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95,521
Statistical Physics
Problem Set #3

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2.4 Schottky Defects. For a system consisting of N atoms and possessing n such defects write down the Helmholtz free energy $F(n)$.

$$F = E - \tau\sigma$$

$$E = n\varepsilon$$

$$\sigma = k\left[N \ln N - n \ln n - (N-n)\ln(N-n)\right]$$

$$\boxed{F = n\varepsilon - \tau k\left[N\ln N - n\ln n - (N-n)\ln(N-n)\right]}$$

for a system in thermal eq w/hb. @T, F = minimum. find $n/N = f(T)$

$$\frac{\partial F}{\partial n} = \frac{\partial E}{\partial n} - \left(\frac{\partial \tau}{\partial n}\right)\sigma - \tau\frac{\partial \sigma}{\partial n} = 0$$

$$\frac{\partial E}{\partial n} = \varepsilon \qquad \frac{\partial T}{\partial n} = 0 \qquad \frac{\partial \sigma}{\partial n} = k\left[-\ln n + \ln(N-n)\right]$$

$$\varepsilon - kT\left[-\ln n + \ln(N-n)\right] = 0$$

$$\frac{\varepsilon}{kT} - \left[\ln\left(\frac{N-n}{n}\right)\right] = 0$$

$$\ln\left(\frac{N}{n} - 1\right) = \frac{\varepsilon}{kT}$$

$$\frac{N}{n} - 1 = e^{\varepsilon/kT}$$

$$\frac{N}{n} = e^{\varepsilon/kT} + 1$$

$$\boxed{\frac{n}{N} = \frac{1}{e^{\varepsilon/kT} + 1}}$$

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3.1 A crystal contains N atoms which possess spin 1 and magnetic moment μ. Placed in a uniform magnetic field B the atoms can orient themselves in 3 directions; parallel, perpendicular, and antiparallel. If the crystal is in thermal equilibrium at temperature T find an expression for its mean magnetic moment M, assuming that only the interactions of the dipoles with the field B need be considered. What is the magnetic moment of the crystal
(i) when placed in a weak field at high temperature
(ii) when placed in a strong field at low temperature

$$M = N\bar{\mu} \qquad \bar{\mu} = \sum_r p_r \mu_r = p_\parallel \mu_\parallel + p_\perp \mu_\perp + p_{\#} \mu_{\#}$$

$$E_\parallel = \mu B \quad E_\perp = 0 \quad E_{\#} = -\mu B \qquad \mu_\parallel = \mu \quad \mu_\perp = 0 \quad \mu_{\#} = -\mu$$

$$Z_i = \sum_r e^{-E_r\beta} = e^{-\mu B\beta} + e^{+\mu B\beta} + \cancel{e^{0B\beta}}^{\,1}$$

$$Z_i = e^{-\mu B\beta} + e^{+\mu B\beta} + 1 = e^{-x} + e^{x} + 1, \; x \equiv \mu B\beta$$

$$p_\parallel = \frac{e^x}{Z_1} \qquad p_\perp = \frac{1}{Z_i} \qquad p_{\#} = \frac{e^{-x}}{Z_1}$$

$$\bar{\mu} = \sum_r p_r \mu_r = \frac{\mu e^x}{Z} + \cancel{\frac{(0)1}{Z_i}}^{\,0} + \frac{(-\mu)e^{-x}}{Z_i}$$

$$\bar{\mu} = \frac{\mu(e^x - e^{-x})}{(e^x + e^{-x} + 1)} = \frac{\mu\, 2\sinh x}{1 + 2\cosh x} \qquad x \equiv \mu B\beta$$

$$\mathcal{M} = N\bar{\mu} = \frac{N\mu\, 2\sinh x}{1 + 2\cosh x} \qquad x \equiv \mu B \beta = \frac{\mu B}{kT}$$

(i) $\mu B << kT \quad x \ll 1$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \sim 1 + x$$

$$\bar{\mu} = \frac{\mu(e^x - e^{-x})}{(e^x + e^{-x} + 1)} = \frac{\mu[(1+x) - (1-x)]}{[(1+x) + (1-x) + 1]}$$

$$\bar{\mu} = \mu \frac{2x}{3} = \frac{2\mu x}{3}$$

$$\mathcal{M} = N\bar{\mu} = \frac{2N\mu x}{3} = \frac{2N\mu^2 B}{3kT} \qquad \text{Curie's Law}$$

(ii) $kT << \mu B \quad x >> 1$

$$e^{-x} \to 0 \qquad 1 + e^x \to e^x$$

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$$\bar{\mu} = \frac{\mu(e^x - e^{-x})}{(e^x + e^{-x} + 1)} = \frac{\mu e^x}{(1 + e^x)} = \frac{\mu \cancel{e^x}}{\cancel{e^x}} = \mu$$

$\mathcal{M} = N\bar{\mu} = N\mu$ complete alignment

3.3 A paramagnetic crystal contains N magnetic ions which possess spin $\frac{1}{2}$ and a magnetic dipole moment μ. The crystal is placed in a heat bath at temperature T and a magnetic field $\mathcal{B}$ is applied to the crystal. Use the fact that under these conditions the Helmholtz free energy is a minimum to find the net magnetic moment of the crystal.

