PS7

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1 Interacting magnetic system

(a) Magnetic free energy of the system is defined as
$d\mathcal{F} = -SdT - PdV + \mu dN - MdH$
where
$M = -(\frac{\partial \mathcal{F}}{\partial H})_{TVN} = aN\frac{H}{1+bnH}\frac{1}{T}$
$C_V = T(\frac{\partial S}{\partial T})_{VN,H=0} = \text{constant}$
$\kappa_T = -\frac{1}{V}(\frac{\partial V}{\partial P})_{TN,H=0} = \text{constant}$
Therefore
$\mathcal{F} = aN(-\frac{H}{bn} + \frac{1}{(bn)^2}\ln(1+bnH))\frac{1}{T} + f(TVN, H=0)$
$S = C_V \ln(T/T_0) + g(N, T_0, V_0)$
$P = -\frac{1}{\kappa_T}\ln(V/V_0) - h(N, T_0, V_0)$
On the other hand, $f(TVN, H=0)$ satisfies
$df = -SdT - PdV + \mu dN = -(C_V \ln(T/T_0) + g(N, T_0, V_0))dT + (\frac{1}{\kappa_T}\ln(V/V_0) + h(N, T_0, V_0))dV + \mu dN$
and
$(\frac{\partial \mu}{\partial T})_{NV} = -(\frac{\partial S}{\partial N})_{TV} = -\frac{dg}{dN}$
$(\frac{\partial \mu}{\partial V})_{NT} = -(\frac{\partial P}{\partial N})_{VT} = \frac{dh}{dN}$
or
$\mu = -\frac{dg}{dN}(T-T_0) + \frac{dh}{dN}(V-V_0) + l(N, T_0, V_0)$
Then
$f = -C_V T(\ln(T/T_0) - 1) - C_V T_0 - g(N, T_0, V_0)(T-T_0) +$
$\frac{1}{\kappa_T}V(\ln(V/V_0) - 1) + \frac{1}{\kappa_T}V_0 + h(N, T_0, V_0)(V-V_0) -$
$(g(N, T_0, V_0) - g(N_0, T_0, V_0))(T-T_0) + (h(N, T_0, V_0) - h(N_0, T_0, V_0))(V-V_0) + l(N, T_0, V_0) - l(N_0, T_0, V_0)$
$f = -C_V T(\ln(T/T_0) - 1) - (2g(N, T_0, V_0) - g(N_0, T_0, V_0))(T-T_0) + \frac{1}{\kappa_T}V(\ln(V/V_0) - 1) + (2h(N, T_0, V_0) - h(N_0, T_0, V_0))(V-V_0) + l(N, T_0, V_0) - l(N_0, T_0, V_0) - C_V T_0 + \frac{1}{\kappa_T}V_0$
Omit a constant offset
$f = -C_V T\ln(T) - g(N)T + \frac{1}{\kappa_T}V\ln(V) + h(N)V + l(N)$
where $g(\cdot), h(\cdot), l(\cdot)$ are new functions of N different from the above
Therefore
$\mathcal{F} = aN(-\frac{H}{bn} + \frac{1}{(bn)^2}\ln(1+bnH))\frac{1}{T} - C_V T\ln(T) - g(N)T + \frac{1}{\kappa_T}V\ln(V) + h(N)V + l(N)$

(b) Define magnetic Gibbs free energy as $\mathcal{G} = \mathcal{F} + PV$
$d\mathcal{G} = -SdT + VdP + \mu dN - MdH$
Then
$(\frac{\partial V}{\partial H})_{PTN} = -(\frac{\partial M}{\partial P})_{HTN} = -\frac{(\frac{\partial M}{\partial n})_{HTN}}{(\frac{\partial P}{\partial n})_{HTN}}$
where
$(\frac{\partial M}{\partial n})_{HTN} = -aN\frac{bH^2}{(1+bnH)^2}\frac{1}{T}$
$(\frac{\partial P}{\partial n})_{HTN} = -(\frac{\partial^2 \mathcal{F}}{\partial n \partial V})_{HTN} = \frac{n^2}{N}(\frac{\partial^2 \mathcal{F}}{\partial n^2})_{HTN} + \frac{2n}{N}\frac{\partial \mathcal{F}}{\partial n}$
where
$(\frac{\partial \mathcal{F}}{\partial n})_{HTN} = aN(\frac{H}{bn^2} - \frac{2}{b^2n^3}\ln(1+bnH) + \frac{1}{b^2n^2}\frac{bH}{1+bnH})\frac{1}{T} + \frac{N}{\kappa_T}\frac{1}{n^2}(\ln(n) - 1) - h(N)\frac{N}{n^3}$
$(\frac{\partial^2 \mathcal{F}}{\partial n^2})_{HTN} = aN(-\frac{2H}{bn^3} - \frac{6}{b^2n^4}\frac{bH}{1+bnH} - \frac{2}{b^2n^3}\ln(1+bnH) - \frac{2}{b^2n^3}\frac{bH}{1+bnH} - \frac{1}{b^2n^2}\frac{b^2H^2}{(1+bnH)^2})\frac{1}{T} - \frac{N}{\kappa_T}\frac{2}{n^3}(\ln(n) - 1) + \frac{N}{\kappa_T}\frac{1}{n^3} - 3h(N)\frac{N}{n^4}$

