THERMODYNAMICS AND STATISTICAL MECHANICS

CHAPTER 5 –STATISTICAL MECHANICS: ENTROPY AND TEMPERATURE

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Outline

i. Fundamental Assumption
ii. Thermal Equilibrium
iii. Entropy: Law of Increasing of Entropy.
iv. Law of Thermodynamics: Entropy as a Logarithm.

Fundamental Assumptions

To proceed we need a few definitions:

Closed System: Is a system that does not exchange energy nor particles with its surroundings. For a closed system:

- ***total energy is a constant***
- ***total number of particles is constant***.

For example, gas inside a sealed, perfect "Thermos" bottle.

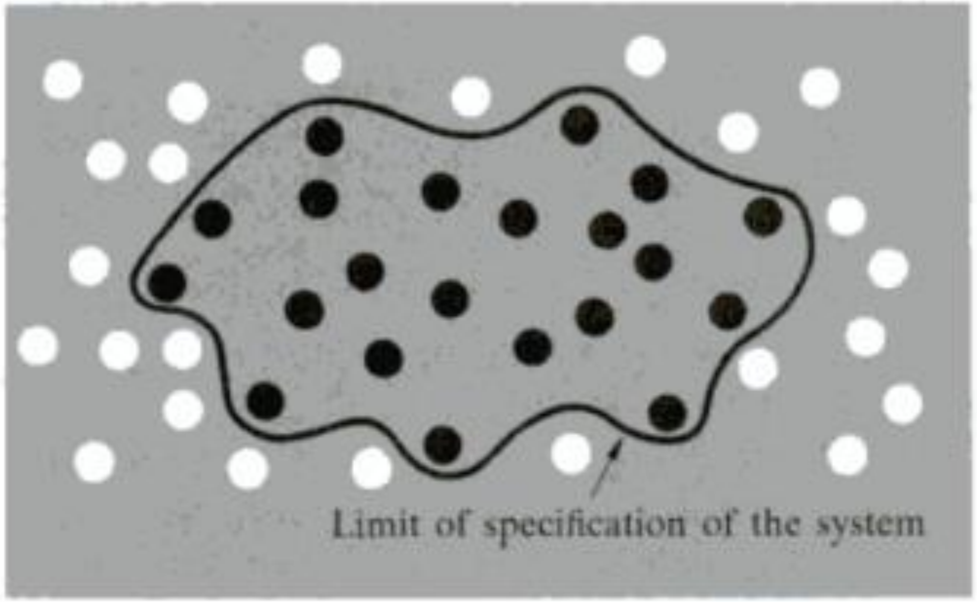
Fundamental Assumptions

Accessible State: An accessible state is a quantum state whose properties are consistent with the physical constraints of the system.

- Energy must lie within the allowed range of the system
- Number of particles must match the system specification

Example: A state with N is not accessible for a system that actually contains N + 5 particles.

Fundamental Assumptions



Each solid dot represents an accessible quantum state of a closed system.

Empty dots represent states that are not accessible, since they do not satisfy the physical constraints of the system.

Fundamental Assumptions

Energy U and the number of particles N of a closed system are perfectly well determined. (In practice, $U = U + \delta U$, with δU small when compared to U; and $N = N + \delta N$, also with δN small when compared to N):

$$\frac{\delta U}{U} \ll 1 \quad and \quad \frac{\delta N}{N} \ll 1$$

Exceptions: Unusual properties of a system sometimes may not allow to access certain stain specific time under observation. For example, states of the crystalline form of SiO_2 are inaccessible at low temperatures in that observation starts with the glassy or amorphous form.

We treat all quantum states as accessible unless they are excluded by a specification of system. ***States that are not accessible are said to have zero probability.***

Statistical Ensemble and Ensemble Average

Statistical Ensemble

- A statistical ensemble is a collection of a large number of identical copies of a system.
- Each copy represents the system in a different accessible microstate.
- There is one copy for every possible accessible state of the system.

Example: A system of spins where each copy corresponds to a different microscopic spin configuration.

Alternative View

- An ensemble can also be viewed as a probability distribution over all possible states of the system.
- For a closed system in equilibrium, all accessible states are equally probable.

