Mecánica Estadística: Tarea 1

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1. Fórmula del virial

Sea $\Omega \subseteq \mathbb{R}^3$ el espacio que ocupa el gas. Entonces el espacio de estados es $\Omega^N \times \mathbb{R}^{3N}$. Tenemos el Hamiltoniano $H : \Omega^N \times \mathbb{R}^{3N} \to \mathbb{R}$ dado por

$$H(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots \mathbf{p}_N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1, j\neq i}^{N} v(\|\mathbf{r}_i - \mathbf{r}_j\|). \tag{1}$$

Consideramos como el espacio de macroestados $\mathbb{R}^+ \times \mathbb{R}^+$ donde los elementos son pares de temperaturas inversas y volumenes. Entonces la función de partición canónica $Z : \mathbb{R}^+ \times \mathbb{R}^+ \to \mathbb{R}$ satisface que $Z(\beta, V)$ es proporcional a

$$\begin{aligned}
&\int_{\Omega^N \times \mathbb{R}^{3N}} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N d^3\mathbf{p}_1 \cdots d^3\mathbf{p}_N \exp(-\beta H(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots \mathbf{p}_N)) \\
&= \int_{\mathbb{R}^{3N}} d^3\mathbf{p}_1 \cdots d^3\mathbf{p}_N \exp\left(-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}\right) \int_{\Omega^N} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\left(-\beta \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1, j\neq i}^{N} v(\|\mathbf{r}_i - \mathbf{r}_j\|)\right) \\
&= \int_{\mathbb{R}^{3N}} d^3\mathbf{p}_1 \cdots d^3\mathbf{p}_N \prod_{i=1}^{N} \exp\left(-\beta \frac{\mathbf{p}_i^2}{2m_i}\right) \int_{\Omega^N/V^{1/3}} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N V^N \exp\left(-\beta \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1, j\neq i}^{N} v(V^{1/3}\|\mathbf{r}_i - \mathbf{r}_j\|)\right) \\
&= V^N \prod_{i=1}^{N} \int_{\mathbb{R}^3} d^3\mathbf{p} \exp\left(-\beta \frac{\mathbf{p}^2}{2m_i}\right) \int_{\Omega^N/V^{1/3}} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\left(-\beta \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1, j\neq i}^{N} v(V^{1/3}\|\mathbf{r}_i - \mathbf{r}_j\|)\right) \\
&= V^N \prod_{i=1}^{N} \left(\int_{\mathbb{R}} dp \exp\left(-\beta \frac{p^2}{2m_i}\right)\right)^3 \int_{\Omega^N/V^{1/3}} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\left(-\beta \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1, j\neq i}^{N} v(V^{1/3}\|\mathbf{r}_i - \mathbf{r}_j\|)\right) \\
&= V^N \prod_{i=1}^{N} \left(\frac{2\pi m_i}{\beta}\right)^{3/2} \int_{\Omega^N/V^{1/3}} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\left(-\beta \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1, j\neq i}^{N} v(V^{1/3}\|\mathbf{r}_i - \mathbf{r}_j\|)\right).
\end{aligned} \tag{2}$$

