

Lecture 4. Entropy and Temperature (Ch. 3)

In Lecture 3, we took a giant step towards the understanding why certain processes in macrosystems are irreversible. Our approach was founded on the following ideas:

- Each accessible microstate of an isolated system is equally probable (the fundamental assumption).
- Every macrostate has a countable number of microstates (follows from Q.M.).
- The probability of a macrostate is proportional to its multiplicity. When systems get large, multiplicities get outrageously large.

On this basis, we will introduce the concept of **entropy** and discuss **the Second Law of Thermodynamics**.

Our plan:

As our point of departure, we'll use the models of an Einstein solid. We have already discussed one advantage of this model – “discrete” degrees of freedom. Another advantage – by considering two ***interacting*** Einstein solids, we can learn about the ***energy exchange*** between these two systems, i.e. how to reach ***thermal equilibrium***.

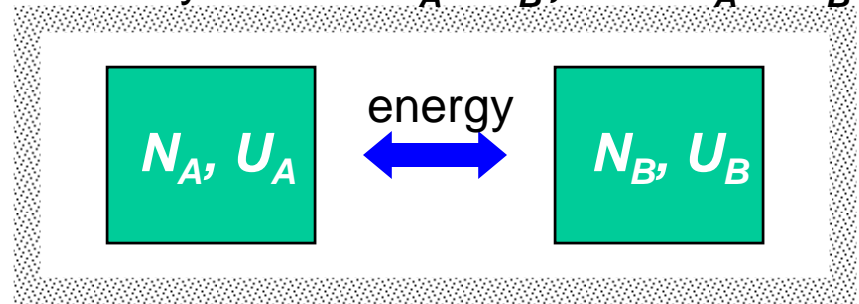
- By using our statistical approach, we'll identify the most probable macrostate of a combined system of two interacting Einstein solids after reaching an equilibrium;
- We'll introduce the entropy as a measure of the multiplicity of a given macrostate
- The Second Law of Thermodynamics

Two Interacting Einstein Solids, Macropartitions

Suppose that we bring two Einstein solids **A** and **B** (two sub-systems with N_A, U_A and N_B, U_B) into thermal contact, to form a larger isolated system. What happens to these solids (macroscopically) after they have been brought into contact?

The combined sys. – $N = N_A + N_B, U = U_A + U_B$

The macropartition of the combined system is defined by macroparameter U_A



Macropartition: a given pair of macrostates for sub-systems **A** and **B** that are consistent with conservation of the total energy $U = U_A + U_B$.

Different macropartitions amount to different ways that the energy can be **macroscopically** divided between the sub-systems.

Example: the pair of macrostates where $U_A = 2 \epsilon$ and $U_B = 4 \epsilon$ is one possible macropartition of the combined system with $U = 6 \epsilon$

As time passes, the system of two solids will randomly shift between different microstates consistent with the constraint that $U = \text{const.}$

Question: what would be the **most probable** macrostate for given N_A, N_B , and U ?

The Multiplicity of Two Sub-Systems Combined

The probability of a macropartition is proportional to its multiplicity:

$$\Omega_{AB} = \Omega_A \times \Omega_B$$

macropartition
 $A+B$

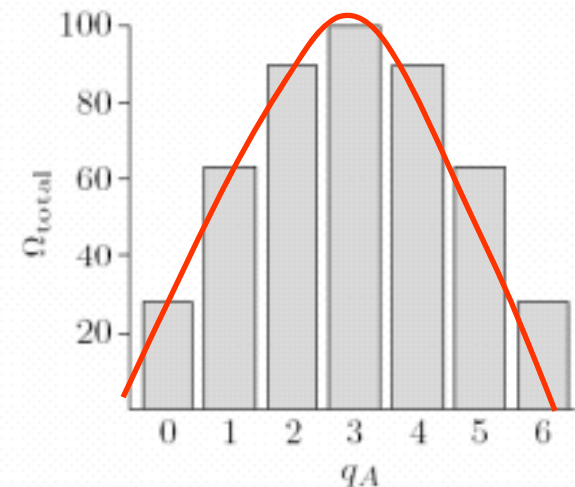
sub-system
 A

sub-system
 B

Example: two one-atom “solids” into thermal contact, with the total $U = 6\varepsilon$.

