Física Estadistica
Tarea 3

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Contents

Chapter 1

1.1

Simplemente desarrollemos como:

$$
\begin{aligned}
-\frac{\partial}{\partial\beta} ln\left(\mathrm{Z}\right) &= -\frac{\partial}{\partial\beta}\ln\left(\sum_i e^{-\beta E_i}\right) \\
&= -\frac{\sum_i \frac{\partial}{\partial\beta} e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \\
&= -\frac{\sum_i -E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \\
&= \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \\
&= \langle E_i \rangle \\
&= U
\end{aligned}
$$

1.2

$$
\begin{aligned}
F &= -\frac{1}{\beta} \ln Z \\
S &= -\left(\frac{\partial F}{\partial T}\right)_{N,V} \\
&= -\frac{\partial}{\partial T}\left(-\frac{1}{\beta} \ln Z\right) \\
&= \frac{\partial}{\partial T}\left(\frac{1}{\beta} \ln Z\right) \\
&= \frac{\partial}{\partial T}\left(kT \ln Z\right) \\
&= k\frac{\partial}{\partial T}\left(T \ln Z\right) \\
&= k\left(\ln Z + T\frac{\partial}{\partial T} \ln Z\right) \\
\frac{\partial \ln Z}{\partial \beta} &= \frac{\partial \ln Z}{\partial \beta}\frac{\partial \beta}{\partial T} \\
\frac{\partial \beta}{\partial T} &= -\frac{1}{kT^2} \\
S &= k\left(\ln Z - \frac{T}{kT^2}\frac{\partial \ln Z}{\partial \beta}\right) \\
&= k\left(\ln Z - \frac{1}{kT}\frac{\partial \ln Z}{\partial \beta}\right) \\
&= k\left(\ln Z - \frac{1}{kT}\frac{\partial \ln Z}{\partial \beta}\right) \\
&= k\left(\ln Z - \beta\frac{\partial \ln Z}{\partial \beta}\right)
\end{aligned}
$$

1.3

$$
\begin{aligned}
C_V &= \left(\frac{\partial E}{\partial T}\right)_{N,V} \\
&= \frac{\partial}{\partial T}\left(-\frac{\partial}{\partial \beta}\ln Z\right) \\
\frac{\partial}{\partial \beta} &= \frac{\partial}{\partial \beta}\frac{\partial \beta}{\partial T} \\
\frac{\partial}{\partial \beta} &= -\frac{\partial}{\partial \beta}\frac{1}{kT^2} \\
C_V &= -\frac{\partial}{\partial \beta}\frac{1}{kT^2}\left(-\frac{\partial}{\partial \beta}\ln Z\right) \\
&= \frac{\partial}{\partial \beta}\frac{1}{kT^2}\frac{k}{k}\left(\frac{\partial}{\partial \beta}\ln Z\right) \\
&= \frac{\partial}{\partial \beta}\frac{1}{k^2T^2}k\left(\frac{\partial}{\partial \beta}\ln Z\right) \\
&= k\beta^2\left(\frac{\partial^2}{\partial \beta^2}\ln Z\right)
\end{aligned}
$$

Chapter 2

Sabemos que para este modelo, la probabilidad

$$P_i = g_i e^{-\frac{E_i}{k_B T}}$$

pero el propio enunciado nos da el degeneramiento. Ahora bien, es importante notar que la degeneración total para el estado $n = 2$ es 8 dada por el enunciado. Sin embargo, esto esta compuesto de dos estados en donde solamente 1 nos interesa (pues tenemos 2s y 2p) por lo tanto partamos estos estados notando que 2s tiene una degeneración de 2. Por lo tanto juntando todo esto la probabilidad simplemente se nos reduce a:

$$P(2p) = \frac{g_{2p} e^{-\frac{E_2}{kT}}}{2e^{-\frac{E_i}{kT}} + 8e^{-\frac{E_2}{kT}}}$$

Chapter 3

3.1

En este caso partimo de:

$$
\begin{aligned}
Z &= \sum_{i=0}^{\infty} e^{-\beta E_i} \\
Z_1 &= \sum_{i=0}^{\infty} e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} \\
&= \sum_{i=0}^{\infty} e^{-\beta\hbar\omega n} e^{-\beta\hbar\omega\frac{1}{2}} \\
&= e^{-\beta\hbar\omega\frac{1}{2}} \sum_{i=0}^{\infty} e^{-\beta\hbar\omega n} \\
&= e^{-\beta\hbar\omega\frac{1}{2}} \sum_{i=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n \\
\sum_{n=0}^{\infty} y^n &= \frac{1}{1-y} \text{ Serie Geometrica} \\
Z_1 &= e^{-\beta\hbar\omega\frac{1}{2}} \frac{1}{1-e^{-\beta\hbar\omega}} \\
&= \frac{1}{e^{-\beta\hbar\omega\frac{1}{2}}\left(1-e^{-\beta\hbar\omega}\right)} \\
&= \frac{1}{e^{-\beta\hbar\omega\frac{1}{2}} - e^{-\frac{1}{2}\beta\hbar\omega}} \\
&= \frac{1}{e^{-\beta\hbar\omega\frac{1}{2}} - e^{-\frac{1}{2}\beta\hbar\omega}} \frac{2}{2} \\
&= \frac{2}{e^{-\beta\hbar\omega\frac{1}{2}} - e^{-\frac{1}{2}\beta\hbar\omega}} \frac{1}{2} \\
&= \frac{1}{\sinh\left(\frac{\beta\hbar\omega}{2}\right)2} \\
&= \left[\sinh\left(\frac{\beta\hbar\omega}{2}\right)2\right]^{-1} \square
\end{aligned}
$$