Por lo tanto, notando que el volumen de $\Omega^N/V^{1/3}$ es 1, se tiene

$$\begin{aligned}
&\beta p(\beta, V) = \frac{\partial \ln Z}{\partial V}(\beta, V) = \frac{1}{Z(\beta, V)}\frac{\partial Z}{\partial V}(\beta, V) \\
&= \frac{N V^{N-1} \int_{\Omega^N/V^{1/3}} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\left(-\beta \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1, j\neq i}^{N} v(V^{1/3}\|\mathbf{r}_i - \mathbf{r}_j\|)\right)}{V^N \int_{\Omega^N/V^{1/3}} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\left(-\beta \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1, j\neq i}^{N} v(V^{1/3}\|\mathbf{r}_i - \mathbf{r}_j\|)\right)} + \\
&\frac{\int_{\Omega^N/V^{1/3}} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N (-\frac{\beta}{2}\sum_{i\neq j} v'(V^{1/3}\|\mathbf{r}_i - \mathbf{r}_j\|)\|\mathbf{r}_i - \mathbf{r}_j\| \frac{1}{3}V^{-2/3}) \exp\left(-\beta \frac{1}{2}\sum_{i\neq j} v(V^{1/3}\|\mathbf{r}_i - \mathbf{r}_j\|)\right)}{\int_{\Omega^N/V^{1/3}} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\left(-\beta \frac{1}{2}\sum_{i\neq j} v(V^{1/3}\|\mathbf{r}_i - \mathbf{r}_j\|)\right)} \\
&= n - \frac{\beta}{6}V^{-2/3} \frac{\sum_{i,j=1, i\neq j}^{N} \int_{\Omega^N} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N v'(\|\mathbf{r}_i - \mathbf{r}_j\|)\|\mathbf{r}_i - \mathbf{r}_j\| \exp\left(-\beta \frac{1}{2}\sum_{i,j=1, i\neq j}^{N} v(\|\mathbf{r}_i - \mathbf{r}_j\|)\right)}{\int_{\Omega^N} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\left(-\beta \frac{1}{2}\sum_{i,j=1, i\neq j}^{N} v(\|\mathbf{r}_i - \mathbf{r}_j\|)\right)}.
\end{aligned} \tag{3}$$

Si el sistema es homogeneo e isotrópico tenemos

$$
\begin{aligned}
&\beta p(\beta, V)\\
&= n - \frac{\beta}{6} V^{-2/3} \frac{N(N-1)\int_{\Omega^N} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N v'(\|\mathbf{r}_1 - \mathbf{r}_2\|)\|\mathbf{r}_1 - \mathbf{r}_2\| \exp\Big(-\beta\frac{1}{2}\sum_{i,j=1,i\neq j}^N v(\|\mathbf{r}_i - \mathbf{r}_j\|)\Big)}{\int_{\Omega^N} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\Big(-\beta\frac{1}{2}\sum_{i,j=1,i\neq j}^N v(\|\mathbf{r}_i - \mathbf{r}_j\|)\Big)}\\
&= n - \frac{\beta V^{-2/3} N(N-1)}{6} \int_{\Omega^2} d^3\mathbf{r}_1 d^3\mathbf{r}_2 v'(\|\mathbf{r}_1 - \mathbf{r}_2\|)\|\mathbf{r}_1 - \mathbf{r}_2\|\\
&\frac{\int_{\Omega^{N-2}} d^3\mathbf{r}_3 \cdots d^3\mathbf{r}_N \exp\Big(-\beta\frac{1}{2}\sum_{i,j=1,i\neq j}^N v(\|\mathbf{r}_i - \mathbf{r}_j\|)\Big)}{\int_{\Omega^N} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\Big(-\beta\frac{1}{2}\sum_{i,j=1,i\neq j}^N v(\|\mathbf{r}_i - \mathbf{r}_j\|)\Big)}\\
&= n - \frac{\beta V^{-2/3}}{6} \int_{\Omega^2} d^3\mathbf{r}_1 d^3\mathbf{r}_2 v'(\|\mathbf{r}_1 - \mathbf{r}_2\|)\|\mathbf{r}_1 - \mathbf{r}_2\|\\
&\frac{\int_{\Omega^N} d^3\mathbf{u}_1 \cdots d^3\mathbf{u}_N \sum_{i=1}^N \sum_{j=1,j\neq i}^N \delta(\mathbf{u}_i - \mathbf{r}_1)\delta(\mathbf{u}_j - \mathbf{r}_2) \exp\Big(-\beta\frac{1}{2}\sum_{i,j=1,i\neq j}^N v(\|\mathbf{u}_i - \mathbf{u}_j\|)\Big)}{\int_{\Omega^N} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \exp\Big(-\beta\frac{1}{2}\sum_{i,j=1,i\neq j}^N v(\|\mathbf{r}_i - \mathbf{r}_j\|)\Big)}\\
&= n - \frac{\beta V^{-2/3}}{6} \int_{\Omega^2} d^3\mathbf{r}_1 d^3\mathbf{r}_2 v'(\|\mathbf{r}_1 - \mathbf{r}_2\|)\|\mathbf{r}_1 - \mathbf{r}_2\| n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\\
&= n - \frac{\beta V^{-2/3}}{6} \int_{\Omega^2} d^3\mathbf{r}_1 d^3\mathbf{r}_2 v'(\|\mathbf{r}_1 - \mathbf{r}_2\|)\|\mathbf{r}_1 - \mathbf{r}_2\| n^2 g(\|\mathbf{r}_1 - \mathbf{r}_2\|) = n - \frac{\beta n^2 V^{1/3}}{6}\int_\Omega d^3\mathbf{r} v'(\|\mathbf{r}\|)\|\mathbf{r}\| g(\|\mathbf{r}\|)
\end{aligned}
\tag{4}
$$