Possible macropartitions for $N_A = N_B = 3$, $U = q_A + q_B = 6\varepsilon$

Macro-partition	U_A	U_B	Ω_A	Ω_B	Ω_{AB}
0 : 6	0 ε	6 ε	1	28	28
1 : 5	1 ε	5 ε	3	21	63
2 : 4	2 ε	4 ε	6	15	90
3 : 3	3 ε	3 ε	10	10	100
4 : 2	4 ε	2 ε	15	6	90
5 : 1	5 ε	1 ε	21	3	63
6 : 0	6 ε	0 ε	28	1	28



Grand total # of microstates:

$$\frac{(U/\varepsilon + N - 1)!}{(U/\varepsilon)!(N - 1)!} = \frac{(6 + 6 - 1)!}{(6)!(6 - 1)!} = 462$$

Exercise: check the multiplicities of macrostates for $N_A = N_B = 100$, $U = q_A + q_B = 200\varepsilon$

The Probability of Macrostates of a Two-State PM ($B=0$)

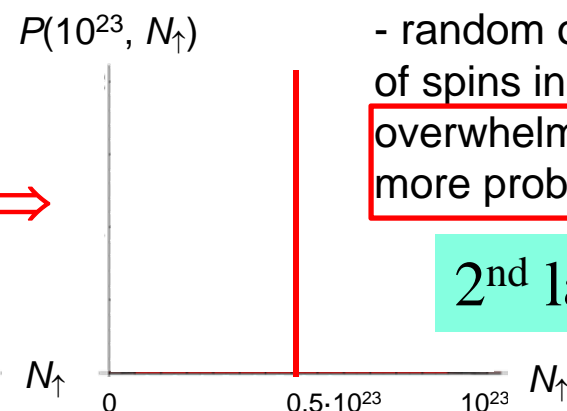
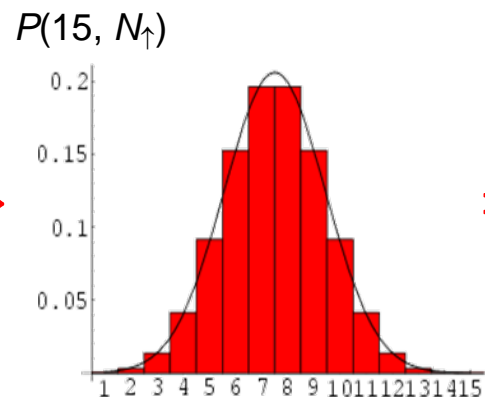
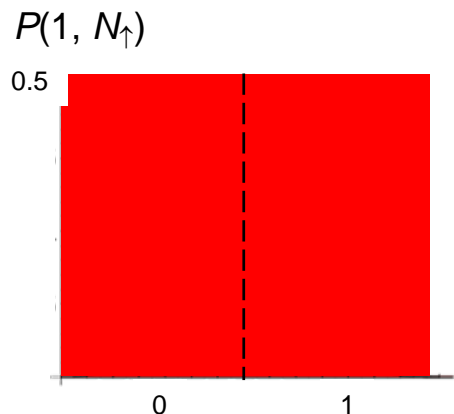
$$P(N, N_{\uparrow}) = \frac{\Omega(N, N_{\uparrow})}{\text{\# of all microstates}} = \frac{\Omega(N, N_{\uparrow})}{\Omega(N, \text{all } N_{\uparrow})} = \frac{\Omega(N, N_{\uparrow})}{2^N}$$

$$P(N, N_{\uparrow}) = \frac{N!}{N_{\uparrow}!(N - N_{\uparrow})! 2^N} \approx \frac{N^N e^{-N}}{N_{\uparrow}^{N_{\uparrow}} e^{-N_{\uparrow}} (N - N_{\uparrow})^{(N - N_{\uparrow})} e^{-(N - N_{\uparrow})} 2^N}$$

$$= \frac{N^N}{N_{\uparrow}^{N_{\uparrow}} (N - N_{\uparrow})^{(N - N_{\uparrow})} 2^N}$$

- as the system becomes larger, the $P(N, N_{\uparrow})$ graph becomes more sharply peaked:

$$N=1 \Rightarrow \Omega(1, N_{\uparrow}) = 1, 2^N = 2, P(1, N_{\uparrow}) = 0.5$$



- random orientation of spins in $B=0$ is overwhelmingly more probable

2nd law!

