MAU34405: Statistical Physics I
Homework 3 due 06/12/2021

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Exercise 1

$$\begin{aligned}
\mathcal{H}_i(q_i, p_i) &= \frac{p_i^2}{2\,m} + \frac{k\,q_i^2}{2} \\
\mathcal{H}(\bar{q}, \bar{p}) &= \sum_{i=1}^{N} \mathcal{H}_i(q_i, p_i) \\
&= \sum_{i=1}^{N} \frac{p_i^2}{2\,m} + \sum_{i=1}^{N} \frac{k\,q_i^2}{2}
\end{aligned}$$

$$x_i = \frac{p_i}{\sqrt{2\,m}} \qquad\qquad x_{i+N} = q_i\sqrt{\frac{k}{2}} \qquad\qquad \text{for } i = 1, \ldots, N$$

$$\begin{aligned}
\implies \mathcal{H}(\bar{q}, \bar{p}) &= \sum_{i=1}^{N} x_i^2 + \sum_{i=1}^{N} x_{i+N}^2 \\
&= \sum_{i=1}^{2N} x_i^2
\end{aligned}$$

$$\begin{aligned}
\Omega(E, V, N) &= \int\limits_{\mathcal{H}\leqslant E} \prod_{i=1}^{N} \frac{dq_i\,dp_i}{h^f} \\
&= \int\limits_{\sum_{i=1}^{2N} x_i^2 \leqslant E} \left(\prod_{i=1}^{N} \frac{1}{h^1}\right) \left(\prod_{i=1}^{N} dx_{i+N}\sqrt{\frac{2}{k}}\right) \left(\prod_{i=1}^{N} dx_i\sqrt{2\,m}\right) \\
&= \left(\frac{2}{h}\sqrt{\frac{m}{k}}\right)^N \int\limits_{\sum_{i=1}^{2N} x_i^2 \leqslant E} \prod_{i=1}^{2N} dx_i \\
&= \left(\frac{2}{h\,\omega}\right)^N V_{2N}\left(\sqrt{E}\right)
\end{aligned}$$

$$\begin{aligned}
V_n(r) &\equiv \text{volume of } n\text{-ball of radius } r \\
&= \frac{\pi^{\frac{n}{2}}\,r^n}{\Gamma\left(\frac{n}{2} + 1\right)} \\
V_{2N}\left(\sqrt{E}\right) &= \frac{\pi^N \left(\sqrt{E}\right)^{2N}}{\Gamma(N+1)} \\
&= \frac{(\pi\,E)^N}{N!}
\end{aligned}$$

$$\Longrightarrow \quad \Omega(E,N) = \frac{1}{N!}\left(\frac{2\,\pi\,E}{h\,\omega}\right)^N$$

$$\begin{aligned}
\mathcal{W}(E,N) &= \frac{\partial \Omega(E,N)}{\partial E} \\
&= \frac{N}{N!}\left(\frac{2\,\pi\,E}{h\,\omega}\right)^{N-1}\left(\frac{2\,\pi}{h\,\omega}\right) \\
\mathcal{W}(E,N) &= \frac{E^{N-1}}{(N-1)!}\left(\frac{2\,\pi}{h\,\omega}\right)^N
\end{aligned}$$

$$\begin{aligned}
S(E,N) &= k_B \ln \Omega(E,N) \\
&= k_B \ln\!\left(\frac{1}{N!}\left(\frac{2\,\pi\,E}{h\,\omega}\right)^N\right) \\
&= k_B\left(N \ln\!\left(\frac{2\,\pi\,E}{h\,\omega}\right) - \ln(N!)\right) \\
&\approx k_B\left(N \ln\!\left(\frac{2\,\pi\,E}{h\,\omega}\right) - N\ln(N) + N\right) && \text{(Stirling's approximation)} \\
S(E,N) &= N\,k_B\left(\ln\!\left(\frac{2\,\pi\,E}{N\,h\,\omega}\right) + 1\right)
\end{aligned}$$

$$\begin{aligned}
\frac{1}{T} &= \left(\frac{\partial S(E,N)}{\partial E}\right)_{V,N} \\
&= \frac{\partial}{\partial E}\left(N\,k_B \ln\!\left(\frac{2\,\pi}{N\,h\,\omega}\right) + N\,k_B \ln(E) + 1\right) \\
&= 0 + \frac{N\,k_B}{E} + 0 \\
\Longrightarrow \quad T(E,N) &= \frac{E}{N\,k_B}
\end{aligned}$$

