Statistical Mechanics - Class Exercise 6

May 17, 2022

Exercise 5024 - Pressure of Lenard Jones gas

A gas of N particles is confined in a box of volume V at temprature of T. The two-body interaction between the particles is given by the Lenard Jones expression:

$$u(r) = \frac{a}{r^{12}} - \frac{b}{r^6}$$

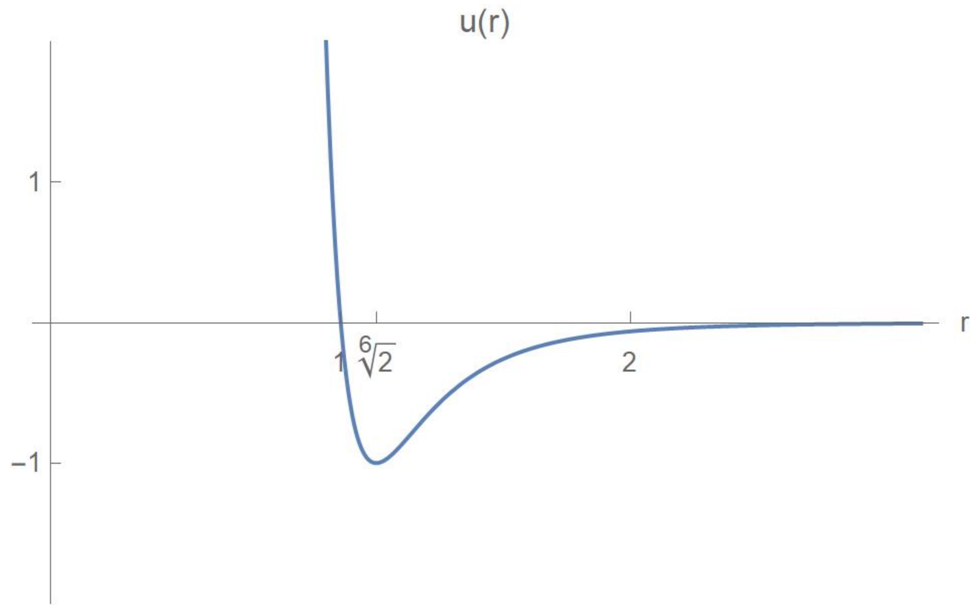
Note that this interaction is characterized by a length scale r_0 and an energy scale ϵ_0 that correspond to the position and the depth of the potential.

1. Find an expression for the pressure via the Virial theorem, assuming that the moments $\langle r^n \rangle_T$ are known.
2. Using the Virial expansion, find an explicit expression for the pressure assuming low temperatures.
3. Using the Virial expansion, find an explicit expression for the pressure assuming high temperatures.
4. Comparing your answers to items (1) and (3) deduce explicit expressions for the $n = -6$ and for the $n = -12$ moments. Express your result in terms of (V, r_0, ϵ_0, T).

Answer

The Lenard Jones potential is:

$$u(r) = \frac{a}{r^{12}} - \frac{b}{r^6}$$



The length scale is r_0, so

$$u(r_0) = \frac{a}{r_0^{12}} - \frac{b}{r_0^6} = 0$$

$$\rightarrow r_0 = \left(\frac{a}{b}\right)^{\frac{1}{6}}$$

the minimum is

$$u'(r) = -12\frac{a}{r^{13}} + 6\frac{b}{r^7} = 0$$

$$\rightarrow r_m = \left(\frac{2a}{b}\right)^{\frac{1}{6}} = 2^{\frac{1}{6}} r_0$$

