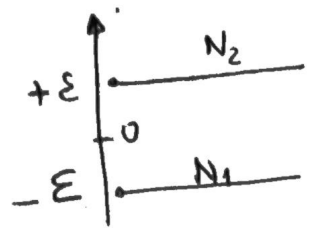


Kikhaou, Boucha.

Système à deux niveaux
à l'énergie non dégénérée

$$N = N_1 + N_2 : \text{particules}$$

$$\varepsilon_{\text{dipôle}} = -\vec{p} \cdot \vec{E}_{\text{ext}} \Rightarrow \begin{cases} pE_{\text{ext}} \\ -pE_{\text{ext}} \end{cases}$$



* Probabilités des deux états:

→ probabilité d'occupation d'un niveau d'énergie E_i :

$$p(E_i) = \frac{1}{Z} \exp\left(-\frac{E_i}{k_B T}\right) \quad \text{Loi de Boltzmann}$$

$$Z = \sum e^{-\beta E_i} = e^{+\beta \varepsilon} + e^{-\beta \varepsilon} = 2 \cosh(\beta \varepsilon)$$

$$Z = 2 \cosh\left(\frac{\varepsilon}{k_B T}\right) = 2 \cosh\left(\frac{\varphi}{T}\right) = 2 \cosh x$$

$$p(E_1) = \frac{1}{Z} \exp\left(\frac{\varepsilon}{k_B T}\right) = \frac{e^x}{e^x + e^{-x}} = \frac{e^x}{2 \cosh x}$$

→ population des deux états

$$p(E_i) = \frac{N_i}{N} \Rightarrow N_i = N p(E_i) \Rightarrow$$

$$N_1 = N p(E_1) = \frac{N e^x}{e^x + e^{-x}}$$

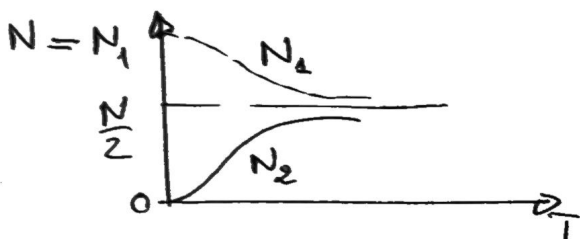
$$N_2 = N p(E_2) = \frac{N e^{-x}}{e^x + e^{-x}}$$

$$\bullet k_B T \ll \varepsilon \Rightarrow x \gg 1$$

$$N_1 \approx N, \quad N_2 \approx 0$$

$$\bullet k_B T \gg \varepsilon \quad x \ll 1$$

$$N_1 \approx N_2 \approx \frac{N}{2}$$



(1)

Énergie moyenne

Kch avon Bonlier

énergie moyenne par particule :

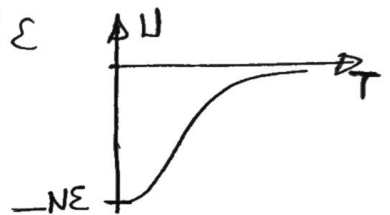
$$\begin{aligned}\langle E \rangle &= \sum E_i p(E_i) = E_1 p(E_1) + E_2 p(E_2) \\ &= \varepsilon \frac{e^{-x} - e^{+x}}{e^{-x} + e^{+x}} = -\varepsilon \operatorname{th} x = -\varepsilon \operatorname{th} \left(\frac{\varepsilon}{k_B T} \right)\end{aligned}$$

énergie moyenne du système.

$$\langle E_S \rangle = U = N \langle E \rangle = -N \varepsilon \operatorname{th} x = -\frac{N \varepsilon (e^x - e^{-x})}{e^x + e^{-x}}$$

• $k_B T \ll \varepsilon \Rightarrow U = \langle E_S \rangle = -N \varepsilon$

• $k_B T \gg \varepsilon \Rightarrow U = \langle E_S \rangle \approx 0$



Fluctuation de l'énergie

ecart quadratique (système) $(\Delta E_S)^2 = N (\Delta E)^2 \Leftrightarrow (\Delta E_S) = \sqrt{N} (\Delta E)$

↙ système ↗
↘ ecart quadratique ↗

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

$$\langle E \rangle = \sum_i E_i p(E_i) = -\varepsilon \operatorname{th} x : \text{par particule}$$

$$\langle E^2 \rangle = \sum_i E_i^2 p(E_i) = \varepsilon^2 [p(E_1) + p(E_2)] = \varepsilon^2$$

La variance de l'énergie d'une particule est

$$\begin{aligned}\operatorname{Var}(E) &= (\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2 = \varepsilon^2 (1 - \operatorname{th}^2 x) \\ &= \frac{\varepsilon^2}{\cosh^2 x} \quad (2)\end{aligned}$$

Variance de l'énergie du système

$$\text{Var}(E_s) = (\Delta E_s)^2 = N (\Delta E)^2 = N \varepsilon^2 (1 - \tanh^2(x))$$

$$\text{Var}(E_s) = \frac{N \varepsilon^2}{\text{ch}^2(x)} = (\Delta E_s)^2$$

Fluctuation de l'énergie du système.

$$\sigma(E_s) = (\Delta E_s) = \sqrt{N} (\Delta E) = \sqrt{N} \varepsilon \sqrt{1 - \tanh^2(x)}$$

$$\sigma(E_s) = \frac{\sqrt{N} \varepsilon}{\text{ch}(x)}$$

fluctuation relative du système autour de sa valeur moyenne :

$$\begin{aligned} \frac{\Delta E_s}{\langle E_s \rangle} &= \frac{\sqrt{N} (\Delta E)}{N \langle E \rangle} = \frac{1}{\sqrt{N}} \frac{\Delta E}{\langle E \rangle} = \frac{1}{\sqrt{N}} \frac{\frac{\varepsilon}{\text{ch} x}}{\varepsilon + \tanh x} \\ &= - \frac{1}{\sqrt{N}} \frac{1}{\text{sh}(x)} ; x = +\beta \varepsilon \end{aligned}$$

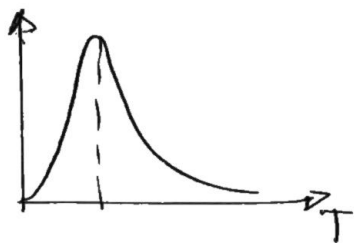
La fluctuation relative de l'énergie du système regresse lorsque la taille du système augmente.