3.2

En este caso :

$$Z_N = \prod_v Z_1$$
$$Z_N = \prod_v \frac{1}{2\sinh\left(\frac{\beta\hbar\omega(v)}{2}\right)}$$

Ahora tenemos la energia libre de Helmholtz como:

$$\begin{aligned}
F &= -\frac{1}{\beta}\ln Z_N \\
&= -\frac{1}{\beta}\ln\prod_v Z_1 \\
\ln(a*b) = \ln(a)+\ln(b) &\implies \ln\prod_n a_n = \sum_n \ln a_n \\
F &= -\frac{1}{\beta}\sum_v \ln Z_1 \\
Z_1 &= e^{-\beta\hbar\omega\frac{1}{2}}\frac{1}{1-e^{-\beta\hbar\omega}} \\
F &= -\frac{1}{\beta}\sum_v \ln e^{-\beta\hbar\omega\frac{1}{2}}\frac{1}{1-e^{-\beta\hbar\omega}} \\
&= -\frac{1}{\beta}\sum_v\left(\ln e^{-\beta\hbar\omega\frac{1}{2}} - \ln 1 - e^{-\beta\hbar\omega}\right) \\
&= -\frac{1}{\beta}\sum_v\left(-\beta\hbar\omega\frac{1}{2} - \ln 1 - e^{-\beta\hbar\omega}\right) \\
&= \sum_v\left(\frac{1}{\beta}\beta\hbar\omega\frac{1}{2} + \frac{1}{\beta}\ln\left(1-e^{-\beta\hbar\omega}\right)\right) \\
&= \sum_v\left(\hbar\omega\frac{1}{2} + \frac{1}{\beta}\ln\left(1-e^{-\beta\hbar\omega}\right)\right) \\
&= \sum_v F_v\square
\end{aligned}$$

3.3

En este caso partimos de

$$\begin{aligned}
U &= -\frac{\partial}{\partial\beta}\ln Z \\
&= -\frac{\partial}{\partial\beta}\ln\prod_v Z_1 \\
&= -\frac{\partial}{\partial\beta}\sum_v \ln Z_1 \\
&= \sum_v -\frac{\partial}{\partial\beta}\ln Z_1
\end{aligned}$$

Ahora definimos:

$$u_v = -\frac{\partial}{\partial\beta}\ln Z_1$$

Con lo que podemos desarrollar como:

$$\begin{aligned}
\ln Z_1 &= \ln\left(e^{-\beta\hbar\omega\frac{1}{2}}\frac{1}{1-e^{-\beta\hbar\omega}}\right)\\
\ln Z_1 &= \ln\left(e^{-\beta\hbar\omega\frac{1}{2}}\right)+\ln\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)\\
\ln Z_1 &= -\beta\hbar\omega\frac{1}{2}-\ln\left(1-e^{-\beta\hbar\omega}\right)
\end{aligned}$$

Que ahora derivamos parcialmente respecto a β con lo que tenemos:

$$\begin{aligned}
u_v &= -\frac{\partial}{\partial\beta}\ln Z_1\\
&= -\frac{\partial}{\partial\beta}\left(-\beta\hbar\omega\frac{1}{2}-\ln\left(1-e^{-\beta\hbar\omega}\right)\right)\\
&= \frac{\partial}{\partial\beta}\beta\hbar\omega\frac{1}{2}+\frac{\partial}{\partial\beta}\ln\left(1-e^{-\beta\hbar\omega}\right)\\
&= \hbar\omega\frac{1}{2}+\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)\frac{\partial-e^{-\beta\hbar\omega}}{\partial\beta}\\
&= \hbar\omega\frac{1}{2}+\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)\hbar\omega e^{-\beta\hbar\omega}\\
&= \hbar\omega\frac{1}{2}+\left(\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)\hbar\omega\\
&= \hbar\omega\frac{1}{2}+\left(\frac{1}{e^{\beta\hbar\omega}\left(1-e^{-\beta\hbar\omega}\right)}\right)\hbar\omega\\
&= \hbar\omega\frac{1}{2}+\left(\frac{1}{e^{\beta\hbar\omega}-1}\right)\hbar\omega\\
&= \hbar\omega\left[\frac{1}{2}+\left(\frac{1}{e^{\beta\hbar\omega}-1}\right)\right]\\
&= \hbar\omega\left[\frac{1}{2}+n_v(\beta)\right]\square
\end{aligned}$$

