At constant temperature T, the probability of observing a system at a given energy state E_ν is $p_\nu = \exp(-\beta E_v)/Z$, with $\beta = 1/k_B T$, and Z a normalization constant. If we now consider the subset of states that all have the same energy E, so that there are $\Omega(E)$ such distinct states with the same energy, then the probability of observing the system having an energy E is

$$p(E) = \frac{1}{Z}\Omega(E)e^{-\beta E} = \frac{1}{Z}e^{\ln \Omega(E) - \beta E},$$

imagining that we have summed p_ν over all the states ν that have an energy E. We wish to show that the probability distribution $p(E)$ is very narrow and centered around $\langle E \rangle$, the average value of E. In other words, observing values of E other than $\langle E \rangle$ is extremely rare.

- Estimate $p(E)$ around its average by expanding $\ln p(E)$ in Taylor series around $\langle E \rangle$ up to second order in $E - \langle E \rangle$. Show that the first order term is zero, and express the second order term as a function of the heat capacity C_V. Remember Boltzmann formula $S(E) = k_B \ln \Omega(E)$.
- Use this expression to estimate the relative probability $(p(E)/p(\langle E \rangle))$ of observing a fluctuation as small as $10^{-6}\langle E \rangle$ for an ideal gas of $N = 0.001$ mol.

Show that $p(E)$ is very narrow around $\langle E \rangle$.

We have that the probability of a certain state E is:

$$p(E) = \frac{1}{Z} W(E) e^{-\beta E}$$

Expand $\ln p(E)$ around the average: $\ln p(\langle E \rangle)$:

$$\ln p(E) = \ln p(\langle E \rangle) + \left(\frac{\partial \ln p(E)}{\partial E} \right)_{\langle E \rangle} (E - \langle E \rangle) + \frac{1}{2} \left(\frac{\partial^2 \ln p(E)}{\partial E} \right)_{\langle E \rangle} (E - \langle E \rangle)^2$$

Compute the first derivative:

$$\left(\frac{\partial \ln p(E)}{\partial E} \right)_{\langle E \rangle} = \left(\frac{\partial (-\ln Z + \ln W(E) - \beta E)}{\partial E} \right)_{\langle E \rangle} = \left(\frac{\partial \ln W(E)}{\partial E} \right)_{\langle E \rangle} - \beta =$$

$$= \frac{1}{k_B} \left(\frac{\partial S}{\partial \langle E \rangle} \right) - \beta = \beta - \beta = 0.$$

Second derivative:

$$\left(\frac{\partial^2 \ln p(E)}{\partial E^2} \right)_{\langle E \rangle} = \left(\frac{\partial^2 (\ln W(E) - \beta E)}{\partial E^2} \right)_{\langle E \rangle} = \left(\frac{\partial^2 \ln W(E)}{\partial E^2} \right)_{\langle E \rangle} =$$

$$= \frac{1}{k_B} \left(\frac{\partial^2 S}{\partial \langle E \rangle^2} \right) = \frac{1}{k_B} \left(\frac{\partial \, 1/T}{\partial \langle E \rangle} \right) = -\frac{1}{k_B T^2} \left(\frac{\partial T}{\partial \langle E \rangle} \right)$$

$\langle E \rangle \equiv U$ is the thermodynamic value of the internal energy.

But $C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)$

$$\Rightarrow \left(\frac{\partial^2 \ln p(E)}{\partial E^2} \right)_{\langle E \rangle} = -\frac{1}{k_B T^2 C_V}$$

$$\Rightarrow \ln p(E) - \ln p(\langle E \rangle) = -\frac{1}{2 k_B T^2 C_V} (E - \langle E \rangle)^2$$

or $$\boxed{p(E) = p(\langle E \rangle) \, e^{-\frac{(E - \langle E \rangle)^2}{2 k_B T^2 C_V}}}$$

Gaussian around $\langle E \rangle$ with standard deviation $2 k_B T^2 C_V$.

We are now asked to estimate the probability of $E - \langle E \rangle = 10^{-6} \langle E \rangle$ for a system of $N = 10^{21}$.

Take an ideal gas $\langle E \rangle = \frac{3}{2} N k_B T$, $C_V = \frac{3}{2} N k_B$

(Note $(E - \langle E \rangle)^2 \sim N^2$, $C_V \sim N$ only, so the standard deviation $\sim \frac{1}{N}$

$$\Rightarrow \boxed{\frac{p(E)}{p(\langle E \rangle)} \sim e^{-10^9}}$$

This is for a monoatomic ideal gas. People may use different models.