Capacité thermique

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = - k_B \beta^2 \left(\frac{\partial U}{\partial \beta} \right)$$

$$\begin{aligned} C_V &= \frac{\partial \langle E_S \rangle}{\partial T} = + N \frac{\partial \langle E \rangle}{\partial T} = N \frac{\partial}{\partial T} \left[- \varepsilon \ln(\beta \varepsilon) \right] \\ &= + N \varepsilon k_B \beta^2 \frac{\partial}{\partial \beta} [\ln(\beta \varepsilon)] = \frac{N k_B \beta^2 \varepsilon^2}{\ln(\beta \varepsilon)} \end{aligned}$$

$$C_V = \frac{N \varepsilon^2}{k_B T^2} (1 - \ln(\beta \varepsilon)) = \frac{N \varepsilon^2}{k_B T^2} \frac{1}{\ln(\beta \varepsilon)}$$



$$\odot (\Delta E_S)^2 = N \varepsilon^2 (1 - \ln(\beta \varepsilon))$$

$$\odot C_V = \frac{N \varepsilon^2}{k_B T^2} (1 - \ln(\beta \varepsilon))$$

$$\Rightarrow (\Delta E_S)^2 = C k_B T^2$$

$$\Rightarrow \sqrt{(\Delta E_S)} = (\Delta E_S) = \sqrt{C k_B} T$$

fluctuation de l'énergie d'un système thermodynamique augmente avec T .

$(\Delta E_S) = \sqrt{C k_B} T$: variable dans le système canonique

Kéran Borhan

Énergie interne Cas général

$$P_r = \frac{g_r}{Z} e^{-\beta E_r} ; Z = \sum g_r e^{-\beta E_r}$$

énergie moyenne $\bar{E} = \sum E_r P_r = \frac{1}{Z} \sum E_r g_r e^{-\beta E_r}$

$$\bar{E} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \left(\sum g_r e^{-\beta E_r} \right) = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$\left\{ \bar{E} = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_{V,N} = -\frac{1}{Z} \left(\frac{\partial Z}{\partial \beta} \right)_{V,N} \right\} \quad \checkmark$$

$$\text{or } \beta = \frac{1}{k_B T} \Rightarrow \frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T}$$

$$\left\{ \bar{E} = k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{V,N} \right\} \quad \checkmark$$

Déterminons maintenant l'écart quadratique moyen de l'énergie E : $(\Delta E)^2 = \overline{E^2} - (\bar{E})^2$

$$\overline{E^2} = \sum E_r^2 P(E_r) = \frac{1}{Z} \sum E_r^2 g_r e^{-\beta E_r}$$

$$\begin{aligned} \text{or } E_r^2 e^{-\beta E_r} &= E_r \frac{\partial}{\partial \beta} (-e^{-\beta E_r}) = -E_r \frac{\partial}{\partial \beta} e^{-\beta E_r} \\ &= + \frac{\partial^2}{\partial \beta^2} e^{-\beta E_r} \end{aligned}$$

$$\text{dnc } \overline{E^2} = \frac{1}{Z} \sum E_r^2 g_r e^{-\beta E_r} = \frac{1}{Z} \frac{\partial^2 \sum g_r e^{-\beta E_r}}{\partial \beta^2}$$

$$\left\{ \overline{E^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \right\} \quad \checkmark$$

Kohn
Bornem

$$\begin{aligned} n \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) &= \left[\frac{\partial}{\partial \beta} \left(\frac{1}{Z} \right) \right] \left(\frac{\partial Z}{\partial \beta} \right) + \frac{\partial^2 Z}{\partial \beta^2} \cdot \frac{1}{Z} \\ &= -\frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 + \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \end{aligned}$$

$$\text{dnc: } \overline{E^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + (\overline{E})^2$$

$$(\Delta E)^2 = \overline{E^2} - (\overline{E})^2 = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$\boxed{(\Delta E)^2 = k_B T^2 \frac{\partial \overline{E}}{\partial T}}$$

$$-\frac{\partial \overline{E}}{\partial \beta}, \quad \frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T}$$

$$\text{dnc } \underline{N.B.} : \boxed{(\Delta E)^2 = k_B T^2 C_V}$$

$$\frac{(\Delta E)}{\overline{E}} : \text{cart relatif} = \frac{\sqrt{k_B T^2 C_V}}{\overline{E}} = \frac{k_B T}{\overline{E}} \sqrt{\frac{C_V}{k_B}}$$

$$\overline{E} = \frac{3}{2} N k_B T; \quad C_V = \frac{3}{2} N k_B; \quad \text{Gaz parfait}$$

$$\frac{\Delta E}{\overline{E}} = \frac{k_B T}{\frac{3}{2} N k_B T} \sqrt{\frac{\frac{3}{2} N k_B}{k_B}} = \frac{2}{3} \frac{1}{\sqrt{N}} \simeq 10^{-12}$$

$$\underline{N \gg 1}$$

Khan Borken