e^N \approx \frac{N^{N+1/2}}{N!} = \cancel{N^{1/2}} \cancel{e^N} \frac{1}{\sqrt{2\pi \cancel{N}}} e^{\frac{1}{12}\frac{1}{N} - R(N)}$

$\epsilon = |1 - \frac{1}{\sqrt{2\pi}} e^{\frac{1}{12}\frac{1}{N} - R(N)}|$

$\lim_{N\to\infty} \epsilon = |1 - \frac{1}{\sqrt{2\pi}}|$

$\frac{\bar{a}^n}{a^{1/2} \cdot a^n} = \frac{1}{a^{1/2}}\left(\frac{\bar{a}}{a}\right)^{n}$

$= \frac{1}{a^{1/2}}\left(\frac{\bar{a}}{a}\right)^{-1/2}\left(\frac{\bar{a}}{a}\right)^{1/2}\left(\frac{n}{n}\right)^{n}$

$= \frac{1}{\bar{a}^{1/2}}\left(\frac{\bar{a}}{a}\right)^{n+\frac{1}{2}}$

(IV) $\log(N!) \approx N\log N - N + \frac{1}{2}\log(N) + \frac{1}{2}\log(2\pi)$

$e^N \approx \frac{N^{N+1/2}\sqrt{2\pi}}{N!} = e^{\frac{1}{12}\frac{1}{N} - R(N)}$; $\epsilon = |1 - e^{\frac{1}{12}\frac{1}{N} - R(N)}|$

$\lim_{N\to\infty} \epsilon = 0$

Problem #5

$\boxed{A}$ $\boxed{B}$ $\boxed{C}$ $\frac{1}{3}$ = car ; $\frac{1}{3}$ = Nothing

1/3 Door ; then another to show Nothing

A=0, B=Car, C=0 [1/3]

A=0, B=0, C=car [1/3]

A=car, B=0, C=0 (1/3)

Game show host Probabilities:

1 A=0, B=car, C=0 ; Host chooses B

~~2 A=0, B=0, C=car ; Host chooses C~~

~~3 A=0, B=0, C=car ; Host chooses B~~ Host does not pick car door.

4 A=0, B=car, C=0 ; Host chooses B

5 A=car ; B=0 ; C=0 ; Host chooses B

~~6 A=car ; B=0 ; C=0 ; Host chooses C~~

then: 1: 1/3 then the host chose B.

3: 1/3

4: 1/3 =

5: 1/6

$\frac{1}{3}$ 1/3, 1/3,

$\frac{4}{5}$ 1/3 + 1/3

Practice:

Car Location	Host opens	Prob	Stay	Switch
1/3 A	1/2 B	1/6	Car	Nothing
	1/2 C	1/6	Car	Nothing
1/3 B	1 C	1/3	Nothing	Car
1/3 C	1 B	1/3	Nothing	Car

Choice		Switch	
1/3 Car		Car, 0	0%
		Nothing, 1	1/3 — 1/3
1/3 Nothing		Car, 1	1/3
		Nothing, 0	1/3, 0 — 2/3
1/3 Nothing		Car, 1	1/3
		Nothing, 0	0

Problem 6: $\underbrace{2s+1 ; s_i = -s, -s+1, \cdots s-1, s}_{\text{Atomic Spin}}$; $\underbrace{M = \sum_{i=1}^{N} s_i}_{\text{Magnetic Moment}}$ Calculate $g(N,M)$; $x = \frac{M}{N} = s$

$= (2s+1)^N = \infty$

$\sum_{s=-s}^{s} N_s = N$; $\sum_{s=-s}^{s} s N_s = M$; $N_{-s}, N_{-s+1}, \cdots, N_{s-1}, N_s$; $\frac{N!}{N_{-s}! N_{-s+1}! \cdots N_{s-1}! N_s!}$

implies $g(N,M) = \sum_{N_{-s}, N_{-s+1} \cdots N_{s-1}, N_s} \frac{N!}{N_{-s}! N_{-s+1}! \cdots N_{s-1}! N_s!} \delta_{\sum_{s=-s}} \cdot \delta_{\sum_{s=-s} sN_s}$; $N! \approx N^N e^{-N}$

$= \sum_{N_{-s}, N_{-s+1} \cdots N_{s-1}, N_s} \left(\frac{N}{N_{-s}}\right)^{N_{-s}} \cdots \left(\frac{N}{N_s}\right)^{N_s} \delta_{\sum_{s=-s}} \cdot \delta_{\sum_{s=-s}}$

In the limit of $N \to \infty$; $\log g(N,M) = \sum_{s=-s}^{s} N_s(\log(N) - \log(N_s))$; with $\sum_{-s}^{s} N_s = N$; $\sum_{-s}^{s} s N_s = M$

With Lagrange Multipliers: $U(N_{-s}, N_{-s+1}, \cdots N_{s-1}, N_s, \kappa, \beta) = \sum_{s=-s}^{s} N_s(\log(N) - \log N_s) + \kappa(\sum N_s - N) + \beta(\sum s N_s - M)$

$\frac{dU}{dN_s} = \log N - \log N_s + \kappa + \beta s - 1 = 0$; $N_s = N e^{\kappa + \beta s - 1}$

$N = \sum_{-s}^{s} N_s = N \sum e^{\kappa + \beta s - 1}$; $M = xN = \sum_{s=-s}^{s} N_s = N \sum s e^{\kappa + \beta s + 1}$

$T_{max} = \sum_{-s}^{s} (\kappa + \beta s - 1) N_s = (1-\kappa) N - \beta x N$

$1 = e^{-1+\kappa} \sum_{-s}^{s} e^{\beta s}$; $x = e^{-1+\kappa} \sum_{-s}^{s} s e^{\beta s}$; $0 = \frac{d\kappa}{dx} e^{-1+\kappa} \sum_{-s}^{s} s e^{\beta s} + e^{-1+\kappa} \sum s e^{\beta s} \frac{d\beta}{dx}$

$= \frac{d\kappa}{\partial x} + x \frac{d\beta}{\partial x}$

$\frac{dT_{max}}{dx} = -\frac{d\kappa}{\partial x} N - \beta N - x \frac{d\beta}{\partial x} = -\beta N$; $\beta = 0, x = 0$.

$T_{max} = \log(2s+1) N - c x^2 N$; $c = \frac{2s+1}{\sum_{-s}^{s} s^2}$; $g(N,x) \approx g(N,0) e^{-cNx^2}$

Problem 7: Total $= 12$

Jackson(%) $= \frac{8J}{12}$; Liboff(%) $= \frac{6L}{12}$; No book(%) $= \frac{2}{12}$

$= 80\%$; $= 60\%$

(Jackson and Liboff) $[J \cup L] = \frac{8}{12} \cdot \frac{6}{12} = \frac{42}{100} = 42\%$

$\frac{1}{T} = \frac{dS}{dU} = \frac{3}{2} N k_B \frac{1}{U}$

$S = \frac{3}{2} N k_B \log U + C(N)$

$g(V,N) = e^{S/k_B}$

$= C'(N) U^{\frac{3}{2}N}$

Problem 8: $U = \frac{3}{2} N k_B T$; $S(V,N)$, $g(V,N)$

$[TdS = dU]_{@N,V}$

$S = \int \frac{du}{T} = \frac{U}{T} = \frac{\frac{3}{2} N k_B T}{T} = \frac{3}{2} N k_B = \ln \Omega$; $e^{-\frac{3}{2} N k_B}$

If Known energy $\hbar^2 k^2 / 2m$

$E_k = \frac{\hbar^2}{2m} \sum_k^N \sum_j^3 k_j^2$; $U = \frac{\hbar^2 k^2}{2m}$

Problem 9: $\epsilon_n = \hbar\omega(n + \frac{1}{2})$

$U = \sum_i^N \epsilon_{n_i} = (M + \frac{1}{2}N)\hbar\omega$

$\frac{(N-1+M)!}{(N-1)! M!}$

$M = \sum n_i$ Calculate $g(M,N)$ to $g(M,N+1)$; $\sum_0^n \binom{n+k}{n} = \binom{n+1+m}{n+1}$

$g(M,N) = \sum_{m=0}^{M} g(m,n) g(M-m, N-m)$; $g(M,1) = 1$

there ; $g(M,N+1) = \sum_{m=0}^{M} g(m,N)$; $g(M,N) = \binom{N+M}{N} \div \binom{N-1+M}{N-1}$; $\log(g[M,N]) = \log(N-1+M)! - \log(N-1)! - \log M!$

$\log N! = N \log N - N + \frac{1}{2}\log(2\pi N)$

therefore $g(M,N) = (N-1+M)\log(N-1+M) - (N-1)\log(N-1) - M\log(M) - \frac{1}{2}\log(2\pi) + \frac{1}{2}\log\frac{N-1+M}{(N-1)M}$

Insert $M = xN$; $\log g(M,N) = N(1+x)\log(N(1+x)) - N\log N - xN\log(xN) - \frac{1}{2}\log(2\pi) + \frac{1}{2}\log\left(\frac{1+x}{xN}\right)$

$$= N(1+x)\log(1+x) - xN\log(x) - \frac{1}{2}\log(2\pi) + \frac{1}{2}\log\left[\frac{(1+x)}{xN}\right]$$

Maximum is at $\frac{\partial}{\partial x} g = 0$; $N\log(1+x) - N\log(x) + \frac{1}{2}\left(\frac{1}{1+x} - \frac{1}{x}\right) = 0$

If $f(x) = N\log(x) + \frac{1}{2}\frac{1}{x}$; $f(x+1) = f(x)$; $\frac{\partial f}{\partial x} = \frac{N}{x} - \frac{1}{2}\frac{1}{x^2}$

Chapter 2: The canonical Ensemble: State variables

Reservoirs are what we need: $\frac{\Delta U_R}{N_R} \propto \frac{1}{\sqrt{N_R}}$; $U_R = \epsilon_R \cdot N_R$; $\Delta U_R \approx \epsilon_R\sqrt{N_R}$

Maximum Energy Fluctuation: $U_S = N_S\epsilon_S$; $N_R \gg N_S^2(\epsilon_S/\epsilon_R)^2$

Probabilities: $g_{S+R}(U_0) = \sum_S g_R(U_0 - \epsilon_S)$ "Multiplicity" ; $P_S(s) \propto g_R(U_0 - \epsilon_s)$

The ratio of probabilities: State 1 and 2 ~ $\frac{P_S(1)}{P_S(2)} = \frac{g_R(U_0-\epsilon_1)}{g_R(U_0-\epsilon_2)} = e^{\frac{1}{k_B}\left[S_R(U_0-\epsilon_1) - S_R(U_0-\epsilon_2)\right]}$

The difference of entropies is: $S_R(U_0-\epsilon_1) - S_R(U_0-\epsilon_2) \approx -(\epsilon_1-\epsilon_2)\left(\frac{\partial S}{\partial U}\right)_{V,N} U_0 = -\frac{\epsilon_1-\epsilon_2}{T_R}$

Therefore: $\frac{P_S(1)}{P_S(2)} = e^{\frac{-\epsilon_1-\epsilon_2}{k_BT}}$; $P_S(s) \propto e^{-\frac{\epsilon_s}{k_BT}}$ "Boltzmann Factor"

A normalization coefficient is needed $Z(t) = \sum e^{-\frac{\epsilon_B}{k_BT}}$; $P_S(s) = \frac{1}{Z}e^{-\epsilon_B/k_BT}$

"Partition Function" "Boltzmann Distribution"

Energy, Entropy, and Temperature:

$U = \sum \epsilon_s P(s)$; $\left(\frac{\partial\log(Z)}{\partial T}\right)_{V,N} = \frac{1}{Z}\left(\frac{\partial Z}{\partial T}\right)_{V,N} = \frac{1}{Z}\sum e^{-\frac{\epsilon_s}{k_BT}} \cdot \frac{\epsilon_s}{k_B \cdot T^2}$ -or- $U(T,V,N) = k_B \cdot T^2\left(\frac{\partial\log Z}{\partial T}\right)$

$S(T,V,N) = S(V,N) + \int_{T_{ref}}^{T} \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)$; $-\frac{U}{k_BT} = \sum_s\left(-\frac{\epsilon_s}{k_BT}\right)P(s)$; $\log P(s) = \frac{-\epsilon_s}{k_B \cdot T} - \log Z$

$$= \sum_s\left(\log P(s) + \log Z\right)P(s)$$

Work and Pressure:

$p\Delta V = \Delta\epsilon_s(V) = -\Delta V\left(\frac{\partial\epsilon_s}{\partial V}\right)_N$

$\Delta U = \sum_s \Delta\epsilon_s P(s) = p\Delta V\sum_s P(s) = p\Delta V$

Therefore, $p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$

-or-

$= -\left(\frac{\partial\epsilon_s}{\partial V}\right)_N$

$Z(T,V) = \sum_s e^{-\frac{V}{V_0}\epsilon_s(V_0)/k_BT} = F\left(\frac{V}{T}\right)$

$U = -k_B \cdot V\frac{F'\left(\frac{V}{T}\right)}{F\left(\frac{V}{T}\right)}$

$S = -k_B\sum P(s)\cdot\log P(s)$

$\frac{\partial}{\partial T}\left(\frac{-U}{k_BT}\right) = \left(\frac{\partial\log(Z)}{\partial T}\right)_{V,N} + \frac{\partial}{\partial T}\sum P(s)\log P(s)$

$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{\partial}{\partial T}\left(-k_B\sum P(s)\log P(s)\right)$

The result of integration is:

$S(T,V,N) = S_0(V,N) - k_B\sum P(s)\log P(s)$

For ground state:

$S(T=0,V,N) = S_0(V,N) - k_B\sum g_0^{-1}\log(g_0^{-1})$

$= \underbrace{S_0(V,N)}_{\equiv 0} + k_B\log(g_0)$

$S(T,V,N) = -k_B\sum P(s)\log P(s)$; $Z(T) = \sum g(E)e^{-E/k_BT}$

More about Pressure: $dS = \left(\frac{\partial S}{\partial V}\right)_V dV + \left(\frac{dS}{dV}\right) dV$; $0 = \left(\frac{dS}{dU}\right)_V \Delta U_S + \left(\frac{dS}{dV}\right)_U \Delta V_S = \left(\frac{dS}{dU}\right)\left(\frac{dU}{dV}\right) + \left(\frac{dS}{dV}\right)$

Helmholtz Free Energy:

$dU = TdS - pdV$;

$dF = TdS - pdV + TdS - SdT = -pdV - SdT$

Changes in variables

$\frac{1}{T} = \left(\frac{dS}{dU}\right)_V (U,V)$

$p = T\left(\frac{dS}{dV}\right)$

Properties of Helmholtz $S_{TOT}(\epsilon) = S_R(U_0 - \epsilon) + S_S(\epsilon) \approx S_R(U_0) - \frac{1}{T}(\epsilon - TS_S(\epsilon))$

Pressure as a function of Temperature: $p(T,V) = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T$

How are pressure and Helmholtz related? $F(T,V,N)$; $Z(T,V,N)$; $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$

Energy Fluctuations: $e^{\frac{-F(T,V,N)}{k_B T}} = \sum_S e^{\frac{-\epsilon_S}{k_B T}}$

$F = U + T\left(\frac{\partial F}{\partial T}\right)_{V,N}$; where $\frac{d}{dT}\left(\frac{F}{T}\right)_S = \frac{-U}{T^2}$

$\left(\frac{\partial \frac{F}{T}}{\partial T}\right)_{V,N} = -k_B\left(\frac{\partial \log Z}{\partial T}\right)_{V,N}$; $F = -k_B T \log Z + c(V,N)T$

$U = \langle\epsilon_S\rangle = \frac{1}{Z}\sum \epsilon_S e^{-\epsilon_S/k_B T}$

$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{1}{Z}\frac{1}{k_B T^2}\sum \epsilon_S^2 e^{-\epsilon_S/k_B T} - \frac{1}{Z^2}\sum \epsilon_S e^{\frac{-\epsilon_S}{k_B T}}\left(\frac{\partial Z}{\partial T}\right)_{V,N}$

$= \frac{1}{k_B T^2}\langle\epsilon_S^2\rangle - \frac{1}{Z}\sum \epsilon_S e^{-\epsilon_S/k_B T}\left(\frac{\partial \log(Z)}{\partial T}\right) = \frac{1}{k_B T^2}\langle\epsilon_S^2\rangle - \langle\epsilon_S\rangle\frac{U}{k_B T^2}$

$U = \langle\epsilon_S\rangle$

$k_B T^2 C_V = \langle\epsilon_S^2\rangle - \langle\epsilon_S\rangle^2 = (\Delta\epsilon)^2$

$\lim_{T\to 0} Z = g_0 e^{-\epsilon_0/k_B T}$; $\frac{U}{T^2} + \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$

$F(T,V,N) = -k_B T \log(g_0) + \epsilon_0 + c(V,N)T$

$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N,T} \approx k_B \log g_0 - c(V,N)$

$= -k_B T \log(Z(T,V,N))$

$Z(T,V,N) = e^{\frac{-F(T,V,N)}{k_B T}}$

Simple Example:

$\epsilon_{nl} = n\hbar\omega$; $l = 1,2,\cdots,n$

$n = 1,2,3\cdots,\infty$: $Z(T) = \sum n\left(e^{\frac{-\hbar\omega}{k_B T}}\right)^n$

Between zero and one

$F = -k_B T \log(Z)$;

$S = k_B \log Z + k_B T \frac{1}{Z}\left(\frac{\partial Z}{\partial T}\right)$;

$= \frac{e^{-\hbar\omega/k_B T}}{(1 - e^{-\hbar\omega/k_B T})^2}$

$F(T) = \hbar\omega + 2k_B T \log(1 - e^{-\hbar\omega/k_B T})$

$S(T) = \hbar\omega\frac{2}{T}\frac{1}{e^{\hbar\omega/k_B T} - 1} - 2k_B \log(1 - e^{-\hbar\omega/k_B T})$

$U(T) = \hbar\omega \coth\left(\frac{\hbar\omega}{2k_B T}\right)$

$T\to 0$; $U \approx \hbar\omega$, $S \approx 0$;

$T\to\infty$; $U \approx 2k_B T$, $S \approx 2k_B - 2k_B \log\left(\frac{\hbar\omega}{k_B T}\right)$; $T\to 0$; $U \approx \hbar\omega$; $S \approx 0$

$T\to\infty$; $U \approx 2k_B T$; $S \approx 2k_B - 2k_B \log\left(\frac{\hbar\omega}{k_B T}\right)$

Heat Capacity: $C(T) = \hbar\omega \frac{d}{dT}\coth\left(\frac{\hbar\omega}{2k_B T}\right) = \frac{(\hbar\omega)^2}{2k_B T^2}\frac{1}{\sinh^2\left(\frac{\hbar\omega}{2k_B T}\right)}$; $T\to 0$: $C \approx 0$

$T\to 0$; $pV \approx -\hbar\omega$; $T\to\infty$; $pV \approx -2k_B T$

$T\to\infty$: $C \approx 2k_B$

$P = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T$

$pV = -\hbar\omega\coth\left(\frac{\hbar\omega}{k_B T}\right)$

Chapter 2: Problems:

Problem 1: $n = 0,1,2,\cdots,\infty$; $\epsilon_n = n\epsilon$ $(\epsilon > 0)$; Temp (T) a) Calculate the partition function $Z(T)$ b) Calculate $U(T)$ & $S(T)$ c) Calculate $T(U)$ d) Calculate $S(U)$ and check $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)$.

$Z(T) = \sum_S n\left(e^{\frac{-\epsilon_S}{k_B T}}\right)^n$

$= \frac{e^{-n\epsilon/k_B T}}{(1 - e^{-n\epsilon/k_B T})^2}$; $F(T) = n\epsilon + 2k_B T \log(1 - e^{-n\epsilon/k_B T})$

$\frac{dF(T)}{dT} = 2k_B \log(1 - e^{-n\epsilon/k_B T}) + 2k_B \frac{+\frac{n\epsilon}{k_B T}}{(1 - e^{-n\epsilon/k_B T})}$

Problem 3: ~~$\epsilon_1 = 0$~~; $\epsilon_2 > 0$ a) Calculate the partition function $Z = e^{-\epsilon_1/k_BT} + e^{-\epsilon_2/k_BT}$

$\boxed{= 1 + e^{-\epsilon_2/k_BT}}$

b) Calculate $U(T)$ and $S(T)$

Helmholtz Free Energy: $F = U + TS$

$$\boxed{U(T,V,N) = k_BT^2\left(\frac{\partial \log Z}{\partial T}\right) = k_BT^2 \frac{\partial}{\partial T}\log\left[1+e^{-\epsilon_2/k_BT}\right] = k_BT^2 \frac{\left(\frac{-\epsilon}{k_BT^2}\right)e^{-\epsilon_2/k_BT}}{1+e^{-\epsilon_2/k_BT}}}$$

$$\boxed{S(T,V,N) = \frac{U}{T} = \frac{1}{T}\left[\frac{e^{-\epsilon_2/k_BT}}{1+e^{-\epsilon_2/k_BT}}\right]}$$

$$\boxed{= \frac{e^{-\epsilon_2/k_BT}}{1+e^{-\epsilon_2/k_BT}}}$$

c) Calculate Heat Capacity: $C_V = \left(\frac{\partial U}{\partial T}\right) = \frac{\frac{\epsilon_2}{k_BT^2} e^{-\epsilon_2/k_BT}}{1+e^{-\epsilon_2/k_BT}} + \frac{\epsilon_2}{k_BT^2}\frac{e^{-2\epsilon_2/k_BT}}{(1+e^{-\epsilon_2/k_BT})^2}$

"Schottky Anomaly" $\boxed{= \frac{\epsilon_2}{k_BT^2} e^{-\epsilon_2/k_BT}\left[\frac{1+2e^{-\epsilon_2/k_BT}}{(1+e^{-\epsilon_2/k_BT})^2}\right]}$

d) Yes, to the second energy state from the first.

Problem 4: $H_1\nu$

$S = 1/2, \mu$
$\epsilon = \pm\mu H$

Bohr condition: $h\nu = 2\mu H$

$\mu H \ll kT$

$\mu H = \frac{h\nu}{2}$

$$Z = e^{-\epsilon/k_BT} + e^{\epsilon/kT} = e^{-\mu H/k_BT} + e^{\mu H/kT}$$
$$= e^{-h\nu/2k_BT} + e^{h\nu/2k_BT}$$

$P \propto \Delta n_{\epsilon_i} = n_{\epsilon_+} - n_{\epsilon_-}$ ~~$P(T) \propto e^{-h\nu/2k_BT} - e^{h\nu/2k_BT}$~~

The internal energy of the sample is $U = -\sum s_i \mu H \propto P$

$$= kT^2 \frac{d}{dT}\log Z(t)$$
$$= kT^2\frac{d}{dT}\log e^{-h\nu/2k_BT} + e^{h\nu/2k_BT}$$
$$= kT^2 \frac{N\left[e^{h\nu/2k_BT} + e^{-h\nu/2k_BT}\right]}{e^{h\nu/2k_BT} + e^{-h\nu/2k_BT}}\left[\frac{-h\nu}{2k_BT^2}\right]$$

$\frac{h\nu}{2} \ll k_BT$; then $e^x = 1 + x$

$$U \approx -N\mu H \frac{\frac{h\nu}{2kT} - \left(-\frac{h\nu}{2k_BT}\right)}{\frac{h\nu}{2k_BT} + \frac{h\nu}{2k_BT}}\left[\frac{-h\nu}{2k_BT^2}\right] = \boxed{-N\frac{\mu^2 \cdot H^2}{kT}}$$

b) $U = F + TS$; $U(T) = \hbar\omega + 2k_BT\log(1-e^{-\hbar\omega/k_BT}) + T\left[\hbar\omega\frac{2}{T}\frac{1}{e^{\hbar\omega/k_BT}-1} - 2k_B\log(1-e^{-\hbar\omega/k_BT})\right]$

$H = U + PV$

$= \hbar\omega + 2k_BT\left[\log(1-e^{-\hbar\omega/k_BT}) - \log(1-e^{-\hbar\omega/k_BT})\right] + \hbar\omega\cdot 2\frac{1}{(e^{\epsilon/k_BT}-1)}$

c) $\frac{2k_BT}{\hbar\omega}\coth\left(\frac{U}{\hbar\omega}\right) = T(U)$

$= \hbar\omega\left[1 + \frac{2}{(e^{\epsilon/k_BT}-1)}\right] = \hbar\omega\left[\frac{e^{\epsilon/k_BT}+1}{(e^{\epsilon/k_BT}-1)^2}\right]$

$= \hbar\omega\left[\frac{\frac{1}{a}+\frac{a}{a}}{\left(\frac{1}{a}+\frac{a}{a}\right)^2}\right]^2 = \hbar\omega\left[\frac{\cosh(\epsilon/k_BT)}{\sinh^2(\epsilon/k_BT)}\right]$

$= \hbar\omega\coth\left(\frac{\hbar\omega}{2k_BT}\right)$

d) $U = TdS + PdV$; $H - TK$

$H = U + PV$; $G = H - TS$; $F = U - TS$

$U = TdS - PdV$; $\left(\frac{dT}{dV}\right) = -\left(\frac{dP}{dS}\right)$; $\left(\frac{dU}{dS} = T\right)$ $-P = \frac{dU}{dV}$

$H = TdS + PdV + PdV + VdP = TdS + VdP$; $\left(\frac{dT}{dP}\right) = \left(\frac{dV}{dS}\right)$

$G = TdS + VdP - TdS - SdT$; $\left(\frac{dV}{dT}\right) = -\left(\frac{dS}{dP}\right)$;

$A = TdS - PdV - TdS - SdT$; $\left(\frac{dP}{dT}\right) = \left(\frac{dS}{dV}\right)$; $\frac{dA}{dt} = -S$

$S(U) = k_B\log\frac{e^{-n\epsilon/k_BT}}{(1-e^{-n\epsilon/k_BT})^2} + k_BT\frac{1}{Z}\left(\frac{+\frac{n\epsilon}{k_BT^2}e^{-n\epsilon/k_BT}}{(1-e^{-n\epsilon/k_BT})^2} - \frac{2\cdot e^{-n\epsilon/k_BT}\, e^{-n\epsilon/k_BT}\,\frac{-n\epsilon}{k_BT^2}}{(1-e^{-n\epsilon/k_BT})^3}\right)$

Problem 2:

$n = 0,1,2,3 \dots \infty$; $\epsilon_1 = f(n)$; $Z_f(T)$; $\epsilon_2 = g(n)$; $Z_g(T)$; $\epsilon_{n,m} = f(n) + g(m)$

$U_f(T)$; $S_f(T)$; $U_g(T)$; $S_g(T)$

(1) $Z(T) = \sum n\left(e^{-f(n)/k_BT}\right)^n + \sum m\left(e^{-g(n)/k_BT}\right)^m = Z_f(T) + Z_g(T)$

$= \frac{e^{-nf(n)/k_BT}}{(1-e^{-nf(n)/k_BT})^2} + \frac{e^{-mg(n)/k_BT}}{(1-e^{-mg(n)/k_BT})}$

(2) $U(T) = U_f(T) + U_g(T) = f(n)\left[\frac{\cosh(f(n)/k_BT)}{\sinh(g(n)/k_BT)}\right] + g(n)\left[\frac{\cosh(g(n)/k_BT)}{\sinh(g(n)/k_BT)}\right] =$

$= -f(n)\coth\left(\frac{f(n)}{k_BT}\right) + g\coth\left(\frac{g(n)}{k_BT}\right)$

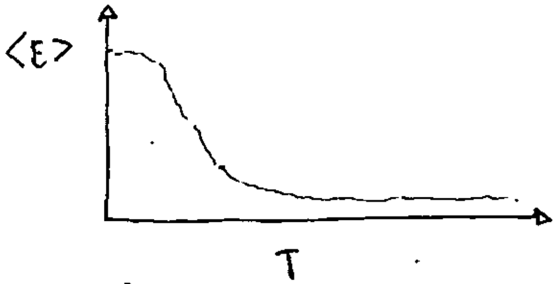
$S(T) = k_B\log Z + k_BT\frac{1}{Z}\left(\frac{\partial Z}{\partial T}\right) = k_B\log\frac{e^{-nf(n)/k_BT}}{(1-e^{-nf(n)/k_BT})} + \frac{e^{-mg(n)/k_BT}}{(1-e^{-mg(n)/k_BT})}$

$\frac{e^{-mf(n)/k_BT}\cdot 2(1-e^{-nf(n)/k_BT})\frac{mg(n)}{k_BT^2}(-e^{-mg(n)/k_BT})}{(1-e^{-mg(n)/k_BT})^4} + k_BT\frac{1}{\left[\frac{e^{-nf(n)/k_BT}}{(1-e^{-nf(n)/k_BT})} + \frac{e^{-mg(n)/k_BT}}{(1-e^{-mg(n)/k_BT})}\right]}$

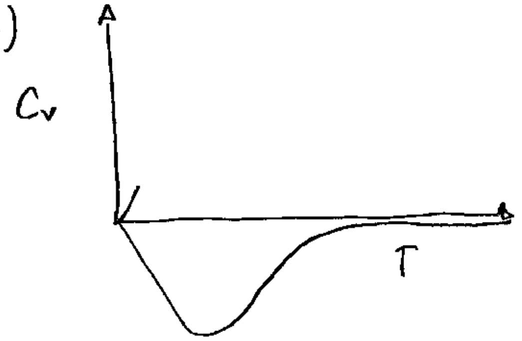
$\frac{e^{-nf(n)/k_BT}\cdot 2(1-e^{-nf(n)/k_BT})\frac{nf(n)}{k_BT^2}(e^{-nf(n)/k_BT})}{(1-e^{-nf(n)/k_BT})^4} + \frac{nf(n)}{k_BT^2}\frac{e^{-nf(n)/k_BT}(1-e^{-nf(n)/k_BT})^2}{(1-e^{-nf(n)/k_BT})^4} + \frac{nf(n)}{k_BT^2}\frac{e^{-mf(n)/k_BT}(1-e^{-mf(n)/k_BT})^2}{(1-e^{-mg(n)/k_BT})^4}$

Problem 5: N interacting particles, ϵ_1 and ϵ_2; Where $\epsilon_1 < \epsilon_2$: $\epsilon_1 < \epsilon_2$

a)



b)



c) See Problem 4.