In this point

$$u(r_m) = \frac{a}{r_m^{12}} - \frac{b}{r_m^6} = \frac{b^2}{4a} - \frac{b^2}{2a} = -\frac{b^2}{4a} = -\epsilon_0$$

so we get

$$u(r) = \left(\frac{b^2}{a}\frac{r_0^{12}}{r^{12}} - \frac{b^2}{a}\frac{r_0^6}{r^6}\right) = 4\epsilon_0\left(\frac{r_0^{12}}{r^{12}} - \frac{r_0^6}{r^6}\right)$$

$$u''(r_m) = 4\epsilon_0\left(12\cdot 13\frac{r_0^{12}}{r_m^{14}} - 6\cdot 7\frac{r_0^6}{r_m^8}\right) = 4\epsilon_0\left(12\cdot 13\frac{1}{2^{\frac{14}{6}}r_0^2} - 6\cdot 7\frac{1}{2^{\frac{8}{6}}r_0^2}\right) = 72\frac{\epsilon_0}{2^{\frac{1}{3}}r_0^2} = 72\frac{\epsilon_0}{r_m^2}$$

1. The pressure is given by the Virial theorem:

$$P = \frac{1}{V}\left[NT - \frac{1}{3}\langle r\cdot\frac{\partial U}{\partial r}\rangle\right]$$

Where

$$U = \sum_{\langle i,j \rangle} u\left(\left|\vec{r}_i - \vec{r}_j\right|\right)$$

$$r \cdot \frac{\partial u}{\partial r} = -24\epsilon_0 \left(2\frac{r_0^{12}}{r^{12}} - \frac{r_0^6}{r^6}\right)$$

The sum is over all the interaction $\frac{N(N-1)}{2} \approx \frac{N^2}{2}$, so we get

$$P = \frac{NT}{V}\left[1 + 4\frac{\epsilon_0}{T} N r_0^6 \left(2r_0^6 \left\langle r^{-12}\right\rangle - \left\langle r^{-6}\right\rangle\right)\right]$$

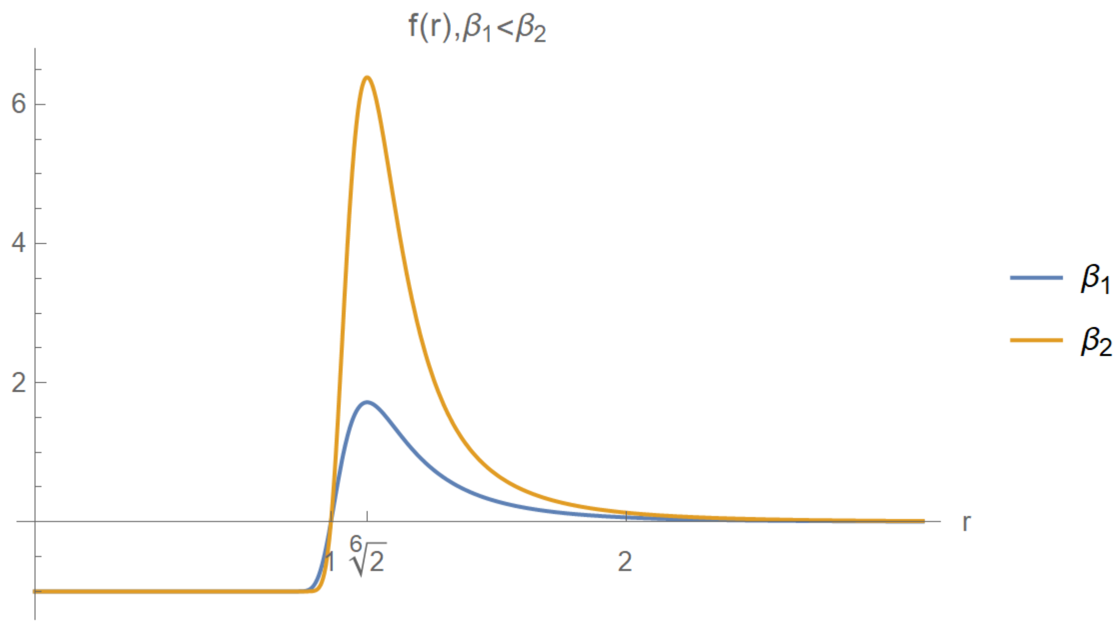
2. The Virial expansion for the pressure is:

$$P = \frac{NT}{V}\left[1 + a_2\left(\frac{N}{V}\right) + a_3\left(\frac{N}{V}\right)^2 + ...\right]$$