The Multiplicity of Two Sub-Systems Combined

The probability of a macropartition is proportional to its multiplicity:

$$\Omega_{AB} = \Omega_A \times \Omega_B$$

Diagram illustrating the equation $\Omega_{AB} = \Omega_A \times \Omega_B$. Arrows point from the labels below to the terms in the equation: Ω_{AB} is labeled "macropartition $A+B$ ", Ω_A is labeled "sub-system A ", and Ω_B is labeled "sub-system B ".

In real systems, $N \sim 10^{23}$, $U \sim 10^{23} \epsilon$

How to count the multiplicity?
(Spreadsheet fails)

How to find out the maximum multiplicity?

Answer: Analytic approximation

Where is the Maximum? The Average Energy per Atom

Let's explore how the macropartition multiplicity for two sub-systems **A** and **B** ($N_A, N_B, \varepsilon_A = \varepsilon_B = \varepsilon$) in thermal contact depends on the energy of one of the sub-systems:

The high- T limit ($q \gg N$): $\Omega_A(N_A, U_A) = \left(\frac{eU_A}{N_A \varepsilon} \right)^{N_A}$, $\Omega_B(N_B, U_B) = \left(\frac{eU_B}{N_B \varepsilon} \right)^{N_B}$ $U_B = U - U_A$

$$\Omega_{AB} = \Omega_A(N_A, U_A) \times \Omega_B(N_B, U_B) = \left(\frac{eU_A}{N_A \varepsilon} \right)^{N_A} \left(\frac{e(U - U_A)}{N_B \varepsilon} \right)^{N_B}$$

$$\frac{d\Omega_{AB}}{dU_A} = N_A \left(\frac{eU_A}{N_A \varepsilon} \right)^{N_A-1} \frac{e}{N_A \varepsilon} \left(\frac{e(U - U_A)}{N_B \varepsilon} \right)^{N_B} + N_B \left(\frac{eU_A}{N_A \varepsilon} \right)^{N_A} \left(\frac{e(U - U_A)}{N_B \varepsilon} \right)^{N_B-1} \left(\frac{-e}{N_B \varepsilon} \right) = 0 \quad \boxed{\frac{U_A}{N_A} = \frac{U_B}{N_B}}$$

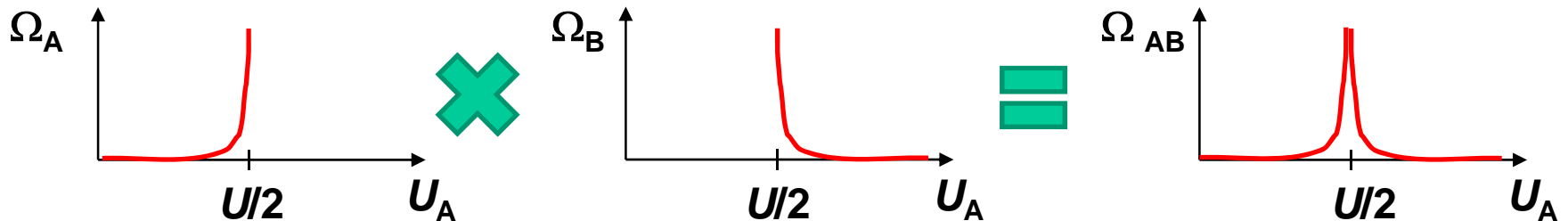
In general, for two systems in thermal contact, the equilibrium (most probable) macropartition of the combined system is the one where ***the average energy per atom in each system is the same*** (the basis for introducing the temperature).

Simpler argument

A special case: two identical sub-systems ($N_A = N_B$), $\Omega_{AB}(U_A)$ is peaked at $U_A = U_B = \frac{1}{2} U$:

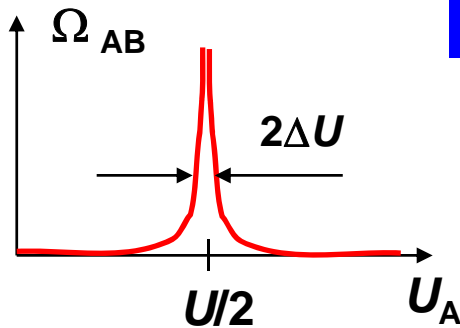
$$\frac{U_A}{N_A} = \frac{U_B}{N_B}$$

$$\Omega_A \times \Omega_B = \Omega_{AB}$$



Take-home exercise: find the position of the maximum of $\Omega_{AB}(U_A)$ for $N_A = 200$, $N_B = 100$, $U = 180 \varepsilon$