Problem 6: $T=0$; N amount of q^- per cm^3
N amount of q^+ per cm^3

	B	
A	(-)	C
	D	

$A+B+C+D=1.0$ for q^+

$A=B=C=D=0.25$ for q^+

Horizontal Probability is $1/2$ a; Energy $\frac{1}{2}eaE$

Vertical Probability is $1/2$ a; Energy $-\frac{1}{2}eaE$

Calculate E

$$Z(T)=\sum_i e^{-(1/KT)\sum_j \epsilon(s_j)} = Z_1(T)^N$$

$$Z_1(T)=2\left(e^{\frac{eaE}{2KT}}+e^{-\frac{eaE}{2KT}}\right)$$

Therefore the probability of finding a state is $(^0/_0) = \frac{1}{Z(T)} e^{-\frac{1}{KT}\sum_j \epsilon(s_j)}$

The average dipole moment is: $\langle P \rangle = \sum_i \sum_j P(s_j)\,Prob(s_1 \dots s_n)$

Which simplifies to - $$= N\frac{\left(\frac{1}{2}ea\right)e^{\frac{eaE}{2KT}}+\left(\frac{-1}{2}\right)e^{-\frac{eaE}{2KT}}}{e^{\frac{eaE}{2KT}}+e^{-\frac{eaE}{2KT}}}$$

$$\langle \nu r \rangle = \frac{N}{2}ae\tanh\left(\frac{eaE}{2KT}\right)$$

Which reduces to: $\langle P \rangle \approx NE\frac{a^2e^2}{4KT}$; When $eaE \ll 2KT$.

Problem 7: $S=-K_B\sum_i P_s\log(P_s)$; Where $S=S_1+S_2$

$$S_1=-K_B\sum_i P_{s_1}\cdot\log(P_{s_1}) : P_{s_1}=\frac{1}{Z(T)}e^{-\frac{1}{KT}\sum_j \epsilon(s_j)}$$

$$Z(T)=\sum_i e^{-\epsilon_1/KT}$$

$$S_2=-K_B\sum_i P_{s_2}\cdot\log(P_{s_2}) ; P_{s_2}=\frac{1}{Z(T)}e^{-\frac{1}{KT}\sum \epsilon(s_2)}$$

$$Z(T)=\sum_i e^{-\epsilon_2/K_BT}$$

$$\boxed{S=-K_B\left[\sum_i P_{s_1}\cdot\log(P_{s_1})+\sum_i P_{s_2}\cdot\log(P_{s_2})\right]}$$

Problem 8: $$\boxed{Z(T,N)=\sum_i e^{-N/K_BT}=Z(T,1)^N=\sum_i e^{(-1/K_BT)^2}}$$

Problem 9: $n=0,1,2,\dots$; $E=0, \epsilon+\Delta, \epsilon+2\Delta, \dots, \epsilon+n\Delta$

$$\boxed{Z(\epsilon) = \sum_{i=1}^{N} e^{-(\epsilon+\Delta n)/k_BT} \; ; \; U(T) = \left[\frac{\cosh[(\epsilon+\Delta n)/k_BT]}{\sinh[(\epsilon+\Delta n)/k_BT]}\right] = \coth\left(\frac{\epsilon+\Delta n}{k_BT}\right)} = F + TS$$

$$= k_BT^2\left(\frac{\partial \log z}{\partial T}\right)$$

$$\boxed{C_p = \frac{dU}{dT} = \left[\frac{\epsilon+\Delta n}{k_BT}\right]\frac{e^{-(\epsilon+\Delta n)/k_BT}}{1+e^{-(\epsilon+\Delta n)/k_BT}}}$$

$$= \cancel{k_B T^2} \frac{\epsilon+\Delta n}{\cancel{k_B T^2}} \frac{e^{-\epsilon_2/k_BT}}{1+e^{-\epsilon_2/k_BT}}$$

$$= \left[\frac{(\epsilon+\Delta n)e^{-(\epsilon+\Delta n)/k_BT}}{1+e^{-(\epsilon+\Delta n)/k_BT}}\right]$$

Chapter 3: Systems ~~with~~ a variable number of particles:

3.1 Chemical Potential | More State variables?

Two systems are in diffusive contact if they can flow back and forth. Consider two systems at Temp(T), and fixed volumes. 1(2) is $N_1(N_2)$. If $\Delta N \to 1$ to 2, the change in free energy is:

$$\Delta F = \left(\frac{\partial F_1}{\partial N}\right)_{T,V}(-\Delta N) + \left(\frac{\partial F_2}{\partial N}\right)_{T,V}(+\Delta N)$$; Where we define chemical potential

$$\mu(T,V,N) = \left(\frac{\partial F}{\partial N}\right)_{T,V}(T,V,N)$$

Free energy is lowest when $\mu_1 = \mu_2$.

This would imply $\mu(T,V,N) = \underbrace{F(T,V,N) - F(T,V,N-1)}$

"Each particle has a chemical potential"

For each particle of the system, $\mu(T,V,N_1,N_2,\ldots) = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}}$

What does chemical potential imply?

Since $\Delta F = (\mu_2 - \mu_1)\Delta N$; P.E. $= \phi_i$; $\Delta E = (\phi_2 - \phi_1)\Delta N$

Total change of free energy: $\Delta F = (\hat{\mu}_2 + \phi_2 - \hat{\mu}_1 - \phi_1)\Delta N$

Therefore, $\mu_2 + \phi_2 = \mu_1 + \phi_1$ "Equilibrium"

Thus, $\mu(T,V,N) = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \hat{\mu} + \phi$; $U_{TOTAL} = U_{internal} + N\phi$

Origin of Internal chemical Potential

$F = U - TS$; $\mu = \left(\frac{\partial U}{\partial N}\right)_{T,V} - T\left(\frac{\partial S}{\partial N}\right)_{T,V}$

$F_{internal} = U_{internal} - TS$

$F_{TOTAL} = F_{internal} + N\phi$

$\mu = \hat{\mu} + \phi$

Simple Models of Chemical Potential

$S = Nf\left(\frac{U}{N}\right)$; for some function

$\frac{1}{T} = f'\left(\frac{U}{N}\right)$ -or- $U = Ng(T)$ and $S = Nf(g(T))$. $F = Nh(T)$ and $\mu = h(T)$

Basic Formulation: Internal Chemical Potential is a thermodynamic Variable which is equal to Standard potential.

Examples of chemical potential: Electricity is always useful.

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^- + 0.8eV \quad (\text{Anode}[-])$$

$$PbO_2 + 2H^+ + H_2SO_4 + 2e^- \longrightarrow PbSO_4 + 2H_2O + 3.2eV$$
$$(\text{Cathode}[+])$$

$$\mathcal{E}_{cell} = \mathcal{E}_{cathode} - \mathcal{E}_{anode} = (3.2 - 0.8)V = 2.6V$$

When the actual reading is $< 2.6V$ because of electrode shape, pressure, electrolyte, etc...

Gravity and Atmospheric Pressure: Chemical potential ideal gas.

$$\mu(n,T) = k_B T \log(N) + \mu_0(T)$$

$$k_B T \log(n(h)) + mgh = k_B T \log(n(0))$$

$$n(h) = n(0) e^{-mgh/k_B T} \quad ; \quad \frac{PV}{RT} = n$$

$$P(h) = P(0) e^{-mgh/k_B T}$$

Differential Relation and Grand Potential: $U = F + TS$; $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$$

Therefore $dS = \left(\frac{\partial S}{\partial U}\right)_{VN} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{UV} dN$; Consider a reversible change in the state variable.

$$\Delta S = \left(\frac{\partial S}{\partial U}\right)_{V,N} (\Delta U)_{T,V} + \left(\frac{\partial S}{\partial N}\right)_{U,V} (\Delta N)_{T,V} \quad \text{under constant volume.}$$

$$\left(\frac{\partial S}{\partial N}\right) = \left(\frac{\partial S}{\partial U}\right)\left(\frac{\partial U}{\partial N}\right) + \left(\frac{\partial S}{\partial N}\right)$$

$$\left(\frac{\partial S}{\partial N}\right) - \frac{1}{T}\left(\frac{\partial U}{\partial N}\right) = \left(\frac{\partial S}{\partial N}\right) \quad ; \quad \frac{1}{T}\left(\frac{\partial F}{\partial N}\right) = \left(\frac{\partial S}{\partial N}\right) = \frac{-\mu}{T}$$

$dU = TdS - pdV + \mu dN$

$dU = C_V dT + \left(-p + T\left(\frac{\partial S}{\partial V}\right)_{T,N}\right)dV + \left(\frac{\partial U}{\partial N}\right)_{T,V} dN$

$dF = -SdT - pdV + \mu dN$

under new definition; $d\Omega = -SdT - pdV - Nd\mu$. "Grand Potential"

3.4: Grand Partition Function:

Calculating Ω via Helmholtz Free Energy $F(T,V,N)$

① $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$ for $N(\mu,T,V)$ ② $\Omega(\mu,T,V) = F(T,V,N(\mu,T,V)) - \mu N(\mu,T,V)$

Total Energy U_0 of R+S:

N_0 in R+S

Number of Quantum States: $g_R(U_0 - \epsilon_s, N_0 - n_s)$

Available Energy: $U_0 - \epsilon_s$

Number of Particles: $N_0 - n_s$

$\frac{Prob(1)}{Prob(2)} = \frac{g_R(U_0-\epsilon_1, N_0 - n_1)}{g_R(U_0 - \epsilon_2, N_0 - n_2)}$

$= \exp\left(\frac{1}{k_B}(n_2 - n_1)\left(\frac{\partial S_R}{\partial N}\right)_{U,V} + \frac{1}{k_B}(\epsilon_2 - \epsilon_1)\left(\frac{\partial S_R}{\partial U}\right)_{V,N}\right)$

$Prob(s) = \frac{1}{\mathcal{Z}} e^{\frac{1}{k_BT}(\mu n_s - \epsilon_s)}$

"Gibbs' Factor" - A generalized Boltzmann Factor

"Grand Partition Function" "Grand Sum" $\boxed{\mathcal{Z}(T,V,\mu) = \sum e^{\frac{1}{k_BT}(\mu n_s - \epsilon_s)}}$

$= \sum_N e^{\frac{\mu N}{k_BT}} \cdot Z(T,V,\hat{N})$

How do we extract information from the Grand Partition?

$\langle n_s \rangle = \sum n_s Prob(s)$

$\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)_{T,V} = \frac{1}{k_BT}\sum_s n_s e^{\frac{1}{k_BT}(\mu n_s - \epsilon_s)} = \frac{1}{k_BT}\mathcal{Z}\langle n_s \rangle$

Therefore, $N(T,V,\mu) = k_BT\left(\frac{\partial \log(\mathcal{Z})}{\partial \mu}\right)_{T,V}$

$\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{\mu,V} = \sum(\mu n_s - \epsilon_s)e^{\beta(\mu n_s - \epsilon_s)}$

$= \mathcal{Z}(\mu N - U)$

New Description; $\beta = \frac{1}{k_BT}$

Absolute Activity: $\lambda = e^{\frac{\mu}{k_BT}}$

Fugacity: $z = e^{\frac{\mu}{k_BT}}$

$(\Delta V)^2 = k_B T \left(\frac{\partial V}{\partial p}\right)_{T,N}$; $Z(T,V,N,M) = \sum e^{-\beta E_s} = e^{-\beta F(T,V,N,M)}$

Laplace Transform

$Z(T,V,N,H) = \sum e^{-\beta(E_s - Hm_s)} = e^{-\beta G(T,V,N,H)}$

$(\Delta M)^2 = k_B T \left(\frac{\partial M}{\partial H}\right)_{T,V,N}$; $\Xi(T,V,\mu) = \sum_N e^{\beta\mu N} \cdot Z(T,V,N)$

A Simple Example: ω = Frequency ; E_n of quantum state ; $n = 0, 1, 2 \ldots$

$\Xi(T,\mu) = \sum_{n=0}^{\infty} e^{\beta(\mu-\hbar\omega)n}$; The summation can be approximated,

$$\Xi(T,\mu) = \frac{1}{1-e^{\beta(\mu-\hbar\omega)}}$$

All thermodynamic properties can now be evaluated from the grand potential:

$\Omega(T,\mu) = k_B T \log\left(1 - e^{\beta(\mu-\hbar\omega)}\right)$

$S(T,\mu) = -k_B \log\left(1 - e^{\beta(\mu-\hbar\omega)}\right) + \frac{1}{T}\frac{\hbar\omega-\mu}{1-e^{\beta(\mu-\hbar\omega)}}$

$N(T,\mu) = \text{frac}\; e^{\beta(\hbar\omega-\mu)} - 1$

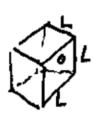
$U(T,\mu) = \Omega + TS + \mu N = N\hbar\omega$

$\mu = \hbar\omega - k_B T \log\left(1 + \frac{1}{N}\right)$

$\frac{\Omega(T,N)}{N} = -k_B T \frac{\log(N+1)}{N}$

$S(T,N) = k_B \log(N+1) + N k_B \log\left(1 + \frac{1}{N}\right)$

Ideal Gas First Approximation:



$\epsilon(n_x, n_y, n_z) = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$

$Z_1 = \sum_{n_x,n_y,n_z} e^{-\beta\epsilon(n_x n_y n_z)} = \sum_{n_x} e^{-\frac{\hbar^2}{2Mk_BT}\left(\frac{\pi}{L}\right)^2 n_x^2} \cdot \sum e^{-\frac{\hbar^2}{2Mk_BT}\left(\frac{\pi}{L}\right)^2 n_y^2} \cdot \sum e^{-\frac{\hbar^2}{2Mk_BT}\left(\frac{\pi}{L}\right)^2 n_z^2}$

$\alpha^2 = \frac{\hbar^2\pi^2}{(2ML^2 k_B T)}$

$Z_1 = \left(\sum_{n=1}^{\infty} e^{-\alpha^2 n^2}\right)^3$; IF $X_i = \alpha n$; $\Delta X = \alpha n$

$\sum_{n=1}^{\infty} e^{-\alpha^2 n^2} = \frac{1}{\alpha}\sum e^{-X_n^2} \cdot \Delta X$

In the limit ΔX is very small, numerical analysis shows,

$$\sum_{n=1}^{\infty} e^{-X_n^2} \cdot \Delta X \approx \underbrace{\int_0^{\infty} e^{-x^2} dx}_{\frac{1}{2}\sqrt{\pi}} - \frac{1}{2}\Delta X + O\left(e^{-\frac{1}{\Delta X}}\right)$$

$Z_1 \approx \left(\frac{\sqrt{\pi}}{2\alpha}\right)^3$; $\alpha \ll 1$; $Z_1 \gg 1$; "Quantum Concentration" $n_Q(T)$

$n_Q(T) = \left(\frac{M k_B T}{2\pi\hbar^2}\right)^{3/2}$

$Z_1(T,V) = V n_Q(T)$

$\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{\mu,V} = \sum (\mu n_s - \epsilon_s)\, e^{\beta(\mu n_s - \epsilon_s)} = \mathcal{Z}(\mu N - U)$; $U = \langle \epsilon_s \rangle$; $U = \mu N - \left(\frac{\partial \log(\mathcal{Z})}{\partial \beta}\right)_{\mu,V} = \left(\frac{\mu}{\beta}\frac{\partial}{\partial \mu} - \frac{\partial}{\partial \beta}\right)\log(\mathcal{Z})$

Grand Partition Measures energy available at constant T, μ, and T.

$\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = -N$; We conclude $\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = -N$; $\Omega = -k_B T \log(\mathcal{Z}) + \underbrace{f(T,V)}_{\text{unknown}}$

$U = \left(\frac{\mu}{\beta}\frac{\partial}{\partial \mu} - \frac{\partial}{\partial \beta}\right)\log(\mathcal{Z}) = \left(\frac{\mu}{\beta}\frac{\partial}{\partial \mu} - \frac{\partial}{\partial \beta}\right)(\beta(f - \Omega))$; $U = \Omega - f + \left(\mu\frac{\partial}{\partial \mu} - \beta\frac{\partial}{\partial \beta}\right)(f - \Omega)$

$= \Omega - f - \mu\left(\frac{\partial \Omega}{\partial \mu}\right)_{\beta,V} - \beta\left(\frac{\partial f}{\partial \beta}\right)_{\mu,V} + \beta\left(\frac{\partial \Omega}{\partial \beta}\right)_{\mu,V}$

Thermodynamical Relationship:

$\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T} = -N$; $\left(\frac{\partial \Omega}{\partial \beta}\right)_{V,\mu} = -T\beta^{-1}\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = TS\beta^{-1}$

To arrive at $U = \Omega - f + \mu N - \beta\left(\frac{\partial f}{\partial \beta}\right)_{\mu,V} + TS$; $U = \Omega + TS + \mu N$

<u>Evaluating the Grand potential</u>

$0 = f + \beta\left(\frac{\partial f}{\partial \beta}\right)_{\mu,V} = \left(\frac{\partial \beta f}{\partial \beta}\right)_{\mu,V}$

$S = \frac{U - \Omega - \mu N}{T} = \frac{1}{T}\sum \epsilon_s \,\mathrm{Prob}(s) + k_B \log(\mathcal{Z}) - \frac{\mu}{T}\sum n_s \,\mathrm{Prob}(s)$

—or—

$f(T,V) = k_B T \log(\mathcal{Z})$

$= k_B \sum \frac{\epsilon_s - \mu n_s}{k_B T}\mathrm{Prob}(s) + k_B \log(\mathcal{Z}) \sum \mathrm{Prob}(s)$

$\mathcal{Z} = e^{-\beta\Omega}$

$= -k_B \sum \left(\frac{\mu n_s - \epsilon_s}{k_B T} - k_B \log(\mathcal{Z})\right)\mathrm{Prob}(s)$; $S = -k_B \sum \mathrm{Prob}(s) \cdot \log \mathrm{Prob}(s)$

Canonical Ensemble: $S(T,V,\mu)$ Canonical Case: $S(T,V,N)$

$\langle N^2 \rangle = \sum n_s^2 \,\mathrm{Prob}(s) = \frac{1}{\beta^2}\cdot\frac{1}{\mathcal{Z}}\left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}\right)$; Using, $\langle N \rangle = \sum n_s \,\mathrm{Prob}(s) = \frac{1}{\beta}\frac{1}{\mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)$

We find; $\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{1}{\beta}\frac{1}{\mathcal{Z}}\left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}\right) - \frac{1}{\beta}\frac{1}{\mathcal{Z}^2}\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)^2$

—or— $k_B T\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \langle n_s^2 \rangle - \langle n_s \rangle^2 = (\Delta N)^2$

"Response Functions" like C_V

<u>Overview of Calculation Methods:</u> Entropy Analogue ; $S(U,V,N) = k_B \log(g(U,V,N))$

$Z(T,V,N) = \sum_{s \in S(V,N)} e^{-\beta \epsilon_s}$; $F(T,V,N) = -k_B T \log(Z(T,V,N))$; $Z(T,V,N) = e^{-\beta F(T,V,N)}$

$\mathcal{Z}(T,V,\mu) = \sum_{s \in S(V)} e^{-\beta(\epsilon_s - \mu n_s)}$; $\Omega(T,V,\mu) = -k_B T \log(\mathcal{Z}(T,V,\mu))$; $\mathcal{Z}(T,V,\mu) = e^{-\beta\Omega(T,V,\mu)}$

$\zeta(T,p,N) = \sum_{s \in S(N)} e^{-\beta(\epsilon_s + pV_s)}$; $G(T,p,N) = -k_B T \log(\zeta(T,p,N))$; $\zeta(T,p,N) = e^{-\beta F(T,p,N)}$

Combining these formulas leads to : $Z_1(T,V) = V n_Q(T)$; Classical Limit : $n = \frac{1}{V}$; $Z_1 \gg 1$

Internal Energy : $U(T,V,N=1) = k_B T^2 \left(\frac{\partial Z_1}{\partial T}\right)_V = \frac{3}{2} k_B T$; $Z(T,V,N) = \frac{1}{N!}(Z_1)^N$

$\underbrace{\text{Ideal Gas Parameters:}}$ $Z(T,V,N) = \frac{1}{N!}(V n_Q(T))^N$; $U = k_B T^2 \left(\frac{\partial \log Z}{\partial T}\right) = \frac{3}{2} N k_B T$

Chemical Potential:

$\mu = k_B T \log\left(\frac{n}{n_Q(T)}\right)$

$\boxed{F = -k_B T \log(Z) = \underbrace{k_B T \log(N!) - N k_B T \log(n_Q V)}_{\text{Sterling's Approximation:}}}$

$= N k_B T\left(\log\left(\frac{n}{n_Q(T)}\right) - 1\right)$

$\mathfrak{Z}(T,\mu,V) = \sum z^{\hat{N}} \cdot \frac{1}{\hat{N}!}(Z_1)^{\hat{N}} = e^{z Z_1}$

"Grand Partition"

$\boxed{p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N k_B T}{V}}$; $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = \underbrace{N k_B\left(\log\left[\frac{n_Q(T)}{n} + \frac{5}{2}\right]\right)}_{\text{Sackur-Tetrode}}$

$\Omega(T,\mu,V) = -k_B T z Z_1 = -k_B T e^{\beta\mu} V n_Q(T)$

"Grand Potential"

The average number of particles $-\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$ leading to $N = e^{\beta\mu} V n_Q(T)$

We can also check Gibbs-Duhem relation:

$TS - pV + \mu N = N k_B T\left(\log\left(\frac{n_Q(T)}{n} + \frac{5}{2}\right)\right) - \frac{N k_B T}{V}\cdot V + k_B T \log\left(\frac{n}{n_Q(T)}\right) N$

$TS - pV + \mu N = \frac{3}{2} N k_B T$; $Z_1 = I(1+\epsilon)$; where I = integral of relative error.

Error is proportional to $(V n_Q(T))^{-1/3}$; $Z_1^N = I^N(1+\epsilon)^N \approx I^N(1+N\epsilon)$

$N^3 \ll V n_Q(T)$; $n \ll n_Q(T) N^{-2}$

$F = F_{ideal} - N k_B T \log(1+\epsilon)$

We would assume the second term is small compared to the first.

$|\log(1+\epsilon)| \ll \left|\log\left(\frac{n}{n_Q(T)}\right) - 1\right|$; $n \ll n_Q(T)$

The two terms in the free energy are:

$F_{ideal} = -N k_B T\left(\log\left(\frac{n}{N_Q(T)}\right) - 1\right)$; $F_{trunc} = -N k_B T \epsilon = -N k_B T f(V,T)(V n_Q(T))^{-1/3}$

Problems : Chapter 3:

1. $F(V,N) = N\log\left(\frac{N}{V}\right) - N$

A. $\boxed{p = -\left(\frac{\partial F}{\partial V}\right)_{T,V} = +\frac{N}{\cancel{N}} \cdot \frac{\cancel{V}\cdot\cancel{N}}{V^2} = \frac{N}{V} \; ; \; \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \log\left(\frac{N}{V}\right) + V - 1}$

B. | ϕ_1 | ϕ_2 | ϕ_3 | ... | ϕ_i |

$M=1$, $V=1$; $M=2$, $V=2$; $M=3$, $V=3$; $M=M_i$, $V=V_i$; N_{total}

$\phi_i = \log\left(\frac{N_i}{V_i}\right) + V_i - 1$; $N_i = V_i e^{\phi_i + 1 - V}$

$\boxed{N_{TOT} = \sum V_i e^{\phi_i + 1 - V}}$

2. $\xrightarrow{B(\vec{r})}$ $\boxed{S = 1/2}$ $\frac{n\uparrow}{V} = C\uparrow$; $\frac{n\downarrow}{V} = C\downarrow$; T = temp ;

a) $\phi_\uparrow = \log\frac{N\uparrow}{\cancel{V}} - V + \log 0 = \log N\uparrow - 1$; $\phi_\downarrow = \log N_\downarrow - 1$

b) The chemical potentials are the same because the function of F is moles.

c). $\mu_m = \frac{B(\vec{r})\cdot V}{\mu_0}$ d) $B(\vec{r}) = \frac{\mu_m \mu_0}{V} = \frac{\mu_m \cdot \mu_0}{n/C} \Rightarrow \boxed{C = \frac{B(\vec{r})\cdot n}{\mu_m \cdot \mu_0}}$

3. a) $\boxed{\mu_\uparrow(\vec r) = k_B T \log\left(\frac{n_\uparrow(\vec r)}{n_Q(T)}\right) - \frac{1}{2}\cdot\gamma\cdot\mu_B\cdot B(\vec r)}$

$\vec m = \gamma\cdot\mu_B\cdot\vec S$; $U_{mag} = -\vec m\cdot\vec B$; $U_{mag} = -\gamma\mu_B\cdot\vec S\cdot B(\vec r)$ ($\vec S \sim 1/2$)

$\mu_\downarrow(\vec r) = \boxed{k_B T \log\left(\frac{n_\downarrow(\vec r)}{n_Q(T)}\right) + \frac{1}{2}\gamma\mu_B B(\vec r)}$

b) If either chemical potential was position dependent, then there would be ~~no~~ equilibrium and particles would shift their spin.

c) $\mu(\vec r) = k_B T \log\left(\frac{n_\uparrow}{n_Q}\right) - \frac{1}{2}\gamma\mu_B\cdot B(\vec r)$; $n_\uparrow(\vec r) = n_Q(T)\, e^{\frac{1}{k_BT}(\mu + \frac{1}{2}\gamma\mu_B B(r))}$

$n_\downarrow(\vec r) = n_Q(\vec r)\, e^{\frac{1}{k_BT}(\mu - \frac{1}{2}\gamma\mu_B B(r))}$

$m(\vec r) = \gamma\mu_B\frac{1}{2}(n_\uparrow(\vec r) - n_\downarrow(\vec r)) = \gamma\mu_B\frac{1}{2}n_Q(T)e^{\frac{\mu}{k_BT}}\left(e^{\frac{\gamma\mu_B B(\vec r)}{2k_BT}} - e^{-\frac{\gamma\mu_B B(\vec r)}{2k_BT}}\right)$ "Subtraction"

$= \gamma\mu_B n_Q(T) e^{\mu/k_BT}\sinh\left(\frac{\gamma\mu_B B(\vec r)}{2k_BT}\right)$

d) Concentration of magnetic particles: $n(\vec r) = n_\uparrow(\vec r) + n_\downarrow(\vec r) = n_Q(T)e^{\frac{\mu}{k_BT}}\left(e^{\frac{\gamma\mu_B B(\vec r)}{2k_BT}} + e^{-\frac{\gamma\mu_B B(\vec r)}{2k_BT}}\right)$

What happens when $\gamma\mu_B B(\vec r) \ll 2k_BT$ $\quad = 2n_Q(T)e^{\frac{\mu}{k_BT}}\cosh\left(\frac{\gamma\mu_B B(\vec r)}{2k_BT}\right)$

$n(\vec r) \approx 2n_Q(T)e^{\frac{\mu}{k_BT}} = n_0$ "Addition"

The magnetization density $m(\vec r) \approx \gamma\mu_B n_Q(T) e^{\frac{\mu}{k_BT}}\frac{\gamma\mu_B B(\vec r)}{2k_BT} = \underbrace{n_0\frac{\gamma^2\mu_B^2}{4k_BT}B(\vec r)}_{\text{Curie-Weiss Law}}$

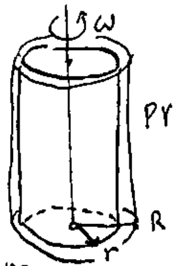
4. $n = 0,1,2,\cdots,\infty$; (n,m) energy is $n\hbar\omega$ for m-particles.
$m = 0,1,2\cdots,n$ $\quad \mathcal{Z} = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} e^{-\beta(n\hbar\omega - \mu m)} = \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}\sum_{m=0}^{n} e^{m\beta\mu} = \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}\frac{1-e^{(n+1)\beta\mu}}{1-e^{\beta\mu}}$

$= \frac{1}{1-e^{\beta\mu}}\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} - \frac{e^{\beta\mu}}{1-e^{\beta\mu}}\sum_{n=0}^{\infty} e^{-n\beta(\hbar\omega-\mu)}$

$= \frac{1}{1-e^{\beta\mu}}\frac{1}{1-e^{-\beta\hbar\omega}} - \frac{e^{\beta\mu}}{1-e^{\beta\mu}}\frac{1}{1-e^{\beta(\mu-\hbar\omega)}}$ Remember $\sum r^n = \frac{1}{1-r}$

$\boxed{= \frac{1}{1-e^{\beta\mu}}\left(\frac{1}{1-e^{-\beta\hbar\omega}} - \frac{1}{e^{-\beta\mu} - e^{-\beta\hbar\omega}}\right)}$

5.



