MSAE3111, Thermodynamics and Statistical Mechanics

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The problem

- Two systems: S_1, S_2

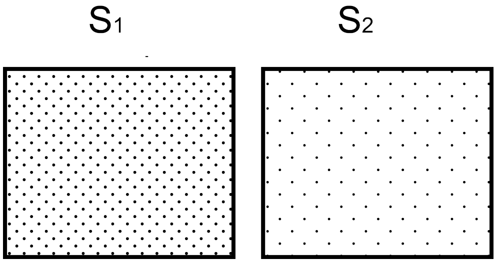

Figure: Isolated systems.

- Different numbers of particles: $N_1 \neq N_2$
- Different properties: spin excess $s_1 \neq s_2 \rightarrow E_1 \neq E_2$

The problem

- Two systems: $\mathbb{S}$

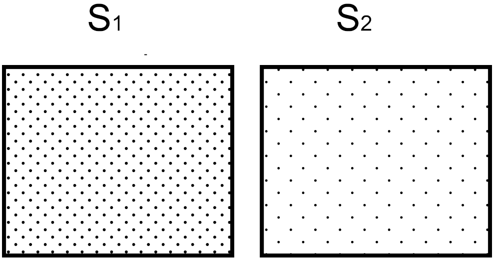

Figure: Isolated systems S_1, S_2

The problem

- Two systems: $\mathbb{S}$

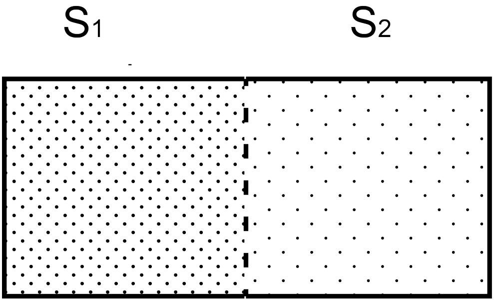

Figure: Joined system $S = S_1 + S_2$

- Brought into contact
- Can exchange energy: $U = U_1 + U_2$ fixed.
- **Can't** exchange particles: N_1, N_2, $N = N_1 + N_2$ fixed. (Relax this later).
- What happens?

To figure out

- Which way does the energy flow?
- Recall: *one* assumption so far. How to introduce temperature T?

Convenient: energy ($\propto s$)

- Apply magnetic field: B
- Magnetic moment m:

$$m = \mu_B \left(N^{\uparrow} - N^{\downarrow} \right) \quad (1)$$

$$= 2\mu_B s \quad (2)$$

- Energy:

$$U = -mB \quad (3)$$

$$= -2\mu_B \, B \, s \quad (4)$$

- Multiplicity for the system: depends on partitioning of s.

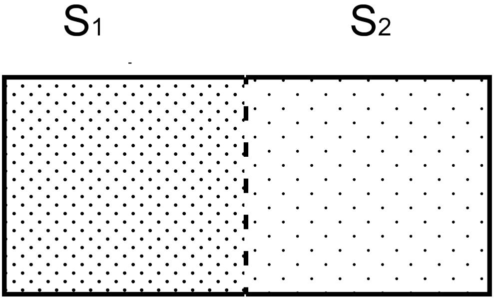

Figure: S_1 on left, S_2 on right

- Take state variable s_1; $s_2 = s - s_1$:

Joint multiplicities

- Total multiplicities: product of g_1, g_2
  - For fixed s_1

$$g(N, s_1) = g_1(N_1, s_1) \cdot g_2(N_2, s - s_1) \tag{5}$$

  - *Accessible* s_1

$$-s \leq s_1 \leq s \tag{6}$$

  - Total multiplicity for all accessible s_1

$$g(N, s_1) = \sum_{s_1} g_1(N_1, s_1) \cdot g_2(N_2, s - s_1) \tag{7}$$

- Most probable state of S: $g_{max} = g(N, \hat{s}_1)$

Finding most likely $s_1 = \hat{s}_1$

- Substituting single-system $g(s, N)$

$$g_1(N_1, s_1) g_2(N_2, s - s_1) = g_1(0, N_1) g_2(0, N_2) e^{\left(-\frac{2s_1^2}{N_1} - \frac{2(s-s_1)^2}{N_2}\right)} \tag{8}$$

- Take logarithm (for entropy):

$$ln(g) = \ln g_1(0, N_1) + \ln g_2(0, N_2) - \frac{2s_1^2}{N_1} - \frac{2(s - s_1)^2}{N_2} \tag{9}$$

- Taking derivative

$$\frac{\partial ln(g)}{\partial s_1} = -\frac{4s_1}{N_1} + \frac{4(s - s_1)}{N_2} \tag{10}$$