Probability

Ensemble average

- The ensemble average of a physical quantity is the average over all members of the ensemble.. We will need the probability distribution, P(s), for the members of the ensemble.
- It represents the macroscopic observable measured in experiments.

The probability distribution takes on a particularly simple form for a closed system.

Probability

If there are g members of the ensemble, all equally likely, and the probabilities are normalized, each individual member of the ensemble has a probability $1/g$:

$$\sum_{all\ g\ accessible\ states} P(r) = 1 = P + P + P + \cdots$$

There are g terms in this sum because there are g accessible states
The probability $P(s)$ of each individual member of ensemble:

$$1 = gP \rightarrow P(s) = \frac{1}{g}$$

Probability

If we can calculate the average value a certain property X(s) which is a function of the state, s, of the system.

$$\langle X(s)\rangle = \sum_{all\ access\ states} X(s)P(s)$$

But in this case $P(s) = 1/g$. So

$$\langle X(s)\rangle = \sum_{all\ access\ states} X(s)\frac{1}{g} = \frac{1}{g}\left(\sum_{all\ access\ states} X(s)\right)$$

Ensemble

How does the ensemble average values relate to experimentally measured values?

- No experimentalist works with g identical copies of a system, each one in a different microscopic state.
- Experimentalists work on one system. And the average values measured are not over an ensemble, but on one system, over a long time.

The theory should yield (predict) the values that can be compared with what is measured.

Ensemble

Why do we go through the ensemble construction?

- Because we know how to calculate ensemble averages (it is easy!!) for any physical property.
- Because calculating $\langle f \rangle_{one\ system\ long\ time}$ is very tough, if at all possible.
- And because $\langle f \rangle_{one\ system\ long\ time}$ is very simply related to $\langle f \rangle_{ensemble}$.

$$\langle f \rangle_{one\ system\ long\ time} = \langle f \rangle_{ensemble}$$

In practice, the <u>ergodic hypothesis is the same thing as assuming that a closed system will evolve in time, in a random manner</u>, in such a way that it will go through all the microscopic states accessible to it.

Ensemble

An ensemble represents a system with 10 spins with energy $-8mB$ and spin excess $2s = 8$. The multiplicity $g(N, s)$ is

$$g(N,s) = \frac{N!}{\left(\frac{N}{2}+s\right)!\left(\frac{N}{2}-s\right)!}$$

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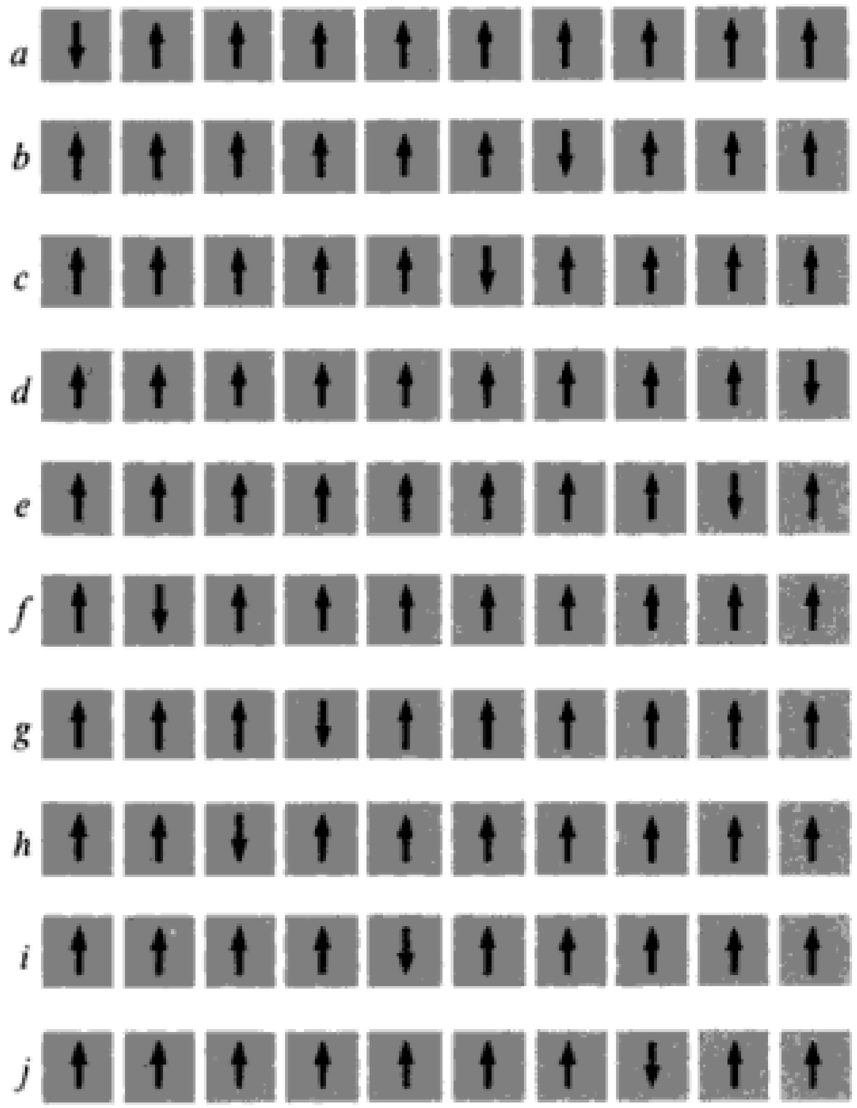
so that the representative ensembles must contain 10 systems.