Sharpness of the Multiplicity Function



How sharp is the peak? Let's consider small deviations from the maximum for two identical sub-systems:

$$U_A = (U/2)(1+x) \quad U_B = (U/2)(1-x) \quad (x \ll 1)$$

$$N_A = N_B = N$$

$$\Omega_{AB} \propto (U_A)^N (U_B)^N = \left(\frac{U}{2}\right)^{2N} (1-x)^N (1+x)^N \propto \Omega_{AB}^{\text{eq}} (1-x^2)^N$$

Example: $N = 100,000 \quad x = 0.01 \Rightarrow (0.9999)^{100,000} \sim 4.5 \cdot 10^{-5} \ll 1$

More rigorously (p. 65):

$$\Omega_{AB} = \left(\frac{e}{N\mathcal{E}}\right)^{2N} (U_A)^N (U_B)^N \propto (U/2)^N \times (U/2)^N \underbrace{\exp\left[-N\left(\frac{\Delta U}{U/2}\right)^2\right]}_{\text{a Gaussian function}}$$

The peak width: $N\left(\frac{\Delta U}{U/2}\right)^2 = 1 \Rightarrow \Delta U = \frac{1}{\sqrt{N}} U/2$

$$\Delta U = \frac{U}{2} x$$

When the system becomes large, the probability as a function of U_A (macropartition) becomes very sharply peaked, i.e. “fluctuation” is very small

Implications? Irreversibility!

The vast majority of microstates are in macropartitions close to the most probable one (in other words, because of the “narrowness” of the macropartition probability graph). Thus,

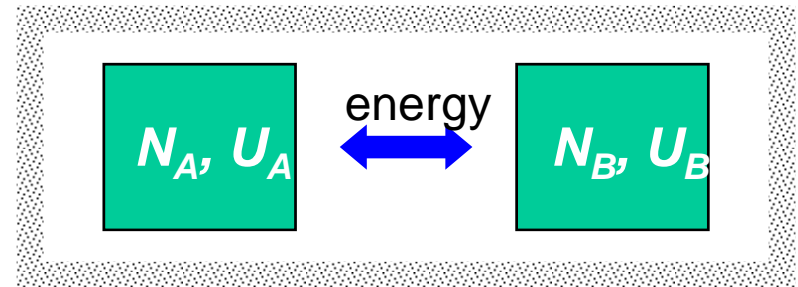
- (a) If the system is not in the most probable macropartition, it will rapidly and inevitably move toward that macropartition. The reason for this “directionality” (irreversibility): there are **far more** microstates in that direction than away. This is why energy flows from “hot” to “cold” and not vice versa.
- (b) It will subsequently stay at that macropartition (or very near to it), in spite of the random shuffling of energy back and forth between the two solids.

When two macroscopic solids are in thermal equilibrium with each other, completely **random and reversible** microscopic processes (leading to random shuffling between microstates) tend at the macroscopic level to push the solids inevitably toward an equilibrium macropartition (**an irreversible macro behavior**). Any random fluctuations away from the most likely macropartition are **extremely small** !

Problem:

Consider the system consisting of two Einstein solids P and Q in thermal equilibrium. Assume that we know the number of atoms in each solid and ε . What do we know if we also know

- (a) the quantum state of each atom in each solid?
- (b) the total energy of each of the two solids?
- (c) the total energy of the combined system?



	the system's macrostate	the system's microstate	the system's macropartition
(a)	✗	✗	✗
(b)	✗		✗
(c)	✗		✗ +fluctuation

Problem:

Imagine that you discover a strange substance whose multiplicity is always 1, no matter how much energy you put into it. If you put an object made of this substance (sub-system **A**) into thermal contact with an Einstein solid having the same number of atoms but much more energy (sub-system **B**), what will happen to the energies of these sub-systems?

- A. Energy flows from **B** to **A** until they have the same energy.
- B. Energy flows from **A** to **B** until **A** has no energy.
- C. No energy will flow from **B** to **A** at all.

Entropy

of a system in a given
macrostate (N, U, V, \dots):

$$S \equiv k_B \ln \Omega(N, U, V, \dots)$$

Units: J/K

The entropy is a **state function**, i.e. it depends on the macrostate alone and not on the path of the system to this macrostate.

Entropy is just another (more convenient) way of talking about multiplicity.