The second Virial coefficient is:

$$a_2 = -\frac{1}{2}\int \left(e^{-\beta u(r)} - 1\right) d^3r = -\frac{1}{2}\int f\left(r\right) d^3r$$

For low temperatures ($\beta\epsilon_0 \gg 1$) we can take the saddle point approximation around the minimum point of $u(r)$



$$a_2 \approx -\frac{1}{2}\int e^{-\beta\left[u(r_m) + \frac{1}{2}u''(r_m)(r-r_m)^2\right]} d^3r = -2\pi e^{-\beta u(r_m)} \int_0^\infty e^{-\frac{1}{2}\beta u''(r_m)(r-r_m)^2} r^2 dr$$

We need to solve

$$\int_0^\infty e^{-\frac{1}{2}\beta u''(r_m)(r-r_m)^2} r^2 dr = \int_{-r_m}^\infty e^{-\frac{1}{2}\beta u'' r^2}\left(r^2 + 2rr_m + r_m^2\right) dr =$$

For the the first integral we use $\left(e^{-\frac{1}{2}\beta u'' r^2}\right)' = -\beta u'' r e^{-\frac{1}{2}\beta u'' r^2}$, so with integration by parts we get

$$\begin{aligned}\frac{1}{-\beta u''}\int_{-r_m}^\infty \left(-\beta u'' e^{-\frac{1}{2}\beta u'' r^2} r\right) r dr =& \frac{1}{-\beta u''} e^{-\frac{1}{2}\beta u'' r^2} r|_{-r_m}^\infty - \frac{1}{-\beta u''}\int_{-r_m}^\infty e^{-\frac{1}{2}\beta u'' r^2} dr \\ =& -\frac{1}{72\beta\epsilon_0} e^{-36\beta\epsilon_0} r_m^3 + \frac{1}{\beta u''}\int_{-r_m}^\infty e^{-\frac{1}{2}\beta u'' r^2} dr\end{aligned}$$

The second part

$$\begin{aligned}\int_{-r_m}^\infty e^{-\frac{1}{2}\beta u'' r^2}(2rr_m)\, dr =& 2r_m\left(\int_0^\infty e^{-\frac{1}{2}\beta u'' r^2} r dr - \int_0^{r_m} e^{-\frac{1}{2}\beta u'' r^2} r dr\right) \\ =& r_m\left(\int_0^\infty e^{-\frac{1}{2}\beta u'' z} dz - \int_0^{r_m^2} e^{-\frac{1}{2}\beta u'' z} dz\right) = r_m\left(\frac{1}{\frac{1}{2}\beta u''} - \frac{e^{-\frac{1}{2}\beta u'' r_m^2} - 1}{-\frac{1}{2}\beta u''}\right) \\ =& 2r_m^3 \frac{e^{-36\beta\epsilon_0}}{72\beta\epsilon_0}\end{aligned}$$

we stay with

$$\begin{aligned}\left(r_m^2 + \frac{1}{\beta u''}\right)\int_{-r_m}^\infty e^{-\frac{1}{2}\beta u'' r^2} dr =& \left(r_m^2 + \frac{1}{\beta u''}\right)\left(\int_0^\infty e^{-\frac{1}{2}\beta u'' r^2} dr + \int_0^{r_m} e^{-\frac{1}{2}\beta u'' r^2} dr\right) \\ =& \left(r_m^2 + \frac{1}{\beta u''}\right)\left(\sqrt{\frac{\pi}{\beta u''}} + \frac{1}{\sqrt{\frac{1}{2}\beta u''}}\int_0^{\sqrt{\frac{1}{2}\beta u''} r_m} e^{-t^2} dt\right) \\ =& r_m^3\left(1 + \frac{1}{72\beta\epsilon_0}\right)\frac{\sqrt{\pi}}{12}\frac{1}{\sqrt{\beta\epsilon_0}}\left(1 + \operatorname{erf}\left(6\sqrt{\beta\epsilon_0}\right)\right)\end{aligned}$$