$PV = nRT$

Calculate the density of gas as function of R.

$\rho = M\cdot\frac{n}{V} = M\cdot\frac{P}{RT}$

$\mu = k_BT\log\left(\frac{n}{n_{TOT}}\right) + \frac{1}{2}mr^2\omega^2$

"Unitof energy" $-\frac{1}{2}\frac{mr^2\omega^2}{k_BT}$ $\quad \mu/k_BT$

$n(\vec r) = n_{TOT}\cdot e^{-\frac{1}{2}\frac{mr^2\omega^2}{k_BT}}\cdot e^{\mu/k_BT}$

$$\boxed{\rho = M\cdot\frac{n_{TOT}\cdot e^{-\frac{1}{2}mr^2\omega^2/k_BT}\cdot e^{\mu/k_BT}}{V}}$$

6. $E(\vec k) = \hbar c|\vec k|$; $n \ll n_{TOT}$

a) Calculate the partition function $(N=1)$

B) Calculate the partition function $(n=\infty)$

c) Calculate $p(T,V,N), S(T,V,N), \mu(T,V,N)$.

6) $Z_1(T,V) = \sum_{n_x,n_y,n_z} e^{-\frac{\hbar c\pi}{k_B T}\sqrt{n_x^2+n_y^2+n_z^2}}$; $\vec{X} = \frac{\hbar c\pi}{k_B T L}(n_x, n_y, n_z)$

$= \int e^{-\frac{\hbar c\pi}{k_B T L}\sqrt{n_x^2+n_y^2+n_z^2}} \cdot dn_x, n_y, n_z$

$X = \frac{\hbar c\pi}{k_B T}\sqrt{n_x^2+n_y^2+n_z^2}$; $\frac{dX}{dn_x} = \frac{1}{2}\frac{\hbar c\pi}{k_B T}(n_x^2+n_y^2+n_z^2)^{-1/2}$

$\frac{dX}{dn_y} = \frac{1}{2}\frac{\hbar c\pi}{k_B T}(n_x^2+n_y^2+n_z^2)^{-1/2}$

$\frac{dX}{dn_z} = \frac{\hbar c\pi}{k_B T}(n_x^2+n_y^2+n_z^2)^{-1/2}$

$\frac{dX}{\left(\frac{\hbar c\pi}{k_B T}\right)(n_x^2+n_y^2+n_z^2)^2} = dn_z$

$\left(\frac{\hbar c\pi}{k_B T}\right)^{-1} \cdot \frac{1}{8} = dn_z$

Quadrants, then, octants.

$= \left(\frac{\hbar c\pi}{k_B T L}\right)^{-3} \cdot \frac{1}{8}\int d^3X\, e^{-X} = \left(\frac{k_B T L}{\hbar \cdot 2c\cdot\pi}\right)^3 \int_0^\infty \underbrace{4\pi X^2}_{\text{surface over sphere}} e^{-X}\, dX$

$= \left(\frac{k_B T L}{\hbar c 2\pi}\right)^3 \cdot 8\pi = \underbrace{V\left(\frac{k_B T}{\hbar c 2\pi}\right)^3 \cdot 8\pi}_{\text{at low density, an approximation is considered}}$

$Z(T,V) = Z(T,V,N) = \frac{1}{N!}V^N\left(\frac{k_B T}{\hbar c 2\pi}\right)^{3N}(8\pi)^N$

$F = -k_B T\log(Z) = \underbrace{-Nk_B T\log\left(8\pi\frac{V}{N}\left(\frac{k_B T}{\hbar c 2\pi}\right)^3\right) - Nk_B T}_{\text{Stirling Approximation.}}$

$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_B T}{V}$; $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B\log\left(8\pi\frac{V}{N}\left(\frac{k_B T}{\hbar c 2\pi}\right)^3\right) + 4Nk_B$

$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_B T\log\left(8\pi\frac{V}{N}\left(\frac{k_B T}{\hbar c 2\pi}\right)^3\right)$

$U = k_B T^2\frac{\partial}{\partial T}\log(Z) = 3Nk_B T$; $TS - pV + \mu N = 3Nk_B T$

Problem 7: $\mu = k_B T\log\left(\frac{n}{n_Q(T)}\right)$; Suppose $n \ll n_Q(T)$; $\mu < 0$; $\frac{n}{V} \ll 1$: one less molecule means μ is larger.

If density is low, then pressure inside the bottle is low,

As such, the chemical potential outside the n bottle $\frac{n}{n_Q} = \frac{n}{(n+1)}$

... is important to the story. $\Delta F = (\mu_m - \mu_{int})\Delta N = k_B T\log\left(\frac{n_m}{n_{int}}\right)\Delta N$

Problem 8: $\langle N\rangle = [e^{\hbar\omega/k_B T} - 1]^{-1}$; ω ; "Plancks Law for Distribution of photons"

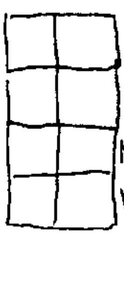
Grand Potential: $\Omega(T,V,\mu) = \Omega(T,V,0) - \int^\mu N d\mu' = \Omega(T,V,0) - N\mu$

Helmholtz Free: $F = \Omega(T,V,\mu(N)) + N\mu(N) = \Omega(T,V,0)$ || which has no N!

Hence, $\underbrace{\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = 0}_{\text{No cost to create or destroy photons}}$

Problem 9:

Energy



$N=0, E=0$; $\epsilon_2 > \epsilon_1 > 0$; $I < 0$; T, μ

$N=1, E=\epsilon_1$ (A) Calculate the Grand Partition

$N=1, E=\epsilon_2$ $\Omega(T,V,\mu(N)) = \sum e^{-E/k_B T} = e^0 + e^{-\epsilon_1/k_B T} + e^{-\epsilon_2/k_B T} + e^{-(\epsilon_1+\epsilon_2+I/k_B T)}$

$N=2, E=\epsilon_1+\epsilon_2+I$ (B) calculate $N(T,\mu)$; $N(T,\mu) = \frac{0+1+1+2}{4}$

$$\mu = k_B T \log\left(\frac{n}{n_Q(T)}\right); \quad \mathcal{Z}(T,\mu,V) = \sum z^{\hat{N}} \frac{1}{\hat{N}!} (Z_1)^{\hat{N}} = e^{z Z_1}$$

$$\boxed{Z(T,\mu)} = 1 + e^{-\frac{1}{k_BT}(\epsilon_1-\mu)} + e^{-\frac{1}{k_BT}(\epsilon_2-\mu)} + e^{-\frac{1}{k_BT}(\epsilon_1+\epsilon_2+I-2\mu)}$$

$$\boxed{N(T,\mu)} = \frac{1}{Z}\left(e^{-\frac{1}{k_BT}(\epsilon_1-\mu)} + e^{-\frac{1}{k_BT}(\epsilon_2-\mu)} + 2e^{-\frac{1}{k_BT}(\epsilon_1+\epsilon_2+I-2\mu)}\right)$$

$$\left(\frac{\partial N}{\partial T}\right)_\mu = -\frac{1}{Z^2}\left(\frac{\partial Z}{\partial T}\right)\left(e^{-\frac{1}{k_BT}(\epsilon_1-\mu)} + e^{-\frac{1}{k_BT}(\epsilon_2-\mu)} + 2e^{-\frac{1}{k_BT}(\epsilon_1+\epsilon_2+I-2\mu)}\right) + \frac{1}{Z}\left((\epsilon_1-\mu)e^{-\frac{1}{k_BT}(\epsilon_1-\mu)} + (\epsilon_2-\mu)e^{-\frac{1}{k_BT}(\epsilon_2-\mu)} + 2(\epsilon_1+\epsilon_2+I-2\mu)e^{-\frac{1}{k_BT}(\epsilon_1+\epsilon_2+I-2\mu)}\right)\frac{1}{k_BT^2}$$

$$Z k_B T^2\left(\frac{\partial N}{\partial T}\right)_\mu = -N(T,\mu)\left((\epsilon_1-\mu)e^{-\frac{1}{k_BT}(\epsilon_1-\mu)} + (\epsilon_2-\mu)e^{-\frac{1}{k_BT}(\epsilon_2-\mu)} + (\epsilon_1+\epsilon_2+I-2\mu)e^{-\frac{1}{k_BT}(\epsilon_1+\epsilon_2+I-2\mu)}\right)$$
$$+\left((\epsilon_1-\mu)e^{-\frac{1}{k_BT}(\epsilon_1-\mu)} + (\epsilon_2-\mu)e^{-\frac{1}{k_BT}(\epsilon_2-\mu)} + 2(\epsilon_1+\epsilon_2+I-2\mu)e^{-\frac{1}{k_BT}(\epsilon_1+\epsilon_2+I-2\mu)}\right)$$
$$= (1-N(T,\mu))(\epsilon_1-\mu)e^{-\frac{1}{k_BT}(\epsilon_1-\mu)} + (1-N(T,\mu))(\epsilon_2-\mu)e^{-\frac{1}{k_BT}(\epsilon_2-\mu)}$$
$$+ (2-N(T,\mu))(\epsilon_1+\epsilon_2+I-2\mu)e^{-\frac{1}{k_BT}(\epsilon_1+\epsilon_2+I-2\mu)}$$

$N(T,\mu) > 1$; means $\epsilon_1+\epsilon_2+I$ is the lowest energy state.

$I < -\epsilon_1 - \epsilon_2$;

$N(T=0,\mu) = 2$; small temp

Look at coefficients

Depends on population at a temperature

Chapter 4: Statistics of independent Particles:

Ideal Gas = Noninteracting particles in a low-density limit

Energy levels - Single particle states.

Orbital - single particle state.

Particle are independendence when $\epsilon_o^s = \epsilon_o$

Quasiparticles - a replacement of electrons with volume around them.

Total Energy of Independent Particles. $E(\text{state } s) = \sum_o n_o^s \epsilon_o$

of course we have

$N(\text{state } s) = \sum_o n_o^s$

Inclusion of Correlation:

$E(n_f) = E(0) + n_f\epsilon_f + \frac{1}{2}n_f^2 U$

coulomb Interaction. "Same magnitude as ϵ_f"

$E(\text{state } s) = E(0) + \sum_o n_o^s\epsilon_o + \frac{1}{2}\sum_{o,o'} n_o^s n_{o'}^s U_{o,o'}$

Inclusion of Quantum Statistics: Fermions have $n=0,1$ particles

Bosons have $n=0,1,2\cdots n$. particles.

Calculations for Independent Subsystems: $\mathcal{Z}_o(T,\mu,V) = \sum_{n=0}^{?} e^{\frac{n(\mu-\epsilon_o)}{k_BT}}$

$\boxed{\text{Fermions}}$: $\mathcal{Z}(T,\mu,V) = 1 + e^{\frac{\mu - \epsilon_0}{k_B T}}$; $\langle n_o \rangle$ is number of particles in orbital.

P_n is probability of finding n particles of

$$\langle n_0 \rangle = 0P_0 + 1P_1$$

$$\langle n^o \rangle = \frac{e^{\frac{\mu-\epsilon_0}{k_BT}}}{1 + e^{\frac{\mu-\epsilon_0}{k_BT}}} = \frac{1}{e^{\frac{\epsilon_0-\mu}{k_BT}} + 1}$$

The number of particles in an orbital with energy ϵ is the distribution function:

$$\underbrace{F_{FD}(\epsilon,T,\mu) = \frac{1}{e^{\frac{\epsilon-\mu}{k_BT}} + 1}}_{\boxed{\text{Fermi-Dirac Distribution}}}$$

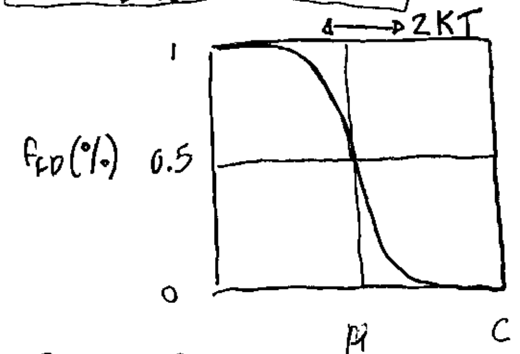
Fermi-Dirac Distribution:

Properties: $\lim_{\epsilon \to \infty} F_{FD}(\epsilon,T,\mu) = 0$

$\lim_{\epsilon \to -\infty} F_{FD}(\epsilon,T,\mu) = 1$

$f_{FD}(\epsilon = \mu, T, \mu) = \frac{1}{2}$

@ $\epsilon = \mu$; value $= \frac{1}{2}$



$\boxed{\text{Bosons}}$: $\mathcal{Z}_0(T,\mu,V) = \sum_{n=0}^{\infty} e^{\frac{n(\mu-\epsilon_0)}{k_BT}} = \frac{1}{(e^{\frac{\mu-\epsilon_0}{k_BT}} - 1)}$ * Due to infinite amount of Bosons vs Fermion

The average number of particles follows:

$$\langle n_o \rangle = k_B T \left(\frac{\partial \log(\mathcal{Z}_0)}{\partial \mu}\right)_{T,V} = \frac{1}{(e^{\frac{\epsilon_0-\mu}{k_BT}} - 1)}$$

The distributions for Bosons is $f_{BE}(\epsilon,T,\mu) = \frac{1}{e^{\frac{\epsilon-\mu}{k_BT}} - 1}$ $\boxed{\text{Bose-Einstein Distribution}}$

Bose-Einstein Distribution:

Properties: $\lim_{\epsilon \to \infty} f_{FD}(\epsilon,T,\mu) = 0$

$\lim_{\epsilon \to \mu} f_{FD}(\epsilon,T,\mu) = \infty$

Limit of Small Occupation Numbers: Negative energy states correspond to positrons and are resolved with Dirac Hamiltonian and not Hamiltonian.

Requirement: $\mu(T) \ll \epsilon_{min} - k_BT$

$e^{\frac{\epsilon-\mu}{k_BT}} \gg 1$, so $f_{MB}(\epsilon;T,\mu) = e^{\frac{\mu-\epsilon}{k_BT}}$

Use of Distribution Functions: Q has T,μ,V from a $Q_o(V)$

$Q(T,V,\mu) = \sum f(\epsilon_o(V);T,\mu)\, Q_o(V)$ $\quad N(T,V,\mu) = \sum_{orb} f(\epsilon_o(V);T,\mu) \longrightarrow \mu(T,V,N) \longrightarrow F(T,V,N)$

$$U(T,V,\mu) = \sum_{orb} f(\epsilon_o(V);T,\mu)\,\epsilon_o(V)$$

Boltzmann Gas Again: 1) Free 2) Noninteracting 3) Classical regime.

No external forces ✓ — Volume — No internal forces — Quantum Effects related to occupation

Ideal Gas Again: Boltzmann Distribution Function $N = \sum_{orb} f_{MB}(\epsilon_0) = \sum_{orb} e^{\frac{\mu - \epsilon_0}{k_B T}} = e^{\frac{\mu}{k_B T}} Z_1$

Quantum concentration: $n_Q(T) = \left(\frac{M k_B T}{2\pi \hbar^2}\right)^{3/2}$; $\mu = k_B T \log\left(\frac{n}{n_Q(T)}\right)$

Requires: $\mu << -k_B T$ and $n << n_Q(T)$

Internal Energy: $U = \sum_{orb} \epsilon_0 e^{\frac{\mu - \epsilon_0}{k_B T}} = e^{\frac{\mu}{k_B T}} \cdot k_B T^2 \frac{\partial}{\partial T} \sum_{orb} e^{-\frac{\epsilon_0}{k_B T}}$

$$= \frac{N k_B T^2}{Z_1}\left(\frac{\partial Z_1}{\partial T}\right)_{N,V} = \frac{3}{2} N k_B T$$

Note: ideal gas $\left(\frac{\partial U}{\partial V}\right)_{T,N} = 0$.

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(\frac{\partial U}{\partial V}\right)_{T,N} + T\left(\frac{\partial S}{\partial V}\right)_{T,N}$$

Note: gas pressure/volume describes distance between particles

Solid pressure/volume describes interaction between particles

Summation of Chemical Potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} ; \quad F(N,T,V) = \int_0^N \mu \, dN' = \int_0^N k_B T \log\left(\frac{N'}{V n_Q(T)}\right) dN' = N k_B T\left(\log\left(\frac{n}{n_Q(T)}\right) - 1\right)$$

Where $\int_0^N \log(cN')\,dN' = N \log(c) + N\log(N) - N$

Remember, chemical potential is the energy needed to add one particle to the system,

$$F(N,T,V) = \sum_{N=1}^{N} \mu(N,T,V) \approx \sum_{n=1}^{N} k_B T \log\left(\frac{\hat{N}}{V n_Q(T)}\right) = k_B T \log(N!) - N \log(n_Q(T) V)$$

Where $\sum_{N=1}^{N} \log(cN) = N\log(c) + \log(N!)$

if N is large, then $\log(N!) = N\log(N) - N$.

Back to Thermodynamics Once Helmholtz Free Energy is known, entropy and pressure are discovered.

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N k_B T}{V}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = N k_B\left(\log\left(\frac{n_Q(T)}{n}\right) + \frac{5}{2}\right)$$

Euler Equation: $G = F + pV$ @ constant pressure. For an ideal gas, we find $G = \mu N$

Heat Capacity: $C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{3}{2}Nk_B$; $C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = \frac{5}{2}Nk_B$

$$\left(\frac{\partial S}{\partial T}\right)_{p,N} = \left(\frac{\partial S}{\partial T}\right)_{V,N} + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{T,N}}_{\frac{Nk_B}{V}} \underbrace{\left(\frac{\partial V}{\partial T}\right)_{p,N}}_{\frac{Nk_B}{p} = \frac{V}{T}} = \frac{5}{2}\frac{Nk_B}{T}$$

Ratio of heat Capacities:

$\gamma = \frac{C_p}{C_V} = \frac{5}{3}$

$$\gamma = 1 + \left(\frac{\partial S}{\partial V}\right)_{T,N}\cdot\left(\frac{\partial V}{\partial T}\right)_{p,N}\cdot\left(\left(\frac{\partial S}{\partial T}\right)_{V,N}\right)^{-1} = 1 + \left(\frac{\partial S}{\partial V}\right)_{T,N}\cdot\left(\frac{\partial V}{\partial T}\right)_{p,N}\cdot\left(\frac{\partial T}{\partial S}\right)_{V,N}$$

$$= 1 - \left(\frac{\partial T}{\partial V}\right)_{S,N}\cdot\left(\frac{\partial V}{\partial T}\right)_{p,N} ; \left(\frac{\partial T}{\partial V}\right)_{S,N} = (1-\gamma)\frac{T}{V}$$

$T \propto V^{1-\gamma}$; pV^{γ}

Gas of poly-atomic molecules:

Internal motion is independent.

$$\epsilon(n_x, n_y, n_z, int) = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2(n_x^2 + n_y^2 + n_z^2) + \epsilon_{int}$$

Degrees of freedom: $3(N-1) - r$: r = rotational

Changes in the partition function:

Note: Heat capacities change.

Ratio of Heat capacities change.

$$\mathcal{Z}_o(T,\mu,V) = 1 + \lambda\sum e^{-\frac{\epsilon_o + \epsilon_{int}}{k_BT}} = 1 + \lambda\mathcal{Z}_{int}e^{-\frac{\epsilon_o}{k_BT}}$$

Where $\mathcal{Z}_{int}(T) = \sum e^{-\frac{\epsilon_{int}}{k_BT}}$

$$\langle n_o\rangle = \sum \frac{\lambda e^{-\frac{\epsilon_{int}}{k_BT}}\cdot e^{-\frac{\epsilon_o}{k_BT}}}{1 + \lambda\sum_{int} e^{-\frac{\epsilon_{int}}{k_BT}}\cdot e^{-\frac{\epsilon_o}{k_BT}}} \approx \lambda\mathcal{Z}_{int}\cdot e^{-\frac{\epsilon_o}{k_BT}}$$

$\ll 1$

Degenerate Gas: A Boltzmann gas is given by Sackur-Tetrode formula.

- Temperature is in quantum concentration.
- Quantum gas or degenerate gas $n \approx n_Q(T)$

$$N = \lambda\mathcal{Z}_{int}(T)n_Q(T)\cdot V$$

$$\mu = k_BT\left(\log\left(\frac{n}{n_Q(T)}\right) - \log(\mathcal{Z}_{int})\right)$$

$$F = Nk_BT\left(\log\left(\frac{n}{n_Q(T)}\right) - 1\right) + F_{int}(T,N)$$

$$F_{int}(T,N) = -Nk_BT\log\mathcal{Z}_{int}(T)$$

Fermi Gas: A quantum gas type.

Fermi energy: $f_{FD}(\epsilon) = \frac{1}{e^{\frac{\epsilon-\mu}{k_BT}} + 1}$

$$@T = 0K, \mu(T=0) = \epsilon_F ; N = \sum_{orb} f_{FD}(\epsilon_o) = g\sum_{n_x,n_y,n_z} f_{FD}(\epsilon(n_x,n_y,n_z))$$

Convergence of Series:

$\sum_{n=1}^{\infty} x_n = S$; $\lim_{N\to\infty} S_N = S$; $N > N_\epsilon \Rightarrow |S_N - S| < \epsilon$: $N > N_\epsilon(T) \Rightarrow |S_N(T) - S(T)| < \epsilon$

$g = 2S+1$; $g = 2$ for electrons

$\sum_{n=1}^{\infty} x_n(T) = S(T)$; for every $\epsilon > 0$; we find $N_\epsilon(T)$

$N > N_\epsilon \Rightarrow |S_N(T) - S(T)| < \Theta$: $\lim_{\epsilon\to\infty} f_{FD}(\epsilon) \approx e^{\frac{\mu-\epsilon}{k_BT}}$;

$[0, T_{max}]$ we have $e^{\frac{-\epsilon}{k_BT}} \cdot e^{\frac{-\epsilon}{k_BT_{max}}}$; $N = \sum_{orb}\Theta(\epsilon_F - \epsilon_o)$

Grand Partition Function:

$$\mathcal{Z}(T,\mu,V) = \sum_{\{n_1,n_2\ldots\}} e^{\frac{1}{k_BT}(\mu N(\{n_1,n_2\ldots\}) - E(\{n_1,n_2\ldots\}))}$$

Total Number of particles:

$N(\{n_1,n_2,\ldots\}) = \sum_o n_o$; Energy: $E(n_1,n_2\ldots) = \sum n_o\epsilon_o$

Many body: $E(\{n_1, n_2 \dots\})$; Single particle Energies: ϵ_0; The grand partition function:

$$\mathcal{Z}(T,\mu,V) = \sum_{\{n_1 n_2 \dots\}} e^{\frac{1}{k_BT}(\mu-\epsilon_0)n_0} = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\cdots\sum_{n_i=0}^{1}\cdots\prod_0 e^{\frac{1}{k_BT}(\mu-\epsilon_0)n_0} = \left(\sum_{n_1=0}^{1} e^{\frac{1}{k_BT}(\mu-\epsilon_1)n_1}\right)\left(\sum_{n_2=0}^{1} e^{\frac{1}{k_BT}(\mu-\epsilon_2)n_2}\right)\dots$$

$$= \prod_{orb}\left(\sum_{n=0}^{1} e^{\frac{1}{k_BT}(\mu-\epsilon_0)n}\right) = \prod \mathcal{Z}_0(T,\mu,V)$$

$$= \sum_{n=0}^{1} e^{n\frac{\mu-\epsilon_0}{k_BT}} = \boxed{1+e^{\frac{\mu-\epsilon_0}{k_BT}}}$$

Grand Energy: $\Omega(T,\mu,V) = -k_BT\log(\mathcal{Z}_0)$

$$= -k_BT\sum_{orb}\log(\mathcal{Z}_0(T,\mu,V))$$

$$N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = k_BT\sum_{orb}\frac{1}{\mathcal{Z}_0(T,\mu,V)}\left(\frac{\partial\mathcal{Z}_0(T,\mu,V)}{\partial\mu}\right);$$

$$= \sum_{orb}\frac{e^{\frac{\mu-\epsilon_0}{k_BT}}}{1+e^{\frac{\mu-\epsilon_0}{k_BT}}} = \sum_{orb} f_{FD}(\epsilon_0;T,\mu)$$

Entropy of a system fermions:

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{\mu,V} = k_B\sum\log(\mathcal{Z}_0(T,\mu,V)) + k_BT\sum\left(\frac{\partial\log(\mathcal{Z}_0(T,\mu,V))}{\partial T}\right)_{\mu,V}$$

$$= k_B\sum\log\left(1+e^{\frac{\mu-\epsilon_0}{k_BT}}\right) + k_BT\sum\frac{e^{\frac{\mu-\epsilon_0}{k_BT}}}{1+e^{\frac{\mu-\epsilon_0}{k_BT}}}\cdot\frac{\mu-\epsilon_0}{-k_BT^2}$$

$$= k_B\sum\log(1+e$$

Note: $e^{\frac{\mu-\epsilon}{k_BT}} = \frac{1}{e^{\frac{\epsilon-\mu}{k_BT}}} = \frac{1}{e^{\frac{\epsilon-\mu}{k_BT}}+1-1} = \frac{1}{\frac{1}{f_{FD}}-1} = \frac{f_{FD}}{1-f_{FD}}$

$$= k_B\sum\log\left(1+\frac{f_{FD}}{1-f_{FD}}\right) - k_B\sum\frac{\frac{f_{FD}}{1-f_{FD}}}{1+\frac{f_{FD}}{1-f_{FD}}}\log\left(\frac{f_{FD}}{1-f_{FD}}\right) = -k_B\sum\log(1-f_{FD}) - k_B\sum f_{FD}\log\left(\frac{f_{FD}}{1-f_{FD}}\right)$$

$$= -k_B\sum\left(f_{FD}\log(f_{FD}) + (1-f_{FD})\log(1-f_{FD})\right)$$

$$= -k_B\sum P_s\log(P_s)$$

Boson Gas:

Distribution: $f_{BE}(\epsilon) = \frac{1}{e^{\frac{\epsilon-\mu}{k_BT}}-1}$

Grand Partition Function: $\mathcal{Z}(T,\mu,V) = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\sum_{n_i} e^{\frac{1}{k_BT}(\mu\sum_0 n_0 - \sum n_0\epsilon_0)} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\sum_{n_i}\prod_{orb} e^{\frac{n_0}{k_BT}(\mu-\epsilon_0)}$

$$= \prod\left[\sum e^{\frac{n(\mu-\epsilon_0)}{k_BT}}\right] = \prod\mathcal{Z}_0(T,\mu,V)$$

Grand Potential: $\Omega(T,\mu,V) = -k_BT\sum(\mathcal{Z}_0(T,\mu,V))$

Total Number of Particles: $N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = \sum f_{BE}(\epsilon_0)$

$$\mathcal{Z}_0(T,\mu,V) = \frac{1}{1-e^{\frac{\mu-\epsilon_0}{k_BT}}}$$

because $\left(\frac{\partial\log\mathcal{Z}_0}{\partial\mu}\right)_{T,V} = \frac{1}{k_BT}\mathcal{Z}_0^{-1}\frac{e^{\frac{\mu-\epsilon_0}{k_BT}}}{\left(1-e^{\frac{\mu-\epsilon_0}{k_BT}}\right)^2}$

Entropy: $S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = -k_B\sum\left(f_{BE}(\epsilon_0)\log(f_{BE}(\epsilon_0)) - (1+f_{BE}(\epsilon_0))\log(1+f_{BE}(\epsilon_0))\right)$

$$= k_B\sum\left(f_{BE}(\epsilon_0)\log\left(\frac{1+f_{BE}(\epsilon_0)}{f_{BE}(\epsilon_0)}\right) + \log(1+f_{BE}(\epsilon_0))\right)$$

"Related to Stimulated Emission!"

Problems for Chapter 4

1) Imaginons here # particles of 0, 1, or 2.

a) $\mathcal{Z}_0(T,\mu,V) = \sum_{n=0}^{2} e^{\frac{n(\mu-\epsilon_0)}{k_BT}} = 1 + e^{\frac{(\mu-\epsilon_0)}{k_BT}} + e^{\frac{2(\mu-\epsilon_0)}{k_BT}}$; $\langle n_0\rangle = 0P_0 + 1P_1 + 2P_2 = 0 + \frac{e^{\frac{(\mu-\epsilon)}{k_BT}} + e^{2(\mu-\epsilon)/k_BT}}{1+e^{\frac{\mu-\epsilon}{k_BT}}+e^{2(\mu-\epsilon)/k_BT}}$

$$f_{IM} = \frac{1}{2e^{(\epsilon-\mu)/k_BT} + e^{(\mu-\epsilon)/k_BT} + 1}$$

b) Black body "Ultra : Chart"

c) See ...