2. Fórmula de compresibilidad

1.

$$
\begin{aligned}
&\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\\
&= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \left\langle \left(\sum_{i=1}^N \delta(\mathbf{x}_i - \mathbf{r}_1)\right)\left(\sum_{i=1}^N \delta(\mathbf{x}_j - \mathbf{r}_2)\right)\right\rangle\\
&= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{1}{Z(\mu, V, \beta)} \sum_{N=0}^\infty \frac{\zeta^N}{N!} \int d^3\mathbf{x}_1 \cdots d^3\mathbf{x}_N \sum_{i=1}^N \sum_{j=1,j\neq i}^N \delta(\mathbf{x}_i - \mathbf{r}_1)\delta(\mathbf{x}_j - \mathbf{r}_2) e^{-\beta U(\mathbf{x}_1,\ldots,\mathbf{x}_N)}\\
&= \sum_{N=0}^\infty \sum_{i=1}^N \sum_{j=1,j\neq i}^N \frac{1}{Z(\mu, V, \beta)} \frac{\zeta^N}{N!} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \int d^3\mathbf{x}_1 \cdots d^3\mathbf{x}_N \delta(\mathbf{x}_i - \mathbf{r}_1)\delta(\mathbf{x}_j - \mathbf{r}_2) e^{-\beta U(\mathbf{x}_1,\ldots,\mathbf{x}_N)}\\
&= \sum_{N=0}^\infty \sum_{i=1}^N \sum_{j=1,j\neq i}^N \frac{1}{Z(\mu, V, \beta)} \frac{\zeta^N}{N!} \int d^3\mathbf{x}_1 \cdots d^3\mathbf{x}_N e^{-\beta U(\mathbf{x}_1,\ldots,\mathbf{x}_N)}\\
&= \sum_{N=0}^\infty N(N-1) \frac{1}{Z(\mu, V, \beta)} \frac{\zeta^N}{N!} \int d^3\mathbf{x}_1 \cdots d^3\mathbf{x}_N e^{-\beta U(\mathbf{x}_1,\ldots,\mathbf{x}_N)}\\
&= \frac{1}{Z(\mu, V, \beta)} \sum_{N=0}^\infty \frac{\zeta^N}{N!} \int d^3\mathbf{x}_1 \cdots d^3\mathbf{x}_N N(N-1) e^{-\beta U(\mathbf{x}_1,\ldots,\mathbf{x}_N)} = \langle N(N-1)\rangle
\end{aligned}
\tag{5}
$$