$$\begin{aligned}
\frac{P}{T} &= \left(\frac{\partial S(E,N)}{\partial V}\right)_{E,N} \\
&= \frac{\partial}{\partial V}\left(N\,k_B\left(\ln\!\left(\frac{2\,\pi\,E}{N\,h\,\omega}\right) + 1\right)\right) \\
&= 0 \\
\Longrightarrow \quad P &= 0
\end{aligned}$$

$$\begin{aligned}
C_P &= \left(\frac{\partial E(T,N)}{\partial T}\right)_P \\
&= \frac{\partial}{\partial T} N\,k_B\,T \\
C_P &= N\,k_B
\end{aligned}$$

$$\begin{aligned}
C_V &= \left(\frac{\partial E}{\partial T}\right)_V \\
&= \frac{\partial}{\partial T} N\,k_B\,T \\
C_V &= N\,k_B
\end{aligned}$$

Exercise 2

$$\begin{aligned}
Z(T,1) &= \int_{\substack{\text{all} \\ \text{energies}}} dE\,\mathcal{W}(E,1)\,e^{-\beta\,E} \\
&= \int_0^\infty dE\,\frac{E^{1-1}}{(1-1)!}\left(\frac{2\,\pi}{h\,\omega}\right)^1 e^{-\frac{E}{k_B T}} \\
&= \frac{2\,\pi}{h\,\omega}\int_0^\infty dE\,e^{-\frac{E}{k_B T}} \\
&= -\frac{2\,\pi}{h\,\omega}\,k_B\,T\,e^{-\frac{E}{k_B T}}\Big|_0^\infty \\
&= -\frac{2\,\pi\,k_B\,T}{h\,\omega}(0-1) \\
&= \frac{2\,\pi\,k_B\,T}{h\,\omega}
\end{aligned}$$

$$
\begin{aligned}
\mathcal{P}(\epsilon)\,d\epsilon &= \frac{e^{-\beta\,\epsilon}}{Z(T,1)}\,\mathcal{W}(\epsilon,1)\,d\epsilon \\
&= e^{-\frac{\epsilon}{k_B\,T}}\,\frac{h\,\omega}{2\,\pi\,k_B\,T}\,\frac{\epsilon^{1-1}}{(1-1)!}\left(\frac{2\,\pi}{h\,\omega}\right)^1 \\
&= \frac{1}{k_B\,T}\,e^{-\frac{\epsilon}{k_B\,T}}
\end{aligned}
$$

$$
\begin{aligned}
\langle\epsilon\rangle &= \int_0^\infty \mathcal{P}(\epsilon)\,\epsilon\,d\epsilon \\
&= \int_0^\infty \frac{1}{k_B\,T}\,e^{-\frac{\epsilon}{k_B\,T}}\,\epsilon\,d\epsilon \\
&= \int_0^\infty \xi\,e^{-\xi}\,k_B\,T\,d\xi && (\xi = \frac{\epsilon}{k_B\,T}) \\
&= k_B\,T\left(-\xi\,e^{-\xi}\Big|_0^\infty + \int_0^\infty e^{-\xi}\,d\xi\right) && (u=\xi,\ dv = e^{-\xi}\,d\xi) \\
&= k_B\,T\left(0-0-e^{-\xi}\Big|_0^\infty\right) \\
&= k_B\,T\,(0+1) \\
\langle\epsilon\rangle &= k_B\,T
\end{aligned}
$$

Exercise 3

$$
\begin{aligned}
\mathcal{H}_i(q_i,p_i) &= p_i\,c \\
\mathcal{H}(\bar{q},\bar{p}) &= \sum_{i=1}^N \mathcal{H}_i(q_i,p_i) \\
&= \sum_{i=1}^N p_i\,c
\end{aligned}
$$