~~d) This would represent the same result as 1B, but in function, rather than graphical representation.~~

2) a) N $\boxed{\text{Fermions}}$; M orbitals; Total Number of Particles: $N = \sum_{M} n_0$; Energy: $E = \sum_{M} n_0 \epsilon_0$

Grand Partition Function: $\mathcal{Z}(T,\mu,V) = \sum e^{\frac{1}{k_BT}\sum_{M}(\mu - \epsilon_0) n_0}$

$$\mathcal{Z}_0(T,\mu,V) = \sum_{n=0}^{M} e^{n\left(\frac{\mu-\epsilon_0}{k_BT}\right)} = \frac{1}{1-e^{(\mu-\epsilon_0)/k_BT}}$$

b) $N \to \infty$; $N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = T\left[\frac{e^{(\mu-\epsilon_0)/k_BT}}{\left(1-e^{(\mu-\epsilon_0)/k_BT}\right)^2}\right]$

$$\Omega(T,\mu,V) = -k_BT\sum_{orb} \log(\mathcal{Z}_0(T,\mu,V))$$

$$\infty = e^{(\mu-\epsilon_0)/k_BT} \Rightarrow (\mu-\epsilon_0)/k_BT$$

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = k_BT \left[\frac{e^{(\mu-\epsilon_0)/(k_BT)}}{k_BT\left(1-e^{(\mu-\epsilon_0)/k_BT}\right)^2}\right]$$

$\boxed{\text{Temperature drops to zero}}$

Entropy of a system of Fermions $= \sum f_{FD}(\epsilon_p; T,\mu)$

3. Starting from $\Omega(T,\mu,V) = -k_BT\sum \log \mathcal{Z}_{orb}(T,\mu,V)$

$\boxed{\text{Bosons}}$

$$f_{BE}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_BT}-1}$$

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{\mu,V} = k_B\sum \log(\mathcal{Z}_0(T,\mu,V)) + k_BT\sum\left(\frac{\partial \log(\mathcal{Z}_0(T,\mu,V))}{\partial T}\right)$$

Grand Partition Function: $\mathcal{Z}(T,\mu,V) = \sum_0^\infty \sum_0^\infty \sum_{n_0} e^{\frac{1}{k_BT}(\mu\sum n_0 - \sum n_0\epsilon_0)}$

$$= \sum_0^\infty\sum_0^\infty \sum_{n_i}\prod_{orb} e^{\frac{n_0}{k_BT}(\mu-\epsilon_0)} = \prod_{orb}\left[\sum_0^\infty e^{n(\mu-\epsilon_0)/k_BT}\right] = \prod_{orb}\mathcal{Z}_0(T,\mu,V)$$

$$= k_B\sum \log(\mathcal{Z}_0(T,\mu,V)) + k_BT\sum \frac{(\mu-\epsilon_0)}{k_BT^2}\frac{e^{\mu/(k_BT)}}{\left(e^{\mu/k_BT} - e^{\epsilon_0/(k_BT)}\right)}$$

Therefore, $\Omega(T,\mu,V) = -k_BT\sum \log\left(\frac{1}{1-e^{(\mu-\epsilon_0)/k_BT}}\right)$; $\frac{1}{1-e^{(\mu-\epsilon_0)/k_BT}}$

$$\boxed{= k_B\sum \log\left(\frac{1}{1-e^{(\mu-\epsilon_0)/k_BT}}\right) - \frac{(\mu+\epsilon_0)}{T}\frac{e^{\mu/(k_BT)}}{\left(e^{\mu/k_BT} - e^{\epsilon_0/k_BT}\right)}}$$

Initial Derivatives require: $N = -\left(\frac{\partial\Omega}{\partial\mu}\right) = \sum f_{BE}(\epsilon_0)$

@ $T=0$; $= 0 + 0 = \boxed{0}$

$$\left(\frac{\partial \log \mathcal{Z}_0}{\partial \mu}\right)_{T,V} = \frac{1}{k_BT}\mathcal{Z}_0(T,\mu,V)^{-1}\frac{e^{(\mu-\epsilon_0)/k_BT}}{\left(1-e^{(\mu-\epsilon_0)/k_BT}\right)^2}$$

Entropy: $S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = k_B\sum \log \mathcal{Z}_0(T,\mu,V) + k_BT\sum \frac{e^{(\mu-\epsilon_0)/k_BT}}{1-e^{(\mu-\epsilon_0)/k_BT}}\frac{(\mu-\epsilon_0)}{k_BT^2}$

$$\mathcal{Z}_0(T,\mu,V) = \frac{1}{1-e^{(\mu-\epsilon_0)/k_BT}} \quad \frac{e^{-(\mu-\epsilon_0)/k_BT}}{e^{(\epsilon-\mu)/k_BT}-1} = f_{BE}(\epsilon)\, e^{-(\mu-\epsilon_0)/k_BT} \quad (\mu-\epsilon_0)^2$$

f_{BE} $\log f_{BE}$

$$= f_{BE}(\epsilon)\cdot e^{(\epsilon-\mu)/k_BT} + 1 - 1 = f_{BE}(\epsilon)\cdot \frac{1}{e^{(\epsilon-\mu)/k_BT}+1-1} = f_{BE}(\epsilon)\frac{1}{\frac{1}{f_{BE}(\epsilon)}+1}$$

$$= f_{BE}(\epsilon)\frac{f_{BE}(\epsilon)}{1+f_{BE}(\epsilon)} =$$

$$\boxed{S = k_B\sum (1+f_{BE}(\epsilon_0))\log(1+f_{BE}(\epsilon_0)) - k_B f_{BE}(\epsilon_0)\log(f_{BE})}$$

$$1 - f_0 = 1 - \frac{1}{e^{(\epsilon-\mu)/k_BT}-1}$$

$$e^{(\epsilon-\mu)} - 1$$

(4) Maxwell Distribution: $f_M(\epsilon, T, \mu) = e^{(\mu-\epsilon)/k_B T}$; Show $S(T, \mu, V) = Nk_B - \sum_o f_M(\epsilon_o; T, \mu)\log(f_M(\epsilon_o; T, \mu))$

Grand Partition Function: $N = -\left(\frac{\partial \Omega}{\partial \mu}\right) = \sum f_M$; $\Omega = -\int f_M(E, T, \mu)\, d\mu$

Entropy: $S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = k_B \sum f_M(\epsilon, \mu, T) + k_B \sum f_M'(\epsilon, \mu, T) = -k_B T \cdot \sum f_M'(\epsilon, T, \mu)$

$= \sum [k_B \cdot N + k_B [(\mu - \epsilon)/k_B T] f_M(\epsilon, T, \mu)] = \boxed{k_B N - \sum [\log f_M] f_M}$

(5) E to $E+dE$ ~~described by~~ $N(E)dE$ = "Density of States"; Energy of a orbital $O_o = O(\epsilon_o)$

Prove $\langle O \rangle = \int_{-\infty}^{\infty} O(E) N(E) F(E, T, \mu)\, dE$; where $f(E, T; \mu)$ = "Distribution function";

$$O = \lim \sum_0^n O(E) N(E) f(E, T, \mu)\, \Delta E = \boxed{\int_{-\infty}^{\infty} O(E) \cdot N(E) f(E, T, \mu)\, dE}$$

(6) Orbital Energies of a system: For Fermions $\epsilon_i = i\Delta$, with $\Delta > 0$; $i = 1, 2, 3 \cdots \infty$

$S = -\left(\frac{\partial \Omega}{\partial T}\right) = 0$ @ low temp $\Omega = -k_B T \sum \log Z(n)$

N particles; $\lim T \to 0$

$\epsilon_F = (N + \frac{1}{2})\Delta$

$\lim_{T \to 0^+} \sum e^{-(\epsilon_i - \mu)/k_B T} \cong 0^+ = -(\sum i\Delta - \mu)/k_B T$; $\boxed{\sum i\Delta = \mu}$

$\mu = i\Delta$

$N = \sum \frac{1}{e^{(i\Delta - \mu)/k_B T} + 1}$; At $T=0$, the lowest N states are occupied $N = \sum_{i=1}^{N} 1$

Taking the difference: $0 = \sum_{i=1}^{N} \left(\frac{1}{e^{(i\Delta - \mu)/k_B T} + 1} - 1\right) + \sum_{i=N+1}^{\infty} \left(\frac{1}{e^{(i\Delta - \mu)/k_B T} + 1}\right)$

$$= \sum_{i=1}^{N} \left(1 - \frac{1}{e^{(i\Delta - \mu)/k_B T} + 1}\right) = \sum_{i=N+1} \left(\frac{1}{e^{(i\Delta - \mu)/k_B T} + 1}\right)$$

$$\sum_{i=1}^{N} \left(\frac{1}{e^{-(i\Delta - \mu)/k_B T} + 1}\right) = \sum_{i=N+1}^{\infty} \left(\frac{1}{e^{(i\Delta - \mu)/k_B T} + 1}\right)$$

$\lim_{T \to 0}$; $\frac{1}{e^{-(N\Delta - \mu)/k_B T} + 1} = \frac{1}{e^{((N+1)\Delta - \mu)/k_B T} + 1}$; $e^{(N\Delta - \mu)/k_B T} + 1 = e^{((N+1)\Delta - \mu)} + 1$

$$-\frac{(N\Delta - \mu)}{k_B T} = \frac{((N+1)\Delta - \mu)}{k_B T}; \quad -(N\Delta - \mu) = ((N+1)\Delta - \mu)$$

Implication @ low temp entering electrons = exiting electrons.

Problem 7: $S = -k_B \sum (f_{FD} \log(f_{FD}) + (1 - f_{FD}) \log(1 - f_{FD}))$ $i = N+1$; $\boxed{f_{FD}(\mu + x; T; \mu) + f_{FD}(\mu - x; T, \mu) = 1}$

Calculate $\lim_{T \to 0} f_{FD}(\epsilon, T, \mu)$ for $\epsilon < \mu$, $\epsilon = \mu$, $\epsilon > \mu$; $N = \sum_{orb} \frac{e^{(\mu - \epsilon_o)/k_B T}}{1 + e^{(\mu - \epsilon_o)/k_B T}} = \sum_{orb} f_{FD}(\epsilon_o; T, \mu)$

$\epsilon < \mu$: $\lim_{T \to 0^+} f_{FD} = 1$; $\epsilon = \mu$: $\lim_{T \to 0} f_{FD} = \frac{1}{2}$; $\epsilon > \mu$: $\lim_{T \to 0} f_{FD} = 0$

@ $T = 0$; $S = -k_B M\left(\frac{1}{2}\log(\frac{1}{2}) + \frac{1}{2}\log(\frac{1}{2})\right) = k_B \log(2^m)$; Entropy is a function of chemical potential.

Chapter 5: Fermi and Bose systems of free, independendent particles:

5.1: Fermions in a box: Free, Independendent Particles: 3-D box - Isotropic

Energy: $\epsilon(n_x,n_y,n_z) = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2(n_x^2+n_y^2+n_z^2)$

Wavevector: $\vec{k} = \frac{\pi}{L}(n_x,n_y,n_z)$

Step sizes: $\Delta k_x = \Delta k_y = \Delta k_z = \frac{\pi}{L}$

Orbitals: $\sum_{orb} = (2S+1)\sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty}$

Arbitrary Function of Energy:

$$\sum_{orb} h(\epsilon_0) = (2S+1)\sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} h(\epsilon(n_x,n_y,n_z))$$

Transformation of Energy: $1 = \Delta k_x \Delta k_y \Delta k_z \left(\frac{\pi}{L}\right)^{-3}$

$$\sum_{orb} h(\epsilon_0) = (2S+1)\left(\frac{L}{\pi}\right)^3 \sum_{\vec{k}} h(\epsilon(\vec{k}))\Delta k_x \Delta k_y \Delta k_z$$

Sum to integral:

$$\frac{1}{V}\sum_{orb} h(\epsilon_0) = \frac{2S+1}{\pi^3}\int d^3k\, h\left(\frac{\hbar^2k^2}{2M}\right) + \text{error}$$

A symmetric integral can be halved.

$$\frac{1}{V}\sum_{orb} h(\epsilon_0) = \frac{2S+1}{(2\pi)^3}\int d^3k\, h\left(\frac{\hbar^2k^2}{2M}\right) + \text{error}$$

"Seems to be the sum of energies for every orbital"

Grand Partition Function: $\Omega(T,\mu,V) = -(2S+1)k_BT\sum_{n_x,n_y,n_z}\log(\mathcal{Z}_{n_x,n_y,n_z}(T,\mu,V))$

$$\mathcal{Z}_{n_xn_yn_z}(T,\mu,V) = 1 + e^{\frac{\mu-\epsilon(n_x,n_y,n_z)}{k_BT}} = 1+\lambda e^{-\epsilon(n_x,n_y,n_z)/k_BT}$$

$$\frac{1}{V}\Omega(T,\mu,V) = -(2S+1)(2\pi)^{-3}k_BT\int d^3k \log\left(1+\lambda e^{\frac{-\hbar^2k^2}{2Mk_BT}}\right)$$

Does not depend on volume.

Free Particles Volume Dependence:

$$\frac{1}{V}\Omega(T,\mu,V) = \left[-(2S+1)(2\pi)^{-3}k_BT\int d^3k \log\left(1+\lambda e^{\frac{-\hbar^2k^2}{2Mk_BT}}\right)\right]\left[1+\mathcal{E}(T,V,\mu)\right]$$

Simplification: $\log(1+\lambda e^{-\epsilon(n_x,n_y,n_z)/k_BT}) \approx \lambda e^{-\epsilon(n_x,n_y,n_z)/k_BT} \approx e^{\frac{\mu_n}{k_BT} - \frac{\hbar^2\pi^2}{2ML_n^2k_BT}(n_x^2+n_y^2+n_z^2)}$

Assuming $x = n_x\sqrt{\frac{\hbar^2\pi^2}{2Mk_BTL^2}}$; $y \cdots z$

$$\frac{\epsilon(n_x,n_y,n_z)}{k_BT} = \frac{\hbar^2\pi^2}{2Mk_BTL^2}(n_x^2+n_y^2+n_z^2) = x_{n_x}^2 + y_{n_y}^2 + z_{n_z}^2$$

Note: Looking at analytical error produced understanding of a phase transition

Evaluating the integral: $\frac{1}{V}\Omega(T,\mu,V) = -(2S+1)(2\pi)^{-3}k_BT\int d^3k \log\left(1+\lambda e^{\frac{-\hbar^2k^2}{2Mk_BT}}\right)$

$$\frac{1}{V}\Omega(T,\mu,V) = -(2S+1)(2\pi)^{-3}k_BT\left(\frac{\hbar^2}{2Mk_BT}\right)^{-3/2}4\pi\int_0^{\infty}x^2dx\log(1+\lambda e^{-x^2})$$

$$\vec{x} = \left(\frac{\hbar^2}{2Mk_BT}\right)^{1/2}\vec{k}$$

Thermal Wavelength: $\lambda_T = \left(\frac{2\pi\hbar^2}{Mk_BT}\right)^{1/2}$

Function $f_{\frac{5}{2}}(\lambda)$: $f_{\frac{5}{2}}(\lambda) = \frac{4}{\sqrt{\pi}}\int_0^{\infty}x^2dx\log(1+\lambda e^{-x^2})$

Grand Energy: $$\Omega(T,\mu,V) = -\underbrace{(2S+1)}_{\text{Spin Degeneracy}}\cdot\underbrace{V}_{\text{simple volume Dependence}}\cdot\underbrace{k_BT}_{\text{Energy Scale}}\cdot\underbrace{\lambda_T^{-3}}_{\text{Volume Scale}}\cdot\underbrace{f_{\frac{5}{2}}(\lambda)}_{\text{Density Effects.}}$$

Density Dependence: $f_\kappa(z) = \sum_{n=1}^{\infty}\frac{z^n}{n^\kappa}(-1)^{n+1}$, $|z|<1$

$$f_0(z) = \sum_{n=1}^{\infty}z^n(-1)^{n+1} = 1-\sum_{n=0}^{\infty}z^n(-1)^n = 1-\frac{1}{1+z} = \frac{z}{1+z}$$

Simple example: $\ddot{x}+x=0$; $x(t)=\sum_0^\infty c_n t^n$; $\sum_0^\infty c_n n(n-1)t^{n-2}+\sum_0^\infty c_n t^n=0$; $\sum_0^\infty (c_{n+2}(n+2)(n+1)+c_n)t^n=0$

General Solution: $\sum_{k=0}^{\infty}\frac{(-1)^k}{(2k)!}t^{2k}$ and $\sum_{k=0}^{\infty}\frac{(-1)^k}{(2k+1)!}t^{2k+1}$

Second example: $\frac{d^3x}{dt^3}+x=0$; $\sum_{k=0}^{\infty}\frac{(-1)^k}{(3k)!}t^{3k}$ Finding chemical potential:

$N(T,\mu,V)=-\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}=-\left(\frac{\partial\Omega}{\partial\lambda}\right)_{T,V}\circ\left(\frac{\partial\lambda}{\partial\mu}\right)_{T,V}$; $N=(2s+1)Vk_BT\lambda_T^{-3}\underbrace{\left(\frac{\partial}{\partial\lambda}f_{\frac{5}{2}}(\lambda)\right)\frac{\lambda}{k_BT}}$

$\frac{d}{dz}\sum_{n=1}^{\infty}\frac{z^n}{n^\alpha}(-1)^{n+1}=\sum_{n=1}^{\infty}n\frac{z^{n-1}}{n^\alpha}(-1)^{n+1}=\frac{1}{z}\sum_{n=1}^{\infty}\frac{z^n}{n^{\alpha-1}}(-1)^{n+1}$; $\frac{d}{dz}f_\alpha(z)=\frac{1}{z}f_{\alpha-1}(z)$ "Evaluated with a power series"

$N(T,\mu,V)=(2s+1)\cdot V\cdot\lambda_T^{-3}f_{\frac{3}{2}}(\lambda)$

Low Temperature Expansions:

$\frac{n}{n_Q(T)}=(2s+1)f_{\frac{3}{2}}(\lambda)$

$f_{\frac{3}{2}}(\lambda)=\frac{4}{\sqrt{\pi}}\int_0^\infty x^2dx\frac{e^{-x^2}}{\lambda^{-1}+e^{-x^2}}=\frac{4}{\sqrt{\pi}}\int_0^\infty x^2dx\frac{1}{\lambda^{-1}e^{x^2}+1}$; $x^2=y$, $\lambda=e^{\nu}$

$f_{5/2},f_{3/2},f_{1/2}$ $\quad d/d\lambda \quad d/d\lambda$

$=\frac{4}{\sqrt{\pi}}\int_0^\infty y\cdot\left(\frac{1}{2}\right)\left(\frac{1}{\sqrt{y}}\right)\frac{e^{-y}}{\lambda^{-1}e^{y}+1}=\frac{2}{\sqrt{\pi}}\int_0^\infty\sqrt{y}\frac{1}{e^{y-\nu}+1}dy$

"Expanding the function near maxima and minima with a Taylor Expansion demonstrate functional theory"

$dy=2x\,dx$

$=\frac{4}{\sqrt{3\pi}}\int_0^\infty\frac{1}{e^{y-\nu}+1}dy^{3/2}=\frac{-4}{\sqrt{3\pi}}\int_0^\infty y^{\frac{3}{2}}d\frac{1}{e^{y-\nu}+1}$

$=\frac{4}{\sqrt{3\pi}}\int_0^\infty y^{\frac{3}{2}}\frac{e^{y-\nu}}{(e^{y-\nu}+1)^2}dy$

$E_F=\left(\frac{6n\pi^2}{2s+1}\right)^{2/3}\frac{\hbar^2}{2m}$ ← Relationship to Fermi Energy and Density"

$=\frac{4}{\sqrt{3\pi}}\nu^{5/2}\int_0^\infty t^{3/2}\frac{e^{\nu(t-1)}}{(e^{\nu(t-1)}+1)^2}dt$

$\frac{n}{n_Q(T)}=(2s+1)\frac{4}{3\sqrt{\pi}}(\beta\mu)^{3/2}\left(1+\frac{\pi^2}{8}(\beta\mu)^{-2}\right)=(2s+1)\frac{4}{3\sqrt{\pi}}(\beta E_F)^{3/2}$

$\left(\frac{\mu}{E_F}\right)^{-3/2}=1+\frac{\pi^2}{8}(\beta\mu)^{-2}$; $\frac{\Delta\mu}{E_F}\approx-\frac{\pi^2}{12}(k_BT)^2E_F^{-2}$; $\mu(T,N,V)\approx E_F\left(1-\frac{\pi^2}{12}\left(\frac{k_BT}{E_F}\right)^2\right)$; $k_BT\ll E_F$

Helmholtz Energy at Low Temperatures: $\int_0^N E_F(N')dN'=\frac{3}{5}NE_F$; $\int_0^N E_F^{-1}(N')dN'=3NE_F^{-1}$

$F(T,N,V)=\int_0^N\mu(T,V,N')dN'=\frac{3}{5}NE_F\left(1-\frac{5\pi^2}{12}\left(\frac{k_BT}{E_F}\right)^2\right)$

Entropy: $S(T,N,V)=-\left(\frac{\partial F}{\partial T}\right)\approx\frac{N\pi^2k_BT}{2E_F}k_B$

@ $T=0$, Fermi Gas has pressure >0

$p=-\left(\frac{\partial\Omega}{\partial V}\right)=\frac{-\Omega}{V}$

Gibbs Energy:

$G(T,V,N)=F+pV$

$\approx NE_F\left(1-\frac{\pi^2}{12}\left(\frac{k_BT}{E_F}\right)^2\right)$

Energy: $U(T,N,V)=F+TS\approx\frac{3}{5}NE_F\left(1+\frac{5\pi^2}{12}\left(\frac{k_BT}{E_F}\right)^2\right)$

Heat Capacity: $C_V(T,V,N)=\left(\frac{\partial U}{\partial T}\right)\approx Nk_B\frac{\pi^2}{2}\frac{k_BT}{E_F}$

"Relationship to Fermi Dirac"

Grand Energy:

$\Omega(T,V,N)=F-\mu N=\frac{-2}{5}NE_F\left(1+\frac{5\pi^2}{12}\left(\frac{k_BT}{E_F}\right)^2\right)$

Pressure:

$p(T,V,N)=-\left(\frac{\partial F}{\partial V}\right)\approx\frac{2}{5}\frac{NE_F}{V}\left(1+\frac{5\pi^2}{12}\left(\frac{k_BT}{E_F}\right)^2\right)$

Large Temperatures: $T \to \infty$; $N(T,\mu,V) \approx (2S+1)V n_Q(T)\lambda$; $\Omega(T,\mu,V) \approx -\underbrace{(2S+1)V k_B T n_Q(T)\lambda}$ $\approx -N k_B T$

$p = \frac{N k_B T}{V}$

Bosons in a Box: Integral Form: $\Omega(T,\mu,V) = -(2S+1)k_B T \sum \log(\mathcal{Z}_{n_x n_y n_z}(T,\mu,V))^N$

$\tilde{\Omega}(T,\mu,V) = V k_B T(2S+1)\frac{1}{(2\pi)^3}\int d^3k \log\left(1 - e^{\frac{\mu - \frac{\hbar^2 k^2}{2M}}{k_B T}}\right)$; $\mathcal{Z}_{n_x n_y n_z}(T,\mu,V) = \left(1 - e^{\frac{\mu - \epsilon(n_x,n_y,n_z)}{k_B T}}\right)^{-1}$

Special functions for Bosons: $g_\alpha(z) = \sum_{n=1}^{\infty}\frac{z^n}{n^\alpha}$; $|z|<1$ $\qquad \mu(T,V,N) = k_B T\log\left(\frac{n}{(2S+1)n_Q(T)}\right)$

$\tilde{\Omega}(T,\mu,V) = -(2S+1)V k_B T n_Q(T) g_{\frac{5}{2}}(\lambda)$; where $g_{\frac{5}{2}}(\lambda) = \frac{-4}{\sqrt{\pi}}\int_0^\infty x^2 dx \log(1-\lambda e^{-x^2})$

Expanding a Taylor series: $g_{\frac{5}{2}}(\lambda) = \frac{-4}{\sqrt{\pi}}\int_0^\infty x^2 dx \log(1-\lambda e^{-x^2}) = \frac{4}{\sqrt{\pi}}\sum_{n=1}^{\infty}\frac{1}{n}\lambda^n \int_0^\infty x^2 dx\, e^{-nx^2}$

$N(T,\mu,V) = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = (2S+1)V n_Q(T) g_{\frac{3}{2}}(\lambda)$; $\frac{d}{dz}g_\alpha(z) = \frac{1}{z}g_{\alpha-1}(z)$ $\qquad = \frac{4}{\sqrt{\pi}}\sum_{n=1}^{\infty}\frac{1}{n^{5/2}}\lambda^n\int_0^\infty y^2 dy\, e^{-y^2}$

Low Temperatures: $\Omega_R(T,\mu,V) = (2S+1)k_B T \sum_{n_x,n_y,n_z}^{\sqrt{n_x^2+n_y^2+n_z^2}} \log\left(1-\lambda e^{\frac{-\hbar^2 k^2}{2M k_B T}}\right)$; $\vec{k} = \frac{\pi}{L}(n_x,n_y,n_z)$

The limit:

$N(T,\mu,V) = (2S+1)\sum\left(e^{\frac{\frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2(n_x^2+n_y^2+n_z^2)-\mu}{k_B T}} - 1\right)^{-1}$; $\lim_{T\to 0} N(T,\mu,V) = (2S+1)\sum \lim_{T\to 0}\left(e^{\frac{\frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2(n_x^2+n_y^2+n_z^2)}{k_B T}} - 1\right)^{-1}$

$N = (2S+1)\sum \lim_{T\to 0}\left(e^{\frac{\frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2(n_x^2+n_y^2+n_z^2)-\mu(T,N,V)}{k_B T}} - 1\right)^{-1}$

Exponent: $\lim_{T\to 0}\frac{\frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 3 - \mu(T,N,V)}{k_B T} = \log\left(1+\frac{2S+1}{N}\right)$; $\mu(T,V,N) \approx \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 3 - k_B T\log\left(\frac{N+2S+1}{N}\right) + O(T^2)$

What is a low temp?

$E \gg k_B T$; $\frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 6 - \mu \gg k_B T$; $\frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2 3 \gg k_B T$ "The limit justify λ"

Grand Energy of Low Temperatures: $\frac{\Omega(T,\mu,V)}{V} = \frac{(2S+1)k_B T}{V}\log\left(1-\lambda e^{-\frac{\epsilon(1,1,1)}{k_B T}}\right) + \frac{(2S+1)k_B T}{V}\sum \log \mathcal{Z}(T,\mu,V)$

When incorporating error: $\frac{\Omega(T,\mu,V)}{V} = \frac{(2S+1)k_B T}{V}\log\left(1-\lambda e^{\frac{-3\hbar^2\pi^2}{2M k_B T L^2}}\right) - (2S+1)k_B T n_Q(T) g_{\frac{5}{2}}(\lambda) + \text{error}(T,\mu,V)$

Bose Einstein Condensation: Density $\left(\frac{N}{V}\right)$; $n = \frac{2S+1}{V}f_{BE}(\epsilon_{111}) + \frac{2S+1}{\lambda_T^3}g_{\frac{3}{2}}(\lambda)$ $\qquad V > V_\epsilon \Rightarrow \left|\frac{\text{error}(T,\mu,V)}{\frac{\Omega}{V}}\right| < \epsilon$

$n = \underbrace{\frac{2S+1}{V}\frac{\lambda}{1-\lambda}} + (2S+1)n_Q(T) g_{\frac{3}{2}}(\lambda)$

Thermodynamic limit ($\epsilon_{111}=0$) & Large Volumes: $n = \frac{2S+1}{V}\frac{\lambda}{1-\lambda} + (2S+1)n_Q(T)g_{\frac{3}{2}}(\lambda)$

$\lim_{V\to\infty}\frac{2S+1}{V}\frac{\lambda}{1-\lambda} = n - (2S+1)n_Q(T)G$; $\lambda = 1 - \frac{2S+1}{V(n-(2S+1)n_Q(T)G)}$

Number of particles with lowest energy.

Einstein Temperature:

$n = n_Q(T_E)(2S+1)G$

$T_E = \left(\frac{2\pi\hbar^2}{M k_B}\right)\left(\frac{n}{(2S+1)G}\right)^{2/3}$

Bose-Einstein Distribution Function: $f_{BE}(\epsilon) = \frac{2S+1}{e^{\frac{\epsilon-\mu}{k_B T}}-1}$

$\boxed{\text{Bose-Einstein Condensation: when the number of particles go into the ground state orbital.}}$

Problems from Chapter 5:

Problem 1: H_2 ; $PV = nRT$; $3N \to 6$ Degrees Freedom; $N=2$; 3 Degrees = x, y, z motion.
2 degrees are rotation.
1 of 3 degrees are vibration.

$E_{rt} = k_B T_r j(j+1)$; $n_Q T_q = n$; $T_r \approx 175K$

$E_{vib} = k_B T_v(n+\frac{1}{2})$; $V = 22.4L$; $T_v \approx 6{,}500K$

(?) $V - V_r \epsilon$?