3.4

En este caso partimos desde el punto anterior

$$
\begin{aligned}
U &= \frac{Na}{2\pi}\int_{-\frac{\pi}{a}}^{+\frac{\pi}{a}}\left[n_v(\beta)+\frac{1}{2}\right]\hbar\omega(v)dv \\
U &= \frac{Na}{2\pi}\int_{-\frac{\pi}{a}}^{+\frac{\pi}{a}}\left[n_v(\beta)+\frac{1}{2}\right]\hbar C_L\left|v\right|dv \\
&= \frac{Na}{\pi}\int_{0}^{\frac{\pi}{a}}\left[n_v(\beta)+\frac{1}{2}\right]\hbar C_L v dv \\
&= \frac{Na}{\pi}\int_{0}^{\frac{\pi}{a}}\left[\frac{1}{e^{\beta\hbar c_L v}-1}+\frac{1}{2}\right]\hbar C_L v dv \\
&= \frac{Na}{\pi}\int_{0}^{\frac{\pi}{a}}\left[\frac{\hbar C_L v}{e^{\beta\hbar c_L v}-1}+\frac{C_L v}{2}\right]\hbar dv \\
x &= \beta\hbar C_L v \\
dv &= \frac{dx}{\beta\hbar c_L} \\
U &= \frac{Na}{\pi}\int_{0}^{\frac{\beta\hbar c_L\pi}{a}}\left[\frac{\frac{x}{\beta}}{e^{x}-1}+\frac{\frac{x}{\beta}}{2}\right]\frac{dx}{\beta\hbar c_L} \\
U &= \frac{Na}{\pi}\int_{0}^{\frac{\beta\hbar c_L\pi}{a}}\left[\frac{x}{e^{x}-1}+\frac{x}{2}\right]\frac{dx}{\beta^2\hbar c_L} \\
U &= \frac{Na}{\beta^2\hbar c_L\pi}\int_{0}^{\frac{\beta\hbar c_L\pi}{a}}\left[\frac{x}{e^{x}-1}+\frac{x}{2}\right]dx \\
\Theta &= \frac{\hbar c_L\pi}{ka} \\
\frac{\Theta}{T} &= \frac{\beta\hbar c_L\pi}{a} \\
U &= \frac{Na}{\beta^2\hbar c_L\pi}\int_{0}^{\frac{\Theta}{T}}\left[\frac{x}{e^{x}-1}+\frac{x}{2}\right]dx
\end{aligned}
$$

Con lo que podemos complementar como

$$U=\frac{Na}{\beta^2\hbar c_L\pi}\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\int_0^{\frac{\Theta}{T}}\frac{x}{2}dx$$
$$U=\frac{Na}{\beta^2\hbar c_L\pi}\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\left(\frac{\Theta}{T}\right)^2$$
$$\beta=\frac{1}{kT}$$
$$U=\frac{k^2T^2Na}{\hbar c_L\pi}\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\left(\frac{\Theta}{T}\right)^2$$
$$U=NkT^2\frac{ka}{\hbar c_L\pi}\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\left(\frac{\Theta}{T}\right)^2$$
$$U=NkT^2\frac{1}{\Theta}\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\left(\frac{\Theta}{T}\right)^2$$
$$U=NkT^2\frac{1}{\Theta}\left[\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\left(\frac{\Theta}{T}\right)^2\right]$$
$$U=NkT^2\frac{1}{\Theta}\left[\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\left(\frac{\Theta}{T}\right)^2\right]$$
$$U=NkT^2\frac{1}{\Theta}\left[\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\left(\frac{\Theta}{T}\right)^2\right]$$
$$U=Nk\left[\frac{T^2}{\Theta}\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\frac{T^2}{\Theta}\left(\frac{\Theta}{T}\right)^2\right]$$
$$U=Nk\left[\frac{T^2}{\Theta}\frac{\Theta}{\Theta}\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\frac{T^2}{\Theta}\left(\frac{\Theta}{T}\right)^2\right]$$
$$U=Nk\left[\Theta\frac{T^2}{\Theta^2}\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\Theta\right]$$
$$U=Nk\Theta\left[\frac{T^2}{\Theta^2}\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx+\frac{1}{4}\right]$$
$$U=Nk\Theta\left[\frac{1}{4}+\left(\frac{T}{\Theta}\right)^2\int_0^{\frac{\Theta}{T}}\frac{x}{e^x-1}dx\right]$$