$$
\begin{aligned}
\Omega(E,V,N) &= \frac{1}{N!}\int\limits_{\mathcal{H}\leqslant E}\prod_{i=1}^{N}\frac{d^3q_i\,d^3p_i}{h^f}\\
&= \frac{1}{N!}\int\limits_{\sum_{i=1}^{N} p_i\, c\leqslant E}\left(\prod_{i=1}^{N}\frac{1}{h^3}\right)\left(\prod_{i=1}^{N} d^3q_i\right)\left(\prod_{i=1}^{N} d^3p_i\right)\\
&= \frac{V^N}{h^{3N}\,N!}\int\limits_{\sum_{i=1}^{N} p_i\leqslant \frac{E}{c}}\prod_{i=1}^{N} V_{p_i}\\
&= \frac{V^N}{h^{3N}\,N!}\int\limits_{\sum_{i=1}^{N} p_i\leqslant \frac{E}{c}}\prod_{i=1}^{N} r_{p_i}^2\,\sin\theta_{p_i}\,dr_{p_i}\,d\theta_{p_i}\,d\phi_{p_i}\\
&= \frac{V^N}{h^{3N}\,N!}\int_0^{2\pi}\prod_{i=1}^{N} d\phi\int_0^{\pi}\prod_{i=1}^{N}\sin\theta\,d\theta\int\limits_{\sum_{i=1}^{N} p_i\leqslant \frac{E}{c}}\prod_{i=1}^{N} p_i^2\,dp_i\\
&= \frac{V^N}{h^{3N}\,N!}\,(2\pi)^N\,(1+1)^N\int\limits_{\sum_{i=1}^{N} x_i\leqslant 1}\prod_{i=1}^{N}\left(\frac{E}{c}\,x_i\right)^2\frac{E}{c}\,dx_i\\
&= \frac{1}{N!}\left(4\,\pi\,V\left(\frac{E}{h\,c}\right)^3\right)^N I_N
\end{aligned}
$$

$$
\begin{aligned}
I_N &= \int\limits_{\sum_{i=1}^{N} x_i\leqslant 1}\prod_{i=1}^{N} x_i^2\,dx_i\\
&= \int\limits_{x_N+\sum_{i=1}^{N-1} x_i\leqslant 1} x_N^2\,dx_N\prod_{i=1}^{N-1} x_i^2\,dx_i\\
&= \int_0^1 x_N^2\,dx_N\int\limits_{\sum_{i=1}^{N-1} x_i\leqslant 1-x_N}\prod_{i=1}^{N-1} x_i^2\,dx_i\\
&= \int_0^1 x_N^2\,dx_N\int\limits_{\sum_{i=1}^{N-1} y_i\leqslant 1}\prod_{i=1}^{N-1}\left(y_i\,(1-x_N)\right)^2(1-x_N)\,dy_i\\
&= \int_0^1 x_N^2\,(1-x_N)^{3(N-1)}\int\limits_{\sum_{i=1}^{N-1} y_i\leqslant 1}\prod_{i=1}^{N-1} y_i^2\,dy_i\\
&= B(2+1,3N-3+1)\,I_{N-1}\\
&= \frac{\Gamma(3)\,\Gamma(3N-2)}{\Gamma(3N+1)}\,I_{N-1}\\
&= 2\,\frac{\Gamma(3N-2)}{\Gamma(3N+1)}\,I_{N-1}
\end{aligned}
$$

$$I_1 = \int\limits_{\sum_{i=1}^{1} x_i \leqslant 1} \prod_{i=1}^{1} x_i^2 \, dx_i = \int_0^1 x^2 \, dx = \frac{1}{3}$$

$$I_2 = 2 \frac{\Gamma(4)}{\Gamma(7)} \frac{1}{3} = \frac{2 \cdot 3!}{3 \, \Gamma(7)} = \frac{2^2}{\Gamma(7)}$$

$$I_3 = 2 \frac{\Gamma(7)}{\Gamma(10)} \frac{2^2}{\Gamma(7)} = \frac{2^3}{\Gamma(10)}$$

$$I_4 = 2 \frac{\Gamma(10)}{\Gamma(13)} \frac{2^3}{\Gamma(10)} = \frac{2^4}{\Gamma(13)}$$

$$\implies I_N = \frac{2^N}{\Gamma(3N+1)} = \frac{2^N}{(3N)!}$$

$$\implies \Omega(E,V,N) = \frac{1}{N!} \left(4 \, \pi \, V \left(\frac{E}{h \, c} \right)^3 \right)^N \frac{2^N}{\Gamma(3N+1)} = \frac{2^N}{(3N)!}$$

$$\Omega(E,V,N) = \frac{1}{N! \, (3N)!} \left(8 \, \pi \, V \left(\frac{E}{h \, c} \right)^3 \right)^N$$

$$\begin{aligned}
S(E,V,N) &= k_B \ln \Omega(E,V,N) \\
&= k_B \ln \left(\frac{1}{N! \, (3N)!} \left(8 \, \pi \, V \left(\frac{E}{h \, c} \right)^3 \right)^N \right) \\
&= k_B \left(-\ln(N!) - \ln((3N)!) + \ln \left(8 \, \pi \, V \left(\frac{E}{h \, c} \right)^3 \right)^N \right) \\
&\approx k_B \left(-N \ln N + N - 3N \ln(3N) + 3N + N \ln \left(8 \, \pi \, V \left(\frac{E}{h \, c} \right)^3 \right) \right) \\
&\qquad \text{(Stirling's approximation)} \\
&= N \, k_B \left(-\ln N - \ln(3N)^3 + 4 + \ln \left(8 \, \pi \, V \left(\frac{E}{h \, c} \right)^3 \right) \right)
\end{aligned}$$

$$S(E,V,N) = N \, k_B \left(\ln \left(\frac{8 \, \pi \, V}{27 \, N^4} \left(\frac{E}{h \, c} \right)^3 \right) + 4 \right)$$