Diatomic Molecule @ High Temp: 3 translational Degrees of Freedom: $\frac{3}{2}kT$ } From $\frac{1}{2}kT$

2 Rotational Degrees of Freedom: kT

Partition Functions:

Translational Contribution: $q^T = \frac{V}{\Lambda^3} = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} = \frac{V}{h^3}(2\pi m k T)^{3/2}$ $\boxed{\text{One Dimension } \langle \epsilon^T \rangle = \frac{1}{2}kT}$

Rotational Contribution: $q^R = \sum_i (2J+1) e^{-\frac{J(J+1)h^2}{8\pi^2 I kT}} = \sum_i (2J+1) e^{-\beta hcBJ(J+1)}$ $\boxed{\text{High Temp } \langle \epsilon^R \rangle = kT}$

Vibrational Component: $q^V = \frac{1}{1-e^{-\beta hc\tilde{\nu}}}$ $\boxed{\text{High Temp } \langle \epsilon^V \rangle = kT}$

i) $q_{TOT} = \sum_i g_i \exp(\epsilon_i/kT) = q_{vib} \cdot q_{rot}$; $Q = q^N/N!$; $A = -kT\ln Q$. $S = P = \left(\frac{\partial F}{\partial V}\right)_T$

$q_{TOT} = q_{vib} \cdot q_{rot} = \sum_i 1 \exp(-\epsilon_{vib}/k_B T_V) \cdot \sum_i (2J+1)\exp(-\epsilon_{rot}/k_B T_r)$; $Q = q_{TOT}^N / N!$

$A = -kT\ln Q$; $P = -\left(\frac{\partial A}{\partial V}\right)_{T_Q}$; $A = -\int P\,dV = \int \frac{nRT}{V}dV = nRT\ln[V_f/V_i]$

$\cancel{-nRT_Q\ln\left[V_f/V_i\right]} = -k_B T_Q \ln Q$

Thermal ~~de Broglie~~ Wavelength:

[Translational]

$q^T = \frac{V}{\Lambda^3}$; $\Lambda = \frac{h}{\sqrt{2\pi m k T}}$

a) $\frac{n}{n_Q}$ @ $n_Q = n$; $P(\text{Boltzmann Distribution}) = \frac{e^{-\epsilon_0/k_B T}}{\sum e^{-\epsilon_0/k_B T}}$;

$1 = \frac{e^{-\epsilon_0/k_B T_Q}}{(1+3e^{-2}+5e^{-6}+\frac{1}{6 \cdot k(1/2)})}$

$\frac{1}{T_Q} = \frac{k_B}{-\epsilon_0}\ln(1+3e^{-2}+5e^{-6}+2)$

$= -1.381\times10^{-23}\,J/K[-1.2291/\epsilon_0]$

$= 1.69\times10^{-24}\,\frac{J}{K}\left(\frac{1}{\epsilon_0}\right)$

$T_Q = 5.91\times10^{23}\,\frac{K}{J}\cdot\epsilon_i$ Assuming 3.2eV ground state:

$= 5.91\times10^{23}\,\frac{K}{J} \cdot 5.127\times10^{-19}\,J = \boxed{302{,}592\,K}$

[Rotational]

$q^R = (2J+1)e^{-k_B T_R J(J+1)/k_B T_R}$

$= 1+3e^{-2}+5e^{-6}$

[Vibrational]

$q^V = \frac{1}{1-e^{k_B T_V(n+1/2)/k_B T}}$; Binomial: $(1+X) = 1-(1-X+\cdots)$

$= \frac{1}{+k_B T_V(n+1/2)/k_B T} = \frac{1}{T_V(n+1/2)}$

b) $C_V = \left(\frac{dU}{dt}\right)_V = \frac{d(N_A\langle\epsilon_V\rangle)}{dT} = \frac{d}{dt}N_A\left(\frac{hc\nu}{e^{\beta hc\nu}-1}\right) = \frac{d}{dt}N_A\left(\frac{k\Theta^V}{e^{\Theta^V/T}-1}\right)$; where Θ_V = characteristic vibrational temp.

$= R\Theta^V\frac{d}{dt}\frac{1}{e^{\Theta^V/T}-1} = R\left(\frac{\Theta^V}{T}\right)^2\frac{e^{\Theta^V/T}}{(e^{\Theta^V/T}-1)^2}$; $C_V = \left(\frac{\Theta^V}{T}\right)^2\left[\frac{e^{-\Theta^V/2T}}{1-e^{-\Theta^V/T}}\right]^2$

$= \left(\frac{k_B T_V(n+1/2)}{T_V}\right)^2\left[\frac{e^{-k_B T_V(n+1/2)/2T}}{1-e^{-k_B T(n+1/2)/T}}\right]^2$

$$=\left[1.381\times10^{-23}\,J/K\left(\tfrac{1}{2}\right)\right]^2\left[\frac{e^{-1.381\times10^{-23}J/K\cdot(1/2)/2(50K)}}{1-e^{-1.381\times10^{-23}J/K\,(1/2)/50K}}\right]^2=\boxed{6.57\times10^{-46}\,J/K^2}$$

50
1000
5000

c) @ 4,000K $=\left[1.381\times10^{-23}\frac{J}{K}\left(\frac{1}{2}\right)\right]\left[\frac{e^{-1.381\times10^{-23}J/K\,(1/2)/2\cdot4000K}}{1-e^{-1.381\times10^{-23}J/K\,(1/2)/4,000K}}\right]^2\approx\left[1.381\times10^{-23}\ldots\right]$

5
binomial - absorb
heat

d) 0.

Problem 2: Using the expansion: $f_{\frac{3}{2}}(z)=\frac{4}{3\sqrt{\pi}}\left((\log z)^{\frac{3}{2}}+\frac{\pi^2}{8}(\log z)^{-1/2}+\frac{7\pi^4}{640}(\log z)^{-5/2}\cdots\right)$

For large values of z, calculate the low temperature behavior of $\mu(T), U(T)$, $S(T)$, $P(T)$

$E_F=\mu(T=0)$: $f_{\frac{3}{2}}(z)=\frac{4}{3\sqrt{\pi}}(\beta\mu)^{3/2}$; $(\beta\mu)^{3/2}=\left[(\log z)^{3/2}+\frac{\pi^2}{8}(\log z)^{-1/2}+\frac{7\pi^4}{640}(\log z)^{-5/2}\right]$

$$\mu=\frac{1}{\beta}\left[(\log z)^{3/2}+\frac{\pi^2}{8}(\log)^{-1/2}+\frac{7\pi^4}{640}(\log z)^{-5/2}\right]^{2/3}$$

$$F(T,N,V)=\int_0^N\mu(T,V,N')dN'=\int_0^N\frac{1}{\beta}\left[\log z^{3/2}+\frac{\pi^2}{8}(\log z)^{-1/2}+\frac{7\pi^4}{640}(\log z)^{-5/2}\right]^{2/3}=\boxed{\frac{3}{5}\frac{N}{\beta}\left[\log z^{3/2}+\frac{\pi^2}{8}\log z^{-1/2}+\frac{7\pi^4}{640}\log z^{-5/2}\right]^{2/3}}$$

$$S(T,N,V)=-\left(\frac{\partial F}{\partial T}\right)=\boxed{+\frac{3}{5}k_B\left[\log z^{3/2}+\frac{\pi^2}{8}\log z^{-1/2}+\frac{7\pi^4}{640}\log z^{-5/2}\right]^{2/3}}$$

$$U(T,N,V)=F+TS=\boxed{\frac{3}{5}k_BT(N+1)\left[\log z^{3/2}+\frac{\pi^2}{8}\log z^{-1/2}+\frac{7\pi^4}{640}\log z^{-5/2}\right]^{2/3}}$$

$$p(T,V,N)=-\left(\frac{\partial F}{\partial V}\right)_{T,N}=\frac{2\cdot3}{5\cdot3}N\cdot k_BT\left[\log z^{3/2}+\frac{\pi^2}{8}\log z^{-1/2}+\frac{7\pi^4}{640}\log z^{-5/2}\right]^{2/3}$$

Problem 3: At large temperatures $\lambda\to0$ for fermions and bosons

Using formula for $\frac{N}{V}$; $\Omega(T,\mu,V)=-(2S+1)Vk_BTn_Q(T)\lambda$ s $\Omega(T,\mu,V)=-Nk_BT$

$P=-\Omega/V$
$=\frac{Nk_BT}{V}$

Expand $f_{3/2}=\frac{4}{3\sqrt{\pi}}\nu^{3/2}\sum\nu^{-n}\binom{3/2}{n}\int_{-\infty}^{\infty}v^n\frac{e^v\,dv}{(e^v+1)^2}+O(\lambda^{-1})$; $v=\nu y$

$$=\frac{4}{3\sqrt{\pi}}\left(\frac{\mu}{k_BT}\right)^{3/2}\left[1+\left(\frac{\mu}{k_BT}\right)^{-2}\frac{3}{2!\sqrt{\pi}}\frac{\pi^2}{3}\right)\text{@ High Temp}=\frac{4}{3\sqrt{\pi}}\left(\frac{\mu}{k_BT}\right)^{3/2}\left(1+\left(\frac{\mu}{k_BT}\right)^{-2}\frac{\pi^2}{8}\right)$$

A) Find the correction term to $\mu(T)$ $-1/2$

$$\Omega(T,\mu,V)=-(2S+1)Vk_BTn_Q(T)\lambda\;;\;N=(2S+1)n_Q(T)\left[\frac{4}{3\sqrt{\pi}}\left(\frac{\mu}{k_BT}\right)^{3/2}\left(1+\left(\frac{\mu}{k_BT}\right)^{-2}\frac{\pi^2}{8}\right)\right]$$

2^{nd} term of $\mu(t)$ $=\frac{4}{3\sqrt{2}}\left(\frac{\mu}{k_BT}\right)^{-1/2}\frac{\pi^2}{8}$

$$g_{\frac{3}{2}}=\frac{4}{\sqrt{\pi}}\sum_{n=1}^{\infty}\frac{1}{n^{3/2}}\lambda^{n-1}\int_0^{\infty}y^2dy\,e^{-y^2}=\sum_{n=1}^{\infty}\frac{1}{n^{3/2}}\lambda^{n-1}$$
$$=1+\boxed{\frac{\lambda}{\sqrt{8}}}+\frac{\lambda^2}{\sqrt{27}}+\cdots$$

b) $P = -\frac{N k_B T}{V}$; $f_{3/2}$: $\Omega(T,\mu,V) = -(2s+1) V k_B T n_Q(T) \lambda \frac{4}{\sqrt{\pi}} \ldots$; $p = \frac{-\Omega}{V} = \boxed{\frac{N k_B T}{V} \frac{8}{\pi^2}}$

$g_{3/2}$: $\Omega(T,\mu,V) = -(2s+1) V k_B T n_Q(T) \lambda = -N k_B T \sqrt{B}$; $p = \frac{-\Omega}{V} = \boxed{\frac{N k_B T \sqrt{B}}{V}}$

4. Pauli Paramagnetism: $\epsilon_{\vec{p},s} = \frac{p^2}{2m} - s\mu_0 B$, where $s = \pm 1$, and μ_0 is magnetic moment.

Assume $\mu_0 B \ll \epsilon_F$. Evaluate the magnetic susceptibility.

~~@ T=0:~~ $N = V h^{-3} \sum_s \int d^3p \, f_{FD}(\epsilon_{\vec{p},s})$; $M = V h^{-3} \mu_0 \sum_s \int d^3p \, s f_{FD}(\epsilon_{\vec{p},s})$ $\qquad I(T,\mu) = V h^{-3} \int d^3p \, f_{FD}\left(\frac{p^2}{2m}, T, \mu\right)$

$= I(T, \mu + \mu_0 B) + I(T, \mu - \mu_0 B)$ $\qquad = \mu_0 \left(I(T, \mu+\mu_0 B) - I(T, \mu - \mu_0 B) \right)$ $\qquad \mu - \epsilon = \mu - \frac{p^2}{2m} + s\mu_0 B$

$\downarrow B \ll 1$ $\qquad \downarrow B \ll 1$

$= 2 I(T,\mu)$ $\qquad = 2\mu_0^2 B \left(\frac{\partial I}{\partial \mu}\right)_T (T,\mu)$

$\chi = 2\mu_0^2 \left(\frac{\partial I}{\partial \mu}\right)(T,\mu)$ $\qquad$ @ T=0: $I(T=0, \epsilon_F) = V h^{-3} \frac{4\pi}{3} p_F^3 = V h^{-3} \frac{4\pi}{3} (2m\epsilon_F)^{3/2}$; $\epsilon_F = \frac{p_F^2}{2m}$

$= N\mu_0^2 \left(\frac{\partial \log I}{\partial \mu}\right)(T,\mu)$ $\qquad \chi(T=0) = N\mu_0^2 \frac{3}{2} \frac{1}{\epsilon_F}$; $\mu = \epsilon_F - \frac{\pi^2}{12} \frac{k_B^2 T^2}{\epsilon_F}$;

$N = 2I\left(T, \epsilon_F - \frac{\pi^2}{12} \frac{k_B^2 T^2}{\epsilon_F}\right)$

$N = V h^{-3} \sum_s \int d^3p \, e^{\frac{1}{k_B T}\left(\mu - \frac{p^2}{2m} + s\mu_0 B\right)}$

$I\left(T, \epsilon_F - \frac{\pi^2}{12}\frac{k_B^2 T^2}{\epsilon_F}\right) = I(T=0, \epsilon_F) = V h^{-3} \frac{4\pi}{3} (2m\epsilon_F)^{3/2}$

$M = V h^{-3} \mu_0 \sum_s \int d^3p \, s \, e^{\frac{1}{k_B T}\left(\mu - \frac{p^2}{2m} + s\mu_0 B\right)}$

$\left(\frac{\partial I}{\partial \mu}\right)_T \left(T, \epsilon_F - \frac{\pi^2}{12}\frac{k_B^2 T^2}{\epsilon_F}\right)\left(1 + \frac{\pi^2}{12}\frac{k_B^2 T^2}{\epsilon_F^2}\right) = V h^{-3} \frac{4\pi}{3} (2m\epsilon_F)^{3/2} \frac{3}{2} \frac{1}{\epsilon_F}$

$\frac{M}{N} = \mu_0 \frac{\sinh\left(\frac{\mu_0 B}{k_B T}\right)}{\cosh\left(\frac{\mu_0 B}{k_B T}\right)}$ $\qquad$ As $T \to \infty$ the ratio becomes zero.

$\chi(T)\left(1 + \frac{\pi^2}{12}\frac{k_B^2 T^2}{\epsilon_F^2}\right) = \chi(T=0)$

$\chi(T) = \chi(T=0)\left(1 - \frac{\pi^2}{12}\frac{k_B^2 T^2}{\epsilon_F^2}\right)$

$\frac{M}{N} = \mu_0 \frac{\mu_0 B}{k_B T}$; $\chi = \frac{N\mu_0^2}{k_B T}$

Problem 5: Virial Expansion: $\frac{P}{k_B T} = \sum_{j=1}^{\infty} B_j(T) \left(\frac{N}{V}\right)^j$ with $B_1(T) = 1$; Find $B_2(T)$.

Using $\Omega = -2V k_B T \lambda_T^{-3} f_{\frac{5}{2}}(\lambda)$; $N = 2V\lambda_T^{-3} f_{\frac{3}{2}}(\lambda)$; Small Density $f_{\frac{5}{2}}(\lambda) = (\lambda - \lambda^2 2^{-5/2})$,

$= -2V k_B T \lambda_T^{-3}(\lambda - \lambda^2 2^{-5/2})$; $N = 2V\lambda_T^{-3}(\lambda - \lambda^2 2^{-3/2})$ $\qquad f_{\frac{3}{2}}(\lambda) = (\lambda - \lambda^2 2^{-3/2})$

$p = \frac{-\Omega}{V} \approx 2k_B T \lambda_T^{-3}(\lambda - \lambda^2 2^{-5/2})$; $n \approx 2\lambda_T^{-3}\lambda(1 - \lambda 2^{-3/2})$

$= 2k_B T \lambda_T^{-3} \lambda (1 - \lambda 2^{-5/2})$ $\qquad$; $n(1 + \lambda 2^{-3/2}) \approx 2\lambda_T^{-3}\lambda$; $n(1 + n\lambda_T^3 2^{-5/2}) \approx 2\lambda_T^{-3}\lambda$

$\approx 2k_B T \lambda_T^{-3} n \frac{1}{2}\lambda_T^3 (1 + n\lambda_T^3 2^{-5/2})(1 - n\frac{1}{2}\lambda_T^3 2^{-5/2})$ $\qquad \lambda \approx n\frac{1}{2}\lambda_T^3(1 + n\lambda_T^3 2^{-5/2})$

$\approx k_B T n \underbrace{(1 + n\lambda_T^3 2^{-5/2} - n\frac{1}{2}\lambda_T^3 2^{-5/2})}$

$\boxed{B_2(T) = \lambda_T^3 2^{-7/2}}$

Problem 6: Relativistic energy of electrons: $\epsilon_{\vec{p},s} = \sqrt{p^2c^2 + m^2c^4}$; Length: L ; Volume: V

1) $\epsilon_F = \mu(T=0)$ $\boxed{\text{Fermi Energy}}$ as a function of N and V. ; $N = \sum f_{FD}(\epsilon_0; T, \mu)$

$$N = \frac{2V}{(2\pi)^3}\int d^3k\, f_{FD}\left(\sqrt{\hbar^2c^2k^2 + m^2c^4}; T, \mu\right) = \frac{2V}{(2\pi)^3}\int d^3k \frac{1}{e^{\beta(\sqrt{\hbar^2c^2k^2+m^2c^4}-\mu)}+1} \text{ ; where } \beta = \frac{1}{k_BT}$$

$T=0$; $N = \frac{2V}{(2\pi)^3}\int_{k<k_F} d^3k$ and $\boxed{\epsilon_F = \sqrt{\hbar^2c^2k_F^2 + m^2c^4}}$; $N = \frac{2V}{(2\pi)^3}\frac{4\pi}{3}k_F^3$ or $k_F = \left(3\pi^2\frac{N}{V}\right)^{1/3}$

$$U(T=0) = \frac{2V}{(2\pi)^3}\int_{k<k_F} d^3k \sqrt{\hbar^2c^2k^2 + m^2c^4} \text{ ; } \sqrt{\hbar^2c^2k^2+m^2c^4} = mc^2\sqrt{\frac{\hbar^2}{m^2c^2}k^2 + 1} \approx mc^2 + \frac{\hbar^2k^2}{2m}$$

2) Calculate the internal energy U : $\boxed{U = Nmc^2 + \frac{3}{5}N\frac{\hbar^2k_F^2}{2m}}$

3) For low densities, $\frac{N}{V} \ll 1$; $\sqrt{\hbar^2c^2k^2 + m^2c^4} = mc^2\sqrt{\frac{\hbar^2}{m^2c^2}k^2 + 1} \approx mc^2 + \frac{\hbar^2k^2}{2m}$; $\boxed{U = Nmc^2 + \frac{3}{5}N\frac{\hbar^2k_F^2}{2m}}$

4) For large densities, $\frac{N}{V} \ll 1$; $\sqrt{\hbar^2c^2k^2 + m^2c^4} \approx \hbar ck$; $U \approx \frac{V\hbar c}{\pi^2}\int_0^{k_F} k^3dk = \frac{V\hbar c}{\pi^2}\frac{1}{4}k_F^4 = \boxed{\frac{3}{4}N\hbar ck_F}$; $\boxed{U = \frac{3}{4}N\epsilon_F}$

Problem 7: Landau Diamagnetism: Orbits of electrons in a magnetic field are quantized. The energy levels are defined by:

a) Grand Partition Function $\mathcal{G}(T, \mu, V)$ $\qquad \epsilon(p_z, j, \kappa, s) = \frac{p_z^2}{2m} + \frac{e\hbar B}{mc}\left(j + \frac{1}{2}\right)$

$$G(T, \mu, V, B) = \Omega - MB = -k_BT\sum \log\left(1 + \lambda e^{\sum\sum -\epsilon_0/(k_BT)}\right)$$

$$= -k_BT\sum \log\left(1 + \lambda e^{-\frac{1}{k_BT}\left(\frac{p_z^2}{2m} + \frac{e\hbar B}{mc}(j+\frac{1}{2})\right)}\right) \qquad p_z = \frac{2\pi}{L}\hbar\ell,\ \ell = 0, \pm1, \pm2$$

$j = 0, 1, \ldots$

$$= -k_BT\cdot 2\frac{eBL^2}{2\pi\hbar c}\frac{L}{2\pi\hbar}\int_{-\infty}^{\infty}dp\sum \log\left(1 + \lambda e^{-\frac{1}{k_BT}\left(\frac{p^2}{2m} + \frac{e\hbar B}{mc}(j+\frac{1}{2})\right)}\right) \qquad \text{Degeneracy } [\kappa] = g = \frac{eBL^2}{2\pi\hbar c}$$

$$= -k_BTV\frac{eB}{2\pi^2\hbar^2c}\int_{-\infty}^{\infty}dp\sum \log\left(1 + \lambda e^{-\frac{1}{k_BT}\left(\frac{p^2}{2m} + \frac{e\hbar B}{mc}(j+\frac{1}{2})\right)}\right)$$

$$N = -\left(\frac{\partial G}{\partial \mu}\right) \text{ ; } N = V\frac{eB}{2\pi^2\hbar^2c}\int_{-\infty}^{\infty}dp\sum_j \frac{1}{\lambda^{-1}e^{\frac{1}{k_BT}\left(\frac{p^2}{2m} + \frac{e\hbar B}{mc}(j+1/2)\right)} + 1} \approx \lambda V\frac{eB}{2\pi^2\hbar^2c}\int_{-\infty}^{\infty}dp\sum e^{-\frac{1}{k_BT}\left(\frac{p^2}{2m} + \frac{e\hbar B}{mc}(j+1/2)\right)}$$

$$G = -k_BTV\frac{eB}{2\pi^2\hbar^2c}\int_{-\infty}^{\infty}dp\sum \lambda e^{-1/k_BT\left(\frac{p^2}{2m} + \frac{e\hbar B}{mc}(j+1/2)\right)} \qquad \approx \lambda V\frac{eB}{2\pi^2\hbar^2c}e^{-\frac{e\hbar B}{2mck_BT}}\sqrt{2mk_BT}\int_{-\infty}^{\infty}dx\, e^{-x^2}\frac{1}{1-e^{-e\hbar B/mck_BT}}$$

For small values of B; $N \approx \lambda V\frac{eB}{2\pi^2\hbar^2c}e^{-\frac{e\hbar B}{2mck_BT}}\sqrt{2\pi k_BT}\frac{1}{1-e^{-e\hbar B/mck_BT}}$

$$\frac{e^{-x}}{1-e^{-2x}} \approx \frac{1-x}{2x - 2x^2 + \frac{4}{3}x^3} = \frac{1}{2x}\frac{1-x}{1-x+\frac{2}{3}x^2} \approx \frac{1}{2x}(1-x)\left(1 + x + \frac{1}{3}x^2\right) \approx \frac{1}{2x}\left(1 - \frac{1}{6}(2x)^2\right)$$

$$N \approx \lambda V\frac{mk_BT}{2\pi^2\hbar^3}\sqrt{2\pi mk_BT}\left(1 - \frac{1}{6}\left(\frac{e\hbar B}{mck_BT}\right)^2\right) \text{ ; } M = k_BT\lambda V\frac{mk_BT}{2\pi^2\hbar^3}\sqrt{2\pi mk_BT}\frac{B}{3}\left(\frac{e\hbar}{mck_BT}\right)^2$$

$$\chi = k_BT\lambda V\frac{mk_BT}{2\pi^2\hbar^3}\sqrt{2\pi mk_BT}\left(\frac{1}{3}\right)\left(\frac{e\hbar}{mck_BT}\right)^2 \text{ ; } = N \text{ @ } T=0$$

$$\chi = k_BTN\left(\frac{1}{3}\right)\left(\frac{e\hbar}{mck_BT}\right)^2 = \frac{N}{3k_BT}\left(\frac{e\hbar}{mc}\right)^2$$

Chapter 6: Density Matrix Formalisms

6.1: Density Operators. $\quad H|n\rangle = E_n|n\rangle$; $\langle n'|n\rangle = \delta_{n'n}$; $\sum_n |n\rangle\langle n| = 1$

"Eigenvalue System" "Normalization" "closure"

Arbitrary operator $\langle A\rangle = \sum p_n \langle n|A|n\rangle$; operator $\underbrace{\rho = \sum_n p_n |n\rangle\langle n|}_{\text{"Density Operator"}}$ ← Density Matrix

Density matrix obeys the following relationship:

$$\mathrm{Tr}\,\rho = \sum \langle n|\rho|n\rangle = \sum p_n = 1 \;;\; \rho = \rho^{\dagger} = (\rho^{*})^{T} \;;\; \rho^2 \le \rho$$

"Trace, or diagonal is $\langle n'|n\rangle = \delta_{n'n}$" "A symmetric matrix" "The square amplitudes are less than the amplitudes"

$\langle A\rangle = \sum \langle n|\rho_n A|n\rangle = \mathrm{Tr}(\rho A)$; Boltzmann Factor: $p_n = \frac{1}{Z} e^{-E_n/k_BT}$; where $Z = \sum e^{-E_n/k_BT} = \sum \langle n| e^{-E_n/k_BT} |n\rangle$

$= \sum \langle n| e^{-H/k_BT} |n\rangle = \mathrm{Tr}(e^{-\beta H})$

$$= \mathrm{Tr}(\rho A) = \frac{\mathrm{Tr}(e^{-\beta H}A)}{\mathrm{Tr}(e^{-\beta H})}$$

$\langle n|\rho^2|n\rangle \le \langle n|\rho|n\rangle = r_n^2 \le r_n$

Therefore, $0 \le r_n \le 1$.

$$\rho = \frac{1}{Z}\sum e^{-\beta E_n} |n\rangle\langle n| = \frac{1}{Z} e^{-\beta H}$$

$$e^{0} = \sum_{n=0}^{\infty} \frac{1}{n!} 0^n$$

$$\langle x|\rho^2|x\rangle = \sum \langle x|\rho|n\rangle\langle n|\rho|x\rangle = \sum \langle x|r_n|n\rangle\langle n|r_n|x\rangle = \sum r_n^2 |\langle n|x\rangle|^2$$

$$\langle x|\rho|x\rangle = \sum \langle x|\rho|n\rangle\langle n|x\rangle = \sum \langle x|r_n|n\rangle\langle n|x\rangle = \sum r_n |\langle n|x\rangle|^2$$

$$\sum r_n^2 |\langle n|x\rangle|^2 \le \sum r_n |\langle n|x\rangle|^2$$

General Ensembles: Grand Partition Function $\mathcal{Z} = \sum e^{-\beta(E_n - \mu N_n)}$

$= \mathrm{Tr}\, e^{-\beta(\mathbb{H} - \mu N)} = e^{-\beta\Omega}$ $\boxed{\text{Fock-Space}}$

$Z(T,V,N) = \mathrm{Tr}(e^{-\beta H})$

When considering every quantum state.

$\rho = \frac{1}{\mathcal{Z}} e^{-\beta(\mathbb{H} - \mu N)}$ $\boxed{\text{Fock-Space Density Matrix}}$

Grand Hamiltonian

$$\mathcal{Z}(T,\mu,N) = \sum_N \mathrm{Tr}\, e^{-\beta(H-\mu N)}$$

$$= \sum e^{\beta\mu N} \cdot \mathrm{Tr}\, e^{-\beta H} = \sum e^{\beta\mu N} Z(T,V,N)$$

$\langle x|\rho|x\rangle$

$\mathrm{Tr}\, e^{-\beta(\mathbb{H} + pV)} = e^{-\beta G}$; $G = U - TS + PV$

$Z(T,V,N,M) = \mathrm{Tr}\, e^{-\beta H}$

As a function of the magnetic field; $\tilde{Z}(T,V,N,h) = \mathrm{Tr}\, e^{-\beta(H - hM)} = \sum e^{\beta h M} Z(T,V,N,M)$

Maximum Entropy Principle: $\underbrace{S = -k_B \mathrm{Tr}\, \rho \log(\rho)}_{\text{"Information-Theoretical Definition of Entropy"}} = -k_B \sum_n \langle n|\rho\log(\rho)|n\rangle = -k_B \sum p_n \log p_n$

- Free parameters are determined by maximizing entropy.

Microcanonical Ensemble: relates the internal energy, volume, and number of particles N.

How to find the maximum Entropy: $X(\rho) = -k_B \mathrm{Tr}\,\rho\log\rho + \lambda k_B(\mathrm{Tr}\,\rho - 1)$

over Hermitian operators. S, urn.

Over a small amount $\Delta X = X(\rho + \Delta\rho) - X(\rho)$

- Density Matrix $R_{ij} = \langle i|\rho|j\rangle$; By notation $\Delta R_{ij} = \langle i|\Delta\rho|j\rangle$

First order: $\Delta X = \sum A_{ji}\Delta R_{ij}$; Density Matrix of Entropy change: $\langle j|\frac{\partial X}{\partial \rho}|i\rangle = A_{ji}$

Therefore, $\Delta X = \sum \langle j|\frac{\partial X}{\partial\rho}|i\rangle\langle i|\Delta\rho|j\rangle = \mathrm{Tr}\left(\frac{\partial X}{\partial\rho}\Delta\rho\right)$.

Simple Partial Derivatives: $\Delta X = \left(\frac{\partial X}{\partial R}\right)\langle m|\Delta\rho|n\rangle$ "Entropy change per density operator" i.e which leads to $\langle n|\frac{\partial X}{\partial \rho}|m\rangle = \left(\frac{\partial X}{\partial R_{mn}}\right)$

such that $\Delta X = \left(\frac{\partial X}{\partial R_{mn}}\right)\langle m|\Delta\rho|n\rangle$.