Evaluating

- Extremum

$$0 = -\frac{\hat{s}_1}{N_1} + \frac{(s - \hat{s}_1)}{N_2} \tag{11}$$

$$0 = -\frac{\hat{s}_1}{N_1} + -\frac{\hat{s}_1}{N_2} + \frac{s}{N_2} \tag{12}$$

$$0 = -\frac{\hat{s}_1(N_1 + N_2)}{N_1 N_2} + \frac{s}{N_2} \tag{13}$$

$$\frac{\hat{s}_1}{N_1} = \frac{s}{N} \tag{14}$$

- No privilege of S_1 over S_2 so

$$\frac{\hat{s}_1}{N_1} = \frac{\hat{s}_2}{N_2} = \frac{s}{N} \tag{15}$$

"Most likely," magnetization is the same

Finding most likely $s_1 = \hat{s}_1$

Look at small deviations from probable state

$$s_1 = \hat{s}_1 + \delta \qquad \delta \ll \hat{s}_1 \tag{16}$$

$$ln(g) = \ln g_1(0, N_1) + \ln g_2(0, N_2) - \frac{2(\hat{s}_1 + \delta)^2}{N_1} - \frac{2(\hat{s}_2 - \delta)^2}{N_2} \tag{17}$$

$$ln(g) = \ln g_1(0, N_1) g_2(0, N_2) - \frac{2({\hat{s}_1}^2 + 2\hat{s}_1\delta + \delta^2)}{N_1} - \frac{2({\hat{s}_2}^2 - 2\hat{s}_2\delta + \delta^2)}{N_2} \tag{18}$$

- Since $\hat{s_{1,2}}/N_{1,2} = s/N$,

$$ln(g) = \ln g_{max} - \frac{2s}{N} + \frac{2s}{N} - \delta^2 \left(\frac{1}{N_1} + \frac{1}{N_2} \right) \quad (19)$$

$$ln(g) = \ln g_{max} - \frac{N}{N_1 N_2} \delta^2 \quad (20)$$

$$g(\delta) = g_{max} \exp - \frac{N}{N_1 N_2} \delta^2 \quad (21)$$

Likelihood of $s \neq \hat{s}$

- How likely are these states? Take $N_1 = N_2 = N/2$ for simplicity

$$g(\delta) \sim g_{max} \exp -\frac{4\delta^2}{N} \tag{22}$$

  - Assume $N \sim 10^{22}$ (cm^3)
  - Tiny deviation (below sensitivity of best magnetometer)

$$\delta/N \sim 10^{-10} \tag{23}$$

  - Implies $\delta \sim 10^{12}$
  - Finally

$$4\delta^2/N = 400 \tag{24}$$

- Even this small deviation is *improbable*

$$\frac{P(\delta)}{P_0} = \frac{g(\delta)}{g(0)} = \exp -400 \tag{25}$$

The meaning of never

- How many measurements are possible?
  - Fastest measurement: 10^{-15} s (fs)
  - Age of universe: 13.75 $\pm$ 0.11 $\times 10^9$ yr (Gyr)
  - 60s/min x 60 min/hr x 24 hr/day x 365 day/yr: $\sim 3\times 10^7$ s/yr
- **Possible measurements in history of universe**

$$N_{big} \sim 10^{33} \tag{26}$$

- If $> N_{big}$ measurements needed for observation: More than sufficient for "never." *i.e. not happening*

Unlikelihood of small δ: equivalent to never

- Measurements to observe $\delta/N \sim 10^{-10}$

$$\frac{P_0}{P(\delta)} = \exp 400 \sim 10^{148} \tag{27}$$

Thermal equilibrium

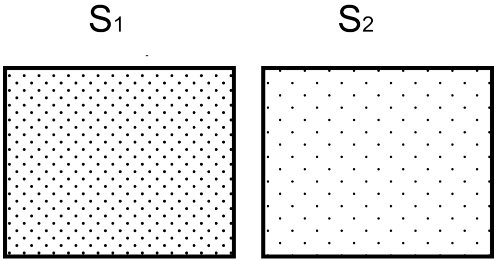

Figure: S_1 on left, S_2 on right

- Assume, before contact:

$$\frac{s_1}{N_1} \neq \frac{s_2}{N_2} \tag{28}$$

Thermal equilibrium

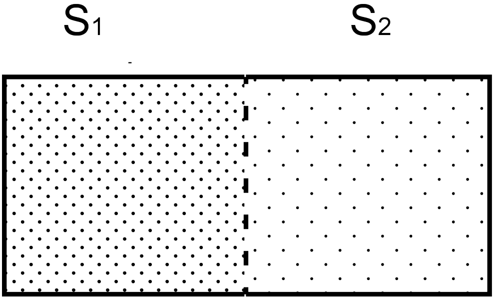

Figure: $S = S_1 + S_2$

- Some time after contact:

$$\frac{s_1}{N_1} = \frac{s_2}{N_2} \tag{29}$$

- This is (by far) the most likely condition
- We must get to this state. How?

