

Problem:

The molecules of a hypothetical ideal gas have internal energy levels that are equally spaced so that the n^{th} energy eigenvalue $E_n = \epsilon n$, where $n = 0, 1, 2, \dots$

The degeneracy of the n^{th} level is $n+1$.

Task: Calculate the contribution of the internal energy states to the thermal energy.

We have an ideal gas (= non-interacting gas).

We start with the single-particle partition function.

Consider only internal contribution:

$$Q_{\text{int},1} = \sum_{n=0}^{\infty} (n+1) e^{-\beta \epsilon n} \quad (\beta = \frac{1}{kT})$$

$$\begin{aligned} &= \sum_{n=0}^{\infty} (n+1) x^n \\ &\quad \nearrow x = e^{-\beta \epsilon} \end{aligned}$$

$$\begin{aligned} &= \sum_{m=1}^{\infty} m x^{m-1} \\ &\quad \nearrow m = n+1 \end{aligned}$$

$$= \frac{d}{dx} \left(\sum_{m=1}^{\infty} x^m \right)$$

$$\begin{aligned} &\text{the constant} \rightarrow \text{does not contribute} \quad = \frac{d}{dx} \left(\sum_{m=1}^{\infty} x^m + 1 \right) \quad \text{constant} \end{aligned}$$

$$= \frac{d}{dx} \left(\underbrace{\sum_{m=0}^{\infty} x^m}_{\frac{1}{1-x}} \right)$$

$$= -\frac{1}{(1-x)^2} (-1)$$

$$x = e^{-\beta \epsilon} \rightarrow = (1-x)^{-2}$$

$$= (1 - e^{-\beta \epsilon})^{-2}$$

$$\Rightarrow \left\{ Q_{int,1} = (1 - e^{-\beta \epsilon})^{-2} \right\}$$

We want thermal energy, i.e., thermal expectation value of \mathcal{H} .

$$U_{int,1} = \frac{1}{Q_{int,1}} \sum_{n=0}^{\infty} \epsilon n (n+1) e^{-\beta \epsilon n}$$

$$= \frac{1}{Q_{int,1}} \sum_{n=0}^{\infty} \left\{ -\frac{\partial}{\partial \beta} \left[(n+1) e^{-\beta \epsilon n} \right] \right\}$$

$$= \frac{-1}{Q_{int,1}} \frac{\partial}{\partial \beta} \left(\underbrace{\sum_{n=0}^{\infty} (n+1) e^{-\beta \epsilon n}}_{\text{from before: } Q_{int,1}} \right)$$

from before: $Q_{int,1}$

$$\Rightarrow U_{\text{int},1} = - \frac{1}{Q_{\text{int},1}} \frac{\partial}{\partial \beta} Q_{\text{int},1}$$

$$= - \frac{\partial}{\partial \beta} \log Q_{\text{int},1}$$

Plug in :

$$U_{\text{int},1} = - \frac{\partial}{\partial \beta} \log \left((1 - e^{-\beta \epsilon})^{-2} \right)$$

$$= + 2 \frac{1}{1 - e^{-\beta \epsilon}} (-e^{-\beta \epsilon}) (-\epsilon)$$

$$\left\{ U_{\text{int},1} = + 2 \epsilon \frac{1}{e^{\beta \epsilon} - 1} \right\}$$

So: internal thermal energy of single particle

$$U_{\text{int},1} = 2 \epsilon (e^{\beta \epsilon} - 1)^{-1}$$

For N particles: $\left\{ U_{\text{int},N} = 2 N \epsilon (e^{\beta \epsilon} - 1)^{-1} \right\}$

Of course: we also have "motional" energy \rightarrow

need to add $\frac{3}{2} N k T$