Max Proft U5190335 Assignment 3.

Q8.13 The partition function is given by:

$$Z = \frac{1}{N!}\frac{1}{h^{3N}}\int d^3r_1 \cdots d^3r_N \, d^3p_1 \cdots d^3p_N \, e^{-\beta U_{kin} - \beta U_{pot}}$$

where $U_{kin} = \sum_{i=1}^{N} \frac{p_i^2}{2m}$, U_{pot} is a function of $(r_1 \ldots r_n)$.

So we can seperate the integral:

$$Z = \frac{1}{N!}\frac{1}{h^{3N}}\int d^3p_1 \cdots d^3p_N \, e^{-\beta U_{kin}} \int d^3r_1 \cdots d^3r_n \, e^{-\beta U_{pot}}$$

But we know that the partition function for an ideal gas is given by

$$Z_{ideal} = \frac{1}{N!}\frac{V^N}{h^{3N}}\int d^3p_1 \cdots d^3p_N \, e^{-\beta U_{kin}}$$

$$\Rightarrow Z = \frac{Z_{ideal}}{V^N}\int d^3r_1 \cdots d^3r_N \, e^{-\beta U_{pot}}$$

$\boxed{\text{Note: } e^{-\beta U_{ij}} \approx 1 + f_{ij}}$

~~good approximation~~

Since $Z_c := \frac{1}{V^N}\int d^3r_1 \cdots d^3r_n \, e^{-\beta U_{pot}} = Exp\left(\sum \text{Connected Diagrams}\right)$

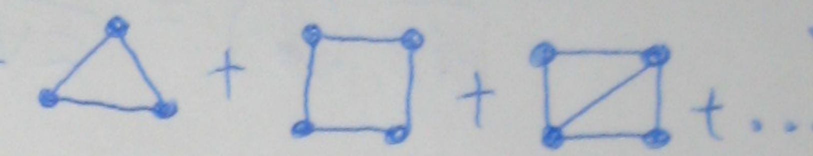
$$Z = Z_{ideal} \, Exp\left(\sum \text{Connected Diagrams}\right)$$

The energy is given by

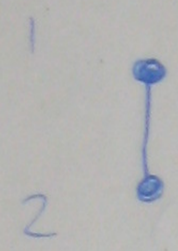
$$E = -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta}\ln(Z_{ideal}) - \frac{\partial}{\partial\beta}\sum \text{Connected Diagrams}$$

$$E_{ideal} = -\frac{\partial}{\partial\beta}\ln(Z_{ideal}) = \frac{3}{2}NkT$$

$$\Rightarrow \quad E = \frac{3}{2}NkT - \frac{\partial}{\partial\beta}\sum \text{Connected Diagrams}$$

$$= \frac{3}{2}NkT - \frac{\partial}{\partial\beta}\Big($$  $$\Big)$$

Taking only the first term of the summation:

 $$= \frac{1}{2}\frac{\cancel{\#}N}{V}\int d^3r_1 \frac{(N-1)}{V}\int d^3r_2\, f_{12} \quad , \quad f_{12} = e^{-\beta U_{12}} - 1$$

$$= \frac{N^2}{2V^2}\int d^3r_1 \int d^3r_2 \,\cancel{f}\left(e^{-\beta U_{12}} - 1\right)$$ since $N-1 \approx N$

$$\Rightarrow -\frac{\partial}{\partial\beta}\Big($$  $$\Big) = \frac{-N^2}{2V^2}\frac{d}{d\beta}\iint d^3r_1 d^3r_2 \left(e^{-\beta U_{12}} - 1\right)$$

$$= \frac{-N^2}{2V^2}\iint d^3r_1 d^3r_2\, (-U_{12})\, e^{-\beta U_{12}}$$ Taking the derivative inside the integral

U_{12} is a function that is only dependent on the distance between two particles. i.e. $U_{12} = U(|\vec{r}_1 - \vec{r}_2|)$