Thermal equilibrium

- Take a small difference of multiplicity

$$\delta g(N_1, U_1)g(N_2, U_2) = \frac{\partial g_1}{\partial U_1} g_2 \delta U_1 + g_1 \frac{\partial g_2}{\partial U_2} \delta U_2 \tag{30}$$

- Total energy is constrained

$$\delta U = \delta U_1 + \delta U_2 \tag{31}$$

$$0 = \delta U_1 + \delta U_2 \tag{32}$$

$$\delta U_1 = -\delta U_2 \tag{33}$$

$$\delta U_1 = -\delta U_2 \tag{34}$$

- At most likely state, $\delta g = 0$

$$g_2 \frac{\partial g_1}{\partial U_1} = g_1 \frac{\partial g_2}{\partial U_2} \tag{35}$$

Thermal equilibrium

- Rewrite:

$$g_2 \frac{\partial g_1}{\partial U_1} = g_1 \frac{\partial g_2}{\partial U_2} \tag{36}$$

$$\frac{\partial \ln g_1}{\partial U_1} = \frac{\partial \ln g_2}{\partial U_2} \tag{37}$$

- Recognize the entropy, $\sigma = \ln g$

$$\frac{\partial \sigma_1}{\partial U_1} = \frac{\partial \sigma_2}{\partial U_2} \tag{38}$$

- If this condition holds, S in its final (equilibrium) state.
- **Thermal equilibrium** (no N exchange) is

$$\frac{\partial \sigma_1}{\partial U_1} = \frac{\partial \sigma_2}{\partial U_2} \qquad \Leftrightarrow \qquad T_1 = T_2 \tag{39}$$

Thermal equilibrium

- Accept (we'll see later):

$$\frac{\partial \sigma}{\partial U} = \frac{1}{k_B T} \tag{40}$$

- Can also say

$$\frac{\partial S}{\partial U} = \frac{1}{T} \tag{41}$$

- where

$$\tau \equiv k_B T \qquad S = k_B \sigma \qquad k_B = 1.381 \times 10^{-21} \mathrm{J/K} \tag{42}$$

Out of equilibrium

- Let's say that $T_1 < T_2$:

$$\delta g(N_1, U_1)g(N_2, U_2) = \frac{\partial g_1}{\partial U_1} g_2 \delta U_1 + g_1 \frac{\partial g_2}{\partial U_2} \delta U_2 \qquad (43)$$

- Rearranging, for $U = U_1 + U_2$, $dU = 0$

$$\delta \ln g_1 g_2 = \frac{\partial \ln g_1}{\partial U_1} \delta U_1 - \frac{\partial \ln g_2}{\partial U_2} \delta U_1 \qquad (44)$$

- Since heat will flow $2 \rightarrow 1$, $\Delta U_1 = |\Delta U| 0$

$$\delta\sigma = \left(\frac{\partial \sigma_1}{\partial U_1} - \frac{\partial \sigma_2}{\partial U_2} \right) |\Delta U| \qquad (45)$$

- **Entropy increases for a spontaneous process!**

$$\delta\sigma = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) |\Delta U| > 0 \qquad (46)$$

Example

- Two bars of Cu, same mass ($m = 10$ g)
- One at $T_1 = 290\mathrm{K}$, one at $T_2 = 350\mathrm{K}$
- Put in contact: you know $T_f = 320\mathrm{K}$.
- $\Delta U = m\, C_p\, \Delta T$
  $= 10\ \mathrm{g} \cdot 0.389\ \mathrm{J} \cdot \mathrm{g}^{-1} \cdot \mathrm{K}^{-1}$
  $= 11.7\ \mathrm{J}$
- Entropy increases:

$$\Delta S = k_B \delta\sigma = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) |\Delta U| \tag{47}$$

$$\Delta S = \left(\frac{1}{290\mathrm{K}} - \frac{1}{350\mathrm{K}}\right) |11.7\ \mathrm{J}| \tag{48}$$

$$\Delta S = 59 \mu\mathrm{J}/\mathrm{K} \tag{49}$$

The laws

1. **Heat is a form of energy**. (and energy is conserved)
2. **Entropy increases**.
   - **if** $s \neq \hat{s}_1$
     If a closed system is in a configuration that is not the equilibrium configuration
   - $\boldsymbol{\Delta\sigma > 0}$
     (the most probable consequence) is that the entropy of the system will increase montonically in successive instants in time
3. **Entropy becomes constant as** $T \rightarrow 0$