$F = E - \tau\sigma$ is a minimum at equilibrium

$n_{\not\parallel}$ = number of antiparallel dipoles

$n_{\parallel}$ = number of parallel dipoles

~~$N - n_{\not\parallel} - n_{\parallel} = n_{\perp}$ = number of perpendicular dipoles~~

$E(n) = n_{\parallel}\mu B + \cancel{n_{\perp}(0)B} + n_{\not\parallel}(\mu B) = (n_{\parallel} - n_{\not\parallel})\mu B$

$E_{tot} = E(n) + E(R) = \text{cnst}$

$\sigma_{total} = \underbrace{\sigma(n_{\parallel}) \cancel{+} \sigma(n_{\not\parallel})}_{\text{magnetic}} + \underbrace{\sigma(R)}_{\text{remainder/vibrational}}$

let $n = (n_{\parallel}, n_{\not\parallel})$

$\frac{\partial F}{\partial n} = \frac{\partial E_{tot}}{\partial n} + \tau\frac{\partial \sigma_{tot}}{\partial n} = 0$ $\quad \frac{\partial E_{tot}}{\partial n} = 0$ because $E_{tot} = \text{cnst}$

$\therefore \frac{\partial \sigma_{tot}}{\partial n} = 0$ is a condition of equilibrium

$$\bar{E} = n\varepsilon_1 + (N-n)\varepsilon_2$$

$$T_0\sigma = -T_0 k \ln(\Omega) = -T_0 k\,[N\ln N - n\ln n - (N-n)\ln(N-n)]$$

$$\Omega = \frac{N!}{n!(N-n)!}$$

$$\frac{\partial F}{\partial n} = \underbrace{\varepsilon_1 - \varepsilon_2}_{2\mu B} - T_0 k \ln\left(\frac{N}{n} - 1\right) = 0$$

$$\frac{2\mu B}{T_0 k} = \ln\left(\frac{N}{n} - 1\right)$$

$$\frac{N}{n} - 1 = e^{2\mu B/T_0 k}$$

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$$\frac{n}{N} = \frac{1}{\left(1 + e^{2\mu B/T_0 k}\right)}$$

$$\frac{n}{N} = \frac{\left(e^{-\mu B/T_0 k}\right)}{\left(e^{-\mu B/T_0 k} + e^{+\mu B/T_0 k}\right)}$$

3.4 The magnetic moment of nuclei is on the order of $10^{-26}\,Am^2$. Estimate the magnetic field required at 0.01 K to produce appreciable alignment of such nuclei.

at low T: $\mathcal{M} = N\mu$ here $kT \ll \mu B$

try $\mu B \sim kT$

$$B \sim \frac{kT}{\mu} = \frac{1.38 \cdot 10^{-23}\,J/K\ 0.01\,K}{10^{-26}\,A\,m^2}$$

$$B \sim 13.8 \left(\frac{N}{A\,m}\right) = 13.8\ \frac{N\,s}{C\,m} = 13.8\ T$$

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KK 3.1 Free Energy of a two state system.

a) Find an expression for the free energy as a function of τ of a system with two states, one at $\emptyset$ and one at ε.

$$F \equiv U - \tau\sigma$$

n = number of particles at energy ε

N = total number of particles

$$\Omega(n) = \frac{N!}{n!(N-n)!} \qquad U = (n\varepsilon + (N-n)\emptyset) = n\varepsilon$$

$$\sigma = k \ln \Omega(n) = k \ln \frac{N!}{n!(N-n)!} =$$

$$= k\{(N\ln N - \cancel{N}) - (n\ln n - \cancel{n}) - ((N-n)\ln(N-n) - \cancel{(N-n)})\}$$

$$= k\{N\ln N - n\ln n - (N-n)\ln(N-n)\}$$

$$F = U - \tau\sigma$$

$$F = n\varepsilon - \tau k\{N\ln N - n\ln n - (N-n)\ln(N-n)\}$$

$$n = \frac{N}{e^{\varepsilon/k\tau}+1} \quad \text{from } \frac{\partial\sigma}{\partial n} = k[-\ln n + \ln(N-n)] \Rightarrow \frac{1}{\tau} = \frac{k}{\varepsilon}\ln\left(\frac{N-n}{n}\right)$$

