4.7 We are given a ton of classical diatomic molecules in a volume V and temperature T w/ Hamiltonian: $H(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2) = \frac{1}{2m}(p_1^2 + p_2^2) + \frac{1}{2}k_0|\vec{r}_1 - \vec{r}_2|^2$

[NOTE: I changed capital K to k_0 for the spring constant for clarity.]

We'll begin by writing the 1-particle partition function Q_1

$$Q_1 = \int d\omega \, e^{-\beta E}$$

In this case, we're using a 6-D phase space, so $d\omega = \frac{dr^6 dp^6}{h^6}$

$$Q_1 = \iint d^6r \, d^6p \, e^{-\beta \frac{p_1^2}{2m}} e^{-\beta p_2^2/2m} e^{-\beta \frac{1}{2}k_0|\vec{r}_1 - \vec{r}_2|^2}$$

Noting that the volume is pretty big, we can pretend it's infinite, and the momentum integrals become easy (just Gaussian integrals.

$(d^6p = dp_{1x}\,dp_{1y}\,dp_{1z}\,dp_{2x}\,dp_{2y}\,dp_{2z}$, and $p_1^2 = p_{1x}^2 + p_{1y}^2 + p_{1z}^2$, etc.)

$$Q_1 = \frac{1}{h^6}\left(\frac{2\pi m}{\beta}\right)^{6/2} \int d^6\vec{r} \, e^{-\frac{\beta}{2}k_0|\vec{r}_1 - \vec{r}_2|^2}$$

Next, let $\vec{x} = \vec{r}_1 - \vec{r}_2$, and $\vec{y} = \vec{r}_2 \Rightarrow \vec{r}_1 = \vec{x} + \vec{y}$ and $\vec{r}_2 = \vec{y}$

This allows us to change variables in our remaining integral.

$\rightarrow |\vec{r}_1 - \vec{r}_2|^2 = x^2$

$\rightarrow d^6\vec{r} = d^3\vec{r}_1 \, d^3\vec{r}_2 = d^3\vec{x}\, d^3y \underbrace{\frac{\partial(\vec{r}_1, \vec{r}_2)}{\partial(x, y)}} = d^3\vec{x}\, d^3y$

This is the Jacobian Determinant. I calculated in Mathematica that it simply equals 1. Nice!

$$Q_1 = \frac{1}{h^6}\left(\frac{2\pi m}{\beta}\right)^{6/2} \int d^3\vec{x}\, d^3\vec{y}\, e^{-\beta/2\, k_0 x^2} = \frac{V}{h^6}\left(\frac{2\pi m}{\beta}\right)^{6/2} \int d^3\vec{x}\, e^{-\frac{\beta}{2}k_0 x^2} \quad ✪$$

This is 3 identical integrals multiplied. We get

$$Q_1 = \frac{V}{h^6}\left(\frac{2\pi m}{\beta}\right)^{6/2}\left(\frac{2\pi}{k_0\beta}\right)^{3/2} = V\left(\frac{2\pi m}{h^2\beta}\right)^3\left(\frac{2\pi}{k_0\beta}\right)^{3/2} = Vf(T) \quad \boxed{\left(\text{where } f(T) = \frac{(2\pi kT)^{9/2}}{h^6}\left(\frac{m^2}{k_0}\right)^{3/2}\right)}$$

Finally, $\boxed{\mathcal{Q}(z, V, T) = e^{zVf(T)}}$ by 4.4.3

Thermodynamics (by 4.4.5–8, we use $f(T)$:)

$P = zkTf(T) \Rightarrow \boxed{P = e^{\mu/kT} kT \frac{(2\pi kT)^{9/2}}{h^6}\left(\frac{m^2}{k_0}\right)^{3/2}}$ $\quad N = zVf(T) \Rightarrow \boxed{N = V\beta P}$

$U = zVkT^2 f'(T) \Rightarrow U = \frac{9e^{\mu/kT}}{2h^6} VkT(2\pi kT)^{9/2}\left(\frac{m^2}{k_0}\right)^{3/2} \Rightarrow \boxed{U = \frac{9}{2}VP = \frac{9}{2}NkT}$

$A = NkT\ln(z) - zVkTf(T) = NkT\left(\frac{\mu}{kT}\right) - PV \Rightarrow \boxed{A = N\mu - PV}$

$S = -Nk\ln(z) + zVkTf'(T) + zVkf(T) = -\frac{Nk\mu}{kT} + \frac{U}{T} + \frac{PV}{T}$

$\Rightarrow \boxed{S = \frac{1}{T}(U + PV - N\mu)}$ $\rightarrow$

4.7, cont

We have called $\vec{r}_{12} = \vec{x}$.

