$\boxed{3.18}$ Prove: $\langle (\Delta E)^3 \rangle = k^2 \left(T^4 \left(\frac{\partial C_v}{\partial T}\right)_V + 2T^3 C_v \right)$

Note: by 3.6.1, $U = \langle E \rangle = \dfrac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \dfrac{\sum_r E_r e^{-\beta E_r}}{Z}$

The first step is to prove that $\dfrac{\partial^2 U}{\partial \beta^2} = \langle (\Delta E)^3 \rangle$

$$\frac{\partial U}{\partial \beta} = \frac{-\cancel{Z} \cdot \sum_r E_r^2 e^{-\beta E_r}}{Z^{\cancel{2}}} - \frac{\left(\sum_r E_r e^{-\beta E_r}\right)(-)\sum_r E_r e^{-\beta E_r}}{Z^2}$$

$$\frac{\partial^2 U}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left[\frac{-\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + \frac{\sum_r E_r^2 e^{-2\beta E_r}}{\sum_r e^{-2\beta E_r}} \right]$$

$$= \frac{\sum_r e^{-\beta E_r} \sum_r E_r^3 e^{-\beta E_r}}{Z^2} - \frac{-\sum_r E_r^2 e^{-\beta E_r}\left(-\sum E_r e^{-\beta E_r}\right)}{Z^2}$$

$$+ \frac{Z^2\left(-\sum_r 2E_r^3 e^{-2\beta E_r}\right)}{Z^4} - \frac{\sum_r 2E_r e^{-2\beta E_r} \sum_r E_r^2 e^{-2\beta E_r}}{Z^4}$$

$$= \langle E^3 \rangle - U\langle E^2 \rangle + \langle 2E_r \rangle - \langle 2E \rangle \langle E^2 \rangle$$

$$= \langle E^3 \rangle - U\langle E^2 \rangle + 2U^3 - 2U\langle E^2 \rangle$$

$$= \langle E^3 \rangle - 3U\langle E^2 \rangle + 2U^3$$

$$= \langle E^3 \rangle - 3U\langle E^2 \rangle + U^3 + 3U^2 \langle E \rangle$$

$$= \langle -U^3 \rangle + \langle 3U^2 E \rangle - \langle 3UE^2 \rangle + \langle E^3 \rangle$$

$$= \langle -U^3 + 3U^2 E - 3UE^2 + E^3 \rangle = \langle (E-U)^3 \rangle = \langle (E - \langle E \rangle)^3 \rangle$$

$$= \langle (\Delta E)^3 \rangle \quad \ldots \text{ Done.}$$

Now $\beta = \frac{1}{kT} \Rightarrow \frac{\partial \beta}{\partial T} = \frac{\partial}{\partial T}\frac{1}{kT} = -\frac{1}{kT^2} \Rightarrow -kT^2 \frac{\partial}{\partial T} = \frac{\partial}{\partial \beta}$

Therefore $\dfrac{\partial^2}{\partial \beta^2} = \left(-kT^2 \frac{\partial}{\partial T}\right)\left(-kT^2 \frac{\partial}{\partial T}\right) = k^2 T^2 \frac{\partial}{\partial T}\left[T^2 \frac{\partial}{\partial T}\right]$

Then $\dfrac{\partial^2 U}{\partial \beta^2} = k^2 T^2 \dfrac{\partial}{\partial T}\left[T^2 \dfrac{\partial U}{\partial T}\right] = k^2 T^2 \left[2T \dfrac{\partial U}{\partial T} + T^2 \dfrac{\partial^2 U}{\partial T^2}\right]$

$$\frac{\partial^2 U}{\partial \beta^2} = \boxed{\langle (\Delta E)^3 \rangle = k^2 \left(T^4 \frac{\partial}{\partial T} C_v \Big|_V + 2T^3 C_v\right)} \qquad \left(\text{since } \frac{\partial U}{\partial T} = C_v\right)$$

ideal gas?

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