($\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2} dt$)
All together we get

$$\begin{aligned}a_2 \approx& -2\pi e^{-\beta u(r_m)}\int_0^\infty e^{-\frac{1}{2}\beta u''(r_m)(r-r_m)^2} r^2 dr \\ =& -2\pi e^{\frac{\epsilon_0}{T}} r_m^3\left[\frac{\sqrt{\pi}}{12}\left(\frac{1}{72}\left(\frac{T}{\epsilon_0}\right)^{\frac{3}{2}} + \left(\frac{T}{\epsilon_0}\right)^{\frac{1}{2}}\right)\left(\operatorname{erf}\left(6\sqrt{\frac{\epsilon_0}{T}}\right) + 1\right) + \frac{T}{\epsilon_0}\frac{e^{-\frac{36\epsilon_0}{T}}}{72}\right] \\ \approx& -\frac{\pi^{\frac{3}{2}}}{6} e^{\frac{\epsilon_0}{T}} r_m^3\left[\frac{1}{72}\left(\frac{T}{\epsilon_0}\right)^{\frac{3}{2}} + \left(\frac{T}{\epsilon_0}\right)^{\frac{1}{2}}\right]\left(\operatorname{erf}\left(6\sqrt{\frac{\epsilon_0}{T}}\right) + 1\right)\end{aligned}$$

For $\frac{\epsilon_0}{T} \gg 1$

$$\operatorname{erf}\left(6\sqrt{\frac{\epsilon_0}{T}}\right) \approx 1$$

$$a_2 \approx -e^{\frac{\epsilon_0}{T}} \frac{r_0^3}{3} \left(2\pi^3\right)^{\frac{1}{2}} \left(\frac{T}{\epsilon_0}\right)^{\frac{1}{2}}$$

$$P = \frac{NT}{V} \left[1 - e^{\frac{\epsilon_0}{T}} \frac{r_0^3}{3} \left(2\pi^3\right)^{\frac{1}{2}} \left(\frac{T}{\epsilon_0}\right)^{\frac{1}{2}} \left(\frac{N}{V}\right)\right]$$

3. For $(\beta\epsilon_0 \ll 1)$

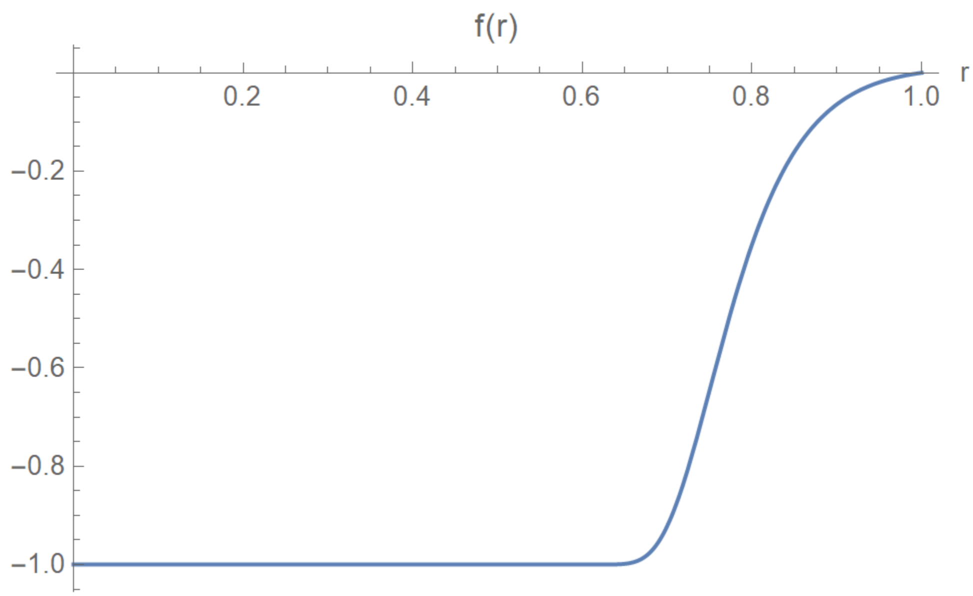
$$f(r) = e^{-\beta u(r)} - 1 \approx -\beta u(r)$$