Example 5-1

Construct an ensemble that represent a closed system of N= 5 spin system, each system with spin excess $2s = 1$.

$$\text{spin excess } 2s = 1 \rightarrow s = \frac{1}{2}$$

$$g(N,s) = \frac{N!}{\left(\frac{N}{2} + s_j\right)!\left(\frac{N}{2} - s_j\right)!}$$

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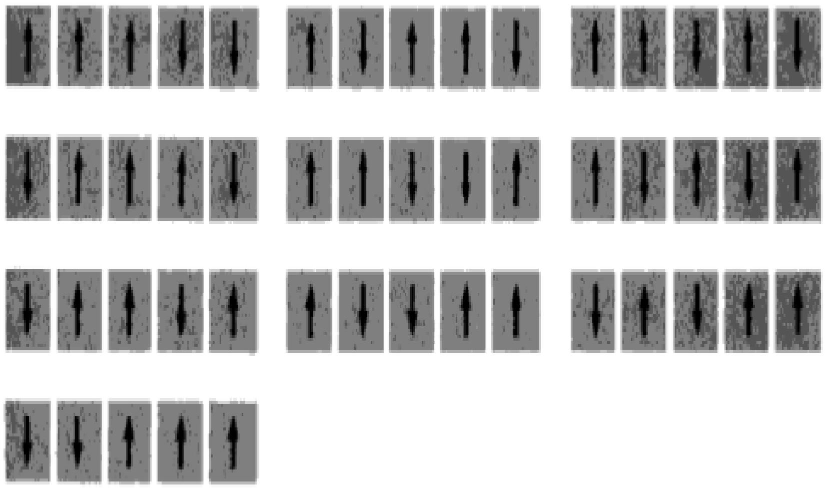
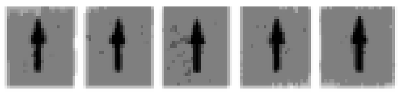


A single system may represent the ensemble when $N = 5$ and spin excess $2s = 5$



Ensemble in Statistical Mechanics

There are three different types of ensembles in Stat. Mech.:

1. **Microcanonical Ensemble**: The one with systems of fixed N and fixed E.
2. **Canonical Ensemble** The one with fixed N but variable E (that is a system in which the particles are fixed but energy can be exchanged with the surroundings). For example, A tank of gas submerged in a pool of water.
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Let's first look at the microcanonical ensemble.

Most Probable Configuration and Thermal Equilibrium

Our combined system S is a closed system (there are energy exchange *between the parts of S*, but not between S and the outside, U is fixed).

Or

S spends a fixed time τ in a given microscopic state, and then in evolves to another microscopic state. The system becomes most probable configuration.

Mathematical expression that defines the most probable configuration

Most Probable Configuration

Let's consider two system S_1 and S_2 are brought together so that the energy can be transferred freely from one to another.

