# Physics 132- Fundamentals of Physics for Biologists II

## Statistical Physics and Thermodynamics

# How does energy move within the system?

- physical description – forces and motion of colliding atoms/molecules
  - The loss of energy of one of the colliding atoms/molecules equals the gain of the other colliding atom/molecule

- Statistical description – what happens on average in many collisions or other interactions

# Statistical Description: Thermal Equilibrium

- ***Internal energy resides in "bins"*** , KE or PE associated with degrees of freedom.
- ***Thermodynamic equilibrium is dynamic*** – Energy moves from bin to bin, changes keep happening in each bin, but total energy remains unchanged.
- ***Key Assumption*** - All sharing arrangements among bins are equally likely to occur.

# Your Questions

**In the case of the sliding chair, I understand the overall concept of molecules more likely to go in random directions rather than collectively going in the same direction, but how does the motion of these molecules transfer and affect the motion of the chair?****  **A better example to visualize first is the smoke.**

**Is there a reason that nature favors entropy?**  **This goes back to our assertion that two microstates with the same energy are equally likely.**

**If the universe always goes towards disorder, when will there be too much disorder for the universe to exist? // Can there ever be too much disorder in the universe?**  **The fate of the universe is an open question.  Right now we don't know how much matter or energy is in the universe.  It is an almost certainty, however, that the universe will last to the end of the semester.**

# Let’s build a simple model of sharing energy

- Total amount of energy is conserved, Energy is divided into small *chunks*, shared among *bins.*
- Each *bin* can have an arbitrary number of *chunks* (but the total number of chunks for all bins is fixed).
- We are going to count, in how many ways this slicing of energy into *chunks* can be done.
- Each way of slicing is assumed to be equally likely.

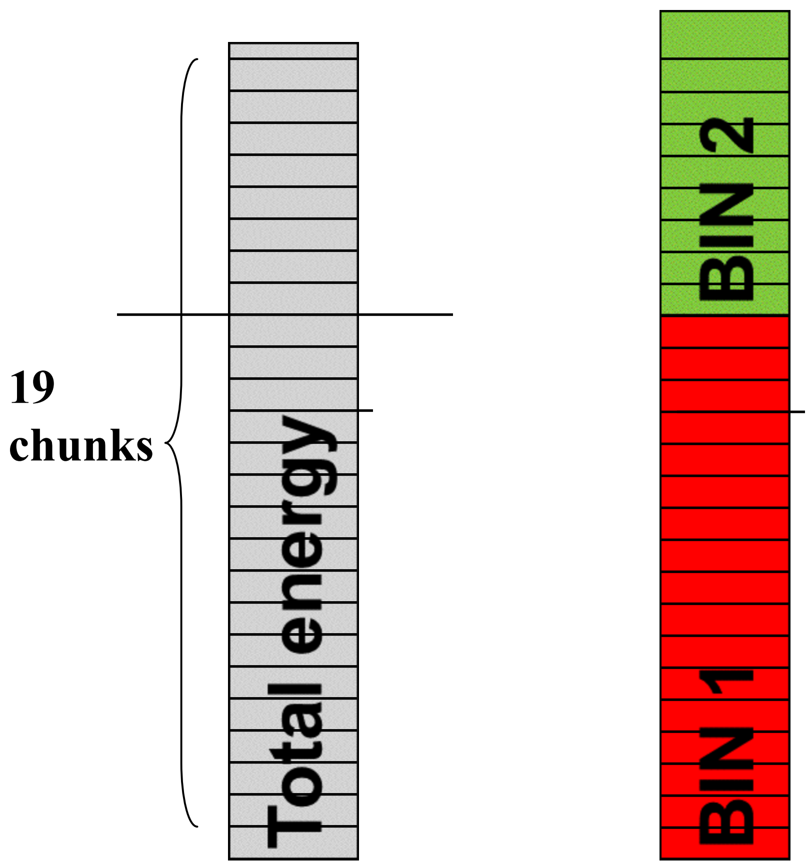
# This simple physical model of sharing of energy will give you a new way to think about the following concepts that are used in chemistry and biology

- Entropy – what is it, and why does it always seem to increase?
- Temperature - Why do two bodies in thermal equilibrium have the same temperature?
- Boltzmann distribution - why does the probability of having a certain energy decrease exponentially? $P(E) \propto e^{-\frac{E}{k_B T}}$

All in a few lectures…

# Now lets calculate!

Two energy "bins" divide up 19 *chunks* of energy randomly




After a "collision", the energy is RANDOMLY divided between Bin 1 and Bin 2

Q: How many ways can this be done?

# Two Bins, 19 energy chunks

| Bin 2 has the following energy | How many ways can this happen |
|---|---|
| 0 | 1 |
| 1 | 1 |
| 2 | 1 |
| 3 | 1 |
| 4 | 1 |
| … | |
| 19 | 1 |

**TOTAL number of "Scenarios": 20**

**Whiteboard, TA & LA**

# Your Questions

**Can we think about energy as finite-sized blocks because energy is quantized, or is it simply for the sake of a simplified model of understanding?   Both**

**How are there fewer arrangements with 9/1 energy in comparison to an 8/2 energy distribution? I tried thinking of it like the way we thought of the energy ?bins? in class. Here there are only 2 bins to divide up the energy. Won?t the way to divide the energies be the same for both considerations? **  So our model is a simple one: Two isolated identical objects that can share a set of energy blocks between them, but that have no exchange of energy or matter with anything else in the universe.   How many bins per object? Someone has to tell us.**

## Micro-state versus Macro-state

**System A**

$m_A$ $n_A$

System A has $n_A$ bins in which to store $m_A$ chunks of energy.

This is referred to as the **macro-state**.
-$n_A$ describes the system - how complicated is it?

- $m_A$ tells how much internal energy it has.

The $m_A$ chunks can be stored $N(m_A, n_A)$ ways.

Each of these is called a **micro-state**.

Two objects, each with 2 bins, sharing 10 chunks

| Number of chunks in A | Number of chunks in B | Number of ways chunks in A can be arranged | Number of ways chunks in B can be arranged | Total number of arrange-ments |
|---|---|---|---|---|
| 1 | 9 | (1+1)= 2 | (9+1)= 10 | 2x10= 20 |
| 2 | 8 | (2+1)= 3 | (8+1)= 9 | 3x9= 27 |
| 5 | 5 | (5+1)= 6 | (5+1)= 6 | 6x6= 36 |

**Whiteboard, TA & LA**

# What would we say is the probability of observing Object A to have 2 chunks and Object B to have 8 chunks?

| Number of chunks in A | Number of chunks in B | Number of ways chunks in A can be arranged | Number of ways chunks in B can be arranged | Total number of arrange-ments |
|---|---|---|---|---|
| 1 | 9 | (1+1)=2 | (9+1)=10 | 2x10=20 |
| 2 | 8 | (2+1)=3 | (8+1)=9 | 3x9= 27 |
| 5 | 5 | (5+1)=6 | (5+1)=6 | 6x6= 36 |

P (A=2)