2. Por una parte tenemos

$$\begin{aligned}
\zeta\frac{\partial\langle N\rangle}{\partial\zeta} &= \zeta\frac{\partial}{\partial\zeta}\frac{1}{Z(\mu,V,\beta)}\sum_{N=0}^{\infty}\frac{\zeta^N}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N N e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&= \frac{1}{Z(\mu,V,\beta)}\sum_{N=0}^{\infty}\frac{\zeta^N}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N N^2 e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&- \frac{1}{Z(\mu,V,\beta)^2}\sum_{N=0}^{\infty}\frac{\zeta^N}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N N e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&\times\sum_{N=0}^{\infty}\frac{N\zeta^N}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&= \frac{1}{Z(\mu,V,\beta)}\sum_{N=0}^{\infty}\frac{\zeta^N}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N N^2 e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&- \left(\frac{1}{Z(\mu,V,\beta)}\sum_{N=0}^{\infty}\frac{\zeta^N}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N N e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\right)^2 = \left\langle N^2\right\rangle - \langle N\rangle^2 .
\end{aligned} \tag{6}$$

Por otra, en el límite termodinámico

$$\begin{aligned}
k_BT\langle N\rangle\frac{\partial n}{\partial p} &= k_BT\langle N\rangle\frac{\partial}{\partial p}\frac{\langle N\rangle}{V} = k_BT\langle N\rangle\frac{\partial\langle N\rangle}{\partial\mu}\left(\frac{\partial p}{\partial\mu}\right)^{-1}\frac{1}{V} = k_BT\langle N\rangle\frac{\partial\langle N\rangle}{\partial\mu}\left(\frac{\partial}{\partial\mu}\frac{-\Omega}{V}\right)^{-1}\frac{1}{V}\\
&= k_BT\langle N\rangle\frac{\partial\langle N\rangle}{\partial\mu}\langle N\rangle^{-1} = k_BT\frac{\partial\langle N\rangle}{\partial\mu} = \frac{1}{\beta}\beta\zeta\frac{\partial\langle N\rangle}{\partial\zeta} = \left\langle N^2\right\rangle - \langle N\rangle^2 ,
\end{aligned} \tag{7}$$

donde se utilizó que

$$\frac{\partial}{\partial\mu} = \frac{\partial\zeta}{\partial\mu}\frac{\partial}{\partial\zeta} = \beta\frac{e^{\beta\mu}}{\lambda}\frac{\partial}{\partial\zeta} = \beta\zeta\frac{\partial}{\partial\zeta} \tag{8}$$

y en el límite termodinámico se tiene $\langle N\rangle = -\frac{\partial\Omega}{\partial\mu}$ y $p = -\frac{\Omega}{V}$.

3. En un sistema homogeneo e isotrópico se tiene

$$\begin{aligned}
k_BT\frac{\partial n}{\partial p} &= \frac{\left\langle N^2\right\rangle - \langle N\rangle^2}{\langle N\rangle} = \frac{\left\langle N^2\right\rangle - \langle N\rangle + \langle N\rangle - \langle N\rangle^2}{\langle N\rangle} = 1 + \frac{\langle N(N-1)\rangle - \langle N\rangle^2}{\langle N\rangle}\\
&= 1 + \frac{1}{\langle N\rangle}\left(\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 n^{(2)}(\mathbf{r}_1,\mathbf{r}_2) - n^2V^2\right) = 1 + \frac{1}{\langle N\rangle}\left(\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 n^2 g(\|\mathbf{r}_1-\mathbf{r}_2\|) - n^2V\int d^3\mathbf{r}\right)\\
&= 1 + \frac{n^2}{\langle N\rangle}\left(\int d^3\mathbf{r}_1 d^3\mathbf{r}\, g(\|\mathbf{r}\|) - V\int d^3\mathbf{r}\right) = 1 + \frac{n^2}{\langle N\rangle}\left(V\int d^3\mathbf{r}\, g(\|\mathbf{r}\|) - V\int d^3\mathbf{r}\right)\\
&= 1 + \frac{n^2}{\langle N\rangle}\left(\int d^3\mathbf{r}_1 d^3\mathbf{r}\, g(\|\mathbf{r}\|) - V\int d^3\mathbf{r}\right) = 1 + \frac{n^2V}{\langle N\rangle}\int d^3\mathbf{r}(g(\|\mathbf{r}\|)-1) = 1 + n\int d^3\mathbf{r}(g(\|\mathbf{r}\|)-1)
\end{aligned} \tag{9}$$