Exercise 4

1.

$$\mathcal{P}(E_1, V_1) \, dE_1 \, dV_1 = \frac{\mathcal{W}_1(E_1, V_1) \, \mathcal{W}_2(E - E_1, V - V_1)}{\mathcal{W}(E, V)} \, dE_1 \, dV_1$$

$$\begin{aligned}
\frac{\mathcal{W}_2(E - E_1, V - V_1)}{\mathcal{W}(E, V)} &= \frac{\mathcal{W}_2(E - E_1, V - V_1) \, \Delta E}{\mathcal{W}(E, V) \, \Delta E} \\
&= \exp(\ln(\mathcal{W}_2(E - E_1, V - V_1) \, \Delta E) - \ln(\mathcal{W}(E, V) \, \Delta E)) \\
&\approx \exp(\ln(\Omega_2(E - E_1, V - V_1)) - \ln(\Omega(E, V))) \\
&= \exp \left(\ln \left(e^{\frac{S_2(E - E_1, V - V_1)}{k_B}} \right) - \ln \left(e^{\frac{S(E,V)}{k_B}} \right) \right) \\
&= \exp \left(\frac{1}{k_B} \left(S_2(E - E_1, V - V_1) - S(E, V) \right) \right)
\end{aligned}$$

$$
\begin{aligned}
S_2(E-E_1,V-V_1) &= S_2(E,V) + E_1\left(\frac{\partial S_2(E-E_1,V-V_1)}{\partial E_1}\bigg|_{E_1,V_1=0}\right) + V_1\left(\frac{\partial S_2(E-E_1,V-V_1)}{\partial V_1}\bigg|_{E_1,V_1=0}\right) + \mathcal{O}(E_1^2,V_1^2)\\
&\approx S_2(E,V) + E_1\left(-\frac{\partial S_2(E-E_1,V-V_1)}{\partial (E-E_1)}\bigg|_{E_1,V_1=0}\right) + V_1\left(-\frac{\partial S_2(E-E_1,V-V_1)}{\partial (V-V_1)}\bigg|_{E_1,V_1=0}\right)\\
&\approx S_2(E,V) - E_1\,\frac{\partial S_2(E,V)}{\partial E} - V_1\,\frac{\partial S_2(E,V)}{\partial V}\\
&\approx S(E,V) - E_1\,\frac{\partial S(E,V)}{\partial E} - V_1\,\frac{\partial S(E,V)}{\partial V}\\
&= S(E,V) - \frac{E_1}{T} - \frac{P\,V_1}{T}
\end{aligned}
$$

$$
\begin{aligned}
\implies \frac{\mathcal{W}_2(E-E_1,V-V_1)}{\mathcal{W}(E,V)} &\approx \exp\!\left(\frac{1}{k_B}\left(-\frac{E_1}{T} - \frac{P\,V_1}{T}\right)\right)\\
&= e^{-\beta(E_1+P\,V_1)}\\
\implies \mathcal{P}(E_1,V_1)\,dE_1\,dV_1 &= \frac{\mathcal{W}_1(E_1,V_1)}{\mathbb{Z}(T,P,N)}\,e^{-\beta(E_1+P\,V_1)}dE_1\,dV_1
\end{aligned}
$$

2.

$$
\begin{aligned}
1 &= \int_{\text{all } E,V} \mathcal{P}(E,V)\,dE\,dV\\
\implies \mathbb{Z}(T,P,N) &= \int_0^\infty\!\int_0^\infty \mathcal{W}(E,V)\,e^{-\beta(E+P\,V)}\,dE\,dV\\
&= \int_0^\infty e^{-\beta\,P\,V}\,dV \int_0^\infty W(E,V)\,e^{-\beta\,E}\,dE\\
\mathbb{Z}(T,P,N) &= \int_0^\infty Z(T,V,N)\,e^{-\beta\,P\,V}\,dV
\end{aligned}
$$

3.