= 27 / Sum

# Giving Leftovers to Bin 3

| Bin 3 has the following energy (1&2 have the rest) | How many ways can this happen |
|---|---|
| 0 | **Students fill in!** |
| 1 | **Students fill in!** |
| 2 | |
| 3 | |
| 4 | |
| | |
| 19 | |

**TOTAL number of "Scenarios":** **Students fill in!**

**Whiteboard, TA & LA**

# Three bins – m *chunks* of energy

| **Bin 3 has the following energy** | **How many ways can this happen** |
|---|---|
| 0 | m+1 |
| 1 | m |
| 2 | m-1 |
| 3 | m-2 |
| 4 | m-3 |
| | |
| m | 1 |

**TOTAL number of "Scenarios":** $\frac{(m+1)^2}{2} \approx \frac{m^2}{2}$

**Whiteboard, TA & LA**

# Now let's add Bin 4

| **Bin 4 has the following energy** | **How many ways can this happen** |
|---|---|
| 0 | $(m+1)^2/2$ |
| 1 | $(m)^2/2$ |
| 2 | $(m-1)^2/2$ |
| 3 | $(m-2)^2/2$ |
| 4 | $(m-3)^2/2$ |
| | |
| m | |

**TOTAL number of "Scenarios":** $\approx (m)^3/(3 \cdot 2)$

# Now let's consider n Bins

- 2 bins: $(m+1)$
- 3 bins: $\frac{(m+1)^2}{2} \approx \frac{m^2}{2}$
- 4 bins: $\approx \frac{(m)^3}{(3 \cdot 2)}$