$$a_2 = \frac{\beta}{2} \int u(r)\, d^3r = 8\pi\beta\epsilon_0 \int_0^\infty \left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6\right] r^2 dr$$

But this integral does not converge for $r \to 0$, so we divide it to two parts $0 < r < r_0, \;\; r_0 < r < \infty$

$$a_{2>} = 8\pi\beta\epsilon_0 \int_{r_0}^\infty \left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6\right] r^2 dr = -\frac{16\pi}{9} \frac{\epsilon_0}{T} r_0^3$$

For the second range we can see that in this range $f(0) = -1$ and $f(r_0) = 0$,So we can approximate $f(r)$ as a step function with the width $\tilde{r}$, when for $\tilde{r}$, $e^{-\beta u(\tilde{r})} = e^{-1}$



$$\beta u(\tilde{r}) = 4\frac{\epsilon_0}{T} \left[\left(\frac{r_0}{\tilde{r}}\right)^{12} - \left(\frac{r_0}{\tilde{r}}\right)^6\right] = 1$$

$$\tilde{r}^{12} + 4\frac{\epsilon_0}{T} r_0^6 \tilde{r}^6 - 4\frac{\epsilon_0}{T} r_0^{12} = 0$$

$$\tilde{r}^6 = -2\frac{\epsilon_0}{T} r_0^6 \pm 2\sqrt{\frac{\epsilon_0}{T}} r_0^6 \sqrt{\left(\frac{\epsilon_0}{T}\right) + 1} = -2\frac{\epsilon_0}{T} r_0^6 \pm 2r_0^6 \sqrt{\frac{\epsilon_0}{T}} \sqrt{1 + \left(\frac{\epsilon_0}{T}\right)} \approx 2r_0^6 \sqrt{\frac{\epsilon_0}{T}}$$

$$\tilde{r} \approx \left(\frac{4\epsilon_0}{T}\right)^{\frac{1}{12}} r_0$$

$$a_{2<} = -2\pi \int_0^{\tilde{r}} (-1)\, r^2 dr = \frac{2\pi}{3} \left(\frac{4\epsilon_0}{T} \right)^{\frac{1}{4}} r_0^3$$

So

$$a_2 = \frac{2\pi}{3} \left[\left(\frac{4\epsilon_0}{T} \right)^{\frac{1}{4}} - \frac{2}{3} \frac{4\epsilon_0}{T} \right] r_0^3$$

$$P = \frac{NT}{V} \left[1 + \frac{2\pi}{3} \left[\left(\frac{4\epsilon_0}{T} \right)^{\frac{1}{4}} - \frac{2}{3} \frac{4\epsilon_0}{T} \right] r_0^3 \left(\frac{N}{V} \right) \right]$$