Let me define $\vec{r} = \vec{r}_1 - \vec{r}_2$

$$\Rightarrow d^3r = d^3r_1$$

And so if we perform the integral with respect to d^3r first we get

$$-\frac{\partial}{\partial\beta}\Big($$  $$\Big) = \frac{N^2}{2V^2}\left(\int d^3r\, U(|\vec{r}|)\, e^{-\beta U(|\vec{r}|)}\right)\left(\underbrace{\int d^3r_2}_{=V}\right)$$

Changing this integral to spherical coordinates

$$= \frac{N^2}{2V}\int U(r)\, e^{-\beta U(r)}\, r^2 \sin\theta \, dr\, d\phi\, d\theta$$

Performing the ϕ and θ integrals

$$-\frac{d}{d\beta}\left(\quad \right) = \frac{N^2}{2V} \times 4\pi \times \int_0^\infty r^2 u(r) e^{-\beta u(r)} dr$$

as required.

Hence the energy is approximately given by:

$$E = \frac{3}{2} NkT + \frac{N^2}{V} 2\pi \int_0^\infty r^2 u(r) e^{-\beta u(r)} dr$$

as required.

See Mathematica for the rest of this question.

8.22 We adjust the dipole energy to get:

$$E_\uparrow = -\varepsilon n \bar{s} - \mu_B B \qquad E_\downarrow = \varepsilon n \bar{s} + \mu_B B$$

For one dipole we have

$$Z_i = e^{-E_\downarrow \beta} + e^{-E_\uparrow \beta} \qquad E_\uparrow = -E_\downarrow$$

$$= e^{-E_\downarrow \beta} + e^{E_\downarrow \beta}$$

$$= 2\cosh(E_\downarrow \beta)$$

The expected value for spin alignment is:

$$\bar{s}_i = \frac{1}{Z_i}\left(s_\uparrow e^{-E_\uparrow \beta} + s_\downarrow e^{-E_\downarrow \beta} \right)$$

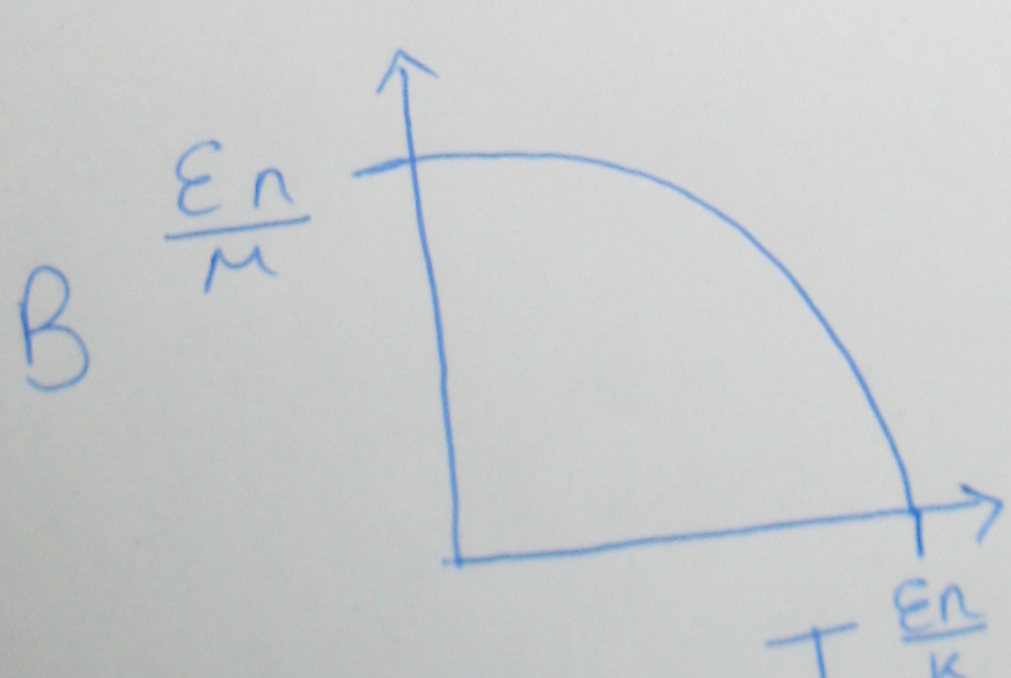
$$= \cancel{2\sinh(E} \frac{1}{Z_i}\left(e^{E_\downarrow \beta} - e^{-E_\downarrow \beta} \right)$$