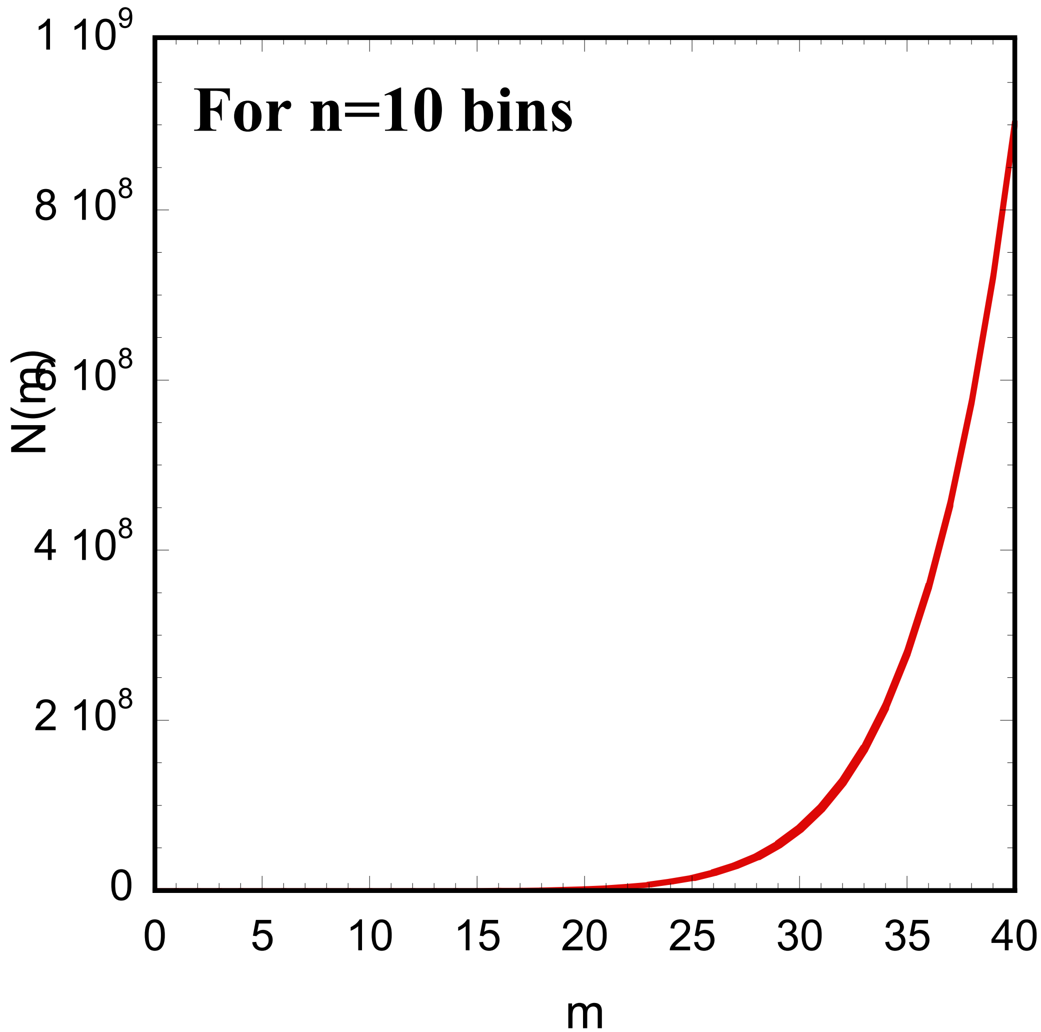
**n bins** $\frac{(m)^{n-1}}{(n-1)!}$

Remember

$$\frac{m^{n+1}}{n+1} = \int_0^m dm\, m^n$$

**Whiteboard, TA & LA**

# How many different ways can *m* chunks of energy be shared by *n*=10 bins




$$N(m,n) \simeq \frac{m^{n-1}}{(n-1)!}$$

**There are many ways!**

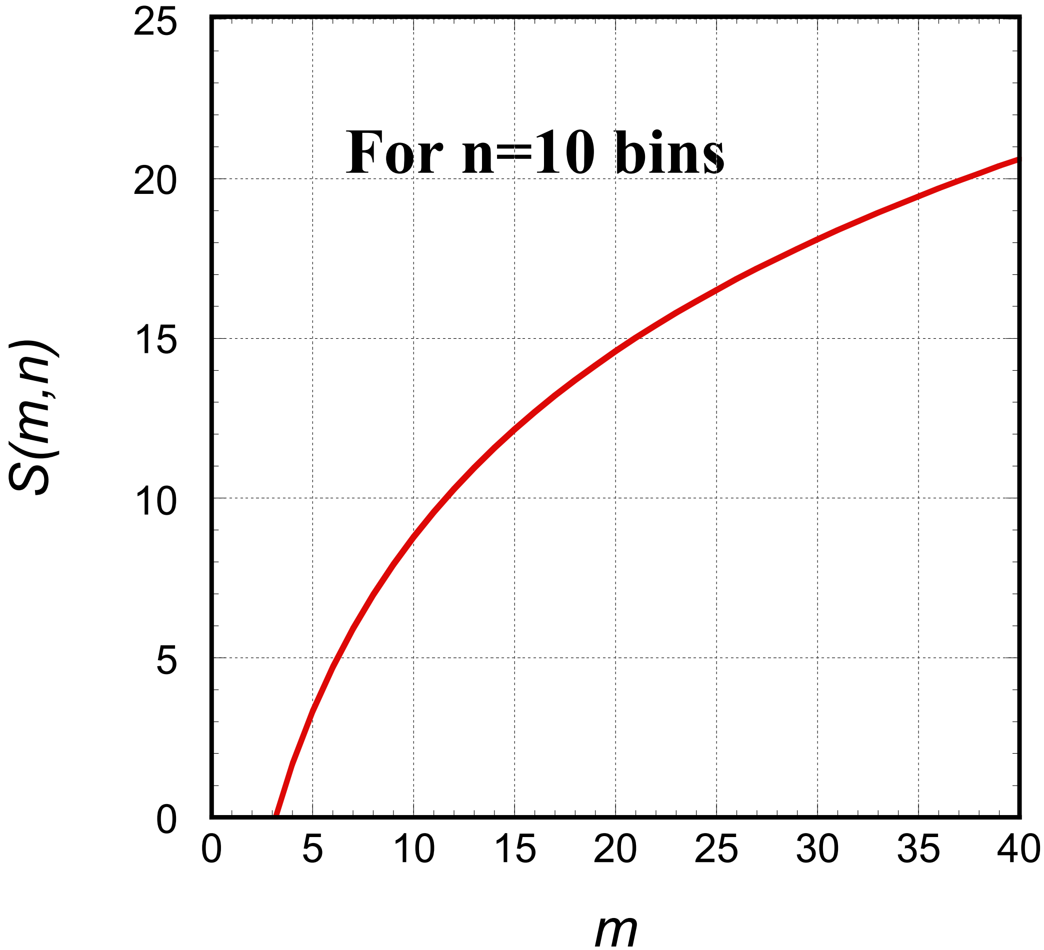
**Increases fast with *m.***

**Maybe we should plot it differently?**

**Suggestions?**

# Plot the log of N(m,n)

$$S(m,n) = \ln N(m,n)$$




**Remember:**

***m*** **represents total internal energy**

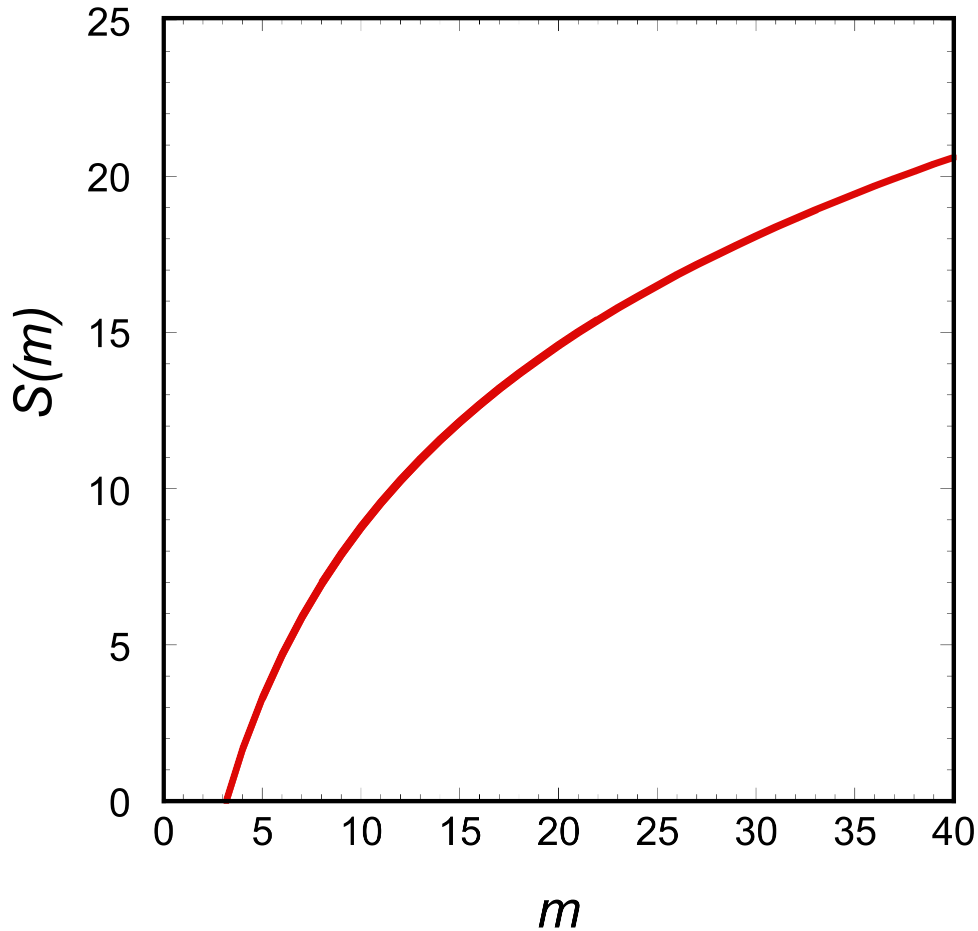
***n*** **represents number of bins**

***N(m,n)*** **is the number of possible arrangements.**

**Much nicer plot**

# S(m,n) is Entropy

$$S(m,n) = \ln N(m,n)$$




**Remember:**

***m*** **represents total internal energy**

***n*** **represents bins**

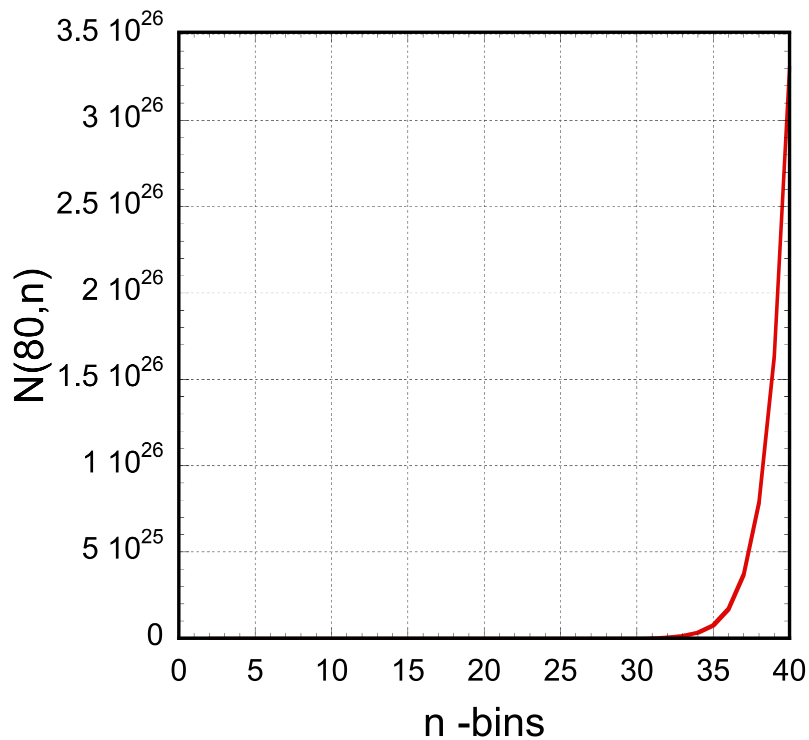
**Entropy increases with internal energy and number of bins**