4. We comperes

$$P = \frac{NT}{V} \left[1 + 4\frac{\epsilon_0}{T} N r_0^6 \left(2r_0^6 \left\langle r^{-12} \right\rangle - \left\langle r^{-6} \right\rangle \right) \right] = \frac{NT}{V} \left[1 + \frac{2\pi}{3} \left[\left(\frac{4\epsilon_0}{T} \right)^{\frac{1}{4}} - \frac{2}{3} \frac{4\epsilon_0}{T} \right] r_0^3 \left(\frac{N}{V} \right) \right]$$

$$8\frac{\epsilon_0}{T} N r_0^{12} \left\langle r^{-12} \right\rangle = \frac{2\pi}{3} \left(\frac{4\epsilon_0}{T} \right)^{\frac{1}{4}} r_0^3 \left(\frac{N}{V} \right)$$

$$\left\langle r^{-12} \right\rangle = \frac{\pi}{3V r_0^9} \left(\frac{4\epsilon_0}{T} \right)^{-\frac{3}{4}}$$

$$\left\langle r^{-6} \right\rangle = \frac{4\pi}{9V r_0^3}$$

Exercise 5963 - Stoner ferromagnetism

Consider Fermi gas of N spin 1/2 electrons, at temperature $T = 0$. Define N_+ and N_- as the number of "up" and "down" electrons respectively, such that $N = N_+ + N_-$. Due to the antisymmetry of the total wave function the energy of the system is $U = \alpha N_+ N_- / \mathsf{V}$, where V is the volume. Note that this interaction favors parallel spin states. Define the magnetization as $M = (N_+ - N_-)/\mathsf{V}$.

1. Write the total energy $E(M)$, including both the kinetic energy and the interaction, and expand up to 4th order in M.

2. Find the critical value α_c, such that for $\alpha > \alpha_c$ the electron gas can lower its total energy by spontaneously developing magnetization. This is known as the Stoner instability.

3. Explain the instability qualitatively, and sketch the behavior of the spontaneous magnetization versus α.

4. Repeat (1) at finite but low temperatures T, and find $\alpha_c(T)$ to second order in T.

Guidance: In the last item explain why the energy $E(M)$ should be replaced by the M-constrained "free energy" $F(M)$. Use know results [Patria] for the free energy of electrons at finite temperature.

Answer

1. the total energy

$$E_T = E_K + U$$

for E_k we need to find k_F

$$N_\pm = V\int_{k<k_F} \frac{d^3k}{(2\pi)^3} = \frac{V}{2\pi^2}\int_0^{k_F} k^2 dk = \frac{Vk_{F\pm}^3}{6\pi^2} \Rightarrow k_{F\pm} = \left(6\pi^2 n_\pm\right)^{1/3}$$

$$E_{K\pm} = V\int_{k_{F\pm}} \epsilon(k)\frac{d^3k}{(2\pi)^3} = V\int_0^{k_{F\pm}} \frac{k^2}{2m}4\pi k^2 \frac{dk}{(2\pi)^3} = \frac{V}{2m}\frac{k_{F\pm}^5}{10\pi^2}$$

So for $T = 0$ the kinetic energy is

$$E_K = \frac{V}{2m}\frac{3}{5}\left(6\pi^2\right)^{2/3}\left(n_+^{5/3} + n_-^{5/3}\right)$$

For $n_+ = n_- = \frac{n}{2}$

$$E_0 = \frac{V}{2m}\frac{6}{5}\left(6\pi^2\right)^{2/3}\left(\frac{n}{2}\right)^{5/3}$$

Now we evaluate $n_+ = \frac{n}{2} + \delta, n_- = \frac{n}{2} - \delta$ so $M = n_+ - n_- = 2\delta$ and expand up to 4th order in M

$$n_\pm^{5/3} = \left(\frac{n}{2}\right)^{\frac{5}{3}}\left(1 \pm \frac{M}{n}\right)^{\frac{5}{3}} \approx \left(\frac{n}{2}\right)^{\frac{5}{3}}\left[1 \pm \frac{5}{3}\frac{M}{n} + \frac{5}{9}\left(\frac{M}{n}\right)^2 \mp \frac{5}{81}\left(\frac{M}{n}\right)^3 + \frac{5}{243}\left(\frac{M}{n}\right)^4\right]$$

so

$$\left(n_+^{5/3} + n_-^{5/3}\right) = 2\left(\frac{n}{2}\right)^{\frac{5}{3}}\left[1 + \frac{5}{9}\left(\frac{M}{n}\right)^2 + \frac{5}{243}\left(\frac{M}{n}\right)^4\right]$$

$$E_K = E_0\left[1 + \frac{5}{9}\left(\frac{M}{n}\right)^2 + \frac{5}{243}\left(\frac{M}{n}\right)^4\right]$$

