Second Law of Thermodynamics

Can calculate no. of configurations W from description of system and then determine entropy

$$S = k_b lnW$$

Or $W = e^{S/k_B}$. Only know S to an additive constant and thus W only known to multiplicative factor

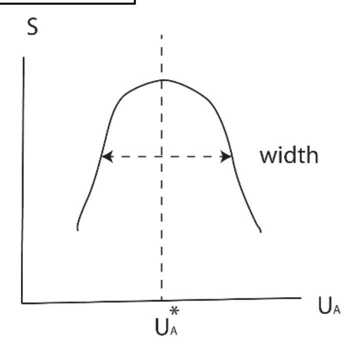
For a give system A with internal energy U_A , S will evolve (i.e approach equilibrium) until S is a maximum

$$S(U_A) = S(U_A) + \frac{(U_A - U_A^*)^2}{2}\left(\frac{\partial^2 S(U_A)}{\partial U_A^2}\right)$$

Negative

write as S''

$$W(U_A) = e^{\frac{S(U_A^*)}{k_B}} e^{\left(\frac{(U_A - U_A^*)^2 \; S''}{2k_B}\right)}$$



How narrow is the width ?

Standard deviation in W is $(\Delta U_A)^2 = -k_B/S''$

Implies that there exists fluctuations in system.

Equilibrium state of macrostate includes fluctuations.

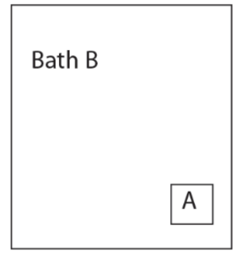
Probabilities of state with energy U_A: $p(U_A) = \frac{W(U_A)}{\sum_A W(U_A)}$ $W(U_A)$ is maximum at ${U_A}^*$

Have $p({U_A}^*) = \frac{W({U_A}^*)}{\sum_A W({U_A}^*)}$,

Ratio $\frac{p(U_A)}{p({U_A}^*)} = \frac{W(U_A)}{W({U_A}^*)} = e^{-\frac{(U_A - U_A^*)^2}{2\Delta U_A^2}}$ typically very very small

e.g. if $U_A - U_A^* = 2\Delta U_A$ $\frac{p(U_A)}{p({U_A}^*)} = e^{-2} = 0.14$

Scale of fluctuations and heat capacity



Consider a small system A embedded in a big thermal bath B

Total Energy $E = U_A + U_B \qquad U_B = E - U_A$ E a constant

For total $S = S_A + S_B$ Use thermodynamic relations

$$\left(\frac{\partial S}{\partial U_A}\right)_V = \frac{\partial}{\partial U_A}[S_A + S_B] = \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_B}\frac{\partial U_B}{\partial U_A} = \frac{1}{T_A} - \frac{1}{T_B}$$

<u>Interested in fluctuations</u>

Determined by $S'' = \left(\frac{\partial^2 S}{\partial {U_A}^2}\right)_V = \frac{\partial}{\partial U_A}(T_A^{-1}) + \frac{\partial}{\partial U_B}(T_B^{-1})$

$$= -\frac{1}{T_A^2}\left(\frac{\partial T_A}{\partial U_A}\right) - \frac{1}{T_B^2}\left(\frac{\partial T_B}{\partial U_B}\right)$$

T_A is near T_B Call it T

Definition of heat capacity $C_A = \frac{\partial U_A}{\partial T_A}$ etc.

Thus $S'' = -\frac{1}{T^2}\left(\frac{1}{C_A} + \frac{1}{C_B}\right)$ By construction C_B is huge so $S'' = -\frac{1}{T^2}\left(\frac{1}{C_A}\right)$

Fluctuations $\Delta U_A^2 = -\frac{k_B}{S''} = k_B T^2 C_A$

Heat capacity C is extensive, and $C \propto N$ therefore fluctuation $\Delta U_A \propto N^{1/2}$

Relative fluctuation $\frac{\Delta U_A}{U_A} \propto N^{-1/2}$ Very very small for most samples.

E.g. one nanomole $N \sim 10^{14}$ and $\frac{\Delta U_A}{U_A} \propto 10^{-7}$

Example problems

Book 4.2

How much heat Q must be added at 300K to change no. of states by 10^6

$$\Delta S = k_B ln\frac{W_f}{W_i} = 1.4\ 10^{-23} ln 10^6 \sim 1.4 * 6 * 2.3\ 10^{-23} = 19\ 10^{-23}$$

Heat needed $\Delta Q = T\Delta S = 3 * 19\ 10^{-21} = 5.7\ 10^{-20}$ J

=0.35 eV (1 eV=1.6 10^{-19} J)