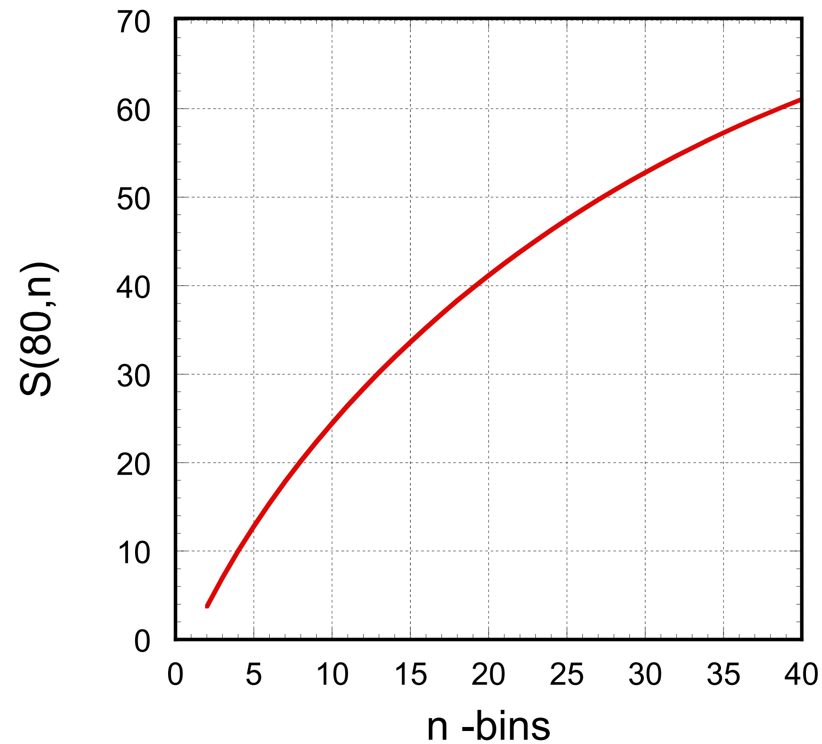
**Entropy also increases with number of bins,**

Number of ways 80 chunks can be shared with different number of bins

80 units of energy $N(m,n)$

$$S(m,n) = \ln N(m,n)$$




Entropy depends on Energy and System Configuration.

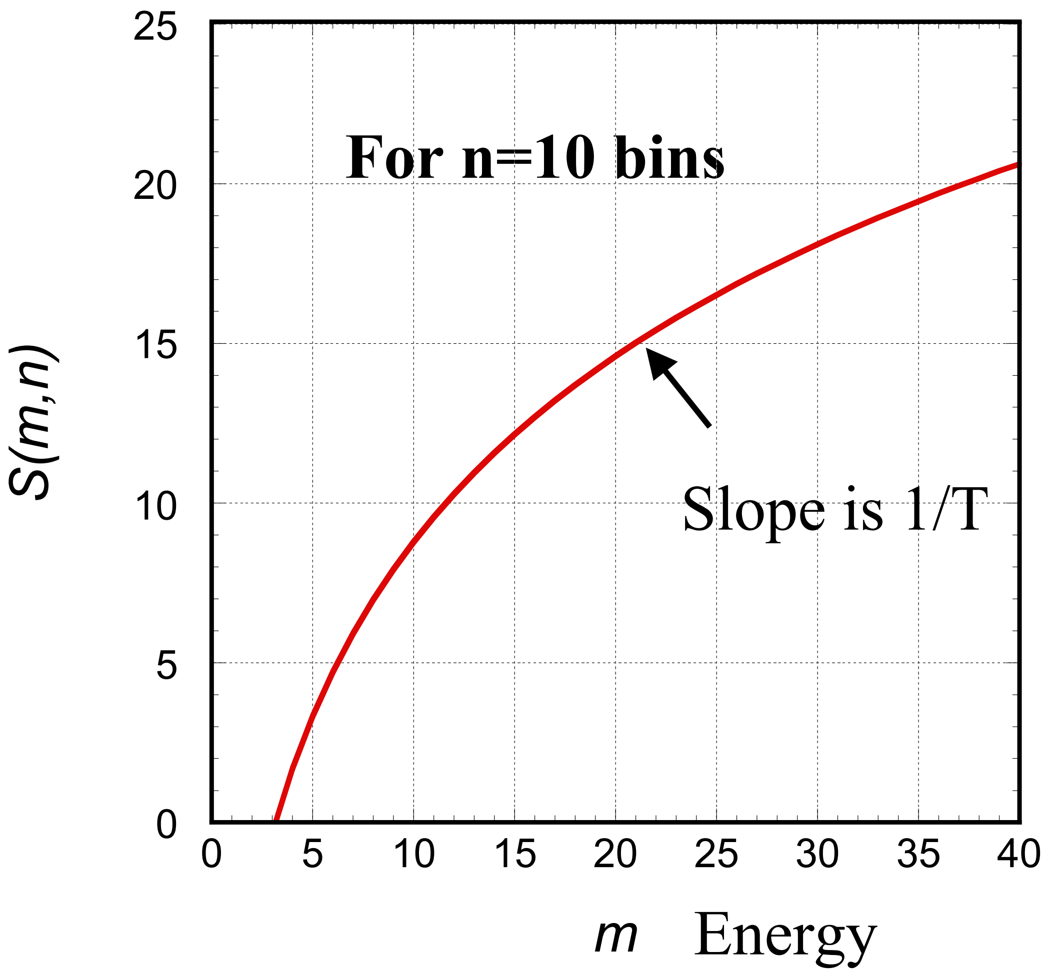
# Relation between entropy, energy and temperature

Do you remember an equation that contains both entropy and energy?

Write on whiteboard!

