Energy fluctuation in canonical ensemble

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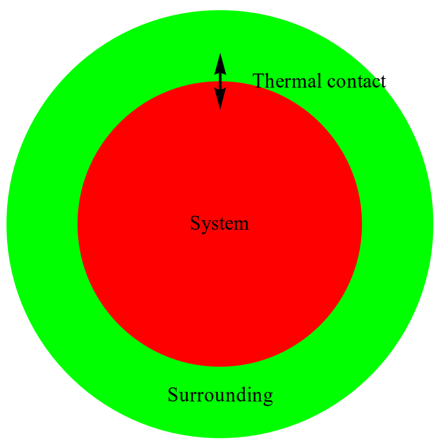
We discuss the energy fluctuation in the canonical ensemble using the following problem. We show that

$$\frac{\Delta E}{\langle E\rangle} \approx \frac{1}{\sqrt{N}}.$$

In the limit of $N \to \infty$ (thermodynamic limit), $\frac{\Delta E}{\langle E\rangle}$ reduces to zero.

Problem



(a) Show that the energy fluctuation in a canonical distribution is given by

$$\left\langle (E - \langle E\rangle)^2 \right\rangle = k_B T^2 C_V ,$$

where the internal energy is given by $U = \langle E\rangle$, T is the absolute temperature, and C_V is the heat capacity at constant volume. (b) Prove the following relation in a similar manner:

$$\left\langle (E - \langle E\rangle)^3 \right\rangle = k_B{}^2 \{T^4 \left(\frac{\partial C_V}{\partial T}\right)_V + 2T^3 C_V\} .$$

(c) Show that, in particular, for an ideal gas consisting of N monatomic molecules (disregard the internal structure, these equations can be reduced to

$$\frac{\langle (E-\langle E\rangle)^2\rangle}{\langle E\rangle^2}=\frac{2}{3N}, \quad \frac{\langle (E-\langle E\rangle)^3\rangle}{\langle E\rangle^3}=\frac{8}{9N^2}.$$

Hint: use $\langle E\rangle = 3Nk_BT/2$ for the ideal gas.

((**Solution**))
The partition function:

$$Z_C = \sum_s e^{-\beta E_s}$$

where $\beta = \frac{1}{k_B T}$

The average values (by definitions):

$$\langle E\rangle = \frac{1}{Z_C}\sum_s E_s e^{-\beta E_s}$$

$$\langle E^2\rangle = \frac{1}{Z_C}\sum_s E_s{}^2 e^{-\beta E_s}$$

$$\langle E^3\rangle = \frac{1}{Z}\sum_s E_s{}^3 e^{-\beta E_s}$$

We take the derivative of Z with respect to β;

$$Z_C' = \frac{\partial Z_C}{\partial \beta} = -Z_C\langle E\rangle \qquad \text{or} \qquad \langle E\rangle = -\frac{Z_C'}{Z_C}$$

$$Z_C'' = \frac{\partial^2 Z_C}{\partial \beta^2} = Z_C\langle E^2\rangle \qquad \text{or} \qquad \langle E^2\rangle = \frac{Z_C''}{Z_C}$$

and

$$Z_C''' = \frac{\partial^3 Z_C}{\partial \beta^3} = -Z_C\langle E^3\rangle \qquad \text{or} \qquad \langle E^3\rangle = -\frac{Z_C'''}{Z_C}$$

(a)

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Here

$$\frac{\partial}{\partial\beta}\langle E\rangle = -k_B T^2 \frac{\partial}{\partial T}\langle E\rangle$$
$$= -k_B T^2 C_V$$

and

$$\frac{\partial}{\partial\beta}\langle E\rangle = \frac{\partial}{\partial\beta}\left(-\frac{Z_C'}{Z_C}\right)$$
$$= (-1)\left(\frac{Z_C'' Z_C - Z_C'^2}{Z_C^2}\right)$$
$$= -\frac{Z_C''}{Z_C} + \left(\frac{Z_C'}{Z_C}\right)^2$$

Then we have the relation

$$(\Delta E)^2 = \left\langle (E - \langle E\rangle)^2 \right\rangle$$
$$= \langle E^2\rangle - \langle E\rangle^2$$
$$= k_B T^2 \frac{\partial}{\partial T}\langle E\rangle$$
$$= k_B T^2 C_V$$

(b)

$$\frac{\partial^2}{\partial \beta^2}\langle E\rangle = 2\left(\frac{Z'}{Z}\right)\left(\frac{Z''Z - Z'^2}{Z^2}\right) - \left(\frac{Z'''Z - Z''Z'}{Z^2}\right)$$
$$= -\frac{Z'''}{Z} + \frac{3Z''Z'}{Z^2} - 2\frac{Z'^3}{Z^3}$$
$$= \langle E^3\rangle - 3\langle E^2\rangle\langle E\rangle + 2\langle E\rangle^3$$
$$= \langle (E - \langle E\rangle)^3\rangle$$

Here we note that

$$\frac{\partial}{\partial \beta}\langle E\rangle = -k_B T^2 C_V$$

$$\frac{\partial^2}{\partial \beta^2}\langle E\rangle = -k_B T^2 \frac{\partial}{\partial T}(-k_B T^2 C_V)$$
$$= k_B{}^2\left(T^4 \frac{\partial C_V}{\partial T} + 2T^3 C_V\right)$$