We are looking for $\langle x^2 \rangle$

Using equation ★ on the previous page, we use

$$\langle x^2 \rangle = \frac{\cancel{\frac{V}{h^6}\left(\frac{2\pi m}{\beta}\right)^{6/2}} \int d^3\vec{x}\, x^2 e^{-\frac{\beta}{2}k_0 x^2}}{\cancel{\frac{V}{h^6}\left(\frac{2\pi m}{\beta}\right)^{6/2}} \int d^3\vec{x}\, e^{-\frac{\beta}{2}k_0 x^2}}$$

$$= \frac{\int dx_1 dx_2 dx_3 (x_1^2 + x_2^2 + x_3^2) e^{-\frac{\beta}{2}k_0(x_1^2+x_2^2+x_3^2)}}{\int dx_1 dx_2 dx_3\, e^{-\frac{\beta}{2}k_0(x_1^2+x_2^2+x_3^2)}}$$

See Mathematica.

$$= \frac{6}{\beta k_0} = \frac{3kT}{k_0}$$

$$\Rightarrow \boxed{\langle r_{12}^2 \rangle = \frac{3kT}{k_0}}$$

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This is the jacobian matrix.

```
x = {x1, x2, x3};
y = {y1, y2, y3};
r1 = x + y;
r2 = y;
Det[{{D[r1[[1]], x[[1]]], D[r1[[1]], x[[2]]],
    D[r1[[1]], x[[3]]], D[r1[[1]], y[[1]]], D[r1[[1]], y[[2]]], D[r1[[1]], y[[3]]]},
   {D[r1[[2]], x[[1]]], D[r1[[2]], x[[2]]], D[r1[[2]], x[[3]]], D[r1[[2]], y[[1]]],
    D[r1[[2]], y[[2]]], D[r1[[2]], y[[3]]]},
   {D[r1[[3]], x[[1]]], D[r1[[3]], x[[2]]], D[r1[[3]], x[[3]]], D[r1[[3]], y[[1]]],
    D[r1[[3]], y[[2]]], D[r1[[3]], y[[3]]]},
   {D[r2[[1]], x[[1]]], D[r2[[1]], x[[2]]], D[r2[[1]], x[[3]]], D[r2[[1]], y[[1]]],
    D[r2[[1]], y[[2]]], D[r2[[1]], y[[3]]]},
   {D[r2[[2]], x[[1]]], D[r2[[2]], x[[2]]], D[r2[[2]], x[[3]]], D[r2[[2]], y[[1]]],
    D[r2[[2]], y[[2]]], D[r2[[2]], y[[3]]]},
   {D[r2[[3]], x[[1]]], D[r2[[3]], x[[2]]], D[r2[[3]], x[[3]]], D[r2[[3]], y[[1]]],
    D[r2[[3]], y[[2]]], D[r2[[3]], y[[3]]]}}]
```

1

This is the integral on the final page. I have replaced the x's with a,b, and c.

$$\left(\int_{-\infty}^{\infty}\left(\int_{-\infty}^{\infty}\left(\int_{-\infty}^{\infty}(a^2+b^2+c^2)\, e^{\frac{-\beta}{2}k0\,(a^2+b^2+c^2)}\, da\right)db\right)dc\right)\Big/\left(\int_{-\infty}^{\infty}\left(\int_{-\infty}^{\infty}\left(\int_{-\infty}^{\infty} e^{\frac{-\beta}{2}k0\,(a^2+b^2+c^2)}\, da\right)db\right)dc\right)$$

$$\text{ConditionalExpression}\left[\frac{3}{k0\,\beta},\ (\text{Re}[k0] \neq 0\ ||\ k0 \notin \text{Reals})\ \&\&\ \text{Re}[k0\,\beta] > 0\ \&\&\ \text{Re}[k0\,\beta] > 0\right]$$