Two system contact and form a larger system

$$S = S_1 + S_2 \quad (closed\ system)$$

And

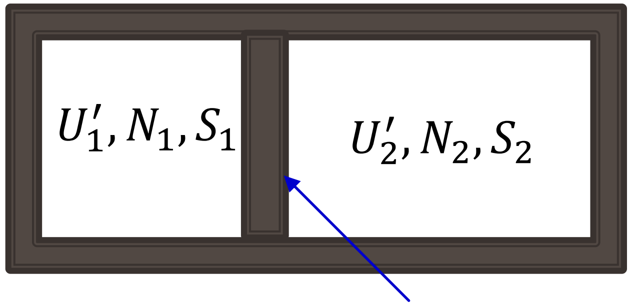
$$U = U_1 + U_2 \quad (constant\ energy)$$

We will solve the problem of thermal contact of two spin systems 1 and 2. So, the spin excess of combine system is

$$s = s_1 + s_2$$

Two closed systems with no contact

Two closed systems are in thermal contact



Thermal conductor allows exchange of energy

Most Probable Configuration

Energy of combine system is

$$U(s) = U_1(s_1) + U_2(s_2)$$
$$= -2mB(s_1 + s_2) = -2mBs$$

The multiplicity function of combined system $\mathcal{S}$ is:

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

Where $s = s_1 + s_2$, $N = N_1 + N_2$, and $U = U_1 + U_2$

The range of s_1 is from $-\frac{1}{2}N_1$ to $\frac{1}{2}N_1$ if $N_1 < N_2$. Here, the first represent the spin excess s_1 and second represent spin excess s_2. $g_1(N_1, s_1)$ and $g_2(N_2, s_2)$ are all accessible state for first and second system. Note the product of two Gaussian functions is always a Gaussian.

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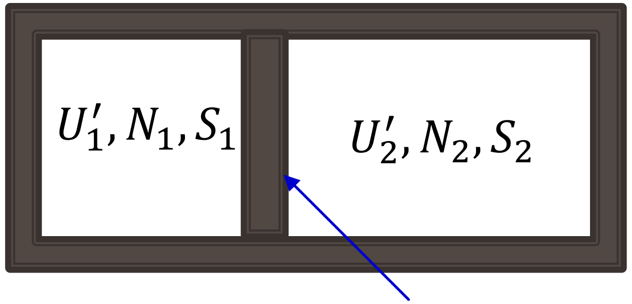

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Two spin System in thermal contact

$$g_1(N_1, s_1)g_2(N_2, s_2) = g_1(0)exp\left(-\frac{2s_1^2}{N_1}\right)g_2(0)\exp\left(-\frac{2s_2^2}{N_2}\right)$$

$$g_1(N_1, s_1)g_2(N_2, s_2) = g_1(0)g_2(0)\exp\left(-\frac{2s_1^2}{N_1} - \frac{2s_2^2}{N_2}\right)$$

$g_1(0)$ and $g_2(0)$ are $g_1(N_1, 0)$ and $g_2(N_2, 0)$.

Replacing s_2 with $s - s_1$

$$g_1(N_1, s_1)g_2(N_2, s_2) = g_1(0)g_2(0)\exp\left(-\frac{2s_1^2}{N_1} - \frac{2(s-s_1)^2}{N_2}\right)$$

Taking log gives us,

$$Log[g_1(N_1, s_1)g_2(N_2, s_2)] = Log[g_1(0)g_2(0)] - \frac{2s_1^2}{N_1} - \frac{2(s-s_1)^2}{N_2}$$