$$
\begin{aligned}
\mathcal{P}(V) &= \int_0^\infty \frac{\mathcal{W}(E,V)}{\mathbb{Z}(T,P,N)}\,e^{-\beta(E+P\,V)}\,dE\\
&= \frac{e^{-\beta\,P\,V}}{\mathbb{Z}(T,P,N)}\int_0^\infty \mathcal{W}(E,V)\,e^{0\beta\,E}\,dE\\
&= \frac{e^{-\beta\,P\,V}}{\mathbb{Z}(T,P,N)}\,Z(T,V,N)\\
1 &\approx \mathcal{P}(\langle V\rangle)\\
&= \frac{e^{-\beta\,P\langle V\rangle}}{\mathbb{Z}(T,P,N)}\,Z(T,\langle V\rangle,N)\\
\ln 1 &= \ln\!\left(\frac{e^{-\beta\,P\langle V\rangle}}{\mathbb{Z}(T,P,N)}\,Z(T,\langle V\rangle,N)\right)\\
0 &= -\beta\,P\,\langle V\rangle - \ln\mathbb{Z} + \ln Z\\
P\,\langle V\rangle - k_B\,T\ln Z &= -k_B\,T\ln\mathbb{Z}\\
P\,\langle V\rangle + F &= -k_B\,T\ln\mathbb{Z}\\
P\,\langle V\rangle + E - T\,S &= -k_B\,T\ln\mathbb{Z}\\
\implies G(P,T,N) &= -k_B\,T\ln\mathbb{Z}
\end{aligned}
$$

Exercise 5

$$
\begin{aligned}
Z(T,V,N) &= \frac{1}{N!}\int\limits_{\substack{\text{all phase}\\ \text{space}}} \prod_{i=1}^{N} \frac{d^3q_i\, d^3p_i}{h^f}\, e^{-\beta\,\mathcal{H}_i} \\
&= \frac{1}{N!}\int\limits_{\substack{\text{all phase}\\ \text{space}}} \left(\prod_{i=1}^{N}\frac{1}{h^3}\right)\left(\prod_{i=1}^{N} d^3q_i\right)\left(\prod_{i=1}^{N} d^3p_i\, e^{-\frac{p_i^2}{2mk_BT}}\right) \\
&= \frac{1}{h^{3N}\,N!}\left(\int\limits_{\substack{\text{available}\\ \text{space}}} d^3q\right)^{N} \left(\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dp_x\,dp_y\,dp_z\, e^{-\frac{p_x^2+p_y^2+p_z^2}{2mk_BT}}\right)^{N} \\
&= \frac{V^N}{h^{3N}\,N!}\left(\int_{-\infty}^{\infty} dp\, e^{-\frac{p^2}{2mk_BT}}\right)^{3N} \\
&= \frac{V^N}{h^{3N}\,N!}\left(\sqrt{2\,\pi\,m\,k_B\,T}\right)^{3N} \\
Z(T,V,N) &= \frac{V^N}{h^{3N}\,N!}\,(2\,\pi\,m\,k_B\,T)^{\frac{3N}{2}}
\end{aligned}
$$

$$
\begin{aligned}
F(T,V,N) &= -k_B\,T\ln Z(T,V,N) \\
&= -k_B\,T\ln\!\left(\frac{V^N}{h^{3N}\,N!}\,(2\,\pi\,m\,k_B\,T)^{\frac{3N}{2}}\right) \\
&= -k_B\,T\left(-\ln(N!) + \ln\!\left(\frac{V}{h^3}\,(2\,\pi\,m\,k_B\,T)^{\frac{3}{2}}\right)^{N}\right) \\
&\approx -k_B\,T\left(-N\ln N + N + N\ln\!\left(\frac{V}{h^3}\,(2\,\pi\,m\,k_B\,T)^{\frac{3}{2}}\right)\right) \qquad \text{(Stirling's approximation)} \\
F(T,V,N) &= -N\,k_B\,T\left(\ln\!\left(\frac{V}{N\,h^3}\,(2\,\pi\,m\,k_B\,T)^{\frac{3}{2}}\right) + 1\right) \\
&= -N\,k_B\,T\left(\ln V - \ln N + \frac{3}{2}\ln T + \ln\!\left(\frac{(2\,\pi\,m\,k_B)^{\frac{3}{2}}}{h^3}\right) + 1\right)
\end{aligned}
$$

$$
\begin{aligned}
F(T,V,N) &= E - T\,S \\
dF &= dE - d(T\,S) \\
&= T\,dS - P\,dV + \mu\,dN - T\,dS - S\,dT \\
&= -S\,dT - P\,dV + \mu\,dN
\end{aligned}
$$