3. Correlaciones en gran-canónico

3.1. Preliminares: derivación funcional

1.

$$\begin{aligned}
\frac{\delta}{\delta f(x)}\int(f(y)\ln(f(y)) - f(y))dy &= \int\left(\delta(y-x)\ln(f(y)) + f(y)\frac{\delta(y-x)}{f(y)} - \delta(y-x)\right)dy\\
&= \ln(f(x)) + 1 - 1 = \ln(f(x))
\end{aligned} \tag{10}$$

2.

$$\frac{\delta G(f(z))}{\delta f(x_0)} = G'(f(z))\delta(z-x_0) \tag{11}$$

3.

$$\begin{aligned}
\frac{\delta}{\delta f(x_0)}\int\int\frac{f(x)f(y)}{|x-y|}dxdy &= \int\int\frac{\delta(x-x_0)f(y) + f(x)\delta(y-x_0)}{|x-y|}dxdy = \int\frac{f(y)}{|x_0-y|}dy + \int\frac{f(x)}{|x-x_0|}dx\\
&= 2\int\frac{f(x)}{|x-x_0|}dx
\end{aligned} \tag{12}$$

3.2. Densidades y correlaciones

1.

$$
\begin{aligned}
n^{(1)}(\mathbf{r}) &= \left\langle \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \right\rangle \\
&= \frac{1}{\Xi(\mu,V,T)} \sum_{N=1}^{\infty} \frac{1}{N!} \int d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \prod_{j=1}^{N} \zeta(\mathbf{r}_j) e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\
&= \frac{1}{\Xi(\mu,V,T)} \sum_{N=1}^{\infty} \sum_{i=1}^{N} \frac{1}{N!} \int d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \delta(\mathbf{r}-\mathbf{r}_i) \prod_{j=1}^{N} \zeta(\mathbf{r}_j) e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\
&= \frac{1}{\Xi(\mu,V,T)} \sum_{N=1}^{\infty} \sum_{i=1}^{N} \frac{1}{N!} \int \prod_{l=1,l\neq i}^{\infty} d^3\mathbf{r}_l \zeta(\mathbf{r}) \prod_{j=1,j\neq l}^{N} \zeta(\mathbf{r}_j) e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_{i-1},\mathbf{r},\mathbf{r}_{i+1},\ldots,\mathbf{r}_N)} \\
&= \frac{\zeta(\mathbf{r})}{\Xi(\mu,V,T)} \sum_{N=1}^{\infty} \sum_{i=1}^{N} \frac{1}{N!} \int \prod_{l=1,l\neq i}^{\infty} d^3\mathbf{r}_l \prod_{j=1,j\neq l}^{N} \zeta(\mathbf{r}_j) e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_{i-1},\mathbf{r},\mathbf{r}_{i+1},\ldots,\mathbf{r}_N)} \\
&= \frac{\zeta(\mathbf{r})}{\Xi(\mu,V,T)} \sum_{N=1}^{\infty} \sum_{i=1}^{N} \frac{1}{N!} \int d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \delta(\mathbf{r}-\mathbf{r}_i) \prod_{j=1,j\neq l}^{N} \zeta(\mathbf{r}_j) e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\
&= \frac{\zeta(\mathbf{r})}{\Xi(\mu,V,T)} \sum_{N=1}^{\infty} \frac{1}{N!} \int d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \prod_{j=1,j\neq l}^{N} \zeta(\mathbf{r}_j) e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\
&= \frac{\zeta(\mathbf{r})}{\Xi(\mu,V,T)} \sum_{N=1}^{\infty} \frac{1}{N!} \int d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \frac{\delta}{\delta\zeta(\mathbf{r})} \left(\prod_{j=1}^{N} \zeta(\mathbf{r}_j) \right) e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\
&= \frac{\zeta(\mathbf{r})}{\Xi(\mu,V,T)} \frac{\delta}{\delta\zeta(\mathbf{r})} \left(1 + \sum_{N=1}^{\infty} \frac{1}{N!} \int d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \prod_{j=1}^{N} \zeta(\mathbf{r}_j) e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \right) \\
&= \frac{\zeta(\mathbf{r})}{\Xi(\mu,V,T)} \frac{\delta\Xi}{\delta\zeta(\mathbf{r})} = \zeta(\mathbf{r}) \frac{\delta \ln(\Xi)}{\delta\zeta(\mathbf{r})}
\end{aligned}
\tag{13}
$$