In a particular case, $X = -k_B\sum\langle i|\rho|j\rangle\langle j|\log(\rho)|i\rangle + \lambda k_B\left(\sum\langle i|\rho|i\rangle - 1\right)$: $\rho \propto e^{-Ht}$, $\rho = \sum_{ij}\rho_i|\psi_i\rangle\langle\psi_j|$

Hence, $\left(\frac{\partial X}{\partial R_{nm}}\right) = -k_B\langle m|\log(\rho)|n\rangle + \lambda k_B\delta_{nm} - k_B\sum\langle i|\rho|j\rangle\left(\frac{\partial\langle j|\log(\rho)|i\rangle}{\partial R_{nm}}\right)$

How to calculate $Tr\,\rho\left(\frac{\partial\rho}{\partial X}\right)$; $\log(\rho) = \tau \Leftarrow e^{\tau} = \rho$; $\frac{\partial}{\partial X}e^{\tau(X)} = \frac{\partial}{\partial X}\sum\frac{1}{n!}\tau^n(X) = \sum\frac{1}{n!}\frac{\partial}{\partial X}\tau^n(X)$

$$Tr\left(\frac{\partial}{\partial X}e^{\tau(X)}\right) = \sum\frac{1}{n!}\sum Tr\left(\tau^{m-1}(X)\left(\frac{\partial\tau}{\partial X}\right)\tau^{n-m}(X)\right) = \sum_n\frac{1}{n!}\sum_1^n Tr\left(\tau^{n-1}(X)\left(\frac{\partial\tau}{\partial X}\right)\right)$$

$$= \sum\frac{1}{n!}n\,Tr\left(\tau^{n-1}(X)\left(\frac{\partial\tau}{\partial X}\right)\right) = Tr\left(\sum\frac{1}{(n-1)!}\tau^{n-1}(X)\left(\frac{\partial\tau}{\partial X}\right)\right) = Tr\left(e^{\tau(X)}\left(\frac{\partial\tau}{\partial X}\right)\right)$$

$$Tr\left(\frac{\partial\rho}{\partial X}\right) = Tr\left(\rho\left(\frac{\partial\log(\rho)}{\partial X}\right)\right) \Rightarrow Tr\left(\frac{\partial\rho}{\partial R_{nm}}\right) = \left(\frac{\partial Tr\rho}{\partial R_{nm}}\right) = \delta_{nm}$$; Partial Derivative:

$$\left(\frac{\partial X}{\partial R_{nm}}\right) = -k_B\langle m|\log(\rho)|n\rangle + (\lambda-1)k_B\delta_{nm}$$

The simple solutions: $\rho = e^{\lambda-1}\mathbb{E}$; $Tr\rho = 1$; $e^{1-\lambda} = Tr\,\mathbb{E}$

When using the multiplicity function: $e^{1-\lambda} = G(U,V,N)$

$S = -k_B Tr\,e^{\lambda-1}(\lambda-1)\mathbb{E} = -k_B g^{-1}(U,V,N)\log(g^{-1}(U,V,N))Tr\,\mathbb{E}$; Also, known as $S = k_B\log(g(U,V,N))$

The extremum of X has been found as a maximum. $\left(\frac{\partial^2 X}{\partial\rho\partial\rho}\right) = -k_B\frac{\partial}{\partial\rho_{ij}}(\log\rho)_{nm}$.

$$\frac{\partial}{\partial X}e^{\tau(X)} = \sum_1^{\infty}\frac{1}{n!}\sum_0^{n-1}\tau^m(X)\left(\frac{\partial\tau}{\partial X}\right)\tau^{n-m-1} = \sum_1\frac{1}{n!}\sum_0^{n-1}(\lambda-1)^m(X)\left(\frac{\partial\tau}{\partial X}\right)(\lambda-1)^{n-m-1}(X)$$

$$= \sum\frac{1}{(n-1)!}(\lambda-1)^{n-1}\left(\frac{\partial\tau}{\partial X}\right) = e^{\lambda-1}\left(\frac{\partial\tau}{\partial X}\right)$$ or $\left(\frac{\partial\rho}{\partial X}\right) = \rho\left(\frac{\partial\log(\rho)}{\partial X}\right)$; using $X = \rho_{ij}$ at the extremum.

$\left(\frac{\partial\rho_{nm}}{\partial\rho_{ij}}\right) = \rho\left(\frac{\partial\log(\rho_{nm})}{\partial\rho_{ij}}\right)$, Therefore, entropy at extremum $\left(\frac{\partial^2 X}{\partial\rho_{ij}\partial\rho_{nm}}\right) = -k_B e^{1-\lambda}\delta_{mi}\delta_{nj}$.

$$\Delta X = \sum_{ijmn}\left(\frac{\partial^2 X}{\partial\rho_{ij}\partial\rho_{nm}}\right)\Delta\rho_{ij}\Delta\rho_{nm} = -k_B e^{1-\lambda}\sum_{ijmn}\delta_{mi}\delta_{nj}\Delta\rho_{ij}\Delta\rho_{nm} = -k_B e^{1-\lambda}\sum_{ij}\Delta\rho_{ij}\Delta\rho_{ji}$$

$$= -k_B e^{1-\lambda}\sum_{ij}|\Delta\rho_{ij}|^2$$ || Where $1 = C\,Tr\,\delta(U-H)$

Discrete Eigenvalues: $\rho = C\delta(U-H)$; Mathematical Details about Delta Function Limits. $\rho = C\frac{1}{\epsilon\sqrt{\pi}}e^{-(U-H)^2/\epsilon^2}$

Entropy of Quantum Systems: $n = 1,2,3\ldots$; $E = \left(\sum_i^N n_i\right)\omega$;

$$S(U,N) = -k_B\sum_{n_1,n_2\ldots n_N}C\frac{1}{\epsilon\sqrt{\pi}}e^{-\frac{(U-(\sum n_i)\omega)^2}{\epsilon^2}}\log\left(C\frac{1}{\epsilon\sqrt{\pi}}e^{-\frac{(U-(\sum n_i)\omega)^2}{\epsilon^2}}\right) = -k_B\left(\frac{N\epsilon}{\omega}\right)^N\int\ldots\int dx_1\ldots dx_n$$

$$C\frac{1}{\epsilon\sqrt{\pi}}e^{-\left(\frac{U}{\epsilon}-Nx_1-\ldots-Nx_n\right)^2}\left[\log\left(C\frac{1}{\epsilon\sqrt{\pi}}\right)-\left(\frac{U}{\epsilon}-Nx_1-\ldots-Nx_n\right)^2\right]$$

$$= -k_B\left(\frac{\epsilon N}{\omega}\right)^N\int dx\,g(x)\,C\frac{1}{\epsilon\sqrt{\pi}}e^{-\left(\frac{U}{\epsilon}-Nx\right)^2}\left[\log\left(C\frac{1}{\epsilon\sqrt{\pi}}\right)-\left(\frac{U}{\epsilon}-Nx\right)^2\right]$$; $C^{-1} = Tr\frac{1}{\epsilon\sqrt{\pi}}e^{-(U-H)^2/\epsilon^2}$

$$= \left(\frac{N\epsilon}{\omega}\right)^N\int\ldots\int dx_1\ldots dx_n\frac{1}{\epsilon\sqrt{\pi}}e^{-\left(\frac{U}{\epsilon}-Nx_1\ldots-Nx_n\right)^2},$$

$$S(U,N) = -k_B\frac{\int dx\,g(x)e^{-\left(\frac{U}{\epsilon}-Nx\right)^2}\left[\log\left(C\frac{1}{\epsilon\sqrt{\pi}}\right)-\left(\frac{U}{\epsilon}-Nx\right)^2\right]}{\int dx\,g(x)e^{-\left(\frac{U}{\epsilon}-Nx\right)^2}}$$

Entropy per Particle: $s = \frac{S}{N}$.

$$S(u,N) = -k_B \frac{\int dx\, g(x) e^{-N^2(\frac{u}{\epsilon}-x)^2}\left[\frac{1}{N}\log\left(C\frac{1}{\epsilon\sqrt{\pi}}\right) - N\left(\frac{u}{\epsilon}-x\right)^2\right]}{\int dx\, g(x) e^{-N^2(\frac{u}{\epsilon}-x)^2}}$$

$$S_1(u,N) = -k_B \frac{1}{N}\log\left(C\frac{1}{\epsilon\sqrt{\pi}}\right)$$

$$S_2(u,N) = N k_B \frac{\int dx\, g(x) e^{-N^2(\frac{u}{\epsilon}-x)^2}\left[\left(\frac{u}{\epsilon}-x\right)^2\right]}{\int dx\, g(x) e^{-N^2(\frac{u}{\epsilon}-x)^2}} = \frac{1}{2}k_B \frac{\partial}{\partial N}\log\left(\int dx\, g(x) e^{-N^2(\frac{u}{\epsilon}-x)^2}\right)$$

When separating the numerator: $S(u,N) = S_1(u,N) + S_2(u,N)$;

.... For large values of N ... $S(u,N) = k_B \frac{1}{N}\log(w^{-N} e^{N} u^{N}) = k_B(\log(\frac{u}{w})+1)$

Equivalence of Entropy Definitions for Canonical Ensemble:

$X = -k_B \mathrm{Tr}\,\rho\log\rho + \lambda k_B(\mathrm{Tr}\rho - 1) - \beta k_B(\mathrm{Tr}\rho H - U)$ "Entropy with a lagrange multiplier"

Maximization of Entropy: $0 = \left(\frac{\partial X}{\partial \rho}\right) = k_B\lambda\delta_{nm} - k_B(\log\rho)_{mn} - k_B\delta_{nm} - \beta k_B H_{mn}$; $k_B(\log\rho)_{mn} = k_B(\lambda-1)\delta_{mn} - \beta k_B H_{mn}$.

$\mathrm{Tr}\rho\log\rho = (\lambda-1)\mathrm{Tr}\rho - \beta\mathrm{Tr}\rho H$. Density Matrix $S = -\underbrace{k_B(\lambda-1)}_{\log C} + \underbrace{k_B\beta U}_{\text{Partition Function}}$ and hence $\rho = e^{\lambda-1}e^{-\beta H} = Ce^{-\beta H}$

With helmholtz: $F(T) = -k_B T\log Z$; Therefore, $\lambda - 1 = \frac{F(T)}{k_B T}$ at Temperature $= \frac{1}{\beta k_B}$; $TS = -k_B T\frac{F(T)}{k_B T} + k_B T\beta U$

Maximized Expression of Entropy: $X = -k_B\mathrm{Tr}\rho\log\rho + \lambda k_B(\mathrm{Tr}\rho - 1) - \beta k_B(\mathrm{Tr}\rho\mathbb{H} - U) + \beta\mu k_B(\mathrm{Tr}\rho\mathbb{N} - N)$

$\rho = Ce^{-\beta(H-\mu N)}$ ← Grand N particles
Grand Hamiltonian

Problems of Chapter 6:

Problem #1: Prove $\rho = Ce^{-\beta(\mathbb{H}-\mu N)}$

Problem #2:
Show that the Solution $\rho = Ce^{-\beta H}$ to $X = -k_B\mathrm{Tr}\rho\log\rho + \lambda k_B(\mathrm{Tr}\rho - 1) - \beta k_B(\mathrm{Tr}\rho H - U)$

$$\frac{\partial X}{\partial\rho} = -k_B[\log\rho + 1] + \lambda k_B - \beta k_B(\mathbb{H}) + \beta\mu k_B(\mathbb{N} - N) = 0$$

$$-[\log\rho + 1] = -\lambda + \beta\mathbb{H} - \beta(\mathbb{N} - N) = -\lambda + \beta(\mathbb{H} - \mathbb{N} + N)$$

$$\rho = e^{-(\lambda-1) + \beta(\mathbb{H} - \mathbb{N} + N)} = \boxed{Ce^{-\beta(\mathbb{H}-\mu N)}}$$

$$\left(\frac{\partial X}{\partial\rho}\right) = 0 = k_B\lambda\delta_{nm} - k_B(\log\rho)_{mn} - k_B\delta_{nm} - \beta k_B H_{mn}$$

$$= k_B\lambda\delta_{mn} - k_B(\log C + \cancel{\beta H}) - k_B\delta_{nm} - \cancel{\beta k_B} H_{mn} = k_B\delta(\lambda-1) - k_B\log C = \delta\underbrace{(\lambda-1)}_{(\lambda-1) = \log C} - \log C = 0$$

Problem #3: Hamiltonian $H = \begin{pmatrix}\epsilon & \alpha^* \\ \alpha & 2\epsilon\end{pmatrix}$; Assume $\epsilon \gg |\alpha|$ and $\beta\epsilon \ll 1$

(A) Calculate the partition function up to second order in β. $Z = e^{-H/k_B T} = 1 - \frac{H}{k_B T} = 1 - \frac{\begin{pmatrix}\epsilon & \alpha^* \\ \alpha & 2\epsilon\end{pmatrix}}{k_B T} = 1 - \beta\begin{pmatrix}\epsilon & \alpha^* \\ \alpha & 2\epsilon\end{pmatrix}$

Possibly $Z = \mathrm{Tr}\, e^{-H/k_B T}$

$$\boxed{= 1 - \beta\mathrm{Tr}\begin{pmatrix}\epsilon & \alpha^* \\ \alpha & 2\epsilon\end{pmatrix}}$$

(B) $C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right) = T\frac{\partial}{\partial T}[-k_B\mathrm{Tr}\rho\log\rho] = T\frac{\partial}{\partial T}[-k_B[(\lambda-1)\mathrm{Tr}\rho - \beta\mathrm{Tr}\rho H]]$

$$= T\frac{\partial}{\partial T}\left[-k_B\left[\mathrm{Tr}e^{-\beta H}\rho - \beta\mathrm{Tr}\rho H\right]\right] = \cancel{k_B}T\frac{1}{k_B T^2}\mathrm{Tr}\begin{pmatrix}\epsilon & \alpha^* \\ \alpha & 2\epsilon\end{pmatrix} = \boxed{\frac{2\epsilon^2}{T}}$$

c) Suppose $\alpha = \frac{N}{V}$. Calculate pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\frac{\partial}{\partial V}\left[-k_B T\log\left(1 - \beta\begin{pmatrix}\epsilon & \alpha^* \\ \alpha & 2\epsilon\end{pmatrix}\right)\right]$$

$$= +\frac{2}{V}k_B T\frac{\beta/V}{1-\beta H}\left(\frac{N}{V}\right)^2 = k_B T\frac{2N^2}{1-\beta H}\frac{1}{V^3} = \boxed{\frac{2k_B TN^2}{V^3(1-\beta H)}}$$

Problem #4:
$H = H_0 + KV$ with $[H_0, V] = 0$. The helmholtz free energy $(F_K(T))$.
Calculate $\Delta F = F_K - F_0$ for the system up to second order $\frac{K}{k_B T}$

$F_K = -k_B T\log Z = -k_B T\log e^{-H_K/k_B T}$
$F_0 = -k_B T\log Z = -k_B T\log e^{-H_0/k_B T}$

$\Delta F = -k_B T[\log(1-\beta H_K) + \log(1-\beta H_0)]$
$= k_B T[\log(1-\beta H_0) - \log(1-\beta H_K)]$

My attempt

$Z = \mathrm{Tr}\, e^{-\beta H} = \mathrm{Tr}\, e^{-\beta H_0 - \beta K V} = \mathrm{Tr}\, e^{-\beta H_0} e^{-\beta K V} = \mathrm{Tr}\, e^{-\beta H_0}(1 - \beta K V + \frac{1}{2}\beta^2 K^2 V^2)$ · Using the thermodynamic average: $\langle x \rangle \mathrm{Tr}\, e^{-\beta H_0} = \mathrm{Tr}\, X e^{-\beta H_0}$

Using $\log Z = -\beta F_K = -\beta F_0 + \log(1 - \beta K \langle v \rangle + \frac{1}{2}\beta^2 K^2 \langle v^2 \rangle)$

and hence: $Z = \mathrm{Tr}\, e^{-\beta H_0}(1 - \beta K \langle V \rangle + \frac{1}{2}\beta^2 K^2 \langle V^2 \rangle)$

$= -\beta F_0 - \beta K \langle v \rangle + \frac{1}{2}\beta^2 K^2 \langle v^2 \rangle - \frac{1}{2}\beta^2 K^2 \langle v \rangle^2$

Problem 5: $F_K - F_0 = K\langle V \rangle - \frac{1}{2}\beta K^2 (\langle V^2 \rangle - \langle V \rangle^2)$

~~Two-dimensional Hilbert Space: Density operator~~ $\rho = \begin{pmatrix} X & R \\ R^* & 1-X \end{pmatrix}$; ~~$\mathrm{Tr}\,\rho = \sum \rho_{\alpha\alpha} = 1$~~

Calculate entropy as a function of X and R; Find X and R that maximize entropy.

$S = -k_B \mathrm{Tr}\,\rho \log \rho = -k_B (X + 1 - X) \log \begin{pmatrix} X & R \\ R^* & 1-X \end{pmatrix} = \boxed{-k_B \log \begin{pmatrix} X & R \\ R^* & 1-X \end{pmatrix}}$; $\frac{dS}{dX} = -k_B \left[\mathrm{Tr}\left(\frac{\partial \rho}{\partial X}\right) \log \rho + \mathrm{Tr}\left(\frac{\partial \rho}{\partial X}\right) \right] = 0$

Setting equal to zero: $0 = \mathrm{Tr}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \log \rho + \mathrm{Tr}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$; $0 = \mathrm{Tr}\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \log \rho + \mathrm{Tr}\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$; $0 = \mathrm{Tr}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \log \rho + \mathrm{Tr}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Problem 6:

or represented as $(\log \rho)_{21} = 0$; $(\log(\rho))_{12} = 0$; $((\log \rho)_{11} - \log \rho_{22}) = 0$

$H^2 = 1$.

$\log(\rho) = \begin{pmatrix} y & 0 \\ 0 & y \end{pmatrix}$; $\rho = \begin{pmatrix} z & 0 \\ 0 & z \end{pmatrix}$; $\rho = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$; $R = 0$; $X = 1/2$

Evaluating the partition function $Z = e^{-\beta H} = e^{-\beta}$; $U = T \cdot S = T[\mp k_B \mathrm{Tr}\,\rho \log \rho] = \boxed{\mp k_B T\, [1-\beta] \log(1-\beta)}$; $\lim_{T \to 0} U = 0$; $\lim_{T \to \infty} U = -\infty$

Problem 7: ρ = Density Operator; E is $[0,1]$; n = number of particles; V = volume of system ; $U = T[k_B \mathrm{Tr}\,\rho \log \rho]$

$\boxed{S = k_B \mathrm{Tr}\,\rho \log}$; $\rho = \prod_{i=1}^{N} \rho_i$ $= \emptyset$

Relation between quantum and classical mechanics:

$= \left(\frac{PV}{NK}\right)\left(\frac{K}{N_A}\right) \mathrm{Tr}\,\rho \log \rho$

$\boxed{N = \frac{PV}{U \cdot N_A} \mathrm{Tr}\,\rho \log_{\rho} \rho_m}$

Chapter 7: Classical Statistical Mechanics:

Choice of Basis: Could be r_i (position), and momenta (p_i)

Wigner Distribution Function: $W(\vec{k}, \vec{r}) = \int d^3x\, e^{i\vec{k}\vec{x}} \langle \vec{r} + \frac{1}{2}\vec{x} | \rho | \vec{r} - \frac{1}{2}\vec{x} \rangle$;

Fourier Transform — Describes the system

$\frac{1}{(2\pi)^3} \int d^3k\, W(\vec{k}, \vec{r}) = \langle \vec{r} | \rho | \vec{r} \rangle$ Position

and

$\frac{1}{(2\pi)^3} \int d^3r\, W(\vec{k}, \vec{r}) = \langle \vec{k} | \rho | \vec{k} \rangle$ Momentum

To arrive at:

$W(\vec{k}, \vec{r}) = \int d^3x\, e^{i\vec{k}\vec{x}} \frac{1}{(2\pi)^3} \int d^3k' \int d^3k''\, e^{i[\vec{k}''(\vec{r} - \frac{1}{2}\vec{x}) - \vec{k}'(\vec{r} + \frac{1}{2}\vec{x})]} \langle \vec{k}' | \rho | \vec{k}'' \rangle$

Remember, $|\vec{x}\rangle = (2\pi)^{-3/2} \int d^3k\, e^{i\vec{k}\vec{x}} |\vec{k}\rangle$

$= \int d^3k' \int d^3k''\, \delta(\vec{k} - \frac{1}{2}[\vec{k}' + \vec{k}''])\, e^{i[\vec{k}''\vec{r} - \vec{k}'\vec{r}]} \langle k' | \rho | \vec{k}'' \rangle$

Classical Density Matrix:

$\langle \vec{X} | \rho | \vec{X} \rangle = \rho(\vec{X}) = C e^{-\beta H(\vec{X})}$

Averages: $\langle O \rangle = \int d^3k \int d^3x\, \underbrace{O(\vec{k}, \vec{x})}_{\text{Classical Operator}} W(\vec{k}, \vec{x})$

Quantum mechanical average

Volume per State:

$\oint p\, dq = n h$ — Plancks constant; q: Generalized Coordinate; p: Generalized Momentum

Classical Integral:

Not-identical: $\sum_{\vec{x}_i} \Rightarrow \frac{1}{h^{3N}} \int d\vec{X}$

Identical: $\sum_{\vec{x}} \Rightarrow \frac{1}{N!\, h^{3N}} \int d\vec{X}$

Classical Partition Function:

$Z = \frac{1}{N!\, h^{3N}} \int d\vec{X}\, e^{-\beta H(X)}$

$\rho(\vec{X}) = \frac{1}{Z} e^{-\beta H(\vec{X})}$

Classical Formulation of Statistical Mechanics Properties:

Entropy: $S(T,V,N) = \frac{-k_B}{Z N!\, h^{3N}} \int d\vec{X}\, e^{-\beta H(X)} \log\left(\frac{1}{Z} e^{-\beta H(X)}\right)$

$= \frac{k_B}{Z N!\, h^{3N}} \int d\vec{X}\, e^{-\beta H(\vec{X})} (\log(Z) + \beta H(X)) = k_B \log Z + k_B \beta U$

Density of States: $\rho(\vec{X}) = C\delta(U - H(\vec{X}))$

$C^{-1} = D(U,V,N) = \frac{1}{N!\, h^{3N}} \int dX\, \delta(U - H(X))$

Micro canonical Ensemble: $Z = \frac{1}{N!h^{3N}}\int d\vec{X} e^{-\beta H(X)} = \frac{1}{N!h^{3N}}\int dX \int du\, \delta(u - H(X)) e^{-\beta u}$

Grand Partition function:

$\Xi(T,\mu,V) = \sum_N \frac{1}{N!h^{3N}}\int d\vec{X} e^{-\beta(H(X,N)-\mu N)}$

$= \sum_N e^{\frac{\mu N}{k_B T}} Z(T,N,V)$

Partition function $\overset{\text{Laplace}}{\underset{\text{Transform}}{\Longleftrightarrow}}$ Density of States

$Z(T,V,N) = \int du\, D(u,V,N) e^{-\beta u}$

$Z(T,V,N) = \int du\, D(u,V,N) e^{-\beta u}$ $\quad D(u,V,N) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} dt\, e^{st} Z(t,V,N)$

Hamilton's Equations:

Ergodic theorem: Connection with experiment: $\langle A \rangle = \frac{1}{N!h^{3N}}\int d\vec{x}\, \rho(\vec{x}) A(\vec{x})$ || $\left(\frac{\partial p_i}{\partial t}\right) = -\left(\frac{\partial H}{\partial x_i}\right)$; $\left(\frac{\partial x_i}{\partial t}\right) + \left(\frac{\partial H}{\partial p_i}\right)$

Equivalency of Averages: Time Evolution of classical system:

$\boxed{\text{Equations of Motion}}$ $\quad \left(\frac{\partial p_i}{\partial t}\right) = -\left(\frac{\partial H}{\partial x_i}\right)$; $\left(\frac{\partial x_i}{\partial t}\right) = \frac{\partial H}{\partial p_i}$ $\qquad \langle A \rangle_\tau(t) = \frac{1}{\tau}\int_t^{t+\tau} A(\vec{X}(t'))\,dt'$

Ergodic: time-average is equal to the ensemble average [ergodic] requires finite volume and energy.

Chaos: An orbit $\vec{X}(t)$ is chaotic if the change of initial conditions leads to a large change of the state of the system at a later time t.

What is chaos? one dimension is not enough! $H(X,p) = \frac{1}{2}(p^2 + x^2)$; $x(t) = x_0\cos(t) + p_0 \sin(t)$

$p(t) = -X_0 \sin(t) + p_0 \cos(t)$

Phase space is two dimensional, and the surface of states with energy U is a circle with radius $\sqrt{2U}$ $\boxed{\text{Small initial change - barely changes the outcome}}$

Two dimensions: Harmonic oscillator at two dimensions:

$H(x,y,p_x,p_y) = \frac{1}{2}(p_x^2 + p_y^2 + x^2 + y^2)$; Solutions: $x(t) = x_0\cos(t) + p_{x0}\sin(t)$; $y(t) = y_0\cos(t) + p_{y0}\sin(t)$

Poincare Surface: a variation of analysis of the Hamiltonian. $\quad p_x(t) = -X_0\sin(t) + p_{x0}\cos(t)$; $p_y(t) = -X_0 \sin(t) + p_{y0}\cos(t)$.

Additional considerations involve Henon-Heiles potential, constraints, and orders of the term.

Ideal Gas in Classical Statistical Mechanics: Classical Hamiltonian: $H = \sum_i^N \frac{p_i^2}{2m}$

Collisions are needed $S(U,V,N) = -k_B \frac{1}{N!h^{3N}}\int d\vec{x}\, C \frac{1}{\epsilon\sqrt{\pi}} e^{-\frac{(U-H)^2}{\epsilon^2}} \log\left(C \frac{1}{\epsilon\sqrt{2\pi}} e^{-(U-H)^2/\epsilon^2}\right)$

Density of States:

$$= -k_B \frac{1}{N!h^{3N}}\int d\vec{X}\, C \frac{1}{\epsilon\sqrt{\pi}} e^{-\frac{(U-H)^2}{\epsilon^2}}\left[\log C - \underbrace{\log(\epsilon\sqrt{\pi})}_{\substack{\text{entropy} \\ =0 \text{ at } T \text{ limit}}} - \underbrace{\frac{(U-H)^2}{\epsilon^2}}_{\text{small}}\right]$$

$U - H \ll \epsilon$

$$D(U,V,N) = C^{-1} = \frac{1}{N!h^{3N}\epsilon\sqrt{\pi}}\int d\vec{X}\, e^{-\frac{(U-H)^2}{\epsilon^2}} =$$

$$= \frac{1}{N!h^{3N}}\int dp_1^3 \cdots dp_N^3\, \delta\left(U - \sum_{i=1}^N \frac{p_i^2}{2m}\right)\int dr_1^3 \cdots dr_N^3$$

$$= \frac{V^N}{N!\,h^{3N}} \frac{2\pi^{3N/2}\left(\sqrt{2mU}\right)^{3N-1}}{\Gamma\left(\frac{3N}{2}\right)}$$

Therefore, $S(U,V,N) = k_B \log\left(\frac{V^N}{N!h^{3N}}\left(\sqrt{2\pi mU}\right)^{3N}\right) - \frac{3}{2}Nk_B\log\left(\frac{3}{2}N\right) + \frac{3}{2}k_B N =$

$$k_B N\log\left(\frac{V(2\pi mU)^{3/2}}{Nh^3}\right) + Nk_B - Nk_B\log\left(\left(3/2\,N\right)^{3/2}\right) + \frac{3}{2}Nk_B$$

$$= Nk_B\log\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}Nk_B$$

Normal Systems: $N \to \infty$; $\frac{U}{N} = u$; $\frac{V}{N} = v$; $\frac{S}{N} \to s$. $\boxed{\text{Normal}}$ Example: $V_{pot} = \int_{r,r'<R} d^3r\, d^3r' \frac{\mu^2}{|\vec{r}-\vec{r}'|}$

Quadratic Variables: $H(\vec{X}) = H' + \alpha c^2$; $Z = Z'\int_{-\infty}^{\infty} dc\, e^{\frac{-\alpha c^2}{k_B T}} = Z'\sqrt{\frac{\pi k_B T}{\alpha}}$

$U = -\frac{\partial}{\partial \beta}\log(Z) = U' + \frac{1}{2}k_B T$

Diatomic Gases: $U = \frac{3}{2}Nk_BT$ $\boxed{\text{Without Rotations}}$

$U = \frac{5}{2}Nk_BT$ $\boxed{\text{With rotations}}$

$\frac{7}{2}Nk_BT$ $\boxed{\text{With momentums}}$

Effects of the Potential Energy: $\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T}$; $pV = Nk_BT$; $H = \sum_i \frac{p_i^2}{2m} + U(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N)$

$U(\lambda\vec{r}_1 \ldots \lambda\vec{r}_N) = \lambda^{\gamma} U(\vec{r}_1 \ldots \vec{r}_N)$; $\gamma = -1$; $Z = \frac{1}{N!\,h^{3N}}\left(\int dp\, e^{-p^2/2mk_BT}\right)^{3N}\int\int d^3r_1 \ldots d^3r_N\, e^{-U(r_1 \ldots r_N)/k_BT}$

$\beta = \frac{1}{k_BT}$; $Z = \frac{1}{N!}\left(\frac{\sqrt{2mk_BT\pi}}{h}\right)^{3N}\int_V d^3r_1 \cdots \int_V d^3r_N\, e^{-U(\beta^{1/\gamma} r_1 \ldots \beta^{1/\gamma} r_N)}$

$= \frac{1}{N!}\left(\frac{\sqrt{2mk_B\pi T}}{h}\right)^{3N}\beta^{-3N/\gamma}\int \cdots \int d^3x_1 \cdots \int_{V\beta^{3/\gamma}} d^3x_N\, e^{-U(x_1 \ldots x_N)}$

Helmholtz Free Energy

$Z(T,V,N) = \frac{1}{N!}\left(\frac{\sqrt{2mk_B\pi}}{h}\right)^{3N} k_B^{3N/\gamma}\, T^{3N(\frac{1}{2}+1/\gamma)}\, g(N, VT^{-3/\gamma})$; $F = -k_BT\log Z$

$F(T,V,N) = k_BT\log(N!) - 3Nk_BT\log\left(\frac{\sqrt{2mk_B\pi}}{h}\right) - \frac{3Nk_BT}{\gamma}\log(k_B) - 3Nk_BT\left(\frac{1}{2}+\frac{1}{\gamma}\right)\log(T) - k_BT\log g(T,VT^{-3/\gamma})$

Pressure $= -\left(\frac{\partial F}{\partial V}\right)_{N,T}$; $pT^{-1+3/\gamma} = f(N, VT^{-3/\gamma})$; $\gamma = -1$ for coulomb interactions.