$(\frac{\partial P}{\partial n})_{HTN} = a(\frac{2H}{bn} - \frac{4}{b^2n^2}\ln(1+bnH) + \frac{2}{b^2n}\frac{bH}{1+bnH})\frac{1}{T} + \frac{1}{\kappa_T}\frac{2}{n}(\ln(n)-1) - h(N)\frac{2}{n^2} + a(-\frac{2H}{bn} - \frac{6}{b^2n^2}\frac{bH}{1+bnH} - \frac{2}{b^2n}\ln(1+bnH) - \frac{2}{b^2n}\frac{bH}{1+bnH} - \frac{1}{b^2}\frac{b^2H^2}{(1+bnH)^2})\frac{1}{T} - \frac{1}{\kappa_T}\frac{2}{n}(\ln(n)-1) + \frac{1}{\kappa_T}\frac{1}{n} - 3h(N)\frac{1}{n^2}$
$= a(-\frac{4}{b^2n^2}\ln(1+bnH) - \frac{6}{b^2n^2}\frac{bH}{1+bnH} - \frac{2}{b^2n}\ln(1+bnH) - \frac{1}{b^2}\frac{b^2H^2}{(1+bnH)^2})\frac{1}{T} + \frac{1}{\kappa_T}\frac{1}{n} - h(N)\frac{2}{n^2} - 3h(N)\frac{1}{n^2}$
Magnetostriction coefficient
$\epsilon = \frac{1}{V}(\frac{\partial V}{\partial H})_{PTN} = \frac{a\frac{bnH^2}{(1+bnH)^2}\frac{1}{T}}{a(-\frac{4}{b^2n^2}\ln(1+bnH) - \frac{6}{b^2n^2}\frac{bH}{1+bnH} - \frac{2}{b^2n}\ln(1+bnH) - \frac{1}{b^2}\frac{b^2H^2}{(1+bnH)^2})\frac{1}{T} + \frac{1}{\kappa_T}\frac{1}{n} - 5h(N)\frac{1}{n^2}}$
$\lim_{H\to 0}\epsilon = \frac{a\frac{bnH^2}{(1+bnH)^2}\frac{1}{T}}{a(-\frac{4}{b^2n^2}(bnH) - \frac{6}{b^2n^2}\frac{bH}{1+bnH} - \frac{2}{b^2n}(bnH) - \frac{1}{b^2}\frac{b^2H^2}{(1+bnH)^2})\frac{1}{T} + \frac{1}{\kappa_T}\frac{1}{n} - 5h(N)\frac{1}{n^2}} = \frac{abn^3\frac{1}{T}}{\frac{1}{\kappa_T}n - 5h(N)}H^2 + o(H^2)$
Hope this is correct…

(c) Since $\mathcal{F} = U^{int} - HM - TS = aN(-\frac{H}{bn} + \frac{1}{(bn)^2}\ln(1+bnH))\frac{1}{T} - C_V T\ln(T) - g(N)T + \frac{1}{\kappa_T}V\ln(V) + h(N)V + l(N)$
Plug in S and M, we have
$U^{int} = aN(-\frac{H}{bn} + \frac{H^2}{1+bnH} + \frac{1}{(bn)^2}\ln(1+bnH))\frac{1}{T} - g^{'}(N)T + \frac{1}{\kappa_T}V\ln(V) + h(N)V + l(N)$
Then
$H^{int} = -(\frac{\partial U^{int}}{\partial M})_{NVT} = -\frac{(\frac{\partial U^{int}}{\partial H})_{NVT}}{(\frac{\partial M}{\partial H})_{NVT}} = \frac{-\frac{1}{bn} + \frac{2H}{1+bnH} + \frac{1}{(bn)^2}\frac{bn}{1+bnH}}{\frac{1}{1+bnH} + \frac{bnH}{(1+bnH)^2}} = \frac{-\frac{1}{bn} + \frac{2H}{1+bnH} + \frac{1}{(bn)^2}\frac{bn}{1+bnH}}{\frac{1}{1+bnH} + \frac{bnH}{(1+bnH)^2}} = \frac{1+bnH}{1+2bnH}H$
If $bnH \in (-\infty, -1)$ or $(-\frac{1}{2}, \infty)$, ferromagnetic
If $bnH \in (-1, -\frac{1}{2})$, antiferromagnetic
If $bnH = -1$, $H^{int} = 0$
If $bnH = -\frac{1}{2}$, H^{int} will diverge