2.

$$
\begin{aligned}
&\zeta(\mathbf{R}_2)\frac{\delta n^{(1)}(\mathbf{R}_1)}{\delta\zeta(\mathbf{R}_2)} = \zeta(\mathbf{R}_2)\frac{\delta}{\delta\zeta(\mathbf{R}_2)}\left(\zeta(\mathbf{R}_1)\frac{\delta\ln(\Xi)}{\delta\zeta(\mathbf{R}_1)}\right) = \zeta(\mathbf{R}_2)\frac{\delta}{\delta\zeta(\mathbf{R}_2)}\left(\zeta(\mathbf{R}_1)\frac{1}{\Xi(\mu,V,T)}\frac{\delta\Xi}{\delta\zeta(\mathbf{R}_1)}\right)\\
&= \zeta(\mathbf{R}_2)\frac{\delta}{\delta\zeta(\mathbf{R}_2)}\left(\frac{1}{\Xi(\mu,V,T)}\sum_{N=1}^{\infty}\frac{1}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\prod_{j=1}^{N}\zeta(\mathbf{r}_j)e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\right)\\
&= -\zeta(\mathbf{R}_2)\frac{1}{\Xi(\mu,V,T)^2}\frac{\delta\Xi}{\delta\zeta(\mathbf{R}_2)}\sum_{N=1}^{\infty}\frac{1}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\prod_{j=1}^{N}\zeta(\mathbf{r}_j)e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&+ \frac{\zeta(\mathbf{R}_2)}{\Xi(\mu,V,T)}\frac{\delta}{\delta\zeta(\mathbf{R}_2)}\left(\sum_{N=1}^{\infty}\frac{1}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\prod_{j=1}^{N}\zeta(\mathbf{r}_j)e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\right)\\
&= -\zeta(\mathbf{R}_2)\frac{\delta\ln(\Xi)}{\delta\zeta(\mathbf{R}_2)}\frac{1}{\Xi(\mu,V,T)}\sum_{N=1}^{\infty}\frac{1}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\prod_{j=1}^{N}\zeta(\mathbf{r}_j)e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&+ \frac{\zeta(\mathbf{R}_2)}{\Xi(\mu,V,T)}\sum_{N=1}^{\infty}\frac{1}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\sum_{k=1}^{N}\delta(\mathbf{R}_2-\mathbf{r}_k)\prod_{j=1,j\neq k}^{N}\zeta(\mathbf{r}_j)e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&= -n^{(1)}(\mathbf{R}_1)n^{(1)}(\mathbf{R}_2)\\
&+ \frac{1}{\Xi(\mu,V,T)}\sum_{N=1}^{\infty}\sum_{k=1}^{N}\frac{1}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\zeta(\mathbf{R}_2)\delta(\mathbf{R}_2-\mathbf{r}_k)\prod_{j=1,j\neq k}^{N}\zeta(\mathbf{r}_j)e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&= \frac{1}{\Xi(\mu,V,T)}\sum_{N=1}^{\infty}\sum_{k=1}^{N}\frac{1}{N!}\int\prod_{l=1,l\neq k}^{N}d^3\mathbf{r}_l\delta(\mathbf{R}_1-\mathbf{R}_2)\sum_{i=1,i\neq k}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\zeta(\mathbf{R}_2)\prod_{j=1,j\neq k}^{N}\zeta(\mathbf{r}_j)e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_{k-1},\mathbf{R}_2,\mathbf{r}_{k+1},\ldots,\mathbf{r}_N)}\\
&- n^{(1)}(\mathbf{R}_1)n^{(1)}(\mathbf{R}_2)\\
&= \frac{1}{\Xi(\mu,V,T)}\sum_{N=1}^{\infty}\sum_{k=1}^{N}\frac{1}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\delta(\mathbf{R}_2-\mathbf{r}_k)\prod_{j=1}^{N}\zeta(\mathbf{r}_j)e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&- n^{(1)}(\mathbf{R}_1)n^{(1)}(\mathbf{R}_2)\\
&= \frac{1}{\Xi(\mu,V,T)}\sum_{N=1}^{\infty}\frac{1}{N!}\int d^3\mathbf{r}_1\cdots d^3\mathbf{r}_N\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\sum_{k=1}^{N}\delta(\mathbf{R}_2-\mathbf{r}_k)\prod_{j=1}^{N}\zeta(\mathbf{r}_j)e^{-\beta V_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\\
&- \langle\hat{n}(\mathbf{R}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\langle\hat{n}(\mathbf{R}_2;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\\
&= \langle\hat{n}(\mathbf{R}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)\hat{n}(\mathbf{R}_2;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle - \langle\hat{n}(\mathbf{R}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\langle\hat{n}(\mathbf{R}_2;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle = U^{(2)T}(\mathbf{R}_1,\mathbf{R}_2)
\end{aligned}
\tag{14}
$$