$$= \frac{2\sinh(E_\downarrow \beta)}{2\cosh(E_\downarrow \beta)} = \tanh(E_\downarrow \beta)$$

The mean field approximation gives us $\bar{s} = \bar{s}_i$

$$\bar{s} = \tanh(\beta \varepsilon n \bar{s} + \beta \mu_B B)$$

The sketch of the region for which there are 3 solutions:



see mathematica for more details.

1	$\uparrow \uparrow$		$e^{+\beta\varepsilon}$
2	$\uparrow \downarrow$		$e^{-\beta\varepsilon}$
3	$\downarrow \uparrow$		$e^{-\beta\varepsilon}$
4	$\downarrow \downarrow$		$e^{+\beta\varepsilon}$

Q 8.17 - Bonus

$$Z = 2\left(e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right)$$

$$\cancel{= 2 \cdot 2\cosh}$$

$$= 4\cosh(\beta\varepsilon)$$

Probability Parallel

$$P_{para} = \frac{2e^{\beta\varepsilon}}{4\cosh(\beta\varepsilon)}$$

Probability Antiparallel

$$P_{anti} = \frac{2e^{-\beta\varepsilon}}{4\cosh(\beta\varepsilon)}$$

Average Energy is.

$$\bar{E} = -\frac{\partial}{\partial\beta} 4\cosh(\beta\varepsilon)$$

$$= -4\varepsilon\sinh(\beta\varepsilon)$$

Finding when it is more likely to find $\uparrow\uparrow$ than to find them antiparallel

Solving:

$$P_{\uparrow\uparrow} > P_{anti}$$

$$\Rightarrow \frac{e^{\beta\varepsilon}}{4\cosh(\beta\varepsilon)} > \frac{2e^{-\beta\varepsilon}}{4\cosh(\beta\varepsilon)}$$

$$\Rightarrow e^{2\beta\varepsilon} > 2$$

$$\Rightarrow \frac{2\varepsilon}{kT} > \ln 2$$

$$\Rightarrow T < \frac{2\varepsilon}{k\ln 2}$$

Q8.13 Continued

ulg[r] is the Leonard Jones Potential
The temperature dependent part is given by U[T]

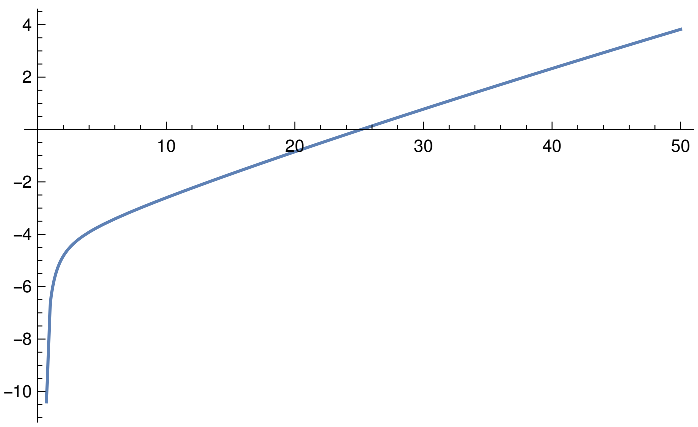
In[34]:= $$\texttt{ulg[r\_] := u0}\left(\left(\frac{\texttt{r0}}{\texttt{r}}\right)^{12} - 2\left(\frac{\texttt{r0}}{\texttt{r}}\right)^{6}\right)$$

$$\texttt{U[T\_]} = \frac{2\,\pi\,\texttt{n}^2}{\texttt{V}}\,\texttt{Integrate}\left[\texttt{r}^2\,\texttt{ulg[r] Exp}\left[-\texttt{ulg[r]}\,/\,(\texttt{k T})\right],\ \{\texttt{r}, 0, \infty\},\ \texttt{Assumptions} \to \{\texttt{r0} > 0, \texttt{k} > 0, \texttt{u0} > 0, \texttt{T} > 0\}\right]$$

