2. let's get the partition function for a single molecule. Then, because we have a system of N non-interacting molecules, the partition function for the whole system is

$$Z_N = \frac{1}{N!}(Z_1)^N .$$

So,

$$Z_1 = \frac{1}{h^6}\int \exp\left[-\beta\frac{\vec{p}_1^{\,2}}{2m} - \beta\frac{\vec{p}_2^{\,2}}{2m} - \frac{L}{2}|\vec{r}_1-\vec{r}_2|^2\right] d^3\vec{p}_1\, d^3\vec{r}_1\, d^3\vec{p}_2\, d^3\vec{r}_2 .$$

$$Z_1 = \frac{1}{h^6}\left(\int \exp\left(-\beta\frac{\vec{p}_1^{\,2}}{2m}\right) d^3\vec{p}_1\right)\left(\int \exp\left(-\beta\frac{\vec{p}_2^{\,2}}{2m}\right) d^3\vec{p}_2\right)\left(\int \exp\left(-\beta\frac{L}{2}|\vec{r}_1-\vec{r}_2|\right) d^3\vec{r}_1\, d^3\vec{r}_2\right)$$

look at the $d^3\vec{p}_1$ integral. it is; because $\vec{p}_1^{\,2} = p_{1x}^2 + p_{1y}^2 + p_{1z}^2$

$$\left(\int \exp\left(-\beta\frac{p_{1x}^2}{2m}\right) dp_{1x}\right)\left(\int \exp\left(-\beta\frac{p_{1y}^2}{2m}\right) dp_{1y}\right)\left(\int \exp\left(-\beta\frac{p_{1z}^2}{2m}\right) dp_{1z}\right)$$

$$= \left[\int_{-\infty}^{\infty} \exp\left(-\frac{\beta}{2m}p^2\right) dp\right]^3$$

Hence

$$Z_1 = \frac{1}{h^6}\left[2\int_0^{\infty} e^{-\frac{\beta}{2m}p^2}\, dp\right]^6 \left[\int \exp\left(-\frac{\beta L}{2}|\vec{r}_1-\vec{r}_2|^2\right) d^3\vec{r}_1\, d^3\vec{r}_2\right].$$

recall $\displaystyle\int_0^{\infty} e^{-\alpha x^2}\, dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$

$$Z_1 = \frac{1}{h^6}\left[\sqrt{\frac{2\pi m}{\beta}}\right]^6 \int \exp\left(-\frac{\beta L}{2}\left|\vec{r}_1 - \vec{r}_2\right|^2\right) d^3\vec{r}_1\, d^3\vec{r}_2$$

Now define $\vec{R} \equiv \dfrac{\vec{r}_1 + \vec{r}_2}{2}$ and $\vec{r} \equiv \vec{r}_1 - \vec{r}_2$.

This means $\vec{r}_1 = \vec{R} + \dfrac{\vec{r}}{2}$ and $\vec{r}_2 = \vec{R} - \dfrac{\vec{r}}{2}$.

The integral can be transformed from ranging over $\vec{r}_1$ & $\vec{r}_2$ to ranging over $\vec{R}$ and $\vec{r}$ by replacing:

$$d^3\vec{r}_1\, d^3\vec{r}_2 \longrightarrow \left|\frac{\partial(\vec{r}_1, \vec{r}_2)}{\partial(\vec{R}, \vec{r})}\right| d^3\vec{R}\, d^3\vec{r}$$

That's the absolute value of the Jacobian of the transformation. So, that's (excuse the abuse of vector notation)

$$\left|\det\begin{pmatrix} \frac{\partial \vec{r}_1}{\partial \vec{R}} & \frac{\partial \vec{r}_2}{\partial \vec{R}} \\ \frac{\partial \vec{r}_1}{\partial \vec{r}} & \frac{\partial \vec{r}_2}{\partial \vec{r}} \end{pmatrix}\right| = \left|\det\begin{pmatrix} 1 & 1 \\ \frac{1}{2} & -\frac{1}{2} \end{pmatrix}\right| = \left|-\frac{1}{2} - \frac{1}{2}\right| = |-1| = \underline{+1}$$

So,

$$Z_1 = \frac{1}{h^6}\left(\frac{2\pi m}{\beta}\right)^{6/2} \int \exp\left(-\frac{\beta L}{2} r^2\right) d^3\vec{R}\, d^3\vec{r}.$$

The integral over $d^3\vec{R}$ simply gives the volume of the container V, and the integration over $d^3\vec{r}$ is the same for each component, so can be written:

$$\left[2\int_0^\infty e^{-\frac{\beta L}{2} r^2} dr\right]^3$$

So

$$Z_1 = \frac{V}{h^6}\left(\frac{2\pi m}{\beta}\right)^3\left(\sqrt{\frac{2\pi}{\beta L}}\right)^3$$

$$Z_1 = \frac{V}{h^6}\left(\frac{4\pi^2 m^2}{\beta^2}\right)^{\frac{3}{2}}\left(\frac{2\pi}{\beta L}\right)^{\frac{3}{2}}$$

$$Z_1 = \frac{V}{h^6}\left(\frac{8\pi^3 m^2}{\beta^3 L}\right)^{3/2}$$

so that $$Z_N = \frac{V^N}{N!\,h^{6N}}\left(\frac{8\pi^3 m^2}{\beta^3 L}\right)^{\frac{3N}{2}}.$$

a) use this to get the Helmholtz free energy.

