6.32) (a) While the potential energy varies with position as $u(x)$, we would have to be a lot more careful in concluding that

$$\bar{x} = \frac{\int dx\ x\ e^{-\beta u(x)}}{\int dx\ e^{-\beta u(x)}}.$$

The text just assumes that the quantum number increases linearly with x, ignores the density of states, or both. Let's play along.

(b) The linear term is zero at equilibrium: $\left.\frac{du}{dx}\right|_{x=x_0} = 0$. Truncating after the quadratic term the series becomes $u = u_0 + k\frac{(x-x_0)^2}{2}$ where $k \equiv \left.\frac{d^2u}{dx^2}\right|_{x=x_0}$

Thus, $$\bar{x} = \frac{\int_{-\infty}^{\infty} dx\ x\ e^{-\beta u_0}\ e^{-\frac{\beta k}{2}(x-x_0)^2}}{\int_{-\infty}^{\infty} dx\ e^{-\beta u_0}\ e^{-\frac{\beta k}{2}(x-x_0)^2}}.$$

Let $y = x - x_0$. Then $$\bar{x} = \frac{\int_{-\infty}^{\infty} dy\ (y+x_0)\ e^{-\beta k y^2/2}}{\int_{-\infty}^{\infty} dy\ e^{-\beta k y^2/2}}$$

The y term in the numerator gives zero (odd function) and so $$\bar{x} = x_0 \frac{\int_{-\infty}^{\infty} dy\ e^{-\beta k y^2/2}}{\int_{-\infty}^{\infty} dy\ e^{-\beta k y^2/2}} = x_0.$$

(c) Now let $u(x) = u_0 + \frac{k}{2}y^2 + \frac{c}{6}y^3 + \ldots$

Now $$\bar{x} = \frac{\int_{-\infty}^{\infty} dy\ (y+x_0)\ e^{-\beta k y^2/2}\ e^{-\beta c y^3/6}}{\int_{-\infty}^{\infty} dy\ e^{-\beta k y^2/2}\ e^{-\beta c y^3/6}}$$

I don't like this very much either because any odd terms like y^3 in the expansion for $u(y)$ make u negative for large negative y (or positive y, depending on the sign of the coefficient).

Once again, we play along and approximate

$$e^{-\beta c y^3/6} \approx 1 - \frac{\beta c}{6} y^3 \quad \text{and compute}$$

$$-\frac{\beta c}{6} \frac{\int_{-\infty}^{\infty} dy \; y^4 e^{-\beta k y^2/2}}{\int_{-\infty}^{\infty} dy \; e^{-\beta k y^2/2}} .$$

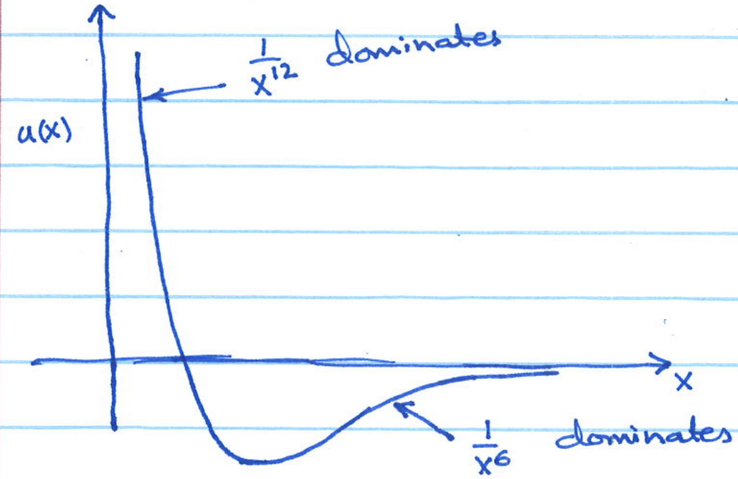
Setting $w = \frac{\beta k}{2} y^2$ we get $y^4 = \left(\frac{2w}{\beta k}\right)^2$, $dy = \frac{dw}{\sqrt{2\beta k w}}$

and our correction term becomes

$$-\frac{\beta c}{6} \cdot \left(\frac{2}{\beta k}\right)^2 \frac{\int_0^\infty dw \; w^{3/2} e^{-w}}{\int_0^\infty dw \; e^{-w} \; w^{-1/2}} = \frac{-2c}{3\beta k^2} \cdot \frac{\Gamma(5/2)}{\Gamma(1/2)}$$

$$= \frac{-2c}{3\beta k^2} \cdot \frac{3}{4} = \frac{-c}{2\beta k^2} = -\frac{c}{2k^2} \cdot kT$$

(d)



The minimum is at x where

$$\left.\frac{du}{dx}\right|_{x=x_0} = 0 \quad , \quad \text{i.e., } u_0\left[-\frac{12}{x}\left(\frac{x_0}{x}\right)^{12} + \frac{12}{x}\left(\frac{x_0}{x}\right)^{6}\right] = 0$$

i.e., $x = x_0$.

We can find our coefficients k and c using

$$k \equiv \left.\frac{d^2u}{dx^2}\right|_{x=x_0} \quad \text{and} \quad c \equiv \left.\frac{d^3u}{dx^3}\right|_{x=x_0} .$$

Thus, $k = u_0\left[\frac{12.13}{x_0^2} - \frac{12.7}{x_0^2}\right] = \frac{72\, u_0}{x_0^2}$.

$$c = u_0\left[\frac{-12.13.14}{x_0^3} + \frac{12.7.8}{x_0^3}\right] = -\frac{1512\, u_0}{x_0^3}.$$

Thus, $\bar{x} \approx x_0 - \frac{(-1512\, u_0/x_0^3)}{2(72\, u_0/x_0^2)^2} . kT = x_0 + 0.146\, x_0 . \left(\frac{kT}{u_0}\right)$

At 80K $\quad \bar{x} \approx x_0 + 0.146\, x_0\left(\frac{80\,k}{u_0}\right)\left(\frac{T}{80}\right) = x_0 + \frac{0.146}{80} . x_0 . \left(\frac{6.93}{10}\right) T$

Giving $\alpha = 0.0013\ K^{-1}$ at 80K.

This is a little higher than the given value of α.