Out[35]= $$-\frac{1}{12\,\texttt{V}}\,e^{\frac{\texttt{u0}}{2\,\texttt{k T}}}\,\texttt{n}^2\,\pi^2\,\texttt{r0}^3\left(3\,\texttt{u0 BesselI}\left[-\frac{1}{4}, \frac{\texttt{u0}}{2\,\texttt{k T}}\right] + (-\texttt{k T} + 3\,\texttt{u0})\,\texttt{BesselI}\left[\frac{1}{4}, \frac{\texttt{u0}}{2\,\texttt{k T}}\right] - \texttt{u0}\left(\texttt{BesselI}\left[\frac{3}{4}, \frac{\texttt{u0}}{2\,\texttt{k T}}\right] + \texttt{BesselI}\left[\frac{5}{4}, \frac{\texttt{u0}}{2\,\texttt{k T}}\right]\right)\right)$$

Plotting the Temperature dependent part, taking all constant equal to 1 for convience.

In[27]:= $$\texttt{Plot}\left[\texttt{U[T] /. }\{\texttt{r0} \to 1, \texttt{k} \to 1, \texttt{u0} \to 1, \texttt{n} \to 1, \texttt{V} \to 1\},\ \{\texttt{T}, 0, 50\}\right]$$

Out[27]= 

When T is very small, the slope of the curve is very steep. As the temperature increases slightly, the slope changes and is essentially a fixed value. This means that the heat capacity can be corrected by a constant value, providing that the temperature is not too small.

Schroeder gives r0 = 3.9 Å, u0=0.010eV, Mass of one argon atom is, $M = 39.948 * 1.660 * 10^{-27}$ kg

Note that $\frac{N^2}{V\text{mass}} = \frac{N^2}{V*M\,N} = \frac{N}{V} * \frac{1}{M} = \frac{P}{k\,T\,M} = \frac{1.01*10^5}{1.381*10^{-23}*300*39.948*1.660*10^{-27}} = 3.676 * 10^{50}$

And hence the specific heat capacity for a fixed volume at 300 $K = 26.8^o\ C$ is given by:

In[38]:= $$\texttt{U'[300] /. }\{\texttt{r0} \to 3.9 * 10^{-10}, \texttt{k} \to 1.381 * 10^{-23}, \texttt{u0} \to 0.01 * 1.6 * 10^{-19}, \texttt{n}^2 \to 3.67624 * 10^{50}\ \texttt{V}\}$$

Out[38]= 0.154049

Q8.22 Continued

If we plot y(s)=s and y(s)=Tanh[$\beta\epsilon$n s+ $\beta\,\mu$ B]=Tanh[$\beta\epsilon$n s+ $\beta\epsilon$n k], where $k = \frac{\mu B}{\epsilon n}$