$$
\begin{aligned}
S(T,V,N) &= -\left(\frac{\partial F}{\partial T}\right)_{V,N} \\
&= N\,k_B\left(\ln V - \ln N + \frac{3}{2}\ln T + \ln\!\left(\frac{(2\,\pi\,m\,k_B)^{\frac{3}{2}}}{h^3}\right) + 1\right) + N\,k_B\,T\left(\frac{3}{2\,T}\right) \\
S(T,V,N) &= N\,k_B\left(\ln\!\left(\frac{V}{N\,h^3}\,(2\,\pi\,m\,k_B\,T)^{\frac{3}{2}}\right) + \frac{5}{2}\right)
\end{aligned}
$$

$$
\begin{aligned}
P(T,V,N) &= -\left(\frac{\partial F}{\partial V}\right)_{T,N} \\
&= N\,k_B\,T\left(\frac{1}{V}\right) \\
P(T,V,N) &= \frac{N\,k_B\,T}{V}
\end{aligned}
$$

$$
\begin{aligned}
\mu(T,V,N) &= \left(\frac{\partial F}{\partial N}\right)_{T,V} \\
&= -k_B\,T\left(\ln V - \ln N + \frac{3}{2}\ln T + \ln\left(\frac{(2\,\pi\,m\,k_B)^{\frac{3}{2}}}{h^3}\right) + 1\right) - N\,k_B\,T\left(-\frac{1}{N}\right) \\
\mu(T,V,N) &= -k_B\,T\ln\left(\frac{V}{N\,h^3}\,(2\,\pi\,m\,k_B\,T)^{\frac{3}{2}}\right)
\end{aligned}
$$

Exercise 6

$$
\begin{aligned}
\mathcal{P}(E)\,dE &= \frac{\mathcal{W}(E)}{Z}\,e^{-\beta\,E}\,dE \\
\frac{\partial\mathcal{P}(E)}{\partial E} &= \frac{1}{Z}\left(\frac{\partial\mathcal{W}(E)}{\partial E}\,e^{-\beta\,E} + \mathcal{W}(E)\,\frac{\partial}{\partial E}e^{-\beta\,E}\right) \\
&= \frac{1}{Z}\left(\frac{\partial^2\Omega}{\partial E^2}\,e^{-\beta\,E} - \beta\,\frac{\partial\Omega}{\partial E}\,e^{-\beta\,E}\right) \\
&= \frac{e^{-\beta\,E}}{Z}\left(\frac{\partial}{\partial E}\left(\frac{\partial}{\partial E}e^{\frac{S}{k_B}}\right) - \frac{1}{k_B\,T}\,\frac{\partial}{\partial E}e^{\frac{S}{k_B}}\right) && \text{(using } S = k_B\ln\Omega\text{)} \\
&= \frac{e^{-\beta\,E}}{Z}\left(\frac{\partial}{\partial E}\left(\frac{1}{k_B}\,e^{\frac{S}{k_B}}\,\frac{\partial S}{\partial E}\right) - \frac{1}{k_B\,T}\,e^{\frac{S}{k_B}}\,\frac{\partial S}{\partial E}\right) \\
&= \frac{e^{-\beta\,E}}{Z}\left(\frac{1}{k_B}\left(\frac{1}{k_B}\,e^{\frac{S}{k_B}}\,\frac{\partial S}{\partial E}\,\frac{\partial S}{\partial E} + e^{\frac{S}{k_B}}\,\frac{\partial^2 S}{\partial E^2}\right) - \frac{1}{k_B\,T}\,e^{\frac{S}{k_B}}\,\frac{\partial S}{\partial E}\right) \\
&\approx \frac{e^{-\beta\,E+\frac{S}{k_B}}}{Z}\left(\frac{1}{k_B^2}\left(\frac{\partial S}{\partial E}\right)^2 - \frac{1}{k_B\,T}\,\frac{\partial S}{\partial E}\right) && \text{(using } \tfrac{\partial^2 S}{\partial E^2}\approx 0\text{)} \\
&= \frac{e^{-\beta\,E+\frac{S}{k_B}}}{Z}\left(\frac{1}{k_B^2}\,\frac{1}{T^2} - \frac{1}{k_B\,T}\,\frac{1}{T}\right) && \text{(using } \tfrac{\partial S}{\partial E} = \tfrac{1}{T}\text{)} \\
&= 0
\end{aligned}
$$

Since the derivative of the probability distribution is approximately 0 for any allowable value of energy E, then we can deduce that the energy of this system is approximately constant and equal to the most probable value E_{mp}. Since we know that the system's energy is almost constant and equal to the average energy $\langle E\rangle$, then we know that the system's nearly constant energy is equal to both the average and most probable energies, i.e. $\langle E\rangle = E_{\text{mp}}$.