3.5

Dado que $\Theta >> T$ entonces hagamos $\frac{\Theta}{T} \to \infty$ Con lo cual desarrollemos primero la integral:

$$\begin{aligned}
\int_0^{\frac{\Theta}{T}} \frac{x}{e^x - 1} dx \to \int_0^{\infty} \frac{x}{e^x - 1} dx \\
= \int_0^{\infty} \frac{x}{e^x - 1} dx \\
= \int_0^{\infty} x \sum_{n=0}^{\infty} e^{-nx} dx \\
= \sum_{n=0}^{\infty} \int_0^{\infty} x e^{-nx} dx \\
u = x;\ du = dx \\
dv = e^{-nx} dx;\ v = -\frac{1}{n} e^{-nx} \\
\int u dv = uv - \int v du \\
\int_0^{\infty} x e^{-nx} dx = -\frac{x}{n e^{nx}}\Big|_0^{\infty} + \frac{1}{n} \int_0^{\infty} e^{-nx} dx \\
-\frac{x}{n e^{nx}}\Big|_0^{\infty} = \lim_{x \to \infty} -\frac{x}{n e^{nx}} - 0 \\
-\frac{x}{n e^{nx}}\Big|_0^{\infty} = 0 - 0 = 0 \\
\int_0^{\infty} x e^{-nx} dx = \frac{1}{n} \int_0^{\infty} e^{-nx} dx \\
\int_0^{\infty} x e^{-nx} dx = \frac{1}{n}\frac{1}{n} \\
\int_0^{\infty} x e^{-nx} dx = \frac{1}{n^2} \\
\sum_{n=0}^{\infty} \int_0^{\infty} x e^{-nx} dx = \sum_{n=0}^{\infty} \frac{1}{n^2}
\end{aligned}$$

Esta es una serie conocida como *Basel Problem* y tiene como resultado $\frac{\pi^2}{6}$. Ahora dado que tenemos la integral podemos volver a la expresión completa de U

$$\begin{aligned}
U = Nk\Theta \left[\frac{1}{4} + \left(\frac{T}{\Theta} \right)^2 \int_0^{\frac{\Theta}{T}} \frac{x}{e^x - 1} x \right] \\
= Nk\Theta \left[\frac{1}{4} + \left(\frac{T}{\Theta} \right)^2 \frac{\pi^2}{6} \right]
\end{aligned}$$

Ahora con esto podemos simplemente derivar para obtener C_V

$$
\begin{aligned}
C_V &= \frac{\partial U}{\partial T} \\
&= \frac{\partial}{\partial T} Nk\Theta \left[\frac{1}{4} + \left(\frac{T}{\Theta} \right)^2 \frac{\pi^2}{6} \right] \\
&= Nk\Theta \left[\frac{\partial}{\partial T} \left(\frac{T}{\Theta} \right)^2 \frac{\pi^2}{6} \right] \\
&= Nk\Theta \left[2T \left(\frac{1}{\Theta} \right)^2 \frac{\pi^2}{6} \right] \\
&= Nk \left[2 \left(\frac{T}{\Theta} \right) \frac{\pi^2}{6} \right] \\
&= Nk \left[\left(\frac{T}{\Theta} \right) \frac{\pi^2}{3} \right] \\
&= Nk \left(\frac{T}{\Theta} \right) \frac{\pi^2}{3} \square
\end{aligned}
$$

Chapter 4

4.1

Para esto partimos con:

$$
\begin{aligned}
Z &= \frac{1}{N!h^{3N}} \int e^{-\beta \sum_{i=0}^{N} p_i c} d^{3N} q d^{3N} p \\
&= \frac{1}{N!h^{3N}} \int e^{-\beta \sum_{i=0}^{N} p_i c} d^{3N} p \int d^{3N} q \\
&= \frac{1}{N!h^{3N}} \int e^{-\beta \sum_{i=0}^{N} p_i c} d^{3N} p V^N \\
&= \frac{V^N}{N!h^{3N}} \int e^{-\beta \sum_{i=0}^{N} p_i c} d^{3N} p \\
&= \frac{V^N}{N!h^{3N}} \left[\int e^{-\beta \sum_{i=0}^{N} p_i c} p_i^2 \sin\theta dpi d\theta d\phi \right]^N \\
&= \frac{V^N}{N!h^{3N}} \left[\int_0^\infty e^{-\beta \sum_{i=0}^{N} p_i c} p_i^2 dpi \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \right]^N \\
&= \frac{V^N}{N!h^{3N}} \left[\int_0^\infty e^{-\beta \sum_{i=0}^{N} p_i c} p_i^2 dpi 4\pi \right]^N \\
&= \frac{1}{N!} \left[\int_0^\infty e^{-\beta \sum_{i=0}^{N} p_i c} \frac{V4pi}{h^3} p_i^2 dpi \right]^N \\
\int_0^\infty e^{-\beta \sum_{i=0}^{N} p_i c} \frac{V4pi}{h^3} p_i^2 dpi &= \frac{8\pi V}{h^3} \frac{1}{\beta^3 C^3} \\
Z &= \frac{1}{N!} \left(\frac{8\pi V}{h^3} \frac{1}{\beta^3 C^3} \right)^N \\
&= \frac{1}{N!} \left(8\pi V \left(\frac{kT}{hC} \right)^3 \right)^N
\end{aligned}
$$