Convenience:

- reduces ridiculously large numbers to manageable numbers

Examples: for $N \sim 10^{23}$, $\Omega \sim 10^{10^{23}}$, $\ln \Omega \sim 10^{23}$, being multiplied by $k_B \sim 10^{-23}$, it gives $S \sim 1 \text{ J/K}$.

The “inverse” procedure: the entropy of a certain macrostate is $4600 k_B$.

What is the multiplicity of the macromacrostate?

$$\Omega = e^{\frac{S}{k_B}} = e^{4600} \sim 10^{2000}$$

- if a system contains two or more interacting sub-systems having their own distinct macrostates, the total entropy of the combined system in a given macropartition is the sum of the entropies of the subsystems they have in that macropartition: $\Omega_{AB} = \Omega_A \times \Omega_B \times \Omega_C \times \dots \Rightarrow S_{AB} = S_A + S_B + S_C + \dots$

Problem:

Imagine that one macropartition of a combined system of two Einstein solids has an entropy of **1 J/K**, while another (where the energy is more evenly divided) has an entropy of **1.001 J/K**. How many times more likely are you to find the system in the second macropartition compared to the first?

$$\frac{\text{Prob}(\text{mp2})}{\text{Prob}(\text{mp1})} = \frac{\Omega_2}{\Omega_1} = \frac{e^{S_2/k_B}}{e^{S_1/k_B}} \approx \frac{e^{0.72464 \cdot 10^{23}}}{e^{0.72536 \cdot 10^{23}}} = e^{7.2 \times 10^{19}}$$

$$e^{7.2 \times 10^{19}} = 10^{\log_{10}\left(e^{7.2 \times 10^{19}}\right)} = 10^{7.2 \times 10^{19} \times \log_{10} e} \approx 10^{3 \times 10^{19}}$$

$$\underbrace{1000 \dots 000}_{3 \times 10^{19}}$$

The Second Law of Thermodynamics

An isolated system, being initially in a non-equilibrium state, will evolve from macropartitions with lower multiplicity (lower probability, lower entropy) to macropartitions with higher multiplicity (higher probability, higher entropy). Once the system reaches the macropartition with the highest multiplicity (highest entropy), it will stay there. Thus,

The entropy of an *isolated* system never decreases.

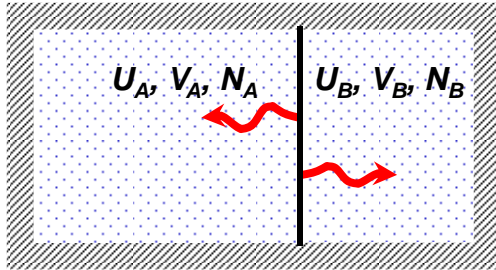
(one of the formulations of the second law of thermodynamics).

(Is it *really* true that the entropy of an isolated system *never* decreases? consider a pair of very small Einstein solids. Why is this statement more accurate for large systems than small systems?)

Whatever increases the number of microstates ***will happen*** if it is allowed by the fundamental laws of physics and whatever constraints we place on the system.

“Whatever” - energy exchange, particles exchange, expansion of a system, etc.

Entropy and Temperature



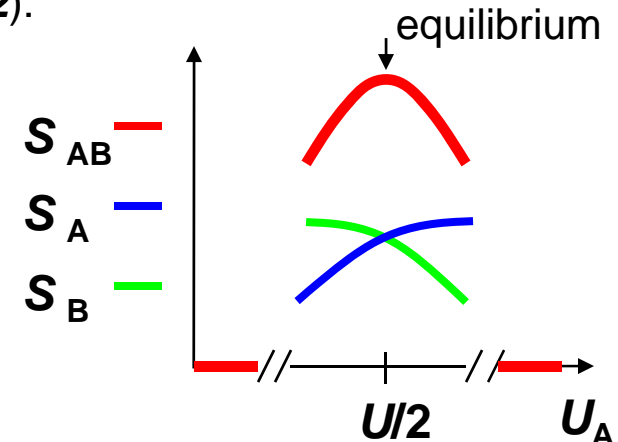
To establish the relationship between S and T , let's consider two sub-systems, A and B , isolated from the environment. The sub-systems are separated by a rigid membrane with finite thermal conductivity (N_i and V_i are fixed, thermal energy can flow between the sub-systems). The sub-systems – with the “**quadratic**” degrees of freedom ($\Omega \sim U^{fN/2}$). For example, two identical Einstein solids ($N_A = N_B = N$) near the equilibrium macropartition ($U_A = U_B = U/2$):

$$\Omega_{AB} = \Omega_A(N, U_A) \times \Omega_B(N, U_B) = \left(\frac{e}{N\epsilon}\right)^{2N} (U_A)^N (U_B)^N$$

$$S_{AB} = S_A + S_B = 2N \ln\left(\frac{e}{N\epsilon}\right) + N \ln(U_A) + N \ln(U_B)$$