**Whiteboard, TA & LA**

$$S(m,n) = \ln N(m,n) \qquad \frac{1}{kT} = \frac{dS(U)}{dU}$$




**Remember:**

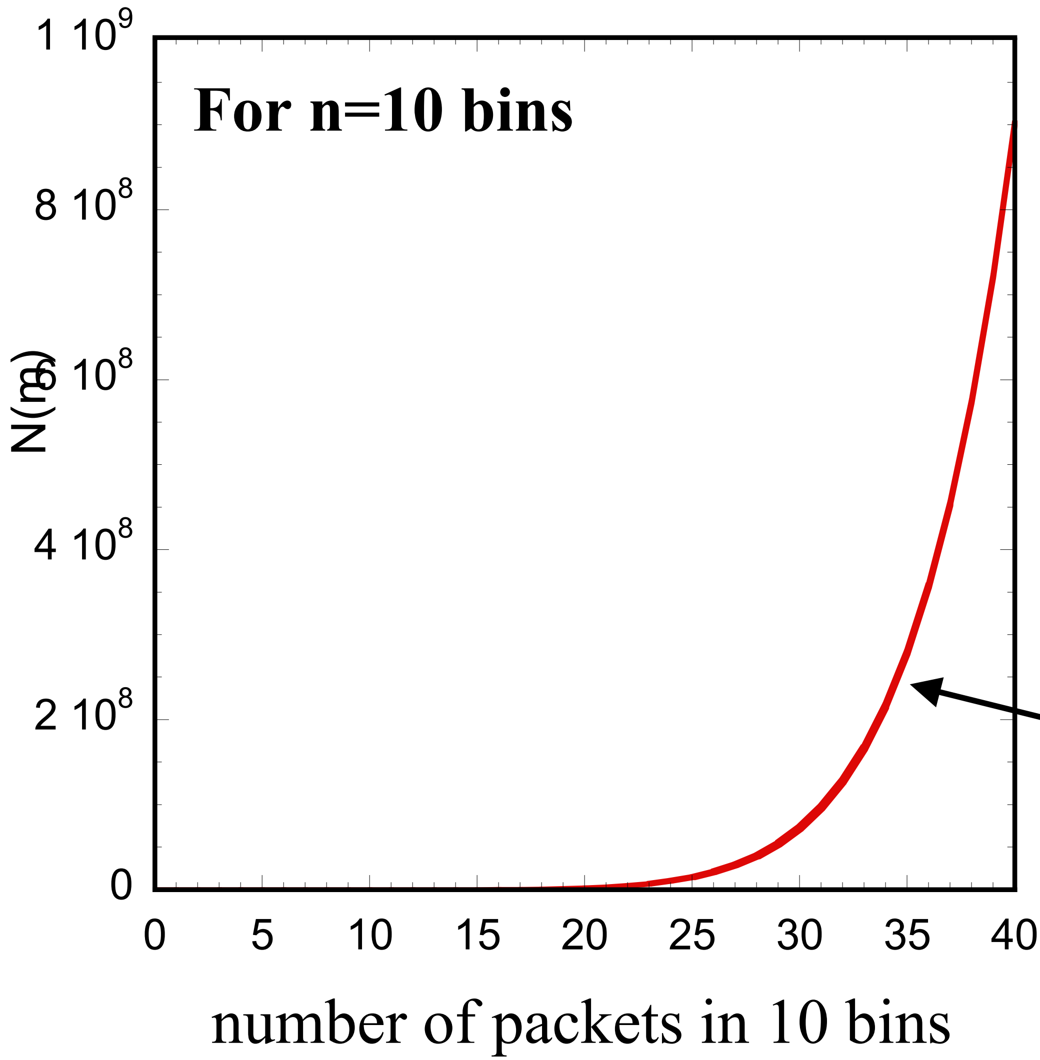
***m*** **represents total internal energy**

***n*** **represents number of bins**

**N represents number of arrangements.**

# Add 11th Bin and Assume 40 shared packets

**How many ways can the 11th bin have *m* packets?**




**If there are m chunks in bin 11,**

**there are 40-m chunks in bins 1 - 10.**

**If m=5, we are here**

# Add 11th Bin and Assume 40 shared packets

**How many ways can the 11th bin have *m* packets?**

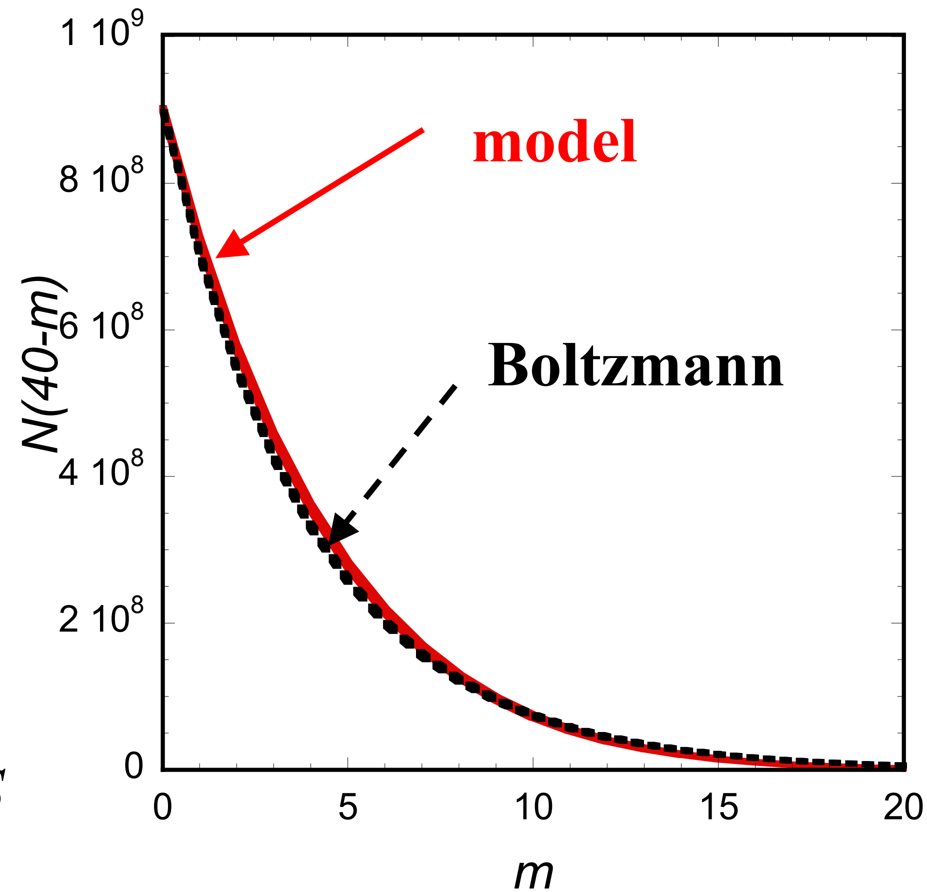
$$N(40-m) \simeq \frac{(40-m)^9}{(9)!}$$

**can show**

$$N(40-m) \simeq N(40)\exp(-\frac{m}{T})$$

**where**

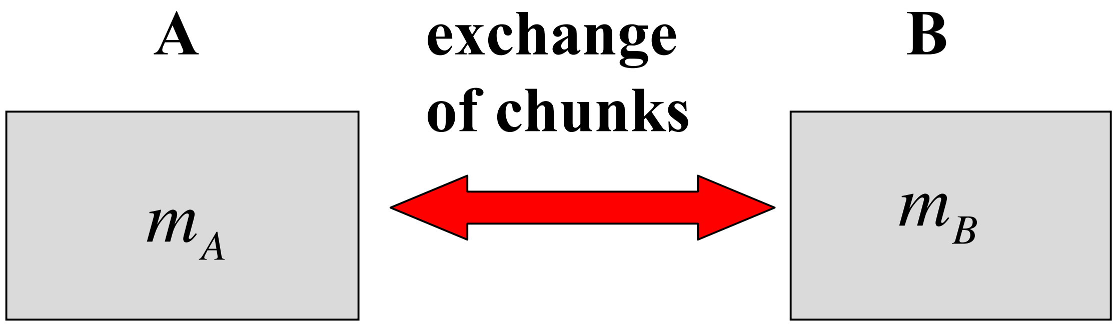
$$\frac{1}{T} = \left.\frac{dS(m)}{dm}\right|_{m=40} \qquad \Delta U = T\Delta S$$




**This is the definition of temperature !**

Why are two systems that can share energy at the same temperature?