4.2

Para este caso

$$
\begin{aligned}
F &= -\frac{1}{\beta}\ln(Z) \\
&= -\frac{1}{\beta}\ln\left(\frac{1}{N!}\left(8\pi V\left(\frac{kT}{hC}\right)^3\right)^N\right) \\
&= -\frac{1}{\beta}\left(N\ln\left(8\pi V\left(\frac{kT}{hC}\right)^3\right)-\ln(N!)\right) \\
&= -\frac{1}{\beta}\left(N\ln\left(8\pi V\left(\frac{kT}{hC}\right)^3\right)-N\ln(N)+N\right) \\
&= -\frac{N}{\beta}\left(\ln\left(8\pi V\left(\frac{kT}{hC}\right)^3\right)-\ln(N)+1\right) \\
&= -\frac{N}{\beta}\left(\ln\left(\frac{8\pi V}{N}\left(\frac{kT}{hC}\right)^3\right)+1\right) \\
&= -kTN\left(\ln\left(\frac{8\pi V}{N}\left(\frac{kT}{hC}\right)^3\right)+1\right)
\end{aligned}
$$

4.3

Tenemos:

$$
\begin{aligned}
S &= -\left(\frac{\partial F}{\partial T}\right)_{N,V} \\
&= -\left(\frac{\partial}{\partial T}-kTN\left(\ln\left(\frac{8\pi V}{N}\left(\frac{kT}{hC}\right)^3\right)+1\right)\right)_{N,V} \\
&= -kN\left(\ln\left(\frac{8\pi V}{N}\left(\frac{kT}{hC}\right)^3\right)+1\right)-kN\cancel{T}\left(\cancel{\frac{N}{8\pi V}}\cancel{\left(\frac{hc}{kT}\right)^3}\right)\cancel{\frac{8\pi V}{N}}3\left(\cancel{\frac{k}{hC}}\right)^3\cancel{T^2} \\
&= -kN\left(\ln\left(\frac{8\pi V}{N}\left(\frac{kT}{hC}\right)^3\right)+1+3\right) \qquad = -kN\left(\ln\left(\frac{8\pi V}{N}\left(\frac{kT}{hC}\right)^3\right)+4\right)
\end{aligned}
$$

4.4

En este caso

$$
\begin{aligned}
U &= -\frac{\partial}{\partial \beta} \ln Z \\
&= -\frac{\partial}{\partial \beta} \left(\ln \left(\frac{1}{N!} \left(\frac{8\pi V}{h^3} \frac{1}{\beta^3 C^3} \right) \right)^N \right) \\
&= -\frac{\partial}{\partial \beta} \left(\ln \left(\frac{1}{N!} \right) - N \ln \left(\frac{\beta^3 C^3}{8\pi V} \right) \right) \\
&= \frac{\partial}{\partial \beta} \left(N \ln \left(\frac{\beta^3 C^3}{8\pi V} \right) \right) \\
&= N \frac{8\pi V}{\beta^3 C^3} \frac{C^3}{8\pi V} 3\beta^2 \\
&= \frac{3N}{\beta} \\
&= 3NkT
\end{aligned}
$$

Ahora nos queda

$$
\begin{aligned}
C_v &= \left(\frac{\partial U}{\partial T} \right)_{N,V} \\
&= 3Nk
\end{aligned}
$$

Por otro lado:

$$
\begin{aligned}
C_p &= \frac{\partial (U + PV)}{\partial T} \\
&= \frac{\partial}{\partial T} (3NkT + NkT) \\
&= 4Nk
\end{aligned}
$$

Por lo tanto

$$
\begin{aligned}
\gamma &= \frac{C_p}{C_v} \\
&= \frac{4Nk}{3Nk} \\
&= \frac{4}{3}
\end{aligned}
$$

Chapter 5

5.1

Partimos desde:

$$
\begin{aligned}
Z &= \frac{1}{h}\int e^{-\beta\frac{p^2}{2m}}dp\int e^{-\beta\left(cq^2-gq^3-fq^4\right)}dq \\
&= \frac{1}{h}\int e^{-\beta\frac{p^2}{2m}}dp\int e^{-\beta\left(cq^2\right)}e^{-\beta\left(-gq^3-fq^4\right)}dq \\
e^{-\beta\left(-gq^3-fq^4\right)} &= \sum_{n=0}^{\infty}\left(-\beta CUq^3-Fq^4\right)^n \\
&= 1+\beta Cgq^3+Fq^4+\frac{\beta}{2}g^2q^6+\ldots \\
Z &= \gamma\left(\sqrt{\frac{\pi}{\beta C}}+\int_{-\infty}^{\infty}e^{-\beta rq^2}\beta gq^3dq+\int_{-\infty}^{\infty}e^{-\beta cq^2}\beta Fq^4dq+\int_{-\infty}^{\infty}e^{-\beta cq^2}\frac{1}{2}\beta^2g^2q^6dq\right) \\
e^{-\beta Cq^2}q^4 &= \frac{\partial^2}{\partial q^2}Ce^{-\beta Cq^2}\frac{1}{\beta F} \\
e^{-\beta Cq^2}q^6 &= \frac{\partial^3}{\partial q^3}Ce^{-\beta Cq^2}\frac{1}{\beta^2g^2} \\
\int_{-\infty}^{\infty}e^{-\beta cq^2}q^4\beta Fdq &= \beta F\left(\frac{3}{4}\sqrt{\frac{\pi}{(\beta C)^2}}\right) \\
\int_{-\infty}^{\infty}\frac{1}{2}\beta g^2e^{-\beta Cq^2}q^6dq &= -\frac{\beta^2g^2}{2}\left(-\frac{15}{8}\sqrt{\frac{\pi}{(\beta C)^7}}\right) \\
Z_1 &= \frac{1}{h}\sqrt{\frac{2m\pi}{\beta C}}\left(\sqrt{\frac{\pi}{\beta C}}+\frac{3}{4}\beta F\sqrt{\frac{\pi}{(\beta C)^5}}+\frac{15}{16}B^2g^2\sqrt{\frac{\pi}{(C\beta)^2}}\right) \\
&= \frac{\pi}{\beta h}\sqrt{\frac{2m}{C}}\left(1+\frac{3}{4}\frac{F}{\beta C^2}+\frac{15}{16}\frac{g^2}{bC^3}\right)
\end{aligned}
$$