$p = T^4 f(N, VT^3)$; In general, $\frac{pV}{T} = vT^{-3/\gamma} f(N, VT^{-3/\gamma})$

$\vec{p}_i - \frac{e}{c}\vec{A}(\vec{r}_i) = $ Momenta; $\vec{A}$ is the potential: $\vec{B} = \vec{\nabla}\times\vec{A}$; $U - TS$

Problems of Chapter 7! 1) $\vec{B} =$ Magnetic Induction. $H(\vec{p}_1, \ldots, \vec{p}_N, \vec{r}_1, \ldots, \vec{r}_N)$

a) Calculate $G(T, \vec{B}, V, N) = U - TS - \vec{M}\cdot\vec{B} = \sum \frac{(p_i - \frac{e}{c}\vec{A}(r_i))^2}{|r_i|^2} + T\frac{\sum(p_i - \frac{e}{c}\vec{A}(r_i))^2}{T^2 |r_i|^2} - \vec{M}\cdot(\vec{\nabla}\times\vec{A})$

b) Prove van Leeuwen's Theorem:

$= T^{-1}\sum(p_i - \frac{e}{c}\vec{A}(r_i))^2 \frac{(T+1)}{T} - \vec{M}(\nabla\times\vec{A})$ $\int \frac{U}{T} dT$

Problem #2:

Rod-like molecules

$H(\vec{p}_i, \vec{r}_i, p_{\theta i}, \theta_i, \phi_i) = \sum_{i=1}^{N}\left(\frac{\vec{p}_i^2}{2m} + \frac{1}{2}I\left[\dot{\theta}_i^2 + \dot{\phi}_i^2\sin^2(\theta_i)\right] - dE\cos(\theta_i)\right)$, where $I =$ moment of inertia, $d =$ electric dipole moment.

A) Calculate the free energy $G(T, E, N, V) = U - TS - \vec{P}\cdot\vec{E}$

$= \frac{1}{2}I[\dot{\theta}_i^2 + \dot{\phi}_i^2\sin^2(\theta_i)] - dE\cos(\theta_i) + \frac{\frac{1}{2}I[\dot{\theta}_i^2 + \dot{\phi}_i^2\sin^2(\theta_i)] - dE\cos(\theta_i)}{T^2}$

B) Calculate the polarization:

$\vec{P}(T, E, N, V) = \prod_{i=0}^{n} e^{-H/k_BT} = \frac{1}{1 + H/k_BT}$ $\boxed{\text{Questionable}}$

Problem #3:

$H(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2) = \frac{1}{2m}(\vec{p}_1^2 + \vec{p}_2^2) + \frac{1}{2}m\omega^2(\vec{r}_1 - \vec{r}_2)^2$; $Z = e^{-H/k_BT} = e^{-\beta\left(\frac{1}{2m}(\vec{p}_1^2+\vec{p}_2^2) + \frac{1}{2}m\omega^2(\vec{r}_1-\vec{r}_2)^2\right)}$

$F = -k_BT\left[-\beta\left[\frac{1}{2m}(\vec{p}_1^2+\vec{p}_2^2) + \frac{1}{2}m\omega^2(r_1-r_2)^2\right]\right] = \frac{1}{2m}(\vec{p}_1^2+\vec{p}_2^2) + \frac{1}{2}m\omega^2(\vec{r}_1-\vec{r}_2)^2$

Problem #4: $r_n = na + x_n$, $n = 1 \ldots N$; $H(x_1, \ldots, x_n, p_1, \ldots, p_n) = \frac{1}{2m}\sum_{i=1}^{N} p_i^2 + \frac{K}{2}\sum_{i=1}^{N}(x_{i-1} - x_i)^2$; $U = -\frac{\partial}{\partial\beta}\log e^{-\beta H} = \boxed{H}$

Asymptotic Behavior $\frac{\partial U}{\partial T} = \boxed{0}$

Problem #5:

$L - x_N - x_1$; $PE = mgx_n$; $PE = nmgx_0$

$\beta_T = \frac{1}{V}\frac{\partial V}{\partial p}$; $\beta_0 = \frac{-1}{L}\frac{\partial L}{\partial p} = \frac{-1}{L}\frac{\partial}{\partial p}\left[\frac{a\,mg\,x_i}{a\cdot(n-1)a}\right] = \boxed{\frac{-1}{L}}$

Problem 6: $H(r_1,r_2,p_1,p_2)=\frac{1}{2m}(p_1^2+p_2^2)+\frac{K}{2}(|r_1-r_2|-d)^2$; $F=-k_BT\log Z=-k_BT[-\beta\cdot H]=H$

$V=-\hbar\frac{\partial}{\partial\beta}\log Z=H$.

Problem 7: Virial Equation: $V=\sum\vec{r}_i\frac{dp_i}{dt}$; Show $E(V(t))=-3Nk_BT$; $PV=nRT[1+B'P+C'P^2]$; $PV=\frac{3}{2}Nk_BT[1+B'P+C'P^2]$

Problem 8: $L(t)=\sum\vec{r}_i(t)\vec{p}_i(t)$; Prove independence of time. $F=\frac{\pi}{r}=\frac{P\pi}{rL}=\frac{p(t)\pi}{\sum r(t)p(t)}$. $PV=\frac{3}{2}Nk_BT[B'+2C'P']$

Chapter 8: Mean-Field Theory: Critical Temperature:

$=\pi/r$ $\quad B'=\frac{PV}{\frac{3}{2}Nk_BT}$

Introduction:

Basis for the Ising Model:

-Pressure $=\frac{F}{A}=\frac{\pi/r}{A}\Rightarrow$ Time Independent. $\quad C'=\frac{PV}{3Nk_BT}$

LoA description of a magnetic solid; Each atom i, with total angular momentum $\vec{S}_i$.

Reminder $S_i=L+s$; Simple model for Heisenberg's model: $H=-\sum_{i<j}\underbrace{J^H_{ij}\vec{S}_i\vec{S}_j}_{\text{"Exchange type"}}$; $\underbrace{\vec{S}=\sum_i\vec{S}_i}_{\text{"Total spin moment"}}$

Gibbs-Duhem Relationship: $V=TS+\mu N+\vec{H}\vec{M}$ "Magnetic Density"

Approximations, $H=-\sum J(|\vec{R}_i-\vec{R}_j|)\vec{S}_i\cdot\vec{S}_j$ where $S=|S_z^1S_z^2\dots S_z^N\rangle$

Eigenvalues of the Projection: $\vec{S}_i\cdot\vec{S}_j=\underbrace{S_i^+S_j^-+S_i^-S_j^+}_{\text{"Unknown"}}+S_{iz}S_{jz}$; Therefore $H=-\sum J(|R_i-R_j|)S_{iz}S_{jz}$

$S_i^{pr}=\frac{1}{2}\hbar\sigma_i$; where $\sigma_i=\pm1$

$$E(\sigma_1,\dots\sigma_n)=-\sum_{i<j}J(|R_i-R_j|)\frac{\hbar^2}{4}\sigma_i\sigma_j=-J\sum_{\langle ij\rangle}\sigma_i\sigma_j;\ \sum_{\langle ij\rangle}1=\frac{1}{2}Nq;\ q=\text{nearest neighbors.}$$

Including a magnetic field:

$$H_{int}(\vec{S}_i)=-\vec{H}\cdot\gamma_G\vec{S}_i;\ \vec{M}_i=\gamma_G\vec{S}_i;\ E_{int}=-\vec{H}\cdot\vec{M}=-h\sum_i\sigma_i;\ M\{\sigma_1,\dots,\sigma_N\}=\sum\sigma_i$$

Thermodynamic Limit: Basic Mean field Theory: $H=\sum_{\sigma_1\dots\sigma_N}|\sigma_1,\dots,\sigma_N\rangle E\{\sigma_1\dots\sigma_N\}\langle\sigma_1\dots\sigma_N|$

operator for magnetic moment: $M=\sum_{\sigma_1\dots\sigma_N}|\sigma_1\dots\sigma_N\rangle M\{\sigma_1\dots\sigma_N\}\langle\sigma_1\dots\sigma_N|$

Magnetic Gibbs Energy: $\quad$ Partition Function $\mathcal{Z}(T,h,N)=Tr\,e^{-\beta(H-hM)}$

$G(T,h,N)=U-TS-hM$

$$\mathcal{Z}(T,h,N)=\sum_{\sigma_1\dots\sigma_N}\langle\sigma_1\dots\sigma_N|e^{-\beta(H-hM)}|\sigma_1\dots\sigma_N\rangle=\sum_{\sigma_1\dots\sigma_N}e^{\beta(J\sum_{\langle ij\rangle}\sigma_i\sigma_j+h\sum_i\sigma_i)}$$

$G(T,h,N)=-k_BT\log(\mathcal{Z}(T,h,N))$ $\quad$ Spin-Variables σ_i: $S_{zi}|\sigma_1\dots\sigma_N\rangle=\sigma_i|\sigma_1\dots\sigma_N\rangle$

$H=-J\sum_{\langle ij\rangle}S_{iz}S_{jz}$; $m(T,h,N)=\frac{1}{N}\sum^N\langle S_i\rangle_{T,h}$ "Average spin" $\quad$ The spin operator arrives to the measurable spin.

Thermodynamic Average: $\langle S_i\rangle_{T,h}=\frac{1}{\mathcal{Z}(T,h,N)}Tr\,S_ie^{-\beta(H-hM)}$ "Expected Spin" on Ensemble

$$m(T,h,N)=\langle S_i\rangle;\ H=-J\sum_{\langle ij\rangle}(S_{iz}-m)(S_{jz}-m)-J\sum_{\langle ij\rangle}S_{iz}m-J\sum_{\langle ij\rangle}mS_{jz}+J\sum m^2$$

Rewritten as number of nearest neighbors q and total number of sights N.

$$H=-J\sum_{\langle ij\rangle}(S_{iz}-m)(S_{jz}-m)-Jm\frac{1}{2}q\sum S_{iz}-Jm\frac{1}{2}q\sum S_{jz}+Jm^2\frac{1}{2}Nq$$

Nearest Neighbors

After combining like terms:

$$H=-J\sum(S_{iz}-m)(S_{jz}-m)-Jmq\sum S_{iz}+Jm^2\frac{1}{2}Nq$$

Internal Energy: $U = \langle H \rangle = -J\sum_{\langle ij \rangle}\langle (S_{iz}-m)(S_{jz}-m)\rangle - Jmq\langle \sum S_{iz}\rangle + Jm^2 \frac{1}{2} Nq$

$$U = -J\sum \langle (S_{iz}-m)(S_{jz}-m)\rangle - Jm^2 \frac{1}{2} Nq$$

Assuming fluctuations on different sites are independent, they are uncorrelated. $\langle (S_{iz}-m)(S_{jz}-m)\rangle = \langle (S_{iz}-m)\rangle\langle (S_{jz}-m)\rangle = 0$

Meanfield Hamiltonian becomes $H^{mf} = -Jmq\sum S_{iz} + Jm^2 \frac{1}{2} Nq$

Linearized would be: $H^{lin} = -h_{eff}\sum S_i + H_0$; $\langle H^{lin}\rangle = -mqJ\langle \sum S_i\rangle + H_0$

Mean Field Results: $m(T,h) = \dfrac{Tr\, S_i e^{-\beta(H^{mf}-hM)}}{Z^{mf}(T,h,N)}$ $\langle H^{lin}\rangle = -m^2 qJN + H_0$

with $Z^{mf}(T,h,N) = Tr\, e^{-\beta(H^{mf}-hM)}$.

Calculating the partition function: $e^{\frac{1}{2}\beta NqJm^2} Z^{mf}(T,h,N) = \sum_{\sigma_1=\pm1}\cdots\sum_{\sigma_N=\pm1} e^{\beta(h+mqJ)\sum \sigma_i} = \sum_{\sigma_1=\pm1}\cdots\sum_{\sigma_N=\pm1}\prod e^{\beta(h+mqJ)\sigma} = \prod_i\left[\sum_{\sigma_i=\pm1} e^{\beta(h+mqJ)\sigma_i}\right]$

$= \left[\sum_{\sigma=\pm1} e^{\beta(h+mqJ)\sigma}\right]^N = 2^N\cosh^N(\beta(h+mqJ))$

Mean Field Includes magnetization

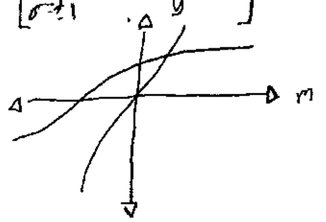
$e^{\frac{1}{2}\beta NqJm^2} Tr\, S_k e^{-\beta(H^{mf}-hm)} = \sum_{\sigma_1=\pm1}\cdots\sum_{\sigma_N=\pm1}\sigma_k e^{\beta(h+mqJ)\sum_i^N \sigma_i}$

$= \sum_{\sigma_1=\pm1}\cdots\sum_{\sigma_N=\pm1}\sigma_k\prod_i e^{\beta(h+mqJ)\sigma_i} = 2^N\cosh^{N-1}(\beta(h+mqJ))\sinh(\beta(h+mqJ))$

Average spin variable: $m = \tanh(\beta(mqJ+h)) = \tanh\left(\beta qJ\left(m+\frac{h}{qJ}\right)\right)$

$= \tanh(\beta^*(m+h^*))$

Spontaneous Magnetic Order:



With no external field: $m = \tanh(\beta^* m)$

$m \approx \beta^* m - \frac{1}{3}(\beta^* m)^3$; $m^2 \approx \dfrac{3(\beta^*-1)}{\beta^{*3}} \approx 3(\beta^*-1)$

$m \propto \sqrt{3(\beta^*-1)} = \sqrt{3\left(\frac{T_c}{T}-1\right)} = \sqrt{\frac{3}{T}(T_c-T)}$

In the thermodynamic limit;

$G(T,h=0,N) = -Nk_BT\log(2\cosh(\beta^* m)) + \frac{1}{2}NqJm^2 \approx -Nk_BT\log(2) - Nk_BT\log\left(1+\frac{1}{2}(\beta^* m)^2\right) + \frac{1}{2}NqJm^2$

$= -Nk_BT\log(2) - Nk_BT\frac{1}{2}(\beta^* m)^2 + \frac{1}{2}NqJm^2 = -Nk_BT\log(2) - \frac{NqJ}{2}\left[k_BT\beta^2 qJ - 1\right]m^2$

$= -Nk_BT\log(2) - \frac{NqJ}{2k_BT}\left[qJ - k_BT\right]m^2 = -Nk_BT\log(2) - \frac{NqJ}{2T}\left[T_c - T\right]m^2$

$G(T>T_c, h=0,N) = -Nk_BT\log(2)$ Density matrix approach (Bragg-Williams Approximation):

$S = -k_B Tr[\rho\log\rho]$; $\rho = \dfrac{e^{-\beta(H-hM)}}{Tr[e^{-\beta(H-hM)}]}$

The function to maximize is $-k_B Tr[\rho\log(\rho)] - \beta k_B[Tr(\rho H) - U] + \beta k_B h[Tr(\rho M) - M]$

Rewritten, $-k_B Tr[\rho\log(\rho)] - \beta k_B Tr(\rho H) + \beta k_B h Tr(\rho M) + k_B\lambda[Tr\rho - 1] + k_B\beta U - k_B\beta hM$ $+ k_B\lambda[Tr\rho - 1]$

Operator of Gibbs Free Energy: $G = \cancel{H} - TS - hM = Tr(\rho H) + k_BT\, Tr[\rho\log(\rho)] - h Tr(\rho M)$

$-\frac{1}{T}G + k_B\lambda[Tr\rho - 1] + k_B\beta U - k_B\beta hM$

$\langle \sigma_1,\dots,\sigma_N|\rho|\sigma_1',\dots,\sigma_N'\rangle = \rho_1(\sigma_1,\sigma_1')\rho_2(\sigma_2,\sigma_2')\cdots\rho_N(\sigma_N,\sigma_N')$; $\rho = \rho_1\otimes\rho_2\otimes\cdots\otimes\rho_N$

$\langle f(\sigma_k)\rangle = \left\{\sum_{\sigma_k=\pm1} f(\sigma_k)\rho_k(\sigma_k,\sigma_k)\right\}\prod_{i\neq k}\left\{\sum \rho_i(\sigma_i,\sigma_i)\right\}$

and since $1 = Tr\rho = \prod_i \{ \sum_{\sigma_i = \pm 1} \rho_i(\sigma_i, \sigma_i) \}$; $\langle f(\sigma_k) \rangle = \dfrac{\sum_{\sigma_k = \pm 1} f(\sigma_k)\rho_k(\sigma_k, \sigma_k)}{\sum \rho_k(\sigma_k, \sigma_k)}$

$\boxed{\text{Independent of sites}}$

Density matrix of true one ; $\sum_{\sigma_1 \cdots \sigma_N} \tilde{\rho}(\sigma_1, \sigma_1) \cdots \tilde{\rho}(\sigma_N, \sigma_N) = 1$ or $[Tr\tilde{\rho}]^N = 1$

Density Matrix is Hermitian:

$$\langle \sigma_1 \cdots \sigma_k' \cdots \sigma_N | \rho | \sigma_1 \cdots \sigma_k \cdots \sigma_N \rangle = (\langle \sigma_1 \cdots \sigma_k \cdots \sigma_N | \rho | \sigma_1 \cdots \sigma_k' \cdots \sigma_N \rangle)^*$$

$$[Tr\tilde{\rho}]^{N-1} \langle \sigma_k' | \tilde{\rho} | \sigma_k \rangle = ([Tr\tilde{\rho}]^{N-1} \langle \sigma_k | \tilde{\rho} | \sigma_k' \rangle)^*, \text{ remembering } [Tr\tilde{\rho}]^N = 1$$

$$\frac{\langle \sigma_k' | \tilde{\rho} | \sigma_k \rangle}{Tr\tilde{\rho}} = \left(\frac{\langle \sigma_k | \tilde{\rho} | \sigma_k' \rangle}{Tr\tilde{\rho}} \right)^*$$; The eigen values are $\tilde{\rho}\vec{e}_m = \lambda_j m [Tr\tilde{\rho}] \vec{e}_m$

Total Density Matrix ρ is positive definite, $\langle \psi | \rho | \psi \rangle \geq \langle \psi | \rho^2 | \psi \rangle$

With components $\langle \sigma_1, \cdots \sigma_N | \psi \rangle = \prod_i e_{n(i)}(\sigma_i)$; Where function $n(i)$ is either one or two.

$$\langle \psi | \rho | \psi \rangle = \lambda_p^p \lambda_2^{N-p} [Tr\tilde{\rho}]^N = \lambda_1^p \lambda_2^{N-p}$$

Where p is the number of times $n(i)$ is equal to one, similarly

$\langle \psi | \rho^2 | \psi \rangle = \lambda_1^{2p} \lambda_2^{2N-2p} [Tr\tilde{\rho}]^{2N} = \lambda_1^{2p} \lambda_2^{2N-2p}$; Generalized: $\tilde{\rho} = \begin{pmatrix} \frac{1}{2}(1+m) & a^* \\ a & \frac{1}{2}(1-m) \end{pmatrix}$

$G(h,T) = \min_\rho Tr[\rho H - \rho h M + k_B T \rho \log \rho]$; $\rho = \tilde{\rho}^N$ $\qquad m = \sum_\sigma \sigma \tilde{\rho}(\sigma, \sigma)$

$G(h,T) = \min_{m,a} Tr[(\tilde{\rho})^N H - (\hat{\rho})^N hM + k_B T (\hat{\rho})^N \log \rho^N]$ $\boxed{\text{Upper Bound}}$

Calculated Energy: $U - Mh = Tr(H - hM)\rho$; $U - Mh = \sum_{\sigma_1} \cdots \sum_{\sigma_N} \tilde{\rho}(\sigma_1, \sigma_1) \cdots \tilde{\rho}(\sigma_N, \sigma_N) [-J \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i]$

$$= -\frac{1}{2} J N q m^2 - h N m$$

Calculated Entropy:

$$S = -k_B \sum_{\sigma_N} \sum_{\sigma_N'} \langle \sigma_1 \cdots \sigma_N | \rho | \sigma_1' \cdots \sigma_N' \rangle \langle \sigma_1' \cdots \sigma_N' | \log \rho | \sigma_1 \cdots \sigma_N \rangle$$

Hence, $\langle \sigma_1, \cdots \sigma_N | \log(\rho) | \sigma_1', \cdots \sigma_N' \rangle = \sum \delta_{\sigma_1, \sigma_1'} \delta_{\sigma_2, \sigma_2'} \cdots \langle \log(\hat{\rho}) \rangle (\sigma_n, \sigma_n) \cdots$

$$Tr \rho \log \rho = \sum_{n=1}^N \sum_{\sigma_1} \langle \sigma_1 | \tilde{\rho} | \sigma_1 \rangle \sum_{\sigma_2} \langle \sigma_2 | \tilde{\rho} | \sigma_2 \rangle \cdots \sum_{\sigma_n \sigma_N} \langle \sigma_n | \tilde{\rho} | \sigma_N' \rangle \langle \sigma_n' | \log(\tilde{\rho}) | \sigma_N \rangle = N Tr \tilde{\rho} \log \tilde{\rho}$$

$$S = -k_B N Tr \tilde{\rho} \log(\tilde{\rho})$$

After minimizing energy, $G(h,T) \leq \min_{m,a} [-\frac{1}{2} J N q m^2 - h N m + N k_B T Tr \tilde{\rho} \log(\tilde{\rho})]$

$\min_a \{ Tr \tilde{\rho} \log(\tilde{\rho}) \}$; to determine a, $\frac{d}{da} Tr \tilde{\rho} \log \tilde{\rho} = 0$; $\frac{d}{da} Tr \rho \log \rho = Tr \frac{\partial \rho}{\partial a} \log \rho + Tr \frac{\partial \rho}{\partial a}$

$\tilde{\rho} = \begin{bmatrix} \frac{1}{2}(1+m) & 0 \\ 0 & \frac{1}{2}(1-m) \end{bmatrix}$; Example $\tilde{\rho} = \begin{bmatrix} 1/2 & a \\ a & 1/2 \end{bmatrix} \xrightarrow{\text{Perturbation}} \frac{1}{2} \pm a$

Finally, $S = -N k_B \left(\frac{1+m}{2} \log\left(\frac{1+m}{2}\right) + \frac{1-m}{2} \log\left(\frac{1-m}{2}\right) \right)$

$$G(h,T) \leq \min_m \left[-\frac{1}{2} J N q m^2 - h N m + N k_B T \left(\frac{1+m}{2} \log\left(\frac{1+m}{2}\right) + \frac{1-m}{2} \log\left(\frac{1-m}{2}\right) \right) \right] \qquad m = \pm 1$$

similar to $\boxed{\text{Landau theory}}$

Slope of $G(T,h,N;m)$ as a function; $\frac{\partial G}{\partial m}(T,h,N;m) = -NqJm - Nh + \frac{1}{2}Nk_BT\log\left(\frac{1+m}{1-m}\right)$

@ $m=-1$, slope $= -\infty$ · @ $m=1$, slope $=\infty$ ∴ $\frac{mqJ+h}{k_BT} = \log\sqrt{\frac{1+m}{1-m}}$; $m = \tanh\beta(qJm+h)$

Second Derivative of Gibbs: $\frac{\partial^2 G}{\partial m^2} = -NqJ + \frac{Nk_BT}{1-m^2}$; $\boxed{\text{Mean Field Results}}$

~~$(1+m)\log(1+m) = (1+m)\sum_1^\infty \frac{(-1)^{k+1}}{k}m^k$~~, $\sum_1^\infty \frac{(-1)^{k+1}}{k}m^k$, $\sum_1^\infty \frac{(-1)^{k+1}}{k}m^{k+1}$ For a single spin

$(1+m)\log(1+m) + (1-m)\log(1-m) = 2\sum_{k=2,\text{even}}^\infty \frac{(-1)^{k+1}}{k}m^k + 2\sum_{k=2,\text{even}}^\infty \frac{(-1)^k}{k-1}m^k = 2\sum_{k=2,\text{even}}^\infty \frac{1}{k(k-1)}m^k$

Therefore, Gibbs free energy $G(h,T,N;m) = -\frac{1}{2}JNqm^2 - hNm + Nk_BT\left(-\log(2) + \frac{1}{2}m^2 + \frac{1}{12}m^4\right)$

$\frac{1}{N}G(h,T,N;m) = -hm - Nk_BT\log(2) + \frac{1}{2}[k_BT - Jq]m^2 + \frac{1}{4}\left[\frac{k_BT}{3}\right]m^4$

Mean Field Theory: contains an average of spins.

Braggs-Williams Approximation: replace density matrix with coupling neighbor sites.

Critical Temperature in Different Dimensions! Finite Size Effects: Low temp, length, N, etc.

$\Delta G = 2J - T\Delta S = 2J - k_BT(\log 2(N-1) - \log(2)) = 2J - k_BT\log(N-1)$

Temperature Described as a diffusion equation: $t_{life} = t_{hop}N^2$

Time averaged spin: $\langle\sigma_i\rangle = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau \sigma_i(t)\,dt$; $\frac{t_{intro}}{t_{life}} \approx \frac{A^{-1}e^{2J\beta}}{A^{-1}N^2}$

Gibbs Free:

$\Delta G = 2JL_W - k_BT\log(2[2L6^{L_W}]) + k_BT\log(2)$

$\Delta G = L_W(2J - k_BT\log(6))$

$k_BT_C = 2J/\log(6)$

$T_C \approx 1.8J$ "lower limit"

Bethe Approximation:

$E_{mf}(\sigma_0) = -(h+h')\sigma_0 + f(h')$; h = regular magnetic field ; h' = Additional Magnetic field.

$E_{mf}(\sigma_0\ldots\sigma_q) = -J\sigma_0\sum_{i=1}^q\sigma_i - h\sum_{i=0}^q\sigma_i - h'\sum_{i=1}^q\sigma_i + f(h')$; $Z = \sum_{\{\sigma_0\ldots\sigma_q\}} e^{-\beta E_0\{\sigma_0\ldots\sigma_q\}}$;

$Z_c = \sum_{\{\sigma_0\ldots\sigma_q\}}\sum_{\sigma_0} e^{\beta J\sigma_0\sum_{i=1}^q\sigma_i}e^{\beta h\sum_0^q\sigma_i}e^{\beta h'\sum_1^q\sigma_i}$

$Z_c = \sum_{\{\sigma_1\ldots\sigma_q\}}\left[e^{\beta H}\prod_{i=1}^q e^{\beta(J+h'+h)\sigma_0} + e^{-\beta H}\prod_{i=1}^q e^{\beta(-J+h+h)\sigma_i}\right]$

$= e^{\beta h}[2\cosh(\beta(J+h+h'))]^q + e^{-\beta h}[2\cosh(\beta(-J+h+h'))]^q$; Spin Averages: $\langle\sigma_0\rangle = \frac{1}{Z_c}\sum\sigma_0 e^{-\beta E_c(\sigma_0\ldots\sigma_q)} = \frac{S_0}{Z_c}$

$S_0 = \sum_{\{\sigma_1\ldots\sigma_q\}}\sum_{\sigma_0}\sigma_0 e^{\beta J\sigma_0}\sum\sigma_i e^{\beta h}\sum\sigma_i\sum\sigma_i$

$\langle\sigma_j\rangle = \frac{1}{Z_c}\sum\sigma_j e^{-\beta E_c(\sigma_0\ldots\sigma_q)} = \frac{S_j}{Z_c}$

$= e^{\beta h}[2\cosh(\beta(J+h+h'))]^q - e^{-\beta h}[2\cosh(\beta(-J+h+h'))]^q$

Resolving the equation: $\frac{\cosh(\beta(J+h+h'))}{\cosh(\beta(J-h-h'))} = e^{\frac{2}{q-1}\beta h'}$

Chapter 8: Problem Set:

Problem 1: Binary Alloy: Atom is A or B @ site i. Energy AA-bond: ϵ_{AA}, AB-Bond $=\epsilon_{AB}$, BB-bond: ϵ_{BB}

A) Energy of Binary Alloy in state $\{\sigma_1\ldots\sigma_N\}$

Total Energy: $\epsilon = \frac{1}{2}\epsilon_{AA} + \frac{1}{2}\epsilon_{BB} - \epsilon_{AB}$

Concentration of A is $C_A = \frac{N_A}{N}$, $N = \frac{N_A}{C_A}$

Concentration of B is $C_B = 1 - C_A$

$N_{A_i} = \frac{1}{2}(1+\sigma_i)$; $\sigma_i = \pm 1$, $n_{B_i} = \frac{1}{2}(1-\sigma_i)$

$E\{\sigma_1\ldots\sigma_N\} = -J[\frac{1}{2}\epsilon_{AA} + \cancel{\frac{1}{2}\epsilon_{BB}} - \cancel{\epsilon_{AB}}]$

$= -J\left[\frac{1}{2}\sum\sigma_i + \frac{1}{2}\sum\sigma_i - \sum\sigma_i\sigma_j\right]$

$= -J\left[\frac{1}{2}N_Aq + \frac{1}{2}N_Bq - \frac{1}{2}Nq\right]$

$\boxed{= -J\left[\frac{1}{2}\left(\frac{1}{2}(1+\sigma_i)\right) + \frac{1}{2}\left(\frac{1}{2}(1-\sigma_i)\right) - \frac{1}{2}\left(1 - \frac{\frac{1}{2}(1+\sigma_i)}{C_A}\right)\right]}$

$= -\frac{J}{4}\left[1+\sigma_i + 1 - \sigma_i - 2C_A - (1+\sigma_i)/2\right] = \boxed{\frac{-J}{4}\left[2 - 2C_A - (1+\sigma_i)/2\right]} = \boxed{-\frac{J}{2}\left[C_B - (1+\sigma_i)/4\right]}$

b) Ising Model: $H(\sigma) = -\sum J_{ij}\sigma_i\sigma_j = \sum h_j \sigma_j$ $J = J$; $h = (1+\sigma_i)/4$

c) My assumption presumes at $T=0$, the system is completely ordered. $T_c > \frac{2J - \Delta G}{k_B}$

If $J>0$, then below T_c, the spontaneity could be $2J - \cancel{k_B T} \le \Delta G \le 2J$ and non-spontaneous.