2 Debye theory of heat capacity in solid

(a) The degrees of freedom of all atoms in the lattice is $f = 3N - 6$, where the 3 translational and 3 rotational degrees of freedom of the mass center are subtracted.
Therefore
$3\frac{V}{8\pi^3}\int_0^{k_{max}} 4\pi k^2 dk = \frac{V}{2\pi^2}k_{max}^3 = \frac{\pi V}{2}\frac{1}{a_{eff}^3} = 3N - 6$
$a_{eff} = (\frac{\pi V}{6N-12})^{\frac{1}{3}} \simeq (\frac{\pi V}{6N})^{\frac{1}{3}} = (\frac{\pi}{6})^{\frac{1}{3}}a$

(b) Given N, V, T, the partition function is $Z = \sum_{n=0}^{\infty} e^{-\beta n\hbar ck} = \frac{1}{1-e^{-\beta\hbar ck}},\ \beta = \frac{1}{T}$
Therefore $n_k = \sum_{n=0}^{\infty}\frac{ne^{-\beta n\hbar ck}}{Z} = -\frac{1}{\hbar ck}\frac{\partial}{\partial\beta}\ln Z = \frac{1}{e^{\beta\hbar ck}-1}$
Then the energy density of phonons are
$\rho_{NV}(T) = \int 3\frac{V}{8\pi^3}\hbar ck n_k dk = \int 3\frac{V}{8\pi^3}\frac{\hbar ck}{e^{\beta\hbar ck}-1}dk = \int_0^{k_{max}} 3\frac{V}{8\pi^3}\frac{4\pi\hbar ck^3}{e^{\beta\hbar ck}-1}dk = \int_0^{k_{max}}\frac{3V}{2\pi^2}\frac{\hbar ck^3}{e^{\beta\hbar ck}-1}dk$
If $T \ll \hbar c\frac{\pi}{a}$, or $\beta\hbar ck \gg 1$ for all k, $\rho_{NV}(T) \simeq \int_0^{k_{max}}\frac{3V}{2\pi^2}\hbar ck^3 e^{-\beta\hbar ck}dk$
Define $\beta\hbar ck = t \gg 1$, $\rho_{NV}(T) = \int_0^{t_{max}}\frac{3V}{2\pi^2}\frac{1}{\beta^4}\frac{1}{(\hbar c)^3}t^3e^{-t}dt = \frac{3V}{2\pi^2}\frac{1}{\beta^4}\frac{1}{(\hbar c)^3}\{e^{-t_{max}}(-t_{max}^3 - 3t_{max}^2 - 6t_{max} - 6) + 6\} \simeq \frac{9V}{\pi^2}\frac{1}{\beta^4}\frac{1}{(\hbar c)^3} = \frac{9V}{\pi^2}T^4\frac{1}{(\hbar c)^3}$
where $t_{max} = \beta\hbar ck_{max} = \frac{\beta\hbar c\pi}{(\frac{\pi}{6})^{\frac{1}{3}}a}$
If $T \gg \hbar c\frac{\pi}{a}$, or $\beta\hbar ck \ll 1$ for all k, $\rho_{NV}(T) \simeq \int_0^{k_{max}}\frac{3V}{2\pi^2}\frac{1}{\beta}k^2dk = \frac{V}{2\pi^2}\frac{1}{\beta}k_{max}^3 = \frac{3N}{\beta} = 3NT$
Or $U = \rho_{NV}(T)V = 3NVT$

(c) Heat capacity
$C_V = (\frac{\partial U}{\partial T})_{V,N} = V\frac{d\rho_{NV}(T)}{dT}$
If $T \ll \hbar c\frac{\pi}{a}$, or $\beta\hbar ck \gg 1$ for all k, $C_V = \frac{36V^2}{\pi^2}T^3\frac{1}{(\hbar c)^3}$
If $T \gg \hbar c\frac{\pi}{a}$, or $\beta\hbar ck \ll 1$ for all k, $C_V = 3N$

(d) Since $(\frac{\partial U}{\partial V})_{T,N} = (\frac{\partial U}{\partial V})_{S,N} + (\frac{\partial U}{\partial S})_{V,N}(\frac{\partial S}{\partial V})_{T,N} = -P + T(\frac{\partial P}{\partial T})_{V,N} = \rho_{NV}(T)$
Or $\frac{\partial}{\partial T}(\frac{P}{T})_{V,N} = \frac{\rho_{NV}(T)}{T^2}$
Then
If $T \ll \hbar c\frac{\pi}{a}$, or $\beta\hbar ck \gg 1$ for all k, $P = \frac{3V}{\pi^2}T^4\frac{1}{(\hbar c)^3}$

If $T \gg \hbar c \frac{\pi}{a}$, or $\beta \hbar c k \ll 1$ for all k, $P = T\{3N\ln(T/T_0) + \frac{P_0}{T_0}\}$. Let $T_0 = 1$, we have $P = T\{3N\ln(T) + P_0\}$ The latter result is very strange...