$$
\begin{aligned}
U &= -\frac{\partial}{\partial\beta}\ln Z \\
&= \frac{\partial}{\partial\beta}\left(\ln\left(\frac{\pi}{\beta h}\sqrt{\frac{2m}{C}}\left(1+\frac{3}{4}\frac{F}{\beta C^2}+\frac{15}{16}\frac{g^2}{bC^3}\right)\right)\right) \\
&= \frac{\partial}{\partial\beta}\left(\ln\left(\frac{\pi}{\beta h}\sqrt{\frac{2m}{C}}\right)+\ln\left(1+\frac{3}{4}\frac{F}{\beta C^2}+\frac{15}{16}\frac{g^2}{bC^3}\right)\right) \\
&= \frac{1}{\beta}+\frac{-\frac{3F}{4\beta^2C^2}+\frac{15g^2}{168^2c^63}}{1+\frac{3f}{4\beta C^2}+\frac{\beta g^2}{16\beta C^3}} \\
&= \frac{1}{\beta}+\frac{\frac{3F}{4C^2}+\frac{15g^2}{16c^3}}{B^2+\frac{3F\beta}{4C^2}+\frac{15g^2}{16C^3}}
\end{aligned}
$$

$$
U \approx \frac{1}{\beta}+\frac{1}{\beta^2}\left(\frac{3F}{4C^2}+\frac{15g^2}{16C^3}\right)
$$

5.2

Tenemos que:

$$
\begin{aligned}
C_V &= \frac{\partial U}{\partial T} \\
&= \frac{\partial}{\partial T}\left(kT+k^2T^2\left(\frac{3F}{4C^2}+\frac{15g^2}{16C^3}\right)\right) \\
&= k+2k^2T\left(\frac{3F}{4C^2}+\frac{15g^2}{16C^3}\right)T
\end{aligned}
$$

5.3

Para este caso partimos desde:

$$
\begin{aligned}
\langle q\rangle &= \frac{1}{h}\int_{-\infty}^{\infty} e^{-\beta\frac{\beta^2}{2m}+\left(q^i-gq^3-Fq^4\right)}q\,dp\,dq \\
&= \frac{\sqrt{\frac{2m\beta}{hz}}}{\int}\Big._{-\infty}^{\infty} e^{-\beta cq^2}\left(q+\beta\left(gq^4+Fq^3\right)\right)+\frac{1}{2}\beta^2g^2q^7dq \\
&= \frac{\sqrt{\frac{2m\pi}{hz}}}{\int}\Big._{-\infty}^{\infty} e^{-\beta cq^2}\beta gq^7 \\
&= \frac{\sqrt{\frac{2m\pi}{hz}}}{\int}\Big._{-\infty}^{\infty} e^{-\beta cq^2}\beta g\left(\frac{3}{4}\sqrt{\frac{\pi}{\beta c^5}}\right) \\
&= \frac{3}{4}\frac{\pi g}{hz}\sqrt{\frac{2m}{\beta^4c^5}} \\
&= \frac{\frac{3\pi g}{4h}\sqrt{\frac{2m}{\beta^4c^3}}}{\frac{\pi}{\beta h}\sqrt{\frac{2m}{c}}\left(1+\frac{3F}{4\beta c^2}+\frac{15g^2}{16\beta c^2}\right)}
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{3}{4}\frac{g}{\beta c^2}\left(1+\frac{3F}{4\beta c^2}+\frac{15g^2}{16\beta c^5}\right)^{-1} \\
\langle q\rangle &= \frac{3g}{4\beta c^2} \\
\frac{1}{q_0}\frac{\partial\langle q\rangle}{\partial T} &= \frac{1}{q_0}\frac{\partial}{\partial T}\left(\frac{3g}{4c^2}kT\right) \\
&= \frac{1}{q_0}\frac{3}{4}\frac{g}{c^2}k = \alpha
\end{aligned}
$$