Two spin System in thermal contact

Maximum or minimum can be found with first derivative with respect to s_1 and set it to zero, and maximum is when negative of second derivative

$$\frac{\partial Log[g_1(N_1,s_1)g_2(N_2,s_2)]}{\partial s_1} = \frac{4s_1}{N_1} - \frac{4\,(s-s_1)}{N_2} = 0$$

$$\frac{s_1}{N_1} = \frac{(s-s_1)}{N_2} = \frac{s_2}{N_2}$$

second derivative of above equation is:

$$-4\left(\frac{1}{N_1} + \frac{1}{N_2}\right)$$

Second derivative is negative, so it is maximum

Two spin System in thermal contact

At the maximum s_1 is $\widehat{s_1}$ and s_2 is $\widehat{s_2}$:

$$\frac{\widehat{s_1}}{N_1} = \frac{\widehat{s_2}}{N_2} = \frac{s}{N}$$

We find

$$(g_1 g_2)_{max} = g_1(\widehat{s_1}) g_2((s - \widehat{s_1})) = g_1(0) g_2(0) \exp\left(-\frac{2\,\widehat{s_1}}{N_1} - \frac{2(s - \widehat{s_1})^2}{N_2}\right)$$

$$= g_1(0) g_2(0) \exp\left(-\frac{2s\,\widehat{s_1}}{N} - \frac{2s\,(s - \widehat{s_1})}{N}\right)$$

$$(g_1 g_2)_{max} = g_1(0) g_2(0) \exp\left(-\frac{2s^2}{N}\right)$$

Sharpness of maximum $g_1 g_2$

Let's investigate the sharpness of maximum $g_1 g_2$. We introduce δ which represent the deviation from the maximum

$$s_1 = \widehat{s_1} + \delta \quad and \;\; s_2 = s - (\widehat{s_1} + \delta) = \widehat{s_2} - \delta$$

$$g_1(N_1, s_1) g_2(N_2, s_2) = g_1(0) g_2(0) \exp\left(-\frac{2(\widehat{s_1} + \delta)^2}{N_1} - \frac{2(\widehat{s_2} - \delta)^2}{N_2}\right)$$

$$= g_1(0) g_2(0) \exp\left(-\frac{2\,\widehat{s_1}^{\,2}}{N_1} - \frac{2\,\widehat{s_2}^{\,2}}{N_2} - \frac{4\,\widehat{s_1}\delta}{N_1} - \frac{2\delta^2}{N_1} + \frac{4\,\widehat{s_2}\delta}{N_2} - \frac{2\delta^2}{N_2}\right)$$

$$= (g_1 g_2)_{max} \exp\left(-\frac{4\,\widehat{s_1}\delta}{N_1} - \frac{2\delta^2}{N_1} + \frac{4\,\widehat{s_2}\delta}{N_2} - \frac{2\delta^2}{N_2}\right)$$

Where $(g_1 g_2)_{max} = g_1(0) g_2(0) \exp(-\frac{2\,\widehat{s_1}}{N_1} - \frac{2(\widehat{s_2})^2}{N_2})$

Sharpness of maximum $g_1 g_2$

$$g_1(N_1, s_1)g_2(N_2, s_2) = (g_1 g_2)_{max} \exp\left(-4\delta\left(\frac{\widehat{s_1}}{N_1}\right) - \frac{2\delta^2}{N_1} + 4\delta\left(\frac{\widehat{s_2}}{N_2}\right) - \frac{2\delta^2}{N_2}\right)$$

here $\frac{\widehat{s_1}}{N_1} = \frac{\widehat{s_2}}{N_2}$

$$g_1(N_1, \widehat{s_1} + \delta)g_2(N_2, \widehat{s_2} - \delta) = (g_1 g_2)_{max} \exp\left(-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}\right)$$

We can see that the fractional deviation from equilibrium is very small numerically.

Let consider $N_1 = N_2 = 10^{23}$ and $\delta = 10^{12}$, then $\frac{\delta}{N_1} = 10^{-10}$ and $\frac{2\delta^2}{N_1} = 200$ and product of $g_1 g_2$ becomes $e^{-400} \approx 10^{-174}$ of its maximum value, which is extremely large drop.

The configuration for which maximum of $g_1 g_2$ is called the **most probable configuration**, which is:

$$g_1(N_1, \widehat{s_1})g_2(N_2, s - \widehat{s_1})$$

Statistical Ensemble and Ensemble Average

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- A statistical ensemble is a collection of a large number of identical copies of a system.
- Each copy represents the system in a different accessible microstate.
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Alternative View

- An ensemble can also be viewed as a probability distribution over all possible states of the system.
- For a closed system in equilibrium, all accessible states are equally probable.