Then

$$\langle (E - \langle E\rangle)^3\rangle = \frac{\partial^2}{\partial \beta^2}\langle \varepsilon\rangle = k_B{}^2\left(T^4 \frac{\partial C_V}{\partial T} + 2T^3 C_V\right)$$

(c) For the ideal gas

$$\langle E\rangle = \frac{1}{Z}\sum_s E_s e^{-\beta E_s} = \frac{3}{2}Nk_B T\ ,$$

$$C_V = \frac{3}{2}Nk_B\,.$$

So that

$$\frac{(\Delta E)^2}{\langle E\rangle^2} = \frac{\langle (E-\langle E\rangle)^2\rangle}{\langle E\rangle^2}$$

$$= \frac{Nk_B{}^2T^2\frac{3}{2}}{\left(\frac{3}{2}Nk_BT\right)^2} \ ,$$

$$= \frac{2}{3N}$$

or

$$\frac{\Delta E}{\langle E\rangle} = \sqrt{\frac{2}{3}}\frac{1}{\sqrt{N}} \approx \frac{1}{\sqrt{N}}$$

In the limit of $N \to \infty$, $\frac{\Delta E}{\langle E\rangle}$ becomes zero. We also have

$$\frac{\langle (E-\langle E\rangle)^3\rangle}{\langle E\rangle^3} = \frac{k_B{}^2\left(2T^3\frac{3}{2}Nk_B\right)}{\left(\frac{3}{2}Nk_BT\right)^3} = \frac{8}{9N^2} \ .$$

((**Example**))

Schottky anomaly of specific heat

$$C_V = Nk_B\left(\frac{\Delta}{k_BT}\right)^2 \frac{e^{\Delta/(k_BT)}}{(e^{\Delta/(k_BT)}+1)^2}$$

The energy fluctuation:

$$(\Delta E)^2 = k_BT^2C_V$$

$$= N\Delta^2 \frac{k_B{}^2T^2}{\Delta^2}\left(\frac{\Delta}{k_BT}\right)^2 \frac{e^{\Delta/(k_BT)}}{(e^{\Delta/(k_BT)}+1)^2}$$

$$= N\Delta^2 \frac{e^{\Delta/(k_BT)}}{(e^{\Delta/(k_BT)}+1)^2}$$

or

$$\frac{(\Delta E)^2}{N\Delta^2} = \frac{e^{\Delta/(k_B T)}}{(e^{\Delta/(k_B T)}+1)^2}$$

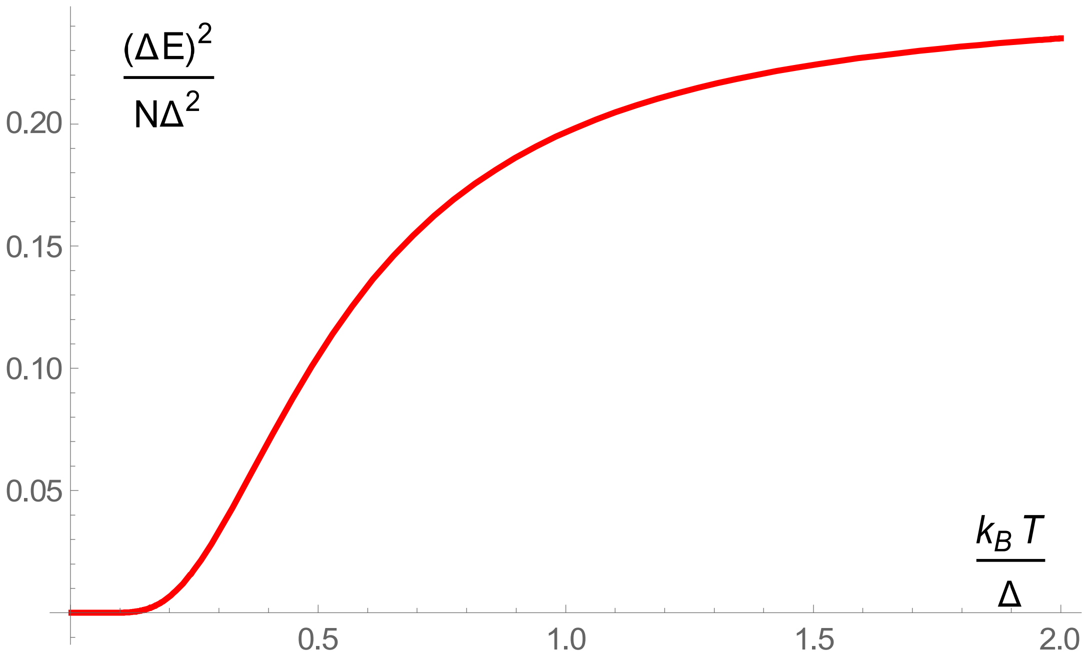

Fig. $\frac{(\Delta E)^2}{N\Delta^2}$ as a function of $x = k_B T/\Delta$. $\frac{(\Delta E)^2}{N\Delta^2} \to \frac{1}{4}$ as $T \to \infty$.