5.4

$$
\begin{aligned}
Z_1 &= \frac{1}{h}\sum_{n=0}^{\infty} e^{-\beta\left[\left(ch+\frac{1}{2}\right)\hbar\omega - X\left(n+\frac{1}{2}\right)^2\hbar\omega\right]} \\
&= \sum_{n=1}^{\infty} e^{-\beta\hbar w\left(n+\frac{1}{2}\right)} - e^{\beta x h w\left(n+\frac{1}{2}\right)} \\
e^{\beta x w\hbar\left(n+\frac{1}{2}\right)} &= 1+\beta x w\hbar\left(n+\frac{1}{2}\right) \\
Z_1 &= \sum_{n=0}^{\infty} e^{-\beta\hbar w\left(n+\frac{1}{2}\right)}\left(1+\beta x w\hbar\left(n+\frac{1}{2}\right)\right) \\
&= e^{-\frac{\beta k w}{2}}\left(\sum_{k=0}^{\infty}\left(e^{-\beta k w}\right)\right)+\beta w x\hbar\left(\frac{1}{2}\sum_{n=0}^{\infty}\left(e^{-\beta\hbar w}\right)^n+\sum_{n=2}^{\infty}e^{-\beta\hbar\omega n}\right) \\
&= \frac{\operatorname{csch}\left(\frac{1}{2}\beta\hbar w\right)}{2}\left(1+\frac{\beta w x\hbar}{2}\right)-\beta w x\hbar\frac{\partial}{\partial\beta\hbar w}\left(\frac{\operatorname{csch}\left(\frac{1}{2}\beta\hbar w\right)}{2}\right) \\
&= \frac{\operatorname{csch}\frac{1}{2}\beta\hbar w}{2}\left(1+\frac{\beta w x\hbar}{2}\left(\frac{1}{2}\coth\left(\frac{1}{2}\beta\hbar w\right)+1\right)\right)
\end{aligned}
$$

5.5

$$
\begin{aligned}
U &= \beta\hbar w \\
&= -\frac{\partial}{\partial\beta}\ln\left(z_1\right) \\
&= -hw\frac{\partial}{\partial u}\ln Z_1 \\
\ln z_1 &= -\ln\left(2\sinh\left(\frac{u}{2}\right)\right)+\frac{xu}{2}\left(\frac{1}{2}\coth\left(\frac{1}{2}u\right)\right)+1 \\
U &= -\hbar w\frac{\partial}{\partial u}\left(\frac{2x}{w}+\frac{xh}{12}+\frac{xu^3}{120}\right) \qquad = -kwx\left(\frac{2k^2T^2}{\hbar^2w^2}-\frac{1}{12}-\frac{\hbar^2w^2}{40k^2T^2}\right)
\end{aligned}
$$

5.6

$$\begin{aligned}
C_V &= \frac{\partial U}{\partial T} \\
&= \frac{\partial U}{\partial u}\frac{\partial u}{\partial}\frac{\partial \beta}{\partial T} \\
&= \frac{h^2 w^2}{kT^2} x \left(\frac{4}{w^3} - \frac{w}{20}\right) \\
&= \frac{4x\hbar^2 w^2}{kT^2\beta^2\hbar^2 w^2}\left(\frac{1}{w} + \frac{u^3}{30}\right) \\
&= 4xk\left(\frac{1}{u} + \frac{u^3}{30}\right)
\end{aligned}$$

5.7

$$\begin{aligned}
C_V &= 4xk\left(\frac{kT}{\hbar w} + \frac{\hbar^3 w^3}{k^3 T^3 80}\right) \\
&= \frac{4xk - T}{\hbar w}\alpha k^2 T \text{ Clasico} \\
C_V &= \frac{3}{2}k^2\left(\frac{F}{c^2} + \frac{5g^2}{4c^3}\right) T\alpha k^2 T \text{ Cuantico}
\end{aligned}$$

Chapter 6

6.1

Podemos tratar esta función como separable para cada grado de libertad. Por lo tanto se veria algo como:

$$Z_1 = Z_r Z_\Omega Z_{dip}$$

Con lo cual:

$$\begin{aligned} Z_r &= \frac{1}{h^3}\int e^{-\beta\frac{p^2}{2m}}d^3p\int d^3r \\ &= (2\pi mkT)^{\frac{3}{2}}\frac{V}{h^3} \end{aligned}$$

$$\begin{aligned} L^2 &= p_\theta^2 + \frac{p_\phi^2}{\sin\theta} \\ E_\Omega &= \frac{L^2}{2I} \\ Z_\Omega &= \frac{1}{h^3}\int e^{-\beta E_\Omega}d^3Ld\Omega \\ Z_\Omega &= \frac{1}{h^3}\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-\beta\frac{L^2}{2I}}L^2dLd\cos\theta_L d\phi_L \\ \int_0^\pi d\cos\theta_L &= 2 \\ \int_0^{2\pi} d\phi_L &= 2\pi \\ u &= \beta\frac{L^2}{2I} \\ du &= \beta\frac{L}{I}dL \\ \int_0^\infty L^2e^{-\beta\frac{L^2}{2I}}dL &= \int_0^\infty Le^{-u}\frac{I}{\beta}du \\ &= \frac{I}{\beta}\int_0^\infty Le^{-u}du \\ &= \frac{I}{\beta}\cdot\frac{4I^2}{\beta} \\ Z_\Omega &= \frac{4\pi^2 IkT}{h^2} \end{aligned}$$

$$
\begin{aligned}
Z_{dip} &= \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} e^{\beta\mu E\cos\theta}\sin d\theta d\phi \\
&= \frac{\sinh\left(\beta\mu E\right)}{\beta\mu E}
\end{aligned}
$$