Key Idea

Ensemble = A tool to connect microscopic states with macroscopic observables.

Probability

Ensemble average

- The ensemble average of a physical quantity is the average over all members of the ensemble. We will need the probability distribution, P(s), for the members of the ensemble.
- It represents the macroscopic observable measured in experiments.

The probability distribution takes on a particularly simple form for a closed system.

Probability of Members in a Statistical Ensemble

- Support there are g accessible states in a system.
- If all states are equally likely, the probabilities must be normalized, each individual member of the ensemble has a probability $1/g$:

$$\sum_{all\ g\ accessible\ states} P(r) = 1 = P + P + P + \cdots$$

- Since there are g terms in this sum and each is equal, and the probability $P(s)$ of each individual member of ensemble.

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- Therefore, the probability of each individual state is

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Connecting Ensemble Averages to Experimental Observables

Experimental reality:

- No experimentalist has access to g identical copies of a system in all possible microstates.
- Experiments are performed on a single system, not an ensemble.

Time averages:

- For systems in equilibrium, long-time averages of observables on one system approximate ensemble averages.
- For systems in equilibrium, time averages ≈ ensemble averages (ergodic hypothesis).

Theory vs Experiment:

Statistical mechanics predicts ensemble averages, which can be directly compared to macroscopic experimental measurements.

Connecting Ensemble Averages to Experimental Observables

Key Takeaway

Ensemble averages allow us to connect microscopic states to experimentally observable macroscopic properties, assuming the system explores all accessible states over time.

Ensemble

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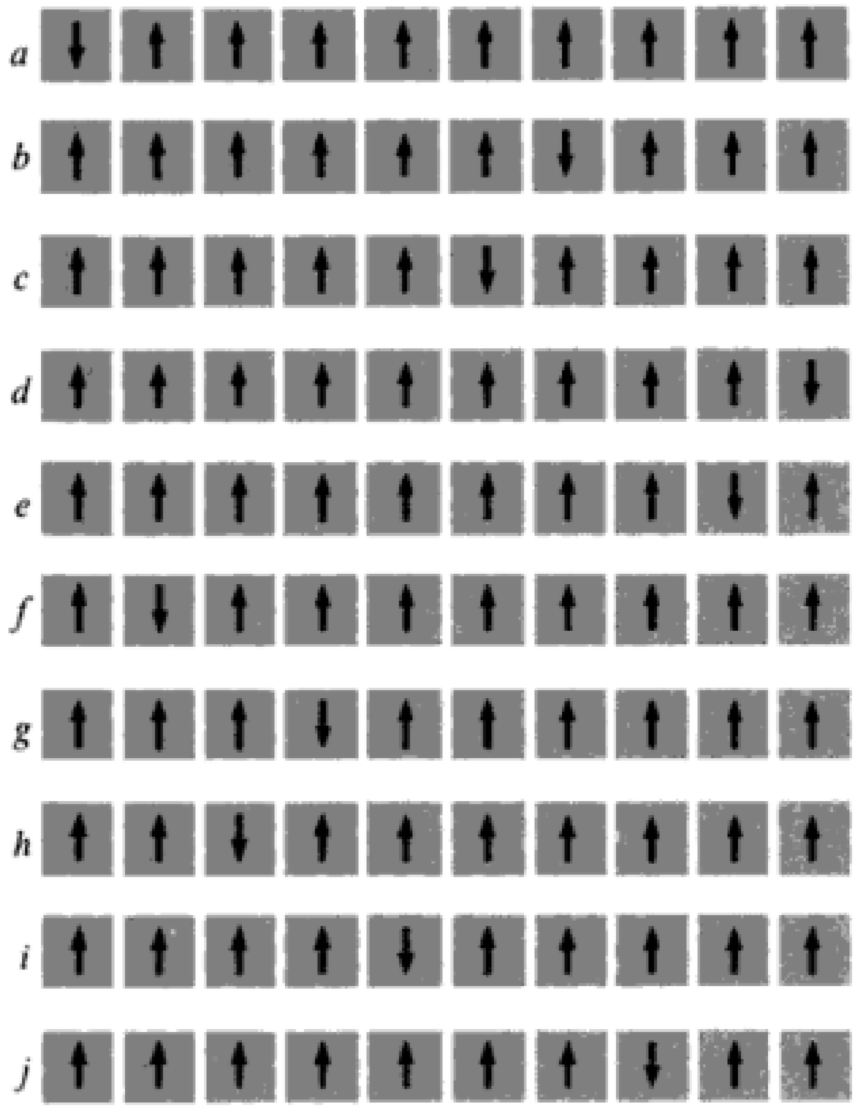