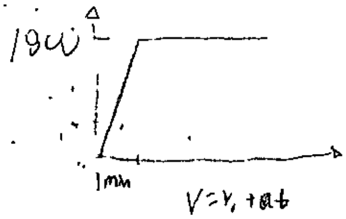
$2J - ec$ $2J > \Delta G$

d) If $J<0$, then there would be spontaneous.

Problem 2: One Dimensional Ising Model ; $J<0$; Spin-variable τ_i relates σ_i

A) Calculate T_c for this system $H(\sigma) = -J\sum \sigma_i + h \sum \sigma_j$; $\tau_i = (-1)^i \sigma_i$

$\Delta G = 2J - \cancel{T}\Delta S = 2J - k_B T \log(2(N-1) - \log 2) = 2J - k_B T \log(N-1)$,



Number walls: $L b_k^{Lw \leftarrow \text{energy of wall}}$

"one starting give" ; average # choices (!)

$\Delta G = 2JLw - k_B T \log(2Lb^{Lw}) + k_B T \log(2) - k_B T \log(2L)$

b) Below T_c, the ΔG would not be spontaneous. $= Lw(2J - k_B T \log(b))$; $k_B T = \frac{2J}{\log(b)}$

Problem 3: $H = -J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j$; Spin Operators $[\vec{S}] = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Spin spinors $\begin{pmatrix} \gamma \\ \mu \end{pmatrix}$; $|1\rangle, |2\rangle, |3\rangle \ldots |N\rangle$

A. Calculate the Internal Energy of a and m. What is the difference?

$\tilde{\rho} = \begin{pmatrix} \frac{1}{2}(1+m) & a^* \\ a & \frac{1}{2}(1-m) \end{pmatrix}$; $m = \sum_\sigma \sigma \tilde{\rho}(\sigma, \sigma)$; Average spin $= \sum \sigma \tilde{\rho}(\sigma, \sigma)$

$H|\psi\rangle = E|\psi\rangle$; $E = \langle \psi^\dagger | H | \psi \rangle = \langle \psi^\dagger | \rho | \psi \rangle = \langle \psi^\dagger | -J \sum \vec{S}_i \vec{S}_j | \psi \rangle$

$= \langle 1 | \langle 2 | \langle 3 | \ldots \langle N | -J \sum_{\langle ij \rangle} \vec{S}_i \vec{S}_j | 1 \rangle | 2 \rangle | 3 \rangle \ldots | N \rangle$

$= \left\langle \begin{matrix} \gamma_1 \\ \mu_1 \end{matrix} \right| \left\langle \begin{matrix} \gamma_2 \\ \mu_2 \end{matrix} \right| \left\langle \begin{matrix} \gamma_3 \\ \mu_3 \end{matrix} \right| \ldots \langle N | J \sum_{1D} \vec{S}_i \vec{S}_j \left| \begin{matrix} \gamma_1 \\ \mu_1 \end{matrix} \right\rangle \left| \begin{matrix} \gamma_2 \\ \mu_2 \end{matrix} \right\rangle \left| \begin{matrix} \gamma_3 \\ \mu_3 \end{matrix} \right\rangle \ldots | N \rangle$

$= \left\langle \begin{matrix} \gamma_{1 \ldots N} \\ \mu_{1 \ldots N} \end{matrix} \right| -J \left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right]^2 \left| \begin{matrix} \gamma_{1 \ldots N} \\ \mu_{1 \ldots N} \end{matrix} \right\rangle$

$= \left\langle \begin{matrix} \gamma_{1 \ldots N} \\ \mu_{1 \ldots N} \end{matrix} \right| -J \begin{bmatrix} 1 & 1-i \\ 1+i & -1 \end{bmatrix} \begin{bmatrix} 1 & 1-i \\ 1+i & -1 \end{bmatrix} \left| \begin{matrix} \gamma_{1 \ldots N} \\ \mu_{1 \ldots N} \end{matrix} \right\rangle = \boxed{\left\langle \begin{matrix} \gamma_{1 \ldots N} \\ \mu_{1 \ldots N} \end{matrix} \right| -J \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix} \left| \begin{matrix} \gamma_{1 \ldots N} \\ \mu_{1 \ldots N} \end{matrix} \right\rangle}$

$\boxed{\frac{1}{2}(1+m) = 3 ; m = 5 ; a = 0}$

B) $\log \tilde{\rho}$, a, m , min ΔG $\quad G(T, h, N) = -H - TS - hM = Tr(\rho H) + k_B T Tr[\rho \log \rho] - h Tr(\rho m)$

$\rho = (\tilde{\rho})^N$ $\quad \frac{dG(\bar{h}, T)}{dm_a} = \frac{d}{dm_a}\left[Tr(\tilde{\rho}^N H) + k_B T Tr[N \tilde{\rho}^N \log \tilde{\rho}] - h Tr(\tilde{\rho}^N m) \right]$

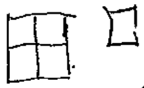
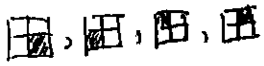
$= \frac{d}{dm_a}\left[Tr\left(\cancel{\tilde{\rho}^N H} + k_B T \cdot N \tilde{\rho}^N \log \tilde{\rho} - \cancel{h \tilde{\rho}^N m} \right) \right]$

$= \frac{d}{dm_a} k_B T N \tilde{\rho}^N \log \tilde{\rho} = k_B T \left[\frac{d\tilde{\rho}^N}{\partial m_a} \log \tilde{\rho} + N \tilde{\rho}^N \frac{d \log \tilde{\rho}}{d m_a} \right]$

$0 = N \frac{d\tilde{\rho}^N}{\partial m} \log \tilde{\rho} + N$; $1 = \frac{\partial \tilde{\rho}}{\partial m} \log \tilde{\rho}$; $\boxed{\frac{1}{N \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}} = \log \tilde{\rho}}$

c. $\log\det A = \mathrm{Tr}\log A$; $\log\tilde{\rho} = \frac{1}{N\tilde{\rho}}$; $\mathrm{Tr}\log\rho = \log\det\rho = \log(\frac{1}{q})$

d) See c.

Problem 4:  a) One inequivalent site:  :

b) Cluster Hamiltonian: $\langle E_c\rangle = -Jq\langle\sigma_0\sigma_j\rangle - h(q+1)m - h'm + f(h') = \hat{H}$

Assuming the neighboring sites $\langle E_c\rangle = -Jq\langle\sigma_i\sigma_j\rangle - h(q+1) - h'm + f(h')$

c) Self-consistency condition: a requirement that the average spin be the same everywhere, usually pertains to spontaneous magnetic order.

$\langle\sigma_i\sigma_j\rangle = \frac{1}{Z_c}\sum_{\sigma_0\cdots\sigma_q}\sigma_0\sigma_j e^{-\beta E_c(\sigma_0\cdots\sigma_q)} = \frac{S_{0j}}{Z_c}$

d) Calculate T_c.

$k_BT_c = 4J$: Mean-field $\quad T_c = 4J/k_B = 4J/1.38\times10^{-23}\,J/K\,mol = \boxed{0.48\,K}$

$k_BT_c = 2.885J$: Cluster value, $T_c = 2.885J/k_B = 2.885/1.38\times10^{-23}\,J/K\,mol = \boxed{0.347\,K}$

Problem 5: A)  $: 6\times4 + 1 + 4 = 29$ B) $\langle\sigma_i\rangle = \langle\sigma_j\rangle$: 3 constraints.

c) Cluster Hamiltonian: $H = \langle E\rangle = -Jq\langle\sigma_0\sigma_j\rangle - h(q+1)m - h'm + f(h')$; $\langle\sigma_0\sigma_j\rangle = \frac{1}{Z_c}\sum\sigma_0\sigma_j e^{-\beta E_c(\sigma_0\cdots\sigma_q)} = \frac{S_0}{Z_c}$

d) To solve the cluster problem: $h' = -1J\langle\sigma_0\sigma_j\rangle - h(80)m - h'm + f(h')$

I would associate σ_j with the neighboring sites, Measure entropy, temperature, partition function. Magnetization dependence of position

Problem 6: $\sigma_1 = \frac{1}{2}, \sigma_2 = 1, \sigma_3 = \frac{1}{2}, \ldots \begin{cases}\sigma_{2N-1} = \frac{1}{2}\\ \sigma_{2N} = 1\end{cases}$; $\{S_1, S_2, \cdots\}$; $S_i = \pm1$; $S_2 = -2, 0, 2$; $E\{S_1S_2\cdots\} = -J\sum_i S_iS_{i+1} - h\sum_i S_i$

$m_{1/2}, m_1$; Mean-Field Approach: 1) Calculate Partition function: $Z_c = \sum e^{-\beta E_c(\sigma_0\cdots\sigma_q)}$

2) Calculate spin averages from expressions.

$$\langle\sigma_0\rangle = \frac{1}{Z_c}\sum_{\sigma_0}^{\sigma_N}\sigma_i e^{-\beta E_c(\sigma_0\cdots\sigma_q)} = \frac{S_0}{Z}$$

$$\langle\sigma_j\rangle = \frac{1}{Z_c}\sum_{\sigma_0}^{\sigma_q}\sigma_j e^{-\beta E_c(\sigma_0\cdots\sigma_q)} = \frac{S_0}{Z}$$

3) Determine Entropy:

$$S_j = e^{\beta h}[2\cosh(\beta(J+h+h'))]^{q-1}[2\sinh(\beta(J+h+h'))] + e^{-\beta h}[2\cosh(\beta(-J+h+h'))]^{q-1}[2\sinh(\beta(-J+h+h'))]$$

4) Determine average spin: $m = \langle\sigma_0\rangle = \langle\sigma_j\rangle$

5) Determine S_0 or S_q.

6) Utilize the Bethe approximation given by $k_BT_c = \frac{J}{\coth^{-1}(q-1)} \approx k_BT_c = qJ \approx 2J$

Problem 7: Bravais Lattice vectors $\vec{R}_i$; $E\{\sigma_i\} = -\frac{1}{2}\sum J(|R_i - R_j|)\sigma_i\sigma_j - h\sum\sigma_i$

Determine T_c: 1) Partition Function: $Z_c = \sum e^{-\beta E}$

2) Calculate spin averages: $\langle\sigma_0\rangle = \frac{1}{Z_c}\sum_{\sigma_1}^{\sigma_N}\sigma_i e^{-\beta E(\sigma_i)} = S_0/Z_c$; $\langle\sigma_j\rangle = S_j/Z_c$

3) Determine Entropy: $S_j = e^{\beta h}[2\cosh(\beta(J|R_i - R_j| + h + h'))]^{q-1}\cdot[2\sinh(\beta(J|R_i - R_j| + h + h'))] + e^{-\beta h}[2\cosh(\beta(-J|R_i - R_j| + h + h'))]^{q-1}[2\sinh(\beta(J|R_i - R_j| + h + h'))]$

4) Determine Spins 5) Evaluate S_0 or S_j 6) Use Bethe approximation $\boxed{k_BT_c = \frac{J|R_i - R_j|}{\coth^{-1}(q-1)}}$

Problem 8: Density Operator: $\langle S_1, S_2, \ldots|\rho|S_1', S_2', \ldots\rangle = \langle S_1|\rho|S_1'\rangle\langle S_2|\rho|S_2'\rangle\cdots$

$$S_T = S_1\cdot S_2\cdots S_n = \prod_{i=1}^{N} -Nk_B\left(\frac{1+m}{2}\log\frac{1+m}{2} - \frac{1-m}{2}\log\frac{1-m}{2}\right)$$

$$= \left[-Nk_B\left(\frac{1+m}{2}\log\frac{1+m}{2} - \frac{1-m}{2}\log\frac{1-m}{2}\right)\right]^N$$

Problem 9: $S_i \propto S_{\pm 1, 0}$; $E\{S_i\} = -J\sum_{\langle ij\rangle} S_i S_j - h\sum_i S_i$ ⋯ $k_B T_c = \frac{2J}{\log\left(\frac{2}{2-2}\right)} = \emptyset$ | Integration over the coupling constant

Problem 10: $q = 6$ $k_B T_c = \frac{2J}{\log\left(\frac{6}{4}\right)} = \boxed{\frac{2J}{\log(3/2)}}$

$$\mathcal{V} = -\sum |\sigma_1 \cdots \sigma_N\rangle \sum \sigma_i \sigma_j \langle \sigma_1 \cdots \sigma_N|$$

$$H_0 = -h\sum |\sigma_1 \cdots \sigma_N\rangle \sum \sigma_i \langle \sigma_1 \cdots \sigma_N|$$

$$H = H_0 + \lambda \mathcal{V}$$

Chapter 9: General Methods: Critical Exponents:

Free Energy as a function of λ: $G(\lambda) = -k_B T \log\left(\mathrm{Tr}\, e^{-\beta H_0 - \beta\lambda\mathcal{V}}\right)$

Derivative with respect to λ: $\frac{dG(\lambda)}{d\lambda} = \frac{-k_B T}{\mathrm{Tr}\, e^{-\beta H_0 - \beta\lambda\mathcal{V}}} \mathrm{Tr} \frac{d}{d\lambda} e^{-\beta H_0 - \beta\lambda\mathcal{V}}$; $[H_0, \mathcal{V}] = 0 \Rightarrow e^{-\beta H_0 - \beta\lambda\mathcal{V}} = e^{-\beta H_0} e^{-\beta\lambda\mathcal{V}}$

$$\frac{d}{d\lambda} e^{-\beta\lambda\mathcal{V}} = \frac{d}{d\lambda}\sum^{\infty} \frac{1}{n!}(-\beta\lambda)^n \mathcal{V}^n = \sum_{n=1}^{\infty} \frac{1}{(n-1)!}\lambda^{n-1}(-\beta)^n \mathcal{V}^n = -\beta\mathcal{V} e^{-\beta\lambda\mathcal{V}}$$

Therefore; $\frac{dG}{d\lambda} = \frac{\mathrm{Tr}\, \mathcal{V} e^{-\beta H_0 - \beta\lambda\mathcal{V}}}{\mathrm{Tr}\, e^{-\beta H_0 - \beta\lambda\mathcal{V}}}$; $\frac{d}{d\lambda} e^{-\beta H_0 - \beta\lambda\mathcal{V}} = \sum_{n=0}^{\infty} \frac{1}{n!}\frac{d}{d\lambda}[-\beta H_0 - \beta\lambda\mathcal{V}]^n$

$$= \sum_{n=1}^{\infty} \frac{1}{n!}\sum_{m=1}^{n} [-\beta H_0 - \beta\lambda\mathcal{V}]^{m-1}[-\beta\mathcal{V}][-\beta H_0 - \beta\lambda\mathcal{V}]^{n-m}$$

$$\mathrm{Tr}\frac{d}{d\lambda} e^{-\beta H_0 - \beta\lambda\mathcal{V}} = \sum_{n=1}^{\infty} \frac{1}{n!}\sum_{m=1}^{n} \mathrm{Tr}\,[-\beta\mathcal{V}][-\beta H_0 - \beta\lambda\mathcal{V}]^{n-1}$$

$$= \sum_{n=1}^{\infty} \frac{1}{(n-1)!}\mathrm{Tr}\,[-\beta\mathcal{V}][-\beta H_0 - \beta\lambda\mathcal{V}]^{n-1} = \mathrm{Tr}\,[-\beta\mathcal{V}]\, e^{-\beta H_0 - \beta\lambda\mathcal{V}}$$

$$G(\lambda) = G(0) + \int_0^J d\lambda \frac{dG}{d\lambda} = G(0) + \int_0^J \frac{d\lambda}{\lambda}\langle\lambda\mathcal{V}\rangle_\lambda \; ; \; \langle\lambda\mathcal{V}\rangle_\lambda = \langle -\lambda\sigma_0 \sum_{i=1}^{2}\sigma_i\rangle_\lambda$$

Cluster partition function

$$Z_c = 8\cosh^2(\beta\lambda)$$

$$E_c = \frac{-\partial}{\partial\beta}\log Z_c = -2\lambda\tanh\beta\lambda$$

$$U = \langle\lambda\mathcal{V}\rangle = \frac{1}{2}N E_c$$

$$G(J) = G(0) - N\int_0^J d\lambda \tanh\beta\lambda = G(0) - Nk_B T\log\cosh\beta J$$

$$= -Nk_B T\log(2\cosh\beta J)$$

$$S = \int_0^T \frac{dT'}{T'}\frac{dU}{dT'} = Nk_B J\int_\beta^\infty \frac{\beta' d\beta'}{\cosh^2\beta' J} \; ; \; E\{\sigma_1, \sigma_2 \cdots\} = -J\sum_{\langle ij\rangle}\sigma_i\sigma_j - h\sum\sigma_0$$

Reference System: $E_0\{\sigma_1, \sigma_2 \cdots\} = -(J\mu q + h)\sum\sigma_i + J\mu^2\frac{1}{2}Nq$; $Z_0(T, h, N) = e^{-\beta J\mu^2\frac{1}{2}Nq}\sum e^{\beta(J\mu q + h)\sum\sigma_i}$

Free Energy: $G_0(T, h, N) = J\mu^2\frac{1}{2}Nq - Nk_B T\log[2\cosh\beta(J\mu q + h)] = e^{-\beta J\mu^2\frac{1}{2}Nq}[2\cosh\beta(J\mu q + h)]^N$

Interaction Term: $\langle\mathcal{V}\rangle_\lambda = -\langle\sum_{\langle ij\rangle}(\sigma_i - \mu)(\sigma_j - \mu)\rangle_\lambda = -\frac{1}{2}Nq\langle(\sigma_i - \mu)(\sigma_j - \mu)\rangle_\lambda$

$$\langle\mathcal{V}\rangle_\lambda = -\frac{1}{2}Nq\langle(\sigma_i - m_\lambda)(\sigma_j - m_\lambda)\rangle_\lambda - \frac{1}{2}Nq\langle 2(m_\lambda - \mu)\sigma_i\rangle_\lambda + \frac{1}{2}Nq(m_\lambda^2 - \mu^2) \approx -\frac{1}{2}Nq\langle 2(m_\lambda - \mu)\sigma_0\rangle + \frac{1}{2}Nq(m_\lambda^2 - \mu^2)$$

$$\approx -Nq(m_\lambda - \mu)m_\lambda + \frac{1}{2}Nq(m_\lambda^2 - \mu^2) \approx -\frac{1}{2}Nq(m_\lambda - \mu)^2 \; ; \; \left(\frac{\partial G}{\partial\lambda}\right) = -\frac{1}{2}Nq(m_\lambda - \mu)^2$$

$$Nm_\lambda = -\left(\frac{\partial G}{\partial h}\right) \; ; \; N\left(\frac{\partial m}{\partial\lambda}\right) = -\left(\frac{\partial^2 G}{\partial h\,\partial\lambda}\right) = Nq(m - \mu)\left(\left(\frac{\partial m}{\partial h}\right) - \left(\frac{\partial\mu}{\partial h}\right)\right)$$

Critical Exponents: $\frac{\cosh\beta(J + h')}{\cosh\beta(J - h')} \approx 1 + h' 2\beta\tanh\beta J + (h')^2 2\beta^2\tanh^2\beta J + O(h')^3$

$$e^{\frac{2\beta h'}{q-1}} \approx 1 + h'\frac{2\beta}{q-1} + (h')^2\frac{2\beta^2}{(q-1)^2} + O(h')^3 \; ; \; h' 2\beta\tanh\beta J + (h')^2 2\beta^2\tanh^2\beta J + a(h')^3 = h'\frac{2\beta}{q-1} + (h')^2\frac{2\beta^2}{(q-1)^2}$$

$$0 = h'\left((T - T_c)(c + dh') + (a - b)(h')^2\right)$$

Susceptibility: $\chi(h, T) = \left(\frac{\partial m}{\partial h}\right)_T$ $\quad m = \tanh\beta(qJm + h)$

$\chi(h=0,T) = \frac{\beta}{\cosh^2\beta Jqm}\{qJ\chi(h=0,T)+1\}$; if $T > T_c$; $m=0$; $\chi(0,T) \approx \frac{1}{k_B(T-T_c)}$ | Relationship between susceptibility

$\cosh^2\beta qJm \approx 1 + (\beta_q J)^2 \kappa^2 (T_c - T)$ | $\chi = \frac{\partial}{\partial h}\frac{Tr S_0 e^{-\beta(H-hm)}}{Tr e^{-\beta(H-hm)}} = \beta\sum\{\langle S_0 S_i\rangle - \langle S_0\rangle\langle S_i\rangle\}$ and Fluctuations

"Fluctuations are correlated to the magnetic field" $= \beta\sum\langle S_0 - m\rangle\langle S_i - m\rangle$

Spin correlation Function:

$T_i(T) = \langle S_0 S_i\rangle_T - \langle S_0\rangle_T\langle S_i\rangle_T$; $\chi = \beta\int d^3r\, T(r,T)$ | $H(\sigma_1\ldots\sigma_N) = -J\sum_{i=1}^{N-1}\sigma_i\sigma_{i+1}$; $Z(T,N) = \sum e^{\beta J\sum\sigma_i\sigma_{i+1}}$

Exact Solution for the Ising Chain:

$G(T,N,h=0) = -Nk_BT\log(2\cosh(\beta J) + k_BT\log\cosh(\beta J))$

$= \sum_{\sigma_1}\sum_{\sigma_2} e^{\beta J\sigma_1\sigma_2}\ldots\sum e^{\beta J\sigma_{N-1}\sigma_N}$

$= \sum_{\sigma_1}\sum_{\sigma_2} e^{\beta J\sigma_1\sigma_2}\cdot 2\cosh(\beta J)$

$= 2^{N-1}\cosh^{N-1}(\beta J)\sum_{\sigma_1} = 2^N\cosh^{N-1}(\beta J)$

$\boxed{\text{Chain of Spins}}$

$\boxed{\text{Periodic Boundary Condition}}$

$H(\sigma_1\ldots\sigma_N) = -\sum_{i=1}^{N} f(\sigma_i,\sigma_{i+1})$; $f(\sigma,\sigma') = J\sigma\sigma' + \frac{h}{2}(\sigma+\sigma')$

$Z(T,N) = \sum e^{\beta\sum f(\sigma_i,\sigma_{i+1})} = \sum_{\sigma_i}\prod_i e^{\beta J(\sigma_i,\sigma_{i+1})}$

Transfer Matrix

$$\mathfrak{T} = \begin{pmatrix} e^{\beta(J+h)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-h)}\end{pmatrix}$$

Partition Function:

$\mathfrak{Z}(T,h,N) = \sum\mathfrak{T}(\sigma_1,\sigma_2)\mathfrak{T}(\sigma_2,\sigma_3)\cdots\mathfrak{T}(\sigma_N,\sigma_1) = Tr\,\mathfrak{T}^N$; $\mathfrak{T}|e\rangle = t|e\rangle$

$(e^{\beta(J+h)} - t)(e^{\beta(J-h)} - t) - e^{-2\beta J} = 0$; $t_\pm = e^{\beta J}\cosh(\beta J) \pm\sqrt{e^{2\beta J}\sinh^2(\beta h) + e^{-2\beta J}}$

$\mathfrak{Z}(T,h,N) = \langle e_+|\mathfrak{T}^N|e_+\rangle + \langle e_-|\mathfrak{T}^N|e_-\rangle = t_+^N + t_-^N$; Magnetic Energy $G(T,h,N) = -k_BT\log(t_+^N + t_-^N)$

$G(T,h,N) = -Nk_BT\log\left(e^{\beta J}\cosh(\beta h) + \sqrt{e^{2\beta J}\sin^2(\beta h) + e^{-2\beta J}}\right)$; $m = -\frac{1}{N}\left(\frac{\partial G}{\partial h}\right) = \frac{e^{\beta J}\sinh(\beta h)}{\sqrt{e^{2\beta J}\sinh^2(\beta h) + e^{-2\beta J}}}$

$\times\frac{\sqrt{e^{2\beta J}\sinh^2(\beta h) + e^{-2\beta J}} + e^{\beta J}\cosh(\beta h)}{e^{\beta J}\cosh(\beta h) + \sqrt{e^{2\beta J}\sinh^2(\beta h) + e^{-2\beta J}}}$

$= \frac{\sinh(\beta h)}{\sqrt{\sinh^2(\beta h) + e^{-4\beta J}}}$

Spin Correlations for the Ising chain $T_i, T=0$

$g_i = \langle S_0 S_i\rangle = \langle\sigma_0\sigma_i\rangle$: correlated | $T_i = \langle(\sigma_0 - m)(\sigma_i - m)\rangle = g_0 - m^2$

$g_i = \langle\sigma_0\rangle\langle\sigma_i\rangle = m^2$: uncorrelated | $= \delta_{i0}(1-m^2)$; $\chi = \beta T_0$

$\langle H\rangle = -JNqm^2 - hN - JNqT_{nn}$

Spin correlations: $T_j = \frac{1}{\mathfrak{Z}(T,h=0,N)}\sum\sigma_0\sigma_j\, e^{\beta J\sum_0^{N-1}\sigma_i\sigma_{i+1}}$; $S(J_0\ldots J_{N-1}) = \sum_{\sigma_0\cdots\sigma_{N-1}} e^{\beta\sum J_i\sigma_i\sigma_{i+1}}$

$\frac{\partial}{\partial J_0}\frac{\partial}{\partial J_1}\cdots\frac{\partial}{\partial J_{j-1}}S = \sum_{\sigma_0\cdots\sigma_{N-1}} e^{\beta\sum J_i\sigma_i\sigma_{N+1}}[\beta\sigma_0\sigma_1][\beta\sigma_1\sigma_2]\cdots[\beta\sigma_{j-1}\sigma_j]$; $g_j = \frac{1}{\beta^j S}\frac{\partial}{\partial J_0}\frac{\partial}{\partial J_1}\cdots\frac{\partial}{\partial J_{j-1}}S\Big|_{J=J}$

Transfer Matrix : $\mathfrak{T}^{(i)} = \begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J}\end{pmatrix} = e^{\beta J\sigma_i\sigma'}$; $S = \sum e^{\beta J_0\sigma_0\sigma_1}e^{\beta J_1\sigma_1\sigma_2}\cdots e^{\beta\sigma_{N-1}\sigma_{N-1}\sigma_0} = Tr\,\mathfrak{T}^{(0)}\mathfrak{T}^{(1)}\cdots\mathfrak{T}^{(N-1)}$

$\mathcal{U}^{(i)} = \frac{\partial\mathfrak{T}^{(i)}}{\partial J_i} = \beta\begin{pmatrix} e^{\beta J_i} & -e^{-\beta J} \\ -e^{-\beta J} & e^{\beta J}\end{pmatrix}$; Spin Correlation Function : $\frac{\partial}{\partial_0}\frac{\partial}{\partial J_1}\frac{\partial}{\partial J_{j+1}}S = Tr\,\mathcal{U}^{(0)}\cdots\mathcal{U}^{(j-1)}\mathfrak{T}^{(j)}\cdots\mathfrak{T}^{(N-1)}$

$T_j = \beta^j\lambda_-^j\lambda_+^{N-j} + \beta^j\lambda_+^j\lambda_-^{N-j}$; $T_j = g_j = \frac{\lambda_-^j\lambda_+^{N-j} + \lambda_+^j\lambda_-^{N-j}}{\lambda_+^N + \lambda_-^N}$; $\frac{\lambda_-}{\lambda_+} = \frac{e^{\beta J} - e^{-\beta J}}{e^{\beta J} + e^{-\beta J}} = \tanh(\beta J)$