use $F = -kT \ln Z_N$.

$$F = -kT\left[N\ln\left(\frac{V}{h^6}\left[\frac{8\pi^3 m^2}{\beta^3 L}\right]^{3/2}\right) - \ln N!\right]$$

use $\ln N! \approx N\ln N - N$

$$F = -kT\left[N\ln\left(\frac{V}{h^6}\left[\frac{8\pi^3 m^2}{\beta^3 L}\right]^{3/2}\right) - N\ln N + N\right]$$

$$F = -kTN\left[\ln\left(\frac{V}{h^6}\left[\frac{8\pi^3 m^2 k^3 T^3}{L}\right]^{3/2}\right) - \ln N + 1\right]$$

$$F = -NkT\left[\frac{9}{2}\ln T + \ln\left(\frac{V}{Nh^6}\left[\frac{8\pi^3 m^2 k^3}{L} \right]^{3/2} \right) + 1 \right]$$

b) get the specific heat at constant volume.

$$C_v \equiv \left(\frac{\delta Q}{dT}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

recall that $F = U - TS$

so $dF = du - Tds - SdT.$

1^{st} law: $du = \delta W + \delta Q = -pdv + Tds$

so $dF = -pdv + Tds - Tds - SdT$

$$dF = -pdv - SdT$$

from which we conclude that

$$\left(\frac{\partial F}{\partial T}\right)_v = -S$$

and hence

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_v = T\frac{\partial}{\partial T}\left(-\frac{\partial F}{\partial T}\Big|_v\right)_v$$

$$C_v = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_v$$

Applying this to the f we got in part (a),

$$\left(\frac{\partial f}{\partial T}\right)_V = -NkT\left[\frac{9}{2}\,\frac{1}{T}\right] - Nk\left[\frac{9}{2}\ln T + \ln\left(\frac{V}{Nh^6}\left[\frac{8\pi^3 m^2 k^3}{L}\right]^{3/2}\right) + 1\right]$$

$$\left(\frac{\partial f}{\partial T}\right)_V = -\frac{9}{2}Nk - Nk\left[\frac{9}{2}\ln T + \ln(\text{blah}) + 1\right]$$

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_V = -\frac{9}{2}Nk\left(\frac{1}{T}\right)$$

So that $C_V = -T\left(\frac{\partial^2 f}{\partial T^2}\right)_V = \boxed{\frac{9}{2}Nk = C_V}$

c) evaluate $\langle|\vec{r}_1 - \vec{r}_2|^2\rangle$ using the canonical ensemble

for a system of one molecule. So, the ensemble average is

$$\langle|\vec{r}_1-\vec{r}_2|^2\rangle = \frac{1}{Z_1}\int \exp\left(-\beta\frac{\vec{p}_1^{\,2}}{2m} - \beta\frac{\vec{p}_2^{\,2}}{2m} - \beta\frac{L}{2}|\vec{r}_1-\vec{r}_2|^2\right) d^3\vec{p}_1\, d^3\vec{p}_2\, d^3\vec{r}_1\, d^3\vec{r}_2$$

with $Z_1 = \frac{V}{h^6}\left(\frac{8\pi^3 m^2}{\beta^3 L}\right)^{3/2}$ as obtained in part (a).

but notice that before integrating,

$$Z_1 = \frac{1}{h^6}\int \exp\left(-\beta\frac{\vec{p}_1^{\,2}}{2m} - \beta\frac{\vec{p}_2^{\,2}}{2m} - \beta\frac{L}{2}|\vec{r}_1-\vec{r}_2|^2\right) d^3\vec{p}_1\, d^3\vec{p}_2\, d^3\vec{r}_1\, d^3\vec{r}_2$$

So that $\frac{\partial}{\partial L}(Z_1) = \frac{1}{h^6}\int \left(-\frac{\beta}{2}|\vec{r_1}-\vec{r_2}|^2\right) \exp(-\beta H)\, d^3\vec{p_1}\, d^3\vec{p_2}\, d^3\vec{r_1}\, d^3\vec{r_2}$

except for the factor $\left(-\frac{\beta}{2}\right)$, This is The numerator of what we need to evaluate. So,

$$\langle|\vec{r_1}-\vec{r_2}|^2\rangle = \frac{-\left(\frac{2}{\beta}\right)\frac{\partial}{\partial L}[Z_1]}{Z_1} = -\frac{2}{\beta}\frac{\partial}{\partial L}[\ln Z_1]$$

$$= -\left(\frac{2}{\beta}\right)\frac{\partial}{\partial L}\left[\ln\left\{\frac{V}{h^6}\left(\frac{8\pi^3 m^2}{\beta^3}\right)^{3/2}\right\} - \frac{3}{2}\ln L\right]$$

$$= -\left(\frac{2}{\beta}\right)\left(-\frac{3}{2}\right)\frac{1}{L} = \frac{3kT}{L}$$

So, yes,

$$\langle|\vec{r_1}-\vec{r_2}|^2\rangle = \frac{3kT}{L}$$