$$F = n\varepsilon - \tau k\{N\ln N + n\ln(1/n) - (N-n)\ln(N-n)\}$$

$$n \ln \frac{1}{n} = n \ln \frac{(e^{\varepsilon/k\tau}+1)}{N} = n \ln(e^{\varepsilon/k\tau}+1) - n \ln N$$

$$\ln(N-n) = \ln\left(N\left(1 - \frac{1}{e^{\varepsilon/k\tau}+1}\right)\right)$$

$$= \ln N + \ln\left(\frac{e^{\varepsilon/k\tau}+1-1}{e^{\varepsilon/k\tau}+1}\right)$$

$$= \ln N + \underbrace{\ln e^{\varepsilon/k\tau}}_{\varepsilon/k\tau} - \ln(e^{\varepsilon/k\tau}+1)$$

$$n \ln\left(\frac{1}{n}\right) - (N-n)\ln(N-n)$$

$$= \cancel{n \ln(e^{\varepsilon/k\tau}+1)} - \cancel{n \ln N} - N \ln N - N\frac{\varepsilon}{k\tau} + N \ln(e^{\varepsilon/k\tau}+1)$$

$$+ \cancel{n \ln N} + n\varepsilon/k\tau - \cancel{n \ln(e^{\varepsilon/k\tau}+1)}$$

$$= -N \ln N - N\frac{\varepsilon}{k\tau} + n\frac{\varepsilon}{k\tau} + N \ln(e^{\varepsilon/k\tau}+1)$$

$$\left\{N \ln N + n \ln\left(\frac{1}{n}\right) - (N-n)\ln(N-n)\right\}$$

$$= \cancel{N \ln N} - \cancel{N \ln N} - (N-n)\frac{\varepsilon}{k\tau} + N \ln(e^{\varepsilon/k\tau}+1)$$

$$F = n\varepsilon - \tau k\left\{N \ln N + n \ln\left(\frac{1}{n}\right) - (N-n)\ln(N-n)\right\}$$

$$F = n\varepsilon - \tau k\left\{-(N-n)\frac{\varepsilon}{k\tau} + N \ln(e^{\varepsilon/k\tau}+1)\right\}$$

$$F = \cancel{n\varepsilon} + N\varepsilon \frac{\cancel{\tau k}}{\cancel{k\tau}} - \cancel{n\varepsilon} \frac{\cancel{\tau k}}{\cancel{k\tau}} - N\tau k \ln(^{\varepsilon/k\tau} + 1)$$

$$\boxed{F = N\varepsilon - N\tau k \ln(e^{\varepsilon/k\tau} + 1)}$$

b) From the free energy, find expressions for the energy and entropy of the system.

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = Nk \ln(e^{\varepsilon/k\tau} + 1) - \frac{N\tau k \left(\frac{-\varepsilon}{k\tau^2}\right)}{(e^{\varepsilon/k\tau} + 1)}$$

$$\sigma = Nk \ln(e^{\varepsilon/k\tau} + 1) + N\left(\frac{\varepsilon}{\tau}\right)(e^{\varepsilon/k\tau} + 1)^{-1}$$

$$U = F + \tau\sigma$$

$$U = N\varepsilon - \cancel{N\tau k \ln(^{\varepsilon/k\tau} + 1)} + \cancel{N\tau k \ln(e^{\varepsilon/k\tau} + 1)}$$

$$+ N\varepsilon (e^{\varepsilon/k\tau} + 1)^{-1}$$

$$U = N\varepsilon \left[1 - \frac{1}{e^{\varepsilon/k\tau} + 1}\right] = \frac{N\varepsilon\,(e^{\varepsilon/k\tau})}{(e^{\varepsilon/k\tau} + 1)}$$

KK 3.3 Free energy of a harmonic oscillator.