Exercise 7

$$Z(T,V,N) = \int_{\substack{\text{all phase}\\ \text{space}}} \prod_{i=1}^{N} \frac{dq_i\, dp_i}{h^f}\, e^{-\beta \mathcal{H}_i}$$

$$= \int_{\substack{\text{all phase}\\ \text{space}}} \left(\prod_{i=1}^{N} \frac{1}{h^1}\right) \left(\prod_{i=1}^{N} dq_i\, dp_i\, e^{-\frac{1}{k_B T}\left(\frac{p_i^2}{2m}+a q_i^4\right)}\right)$$

$$= \frac{1}{h^N} \int_{\substack{\text{all phase}\\ \text{space}}} \left(\prod_{i=1}^{N} dq_i\, e^{-\frac{a q_i^4}{k_B T}}\right) \left(\prod_{i=1}^{N} dp_i\, e^{-\frac{p_i^2}{2 m k_B T}}\right)$$

$$= \frac{1}{h^N} \left(\int_{-\infty}^{\infty} dq\, e^{-\frac{a q^4}{k_B T}}\right)^N \left(\int_{-\infty}^{\infty} dp\, e^{-\frac{p^2}{2 m k_B T}}\right)^N$$

$$= \frac{1}{h^N} \left(2 \int_{0}^{\infty} dx\, \frac{1}{4} \left(\frac{k_B T}{a}\right)^{\frac{1}{4}} x^{-\frac{3}{4}}\, e^{-x}\right)^N \left(\int_{-\infty}^{\infty} dp\, e^{-\frac{p^2}{2 m k_B T}}\right)^N$$

(first integrand is even, change of variables $x = \frac{a\, q^4}{k_B T}$)

$$= \frac{1}{h^N} \left(\frac{1}{2} \left(\frac{k_B T}{a}\right)^{\frac{1}{4}} \Gamma\left(\frac{1}{4}\right)\right)^N \left(\sqrt{2\, \pi\, m\, k_B T}\right)^N$$

$$Z(T,V,N) = \left(\frac{\Gamma\left(\frac{1}{4}\right)}{h}\right)^N (k_B T)^{\frac{3N}{4}} \left(\frac{\pi\, m}{2}\right)^{\frac{N}{2}} \left(\frac{1}{a}\right)^{\frac{N}{4}}$$

$$= \left(\frac{\Gamma\left(\frac{1}{4}\right)}{h} \frac{(k_B T)^{\frac{3}{4}}}{a^{\frac{1}{4}}} \left(\frac{\pi\, m}{2}\right)^{\frac{1}{2}}\right)^N$$

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

$$= -k_B T \ln\left(\frac{\Gamma\left(\frac{1}{4}\right)}{h} \frac{(k_B T)^{\frac{3}{4}}}{a^{\frac{1}{4}}} \left(\frac{\pi\, m}{2}\right)^{\frac{1}{2}}\right)^N$$

$$F(T,V,N) = N\, k_B T \ln\left(\frac{h}{\Gamma\left(\frac{1}{4}\right)} \frac{a^{\frac{1}{4}}}{(k_B T)^{\frac{3}{4}}} \left(\frac{2}{\pi\, m}\right)^{\frac{1}{2}}\right)$$

$$= N\, k_B T \left(-\frac{3}{4} \ln T + \ln\left(\frac{h}{\Gamma\left(\frac{1}{4}\right)} \frac{a^{\frac{1}{4}}}{k_B^{\frac{3}{4}}} \left(\frac{2}{\pi\, m}\right)^{\frac{1}{2}}\right)\right)$$

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

$$= -N\, k_B \left(-\frac{3}{4} \ln T + \ln\left(\frac{h}{\Gamma\left(\frac{1}{4}\right)} \frac{a^{\frac{1}{4}}}{k_B^{\frac{3}{4}}} \left(\frac{2}{\pi\, m}\right)^{\frac{1}{2}}\right)\right) - N\, k_B T \left(-\frac{3}{4\, T}\right)$$

$$S(T,V,N) = N\, k_B \left(\ln\left(\frac{\Gamma\left(\frac{1}{4}\right)}{h} \frac{(k_B T)^{\frac{3}{4}}}{a^{\frac{1}{4}}} \left(\frac{\pi\, m}{2}\right)^{\frac{1}{2}}\right) + \frac{3}{4}\right)$$