Equilibrium:

$$\frac{\partial S_{AB}}{\partial U_A} = \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = \frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0 \Rightarrow \boxed{\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}}$$



Thus, when two solids are in equilibrium, the slope is the same for both of them.

On the other hand, when two solids are in equilibrium, they have the same temperature.

The stat. mech. definition of the temperature

$$\boxed{T \equiv \left(\frac{\partial S}{\partial U}\right)^{-1}_{V,N}}$$

Units: T – K, S – J/K, U – J

1. Note that the partial derivative in the definition of T is calculated at $V=\text{const}$ and $N=\text{const}$.

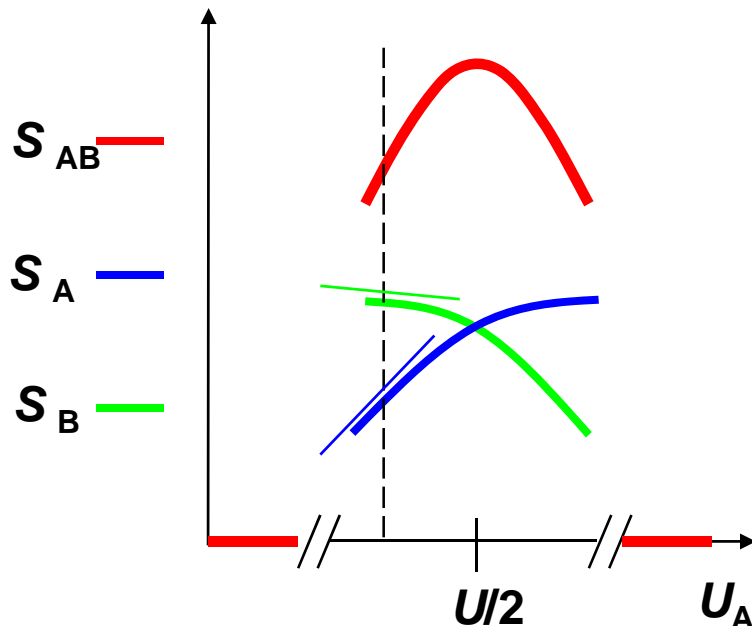
$$T \equiv \left(\frac{\partial S}{\partial U} \right)^{-1}_{V,N}$$

We have been considering the entropy changes in the processes where two interacting systems exchanged the thermal energy but the volume and the number of particles in these systems were fixed. In general, however, we need more than just one parameter to specify a macrostate:

$$S \equiv k_B \ln \Omega(U, V, N)$$

The physical meaning of the other two partial derivatives of S will be considered in L.7.

2. The slope $\partial S / \partial U$ is *inversely* proportional to T .



- the energy should flow from higher T to lower T ; in thermal equilibrium, T_A and T_B should be the same.

The sub-system with a larger $\partial S / \partial U$ (lower T) should receive energy from the sub-system with a smaller $\partial S / \partial U$ (higher T), and this process will continue until $\partial S_A / \partial U_A$ and $\partial S_B / \partial U_B$ become the same.

Problems

$$T \equiv \left(\frac{\partial S}{\partial U} \right)^{-1}_{V,N}$$

Problem: An object whose multiplicity is always 1, no matter what its thermal energy is has a temperature that: (a) is always 0; (b) is always fixed; (c) is always infinite.

Problem: Imagine that you discover a strange substance whose multiplicity is always 1, no matter how much energy you put into it. If you put an object made of this substance (sub-system **A**) into thermal contact with an Einstein solid having the same number of atoms but much more energy (sub-system **B**), what will happen to the energies of these sub-systems?

Problem: If an object has a multiplicity that decreases as its thermal energy increases (e.g., a two-state paramagnetic over a certain **U** range), its temperature would: (a) be always 0; (b) be always fixed; (c) be negative; (d) be positive.