# Two systems each with <u>10</u> bins and a total of <u>$m$</u> chunks of energy




**Conservation of energy** $m_A + m_B = m$

**Number of states with a given $\mathbf{m_A}$, $\mathbf{m_B}$** $N(m_A) \times N(m_B)$

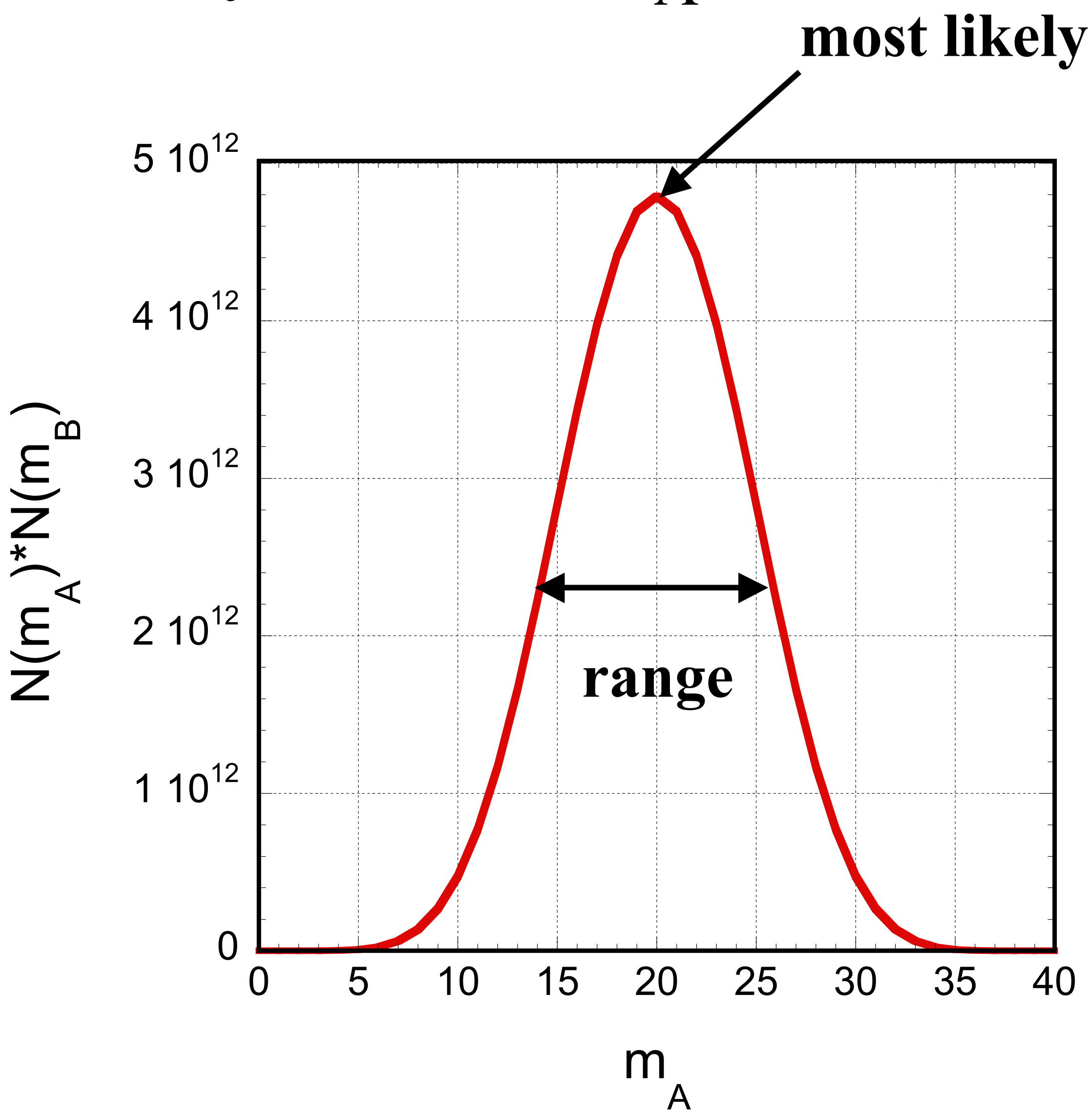
$$S_T = \ln(N(m_A) \times N(m_B)) = S(m_A) + S(m_B)$$