Ahora para construir toda la función de partición simplemente multiplicamos por todos los resultados lo que nos da:

$$
Z_1 = (2\pi mkT)^{\frac{3}{2}}\frac{V}{h^3}\frac{4\pi^2 IkT}{h^2}\frac{\sinh\left(\beta\mu E\right)}{\beta\mu E}
$$

Para encontrar la función de partición total simplemente es la función de partición de cada molecula y se multiplica por la corrección de Gibbs con lo que nos da:

$$
\begin{aligned}
Z_N &= \frac{1}{N!}\left[Z_1\right]^N \\
Z_N &= \frac{1}{N!}\left[(2\pi mkT)^{\frac{3}{2}}\frac{V}{h^3}\frac{4\pi^2 IkT}{h^2}\frac{\sinh\left(\beta\mu E\right)}{\beta\mu E}\right]^N
\end{aligned}
$$

6.2

En este caso

$$
\begin{aligned}
\left\langle\mu\cos\theta\right\rangle &= \frac{\int_0^{\pi}\mu\cos\theta e^{\beta\mu E\cos\theta}\sin\theta d\theta}{\int_0^{\pi} e^{\beta\mu E\cos\theta}\sin\theta d\theta} \\
\int_0^{\pi} e^{\beta\mu E\cos\theta}\sin\theta d\theta &= \frac{\sinh\left(\beta\mu E\right)}{\beta\mu E} \\
\int_0^{\pi}\mu\cos\theta e^{\beta\mu E\cos\theta}\sin\theta d\theta &= mu\frac{d}{d\left(\beta\mu E\right)}\int_0^{\pi} e^{\beta\mu E\cos\theta}\sin\theta d\theta \\
&= \frac{d}{d\left(\beta\mu E\right)}\frac{\sinh\left(\beta\mu E\right)}{\beta\mu E} \\
&= \frac{\beta\mu E\cosh\left(\beta\mu E\right)-\sinh\left(\beta\mu E\right)}{\left(\beta\mu E^2\right)} \\
\left\langle\mu\cos\theta\right\rangle &= \mu\frac{\cosh\left(\beta\mu E\right)}{\sinh\left(\beta\mu E\right)}-\frac{1}{\beta\mu E} \\
&= \mu L\left(\beta\mu E\right)
\end{aligned}
$$

Donde $L(x) = \coth x - \frac{1}{x}$ es la función de Langevin.

6.3

Para este caso vamos a usar:

$$
\begin{aligned}
P &= \frac{N}{V}\left\langle \mu\cos\theta \right\rangle \\
&= \frac{N}{V}\mu L\left(\beta\mu E\right) \\
x \ll 1 \implies L(x) &= \frac{x}{3} \\
P &\approx \frac{N}{V}\mu\left(\frac{\beta\mu E}{3}\right) \\
&\approx \frac{N}{V}\mu\left(\frac{\beta\mu}{3}\right)E \\
\alpha &= \frac{N}{V}\mu\left(\frac{\beta\mu}{3}\right) \\
&\approx \alpha E
\end{aligned}
$$

Ahora, para mostar que

$$
\begin{aligned}
\alpha &= \lim_{E\to 0}\frac{\partial \frac{N}{V3}\left\langle \mu\cos\theta \right\rangle}{\partial E} \\
\alpha &= \lim_{E\to 0}\frac{N}{V3}\mu\frac{\partial L\left(\beta\mu E\right)}{\partial E} \\
\alpha &= \lim_{E\to 0}\frac{N}{V3}\mu\left(\beta\mu\left(1 - L\left(\beta\mu E\right)^2\right)\right) \\
\alpha &= \frac{N}{V3}\mu\left(\beta\mu\left(1-0^2\right)\right) \\
\alpha &= \frac{N}{V3}\mu\beta\mu \\
\alpha &= \frac{N}{V}\mu\left(\frac{\beta\mu}{3}\right)
\end{aligned}
$$

6.4

Salimos de

$$
\begin{aligned}
P &= \frac{N}{V}\mu\left(\frac{\beta\mu}{3}\right)E \\
P &= \epsilon_0\chi_e E \\
\chi_e &= \frac{P}{\epsilon_0 E} \\
&= \frac{N}{V}\frac{\mu^2}{3\epsilon_0 kT} \\
k &= 1 + \chi_e \\
&= 1 + \frac{N}{V}\frac{\mu^2}{3\epsilon_0 kT} \\
&= 1 + f\left(\frac{1}{T}\right) \square
\end{aligned}
$$