A 1D harmonic oscillator has an infinite series of equally spaced energy states, with $\varepsilon_s = s\hbar\omega$, where s is a positive integer or zero, and ω is the classical frequency of the oscillator. We have chosen the zero of energy at the state $s=0$.

a) Show that for a harmonic oscillator the free energy is

$$F = \tau \ln\left[1 - e^{-\hbar\omega/\tau}\right]$$

(Note: at $\tau >> \hbar\omega$, can expand to obtain $F \sim \tau \ln\left(\frac{\hbar\omega}{\tau}\right)$)

$F \equiv U - \tau\sigma$

start with the partition function

$$Z = \sum_{E_r} g(E_r) e^{-\beta E_r} = \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau} = \sum_{s=0}^{\infty} \left(e^{-\hbar\omega/\tau}\right)^s = \frac{1}{1-e^{-\hbar\omega/\tau}}$$

$$F = -\tau \ln Z = -\tau \ln\left(1-e^{-\hbar\omega/\tau}\right)^{-1} = \tau \ln\left(1-e^{-\hbar\omega/\tau}\right)$$

b) From 87 show that $\sigma = \frac{\hbar\omega/\tau}{e^{(\hbar\omega/\tau)}-1} - \ln(1-e^{(-\hbar\omega/\tau)})$

from results of problem 2.3, $U = \frac{N\hbar\omega}{e^{(\hbar\omega/\tau)}-1}$ with $N=1$

$$\sigma = \frac{1}{\tau}(U-F) = \frac{1}{\tau}\left[\frac{\hbar\omega}{\exp(\hbar\omega/\tau)-1} - \tau\ln(1-\exp(-\hbar\omega/\tau))\right]$$

$$\sigma = \frac{\hbar\omega/\tau}{\exp(\hbar\omega/\tau)-1} - \ln(1-\exp(-\hbar\omega/\tau))$$

7. Zipper Problem. A zipper has N links; each link has a state in which it is closed with energy ϕ and a state in which it is open with energy ε. We require that the zipper can only unzip from the left end, and that the link numbers s can only open if all links to the left $(1, 2, \dots, s-1)$ are already open.

a) Show that the partition function can be summed in the form $Z = (1-\exp[-(N+1)\varepsilon/\tau])/(1-\exp(-\varepsilon/\tau))$

n = number opened
N = number links
ε = energy open $\qquad \phi$ = energy closed.
$U = n\varepsilon \qquad n = (U/\varepsilon)$
$g(N,U) = 1$ only one way to have energy U

$$Z = \sum_s e^{-\varepsilon_s/\tau} = \sum_{n=0}^{N} e^{-n\varepsilon/\tau} = \sum_{n=0}^{N} (e^{-\varepsilon/\tau})^n = 1 + \sum_{n=1}^{N} (e^{-\varepsilon/\tau})^n$$

use $\sum_{k=1}^{m} s^k = s\left(\frac{s^m - 1}{s-1}\right)$

$$Z = \frac{(e^{-\varepsilon/\tau})((e^{-\varepsilon/\tau})^N - 1)}{(e^{-\varepsilon/\tau} - 1)} + 1$$

$$Z = \frac{e^{-(N+1)\varepsilon/\tau} - e^{-\varepsilon/\tau}}{e^{-\varepsilon/\tau} - 1} + \frac{e^{-\varepsilon/\tau} - 1}{e^{-\varepsilon/\tau} - 1}.$$

$$Z = \frac{e^{-(N+1)\varepsilon/\tau} - 1}{e^{-\varepsilon/\tau} - 1}$$

$$\boxed{Z = \frac{1 - e^{-(N+1)\varepsilon/\tau}}{1 - e^{-\varepsilon/\tau}}}$$

b) In the limit $\varepsilon >> \tau$, find the average number of open links. n/N n

$$\langle n \rangle = \frac{1}{\varepsilon} \sum_r p_r(\varepsilon_r)\, \varepsilon_r = \sum_r r p_r \; ; \; n = \frac{U}{\varepsilon} \Rightarrow \langle n \rangle = \frac{\langle \varepsilon \rangle}{\varepsilon}$$

$$\langle n \rangle = \frac{kT^2}{\varepsilon} \frac{\partial}{\partial T} \ln Z = \frac{kT^2}{\varepsilon} \frac{1}{Z} \frac{\partial Z}{\partial T}$$

1

$$\frac{\partial Z}{\partial T} = \frac{\partial}{\partial T} \sum_{n=0}^{N} e^{-n\varepsilon/kT} = \sum_{n=0}^{N} \frac{n\varepsilon}{kT^2} e^{-n\varepsilon/kT}$$

$$\langle n \rangle = \frac{\cancel{kT^2}}{\varepsilon} \frac{\sum^{\infty} n\varepsilon/\cancel{kT^2}\, e^{-n\varepsilon/kT}}{\cancel{\sum_{n=0}^{N} e^{-n\varepsilon/kT}}\ 1} = 1 e^{-\varepsilon/kT} + 2\cancel{(e^{-\varepsilon/kT})^2}^{\,0} + 3\cancel{(e^{-\varepsilon/kT})^3}^{\,0} + \dots$$

$$\boxed{\langle n \rangle \sim e^{-\varepsilon/k\tau}}$$