In[79]:=
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Manipulate[Plot[{s, Tanh[βϵn s + βϵn k]}, {s, -5, 5}, PlotRange → {-2, 2}],
 {{βϵn, 1, "βϵn"}, 0, 100}, {{k, 1, "μB/ϵn"}, 0, 2}]
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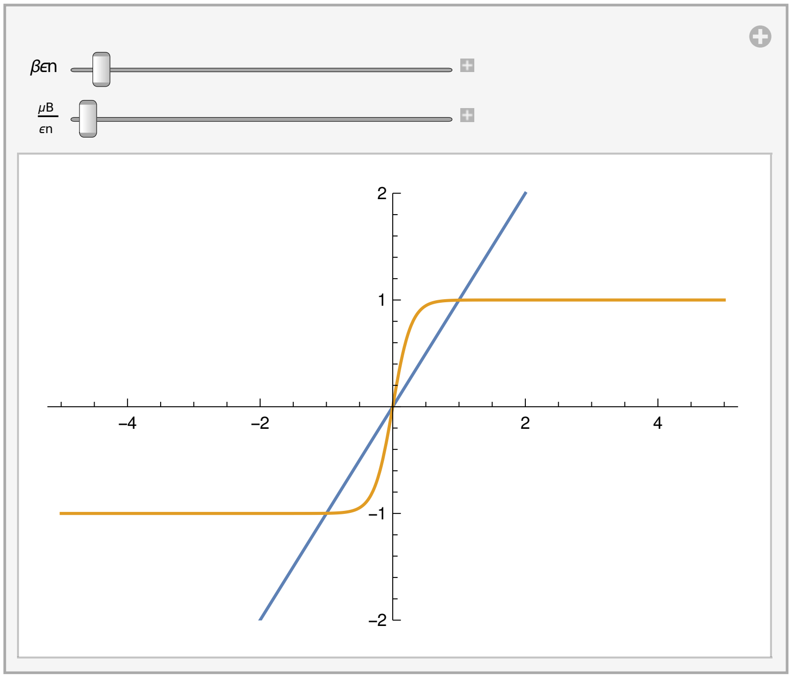
Out[79]=



By manipulating the above plot, we see that as $\beta\epsilon n \to 0$ (T→0) to get three solutions we must have we have $\frac{\mu B}{\epsilon n} < 1 \Rightarrow B < \frac{\epsilon n}{\mu}$

By manipulating the above plot, we see that as $\frac{\mu B}{\epsilon n} \to 0$ (B→0) we have $\beta \epsilon n > 1 \Rightarrow T < \frac{\epsilon n}{k}$

On the original sheet of paper, I have attached a sketch of this region.

Q8.17 Continued

$X = kT/\epsilon$

The Probabilities of being parallel/antiparallel:

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In[10]:= Plot[{Exp[-1 / X]/(2 Cosh[1 / X]), Exp[1 / X]/(2 Cosh[1 / X])},
  {X, 0, 10}, PlotLegends → {"Antiparallel", "Parallel"}]
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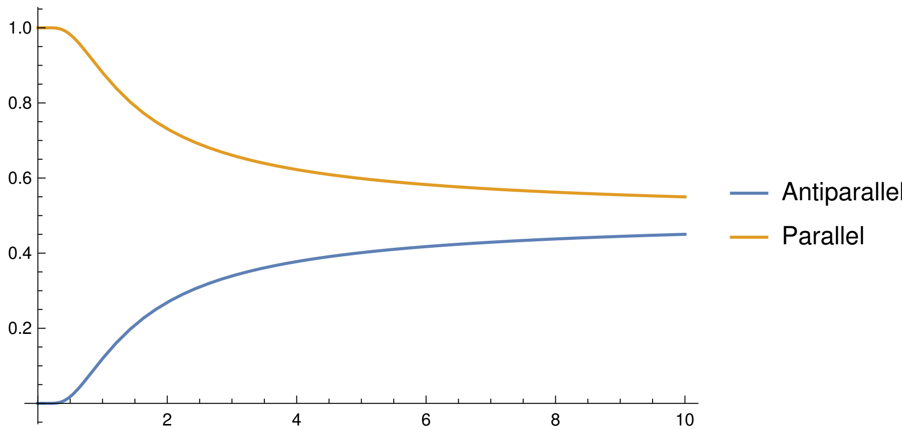
Out[10]=



The Average energy (Vertical axis is in units ϵ)

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In[4]:= Plot[-4 Sinh[1 / X], {X, 0, 10}]
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Out[4]=