3.Obtenemos la relación

$$
\begin{aligned}
U^{(2)T}(\mathbf{R}_1,\mathbf{R}_2) &= \langle\hat{n}(\mathbf{R}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)\hat{n}(\mathbf{R}_2;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle - \langle\hat{n}(\mathbf{R}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\langle\hat{n}(\mathbf{R}_2;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\\
&= \left\langle\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\sum_{j=1}^{N}\delta(\mathbf{R}_2-\mathbf{r}_j)\right\rangle - \langle\hat{n}(\mathbf{R}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\langle\hat{n}(\mathbf{R}_2;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\\
&= \left\langle\sum_{i=1}^{N}\sum_{j=1,j\neq i}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\delta(\mathbf{R}_2-\mathbf{r}_j)\right\rangle + \left\langle\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\delta(\mathbf{R}_2-\mathbf{r}_i)\right\rangle\\
&- \langle\hat{n}(\mathbf{R}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\langle\hat{n}(\mathbf{R}_2;\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\\
&= n^{(2)}(\mathbf{R}_1,\mathbf{R}_2) - n^{(1)}(\mathbf{R}_1)n^{(1)}(\mathbf{R}_2) + \delta(\mathbf{R}_1-\mathbf{R}_2)\left\langle\sum_{i=1}^{N}\delta(\mathbf{R}_1-\mathbf{r}_i)\right\rangle\\
&= n^{(2)}(\mathbf{R}_1,\mathbf{R}_2) - n^{(1)}(\mathbf{R}_1)n^{(1)}(\mathbf{R}_2) + \delta(\mathbf{R}_1-\mathbf{R}_2)n^{(1)}(\mathbf{R}_1)\\
&= n^{(2)}(\mathbf{R}_1,\mathbf{R}_2) - n^{(1)}(\mathbf{R}_1)\Big(n^{(1)}(\mathbf{R}_2) + \delta(\mathbf{R}_1-\mathbf{R}_2)\Big)
\end{aligned}
\tag{15}
$$