In the same way the interaction:

$$U = \alpha\frac{N_+N_-}{V} = \alpha V n_+ n_- = \alpha V\left(\frac{n}{2} + \frac{M}{2}\right)\left(\frac{n}{2} - \frac{M}{2}\right) = \alpha V\left(\frac{n}{2}\right)^2\left(1 + \frac{M}{n}\right)\left(1 - \frac{M}{n}\right)$$

$$= \alpha V\left(\frac{n}{2}\right)^2\left(1 - \left(\frac{M}{n}\right)^2\right)$$

notice that $0 \le \left(\frac{M}{n}\right)^2 \le 1$,we are in the limit $\frac{M}{n} \ll 1$.
And we get

$$\frac{E_T}{V} = \frac{E_0}{V} + \alpha\left(\frac{n}{2}\right)^2 + \left[\frac{5}{9}\frac{E_0}{V} - \alpha\left(\frac{n}{2}\right)^2\right]\left(\frac{M}{n}\right)^2 + \frac{5}{243}\frac{E_0}{V}\left(\frac{M}{n}\right)^4$$

2. To find the critical value α_c, we can see that the coefficient of M^4 is always positive but on the other hand for different values of α the coefficient of M^2 can change its sign. The critical value α_c is defined when the coefficient equals zero

$$\alpha_c = \frac{5}{9}\frac{E_0}{V}\left(\frac{n}{2}\right)^{-2} = \frac{1}{2m}\frac{2}{3}\left(6\pi^2\right)^{2/3}\left(\frac{n}{2}\right)^{-\frac{1}{3}}$$

we can see that for:

$$n_+ = n_- = \frac{n}{2} = \frac{k_F^3}{6\pi^2} = \frac{(2m\epsilon_F)^{\frac{3}{2}}}{6\pi^2}$$

$$\alpha_c = \frac{(2\pi)^2}{(2m)^{\frac{3}{2}}} (\epsilon_F)^{-\frac{1}{2}} = \frac{V}{g(\epsilon_F)}$$

3. To find the magnetization for minimum energy we need to derive the energy:

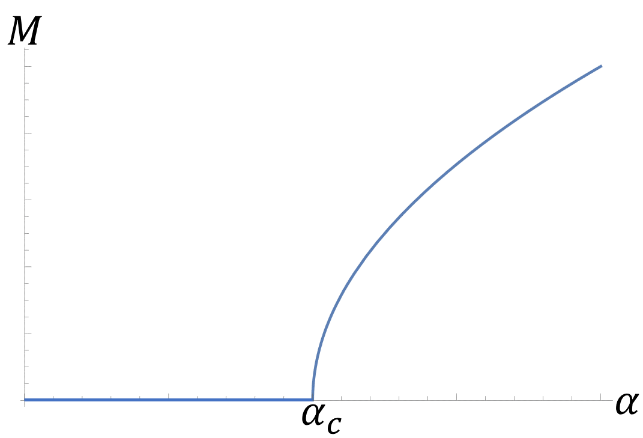
$$\frac{E_T}{V} = const + \frac{1}{4}[\alpha_c - \alpha] M^2 + C_4 M^4$$

$$\frac{\partial}{\partial M}\left(\frac{E_T}{V}\right) = \frac{1}{2}[\alpha_c - \alpha] M + 4C_4 M^3 = 0$$

we get

$$M = 0 \text{ OR} M = \pm\sqrt{\frac{1}{8C_4}[\alpha - \alpha_c]}$$

so we can see that when $\alpha < \alpha_c$ we have not spontaneous magnetization and when $\alpha > \alpha_c$ the spontaneous magnetization grow as a sours function