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

$$P = 0$$

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

$$\mu(T,V,N) = k_B\,T\ln\left(\frac{h}{\Gamma(\frac{1}{4})}\,\frac{a^{\frac{1}{4}}}{(k_B\,T)^{\frac{3}{4}}}\left(\frac{2}{\pi\,m}\right)^{\frac{1}{2}}\right)$$

Exercise 8

$$\begin{aligned}
Z(T,N) &= \int\limits_{\substack{\text{all phase}\\\text{space}}} \prod_{i=1}^{N}\frac{d^3\theta_i\,d^3L_i}{h^f}\,e^{-\beta\,\mathcal{H}_i}\\
&= \int\limits_{\substack{\text{all phase}\\\text{space}}} \left(\prod_{i=1}^{N}\frac{1}{h^3}\right)\left(\prod_{i=1}^{N}d^3\theta_i\right)\left(\prod_{i=1}^{N}d^3L_i\,e^{-\beta\left(\frac{L_1^2}{2I_1}+\frac{L_2^2}{2I_2}+\frac{L_1^3}{2I_3}\right)}\right)\\
&= \frac{1}{h^{3N}}\left(\int_0^{2\pi}d\theta\right)^{3N}\left(\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dL_1\,dL_2\,dL_3\,e^{-\frac{L_1^2}{2k_BTI_1}}\,e^{-\frac{L_2^2}{2k_BTI_2}}\,e^{-\frac{L_3^2}{2k_BTI_3}}\right)^N\\
&= \left(\frac{2\,\pi}{h}\right)^{3N}\left(\sqrt{2\,\pi\,k_B\,T\,I_1}\sqrt{2\,\pi\,k_B\,T\,I_2}\sqrt{2\,\pi\,k_B\,T\,I_3}\right)^N
\end{aligned}$$

$$Z(T,N) = \frac{(2\,\pi)^{\frac{9N}{2}}\,(k_B\,T)^{\frac{3N}{2}}\,(I_1\,I_2\,I_3)^N}{h^{3N}}$$

$$\begin{aligned}
F(T,N) &= -k_B\,T\ln Z(T,N)\\
&= -k_B\,T\ln\left(\frac{(2\,\pi)^{\frac{9N}{2}}\,(k_B\,T)^{\frac{3N}{2}}\,(I_1\,I_2\,I_3)^N}{h^{3N}}\right)\\
&= -N\,k_B\,T\ln\left(\frac{(2\,\pi)^{\frac{9}{2}}\,(k_B\,T)^{\frac{3}{2}}\,I_1\,I_2\,I_3}{h^3}\right)
\end{aligned}$$

$$\begin{aligned}
S(T,N) &= -\left(\frac{\partial F}{\partial T}\right)_N\\
&= N\,k_B\ln\left(\frac{(2\,\pi)^{\frac{9}{2}}\,(k_B\,T)^{\frac{3}{2}}\,I_1\,I_2\,I_3}{h^3}\right) + N\,k_B\,T\left(\frac{3}{2\,T}\right)
\end{aligned}$$

$$S(T,N) = N\,k_B\left(\ln\left(\frac{(2\,\pi)^{\frac{9}{2}}\,(k_B\,T)^{\frac{3}{2}}\,I_1\,I_2\,I_3}{h^3}\right)+\frac{3}{2}\right)$$

$$\begin{aligned}
\langle E\rangle &= -\frac{\partial}{\partial\beta}\ln Z(T,N)\\
&= \frac{\partial}{\partial\beta}\left(\ln\left(\frac{h^{3N}}{(2\,\pi)^{\frac{9N}{2}}\,(k_B\,T)^{\frac{3N}{2}}\,(I_1\,I_2\,I_3)^N}\right)\right)\\
&= N\,\frac{\partial}{\partial\beta}\left(\ln\beta^{\frac{3}{2}}+\ln\left(\frac{h^3}{(2\,\pi)^{\frac{9}{2}}\,I_1\,I_2\,I_3}\right)\right)\\
&= N\left(\frac{3}{2\,\beta}\right)
\end{aligned}$$

$$\langle E\rangle = \frac{3\,N\,k_B\,T}{2}$$

$$\lim_{T\to 0} S(T,N) = \lim_{T\to 0} N\,k_B \left(\ln\left(\frac{(2\,\pi)^{\frac{9}{2}}\,(k_B\,T)^{\frac{3}{2}}\,I_1\,I_2\,I_3}{h^3}\right) + \frac{3}{2}\right) = -\infty \neq 0$$

Thus this system does not obey the 3rd Law of thermodynamics, as the given system is not a thermodynamic system.