**Entropy is additive & most likely division has highest entropy**

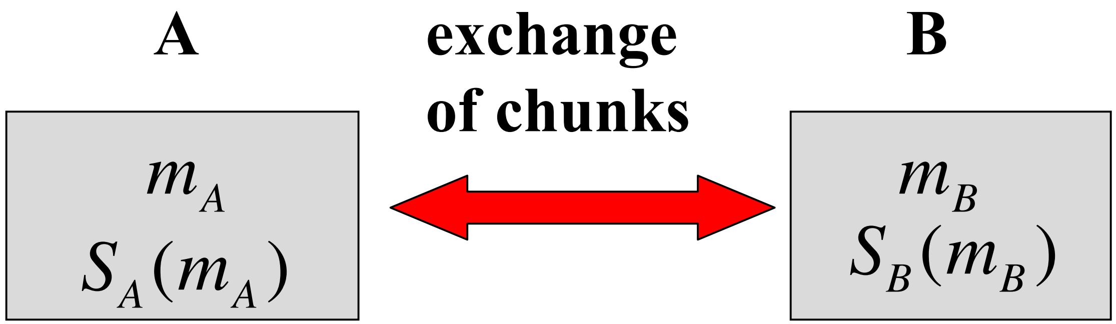
# Likelyhood of $m_A$

**Equal sharing is most likely**

**Range of values shrinks as number of bins goes up.**



# Condition for Maximum Entropy




**no longer identical systems**

$$m_A + m_B = m$$

$$S_T = S_A(m_A) + S_B(m_B = m - m_A)$$

**Total entropy maximum when** $$\frac{dS_T}{dm_A} = 0$$

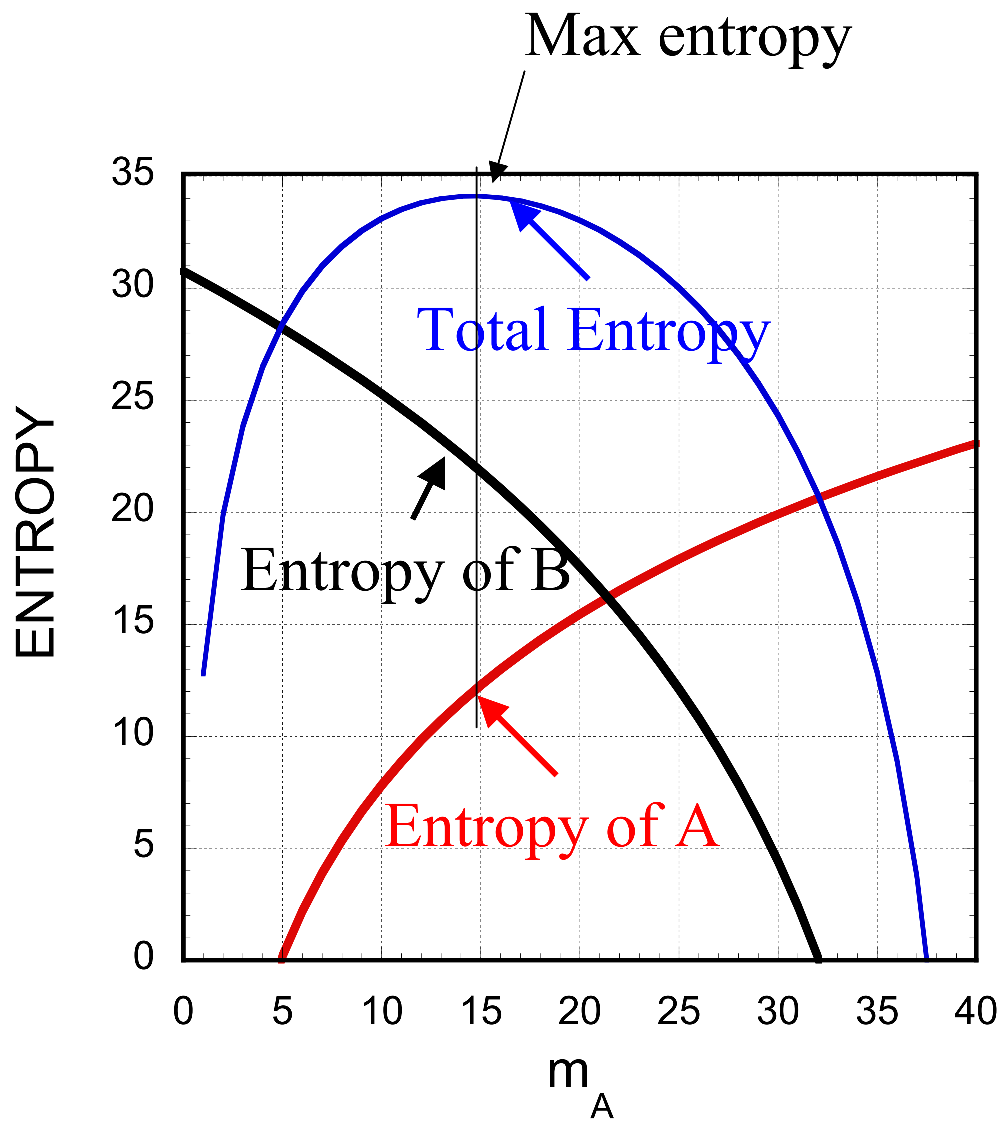
**Temperatures equal** $T_A = T_B$

# Two systems share 40 chunks of energy

**System A**
**12 bins**

**System B**
**20 bins**

**Who will wind up with more chunks of energy?**



# Result

- What is entropy? $S = \ln(N)$
- Why does entropy increase ? Max S most likely
- What is temperature? $1/T = dS/dU$
- Why do two bodies in thermal equilibrium have the same temperature? Condition for maximum total S
- Where does the Boltzmann distribution come from? 1 Bin sharing with many Bins leads to $\exp[-U/kT]$

Ta Da!

# Foothold ideas: Entropy

- Entropy – an <u>extensive</u> measure of how well energy is spread in a system.
- Entropy measures
  - The number of microstates in a given macrostate $S = k_B \ln(W)$
  - The amount that the energy of a system is spread among the various degrees of freedom
- Change in entropy upon heat flow $\Delta S = \frac{Q}{T}$

# More thermal energy packets are in the water molecules

1. Water is hotter than gas
2. Water is colder than gas
3. Water is at the same temperature as gas

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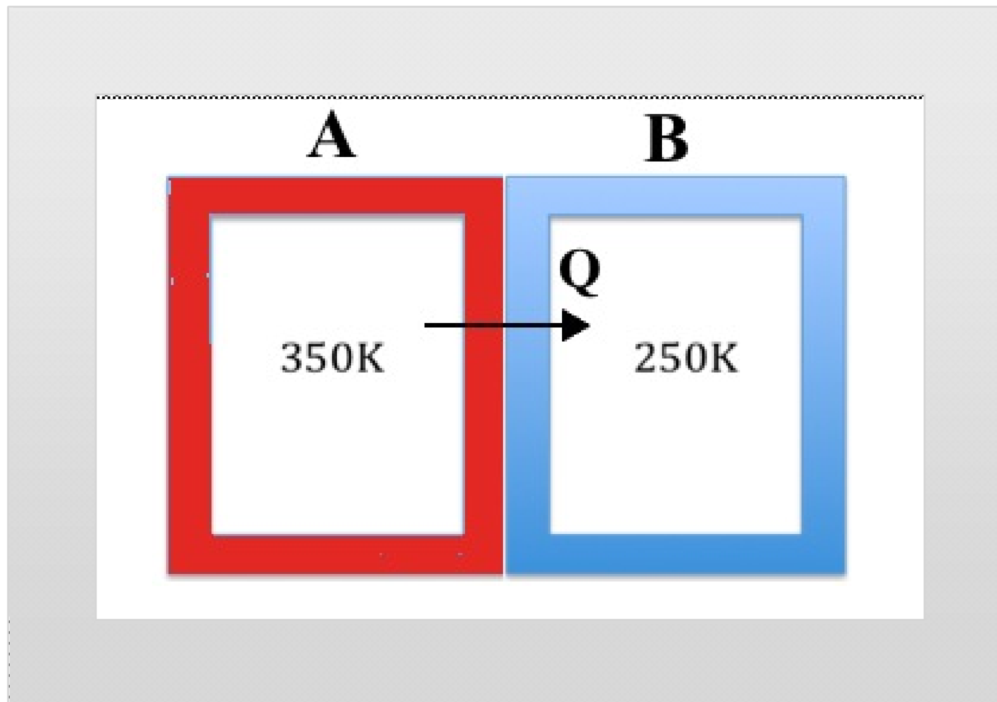
# Foothold ideas:
# The Second Law of Thermodynamics

- Systems spontaneously move toward the thermodynamic (macro)state that correspond to the largest possible number of particle arrangements (microstates).
  - The $2^{nd}$ law is probabilistic. Systems show fluctuations – violations that get proportionately smaller as N gets large.
- Systems that are not in thermodynamic equilibrium will spontaneously transform so as to increase the entropy.
  - The entropy of any particular system can decrease as long as the entropy of the rest of the universe increases more.
- The universe tends towards states of increasing chaos and uniformity. (Is this contradictory?)

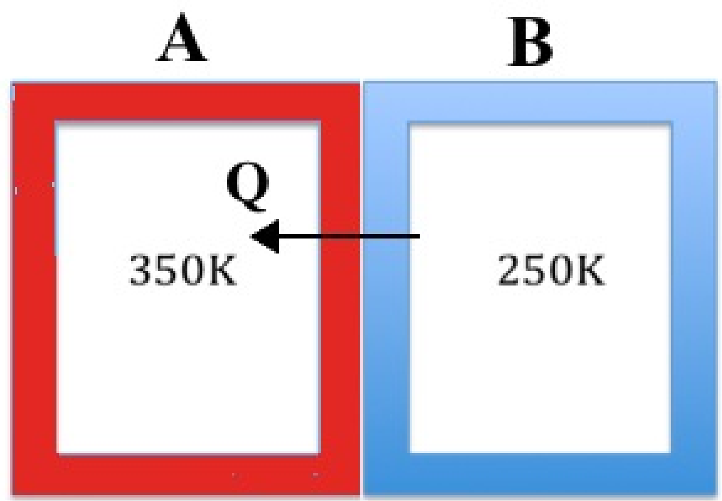
A small amount of heat Q flows out of a hot system A (350K) into a cold system B (250K). Which of the following correctly describes the entropy changes that result? (The systems are thermally isolated from the rest of the universe.)