4.At finite but low temperatures T, The the energy $E(M)$ should be replaced by the M-constrained "free energy" $F(M)$, we can use the Sommerfeld expansion (equation 6.43 in the lecture notes):

$$F = \frac{3}{5}N\epsilon_F\left[1 - \frac{5\pi^2}{12}\left(\frac{T}{\epsilon_F}\right)^2 + O\left(\frac{T}{\epsilon_F}\right)^4\right]$$

we see that

$$k_{F\pm} = (6\pi^2 n_\pm)^{1/3} \rightarrow \epsilon_{F\pm} = \frac{(6\pi^2 n_\pm)^{\frac{2}{3}}}{2m}$$

$$F_\pm = \frac{3}{5}\frac{V}{2m}(6\pi^2)^{\frac{2}{3}}(n_\pm)^{\frac{5}{3}}\left[1 - \frac{5\pi^2}{12}\left(\frac{T}{\epsilon_F}\right)^2\right] = E_{K\pm} - 2mV(n_\pm)^{\frac{1}{3}}\frac{\pi^2}{4(6\pi^2)^{\frac{2}{3}}}T^2$$

$$n_{\pm}^{1/3} = \left(\frac{n}{2}\right)^{\frac{1}{3}} \left(1 \pm \frac{M}{n}\right)^{\frac{1}{3}} \approx \left(\frac{n}{2}\right)^{\frac{1}{3}} \left[1 \pm \frac{1}{3}\frac{M}{n} - \frac{1}{9}\left(\frac{M}{n}\right)^2 \pm \frac{5}{81}\left(\frac{M}{n}\right)^3 - \frac{40}{243}\left(\frac{M}{n}\right)^4\right]$$

$$\left((n_+)^{\frac{1}{3}} + (n_-)^{\frac{1}{3}}\right) = 2\left(\frac{n}{2}\right)^{\frac{1}{3}} \left[1 - \frac{1}{9}\left(\frac{M}{n}\right)^2 - \frac{40}{243}\left(\frac{M}{n}\right)^4\right]$$

we need to add the interactions:

$$\rightarrow \frac{F}{V} = \frac{E_0}{V}\left[1 + \frac{5}{9}\left(\frac{M}{n}\right)^2 + \frac{5}{243}\left(\frac{M}{n}\right)^4\right] + \alpha\left(\frac{n}{2}\right)^2 - \alpha\left(\frac{n}{2}\right)^2\left(\frac{M}{n}\right)^2 - 2m\frac{\pi^2}{4\left(6\pi^2\right)^{\frac{2}{3}}}T^2 2\left(\frac{n}{2}\right)^{\frac{1}{3}}\left[1 - \frac{1}{9}\left(\frac{M}{n}\right)^2 - \frac{40}{243}\left(\frac{M}{n}\right)^4\right]$$

$$\rightarrow \frac{F}{V} = const + \left(\frac{n}{2}\right)^2\left[\alpha_c\left(0\right) - \alpha + \Delta\alpha T^2\right]\left(\frac{M}{n}\right)^2 + \left[\frac{5}{243}\frac{E_0}{V} + 2m\frac{\pi^2}{2\left(6\pi^2\right)^{\frac{2}{3}}}T^2\frac{40}{243}\left(\frac{n}{2}\right)^{\frac{1}{3}}\right]\left(\frac{M}{n}\right)^4$$

where

$$\Delta\alpha = 2m\frac{\pi^2}{18\left(6\pi^2\right)^{\frac{2}{3}}}\left(\frac{n}{2}\right)^{-\frac{5}{3}}$$

So we find

$$\alpha_c(T) = \alpha_c\left(0\right) + \Delta\alpha T^2$$