1. $|\Delta S_A| > |\Delta S_B|$
2. $|\Delta S_B| > |\Delta S_A|$
3. $|\Delta S_A| = |\Delta S_B|$
4. It cannot be determined from the information given



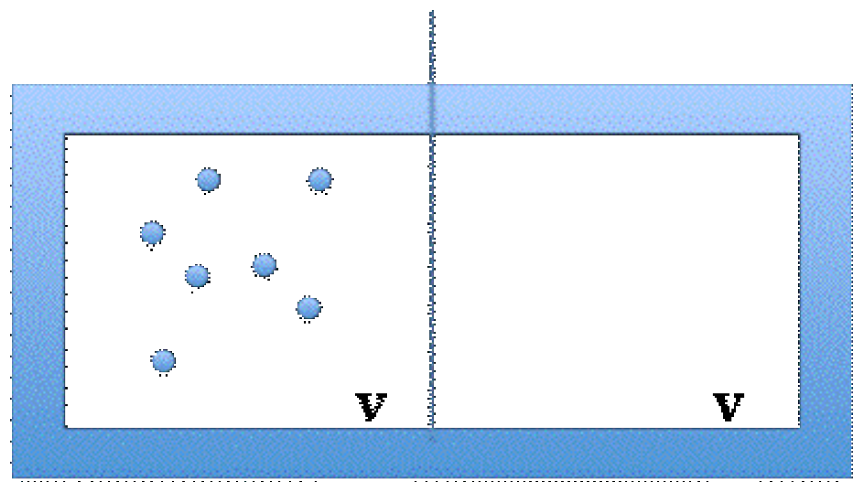
Suppose a small amount of heat Q flows from a system A at low temperature (250K) to a system B at high temperature (350K). Which of the following must be true regarding the entropy of the rest of the universe during this process?

1. It increases by an amount greater than $(|\Delta S_A| - |\Delta S_B|)$
2. It increases by an amount less than $(|\Delta S_A| - |\Delta S_B|)$
3. It decreases
4. It stays the same
5. It cannot be determined from the information given



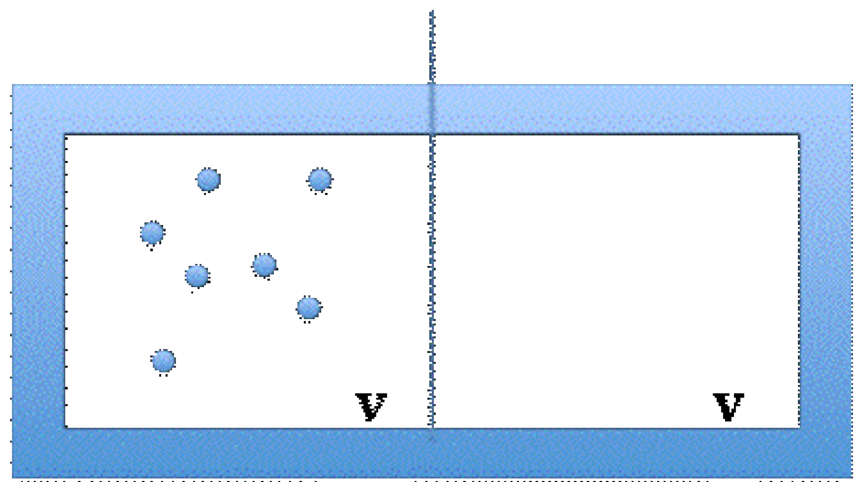
Suppose an isolated box of volume 2V is divided into two equal compartments. An ideal gas occupies half of the container and the other half is empty.
When the partition separating the two halves of the box is removed and the system reaches equilibrium again, how does the new **internal energy** of the gas compare to the internal energy of the original system?

1. The energy increases
2. The energy decreases
3. The energy stays the same
4. There is not enough information to determine the answer



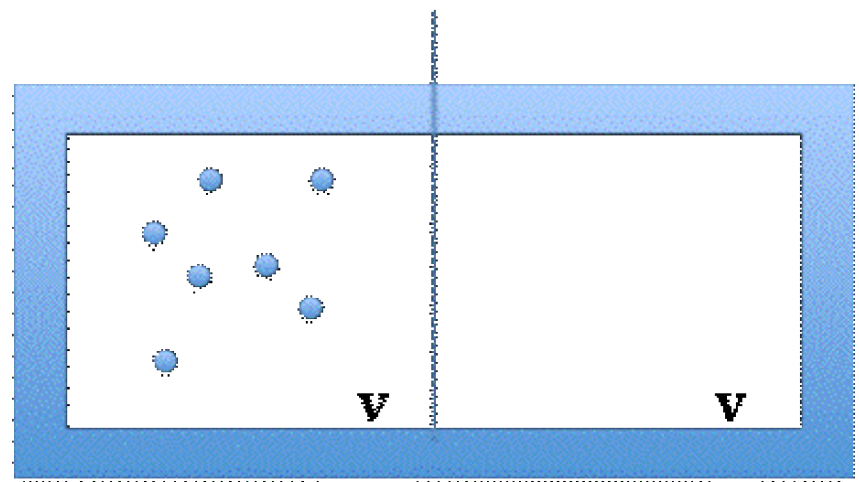
Suppose an isolated box of volume 2V is divided into two equal compartments. An ideal gas occupies half of the container and the other half is empty.
When the partition separating the two halves of the box is removed and the system reaches equilibrium again, how does the new **pressure** of the gas compare to the **pressure** of the original system?

1. The pressure increases
2. The pressure decreases
3. The pressure stays the same
4. There is not enough information to determine the answer



Suppose an isolated box of volume 2V is divided into two equal compartments. An ideal gas occupies half of the container and the other half is empty.
When the partition separating the two halves of the box is removed and the system reaches equilibrium again, how does the new **entropy** of the gas compare to the entropy of the original system?

1. The entropy increases
2. The entropy decreases
3. The entropy stays the same
4. There is not enough information to determine the answer



# Does the volume affect entropy?

1. In an ideal gas, atoms take up no volume so atoms have infinitely many microstates they may choose
2. Each atom has a finite volume, so the number of microstates increases with the available  volume

# Lets test this model with a simple experiment: Let's represent energy *chunks* with pennies

1. Everyone starts with 6 pennies!
   ***(i.e. 6 chunks of energy)***
2. Turn to a random group of neighbors and "interact"
   ***(random exchange of chunks of energy)***
   1. Interaction means to pool pennies of all people
   2. One person takes a **random** amount, a second person takes a **random** amount from the rest (or nothing if nothing is left).

Before we start: How many pennies do you expect to end up with?

**Clicker**

(raise your hand if more than 9)

- How many pennies do you have? (raise your hand if you have more than 9

**Clicker**