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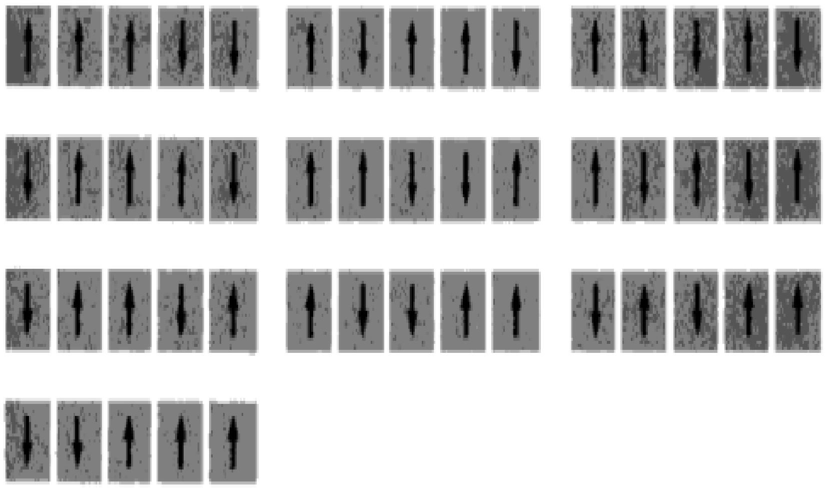

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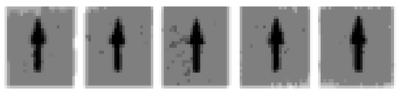

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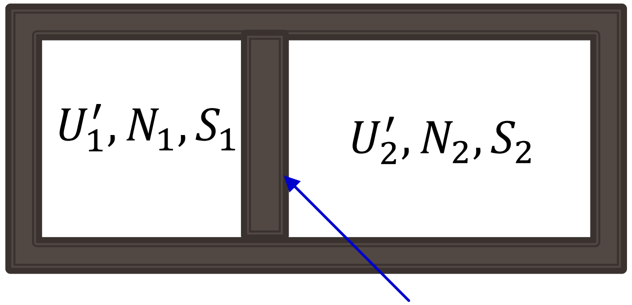

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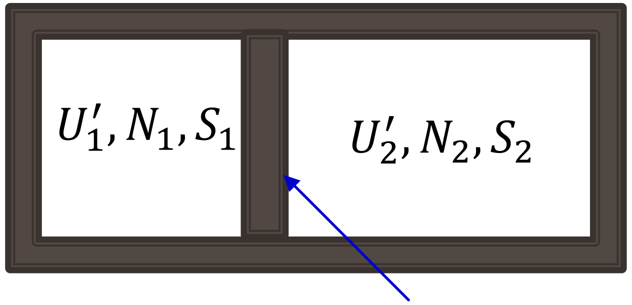

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Replacing s_2 with $s - s_1$

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Two spin System in thermal contact

Maximum or minimum can be found with first derivative with respect to s_1 and set it to zero, and maximum is when negative of second derivative

$$\frac{\partial Ln[g_1(N_1, s_1)g_2(N_2, s_2)]}{\partial s_1} = \frac{4s_1}{N_1} - \frac{4\,(s - s_1)}{N_2} = 0$$

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second derivative of above equation is:

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Second derivative is negative, so it is maximum

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At the maximum s_1 is $\widehat{s_1}$ and s_2 is $\widehat{s_2}$:

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We find

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$$= g_1(0) g_2(0) \exp\left(-\frac{2s\,\widehat{s_1}}{N} - \frac{2s\,(s - \widehat{s_1})}{N}\right)$$

$$(g_1 g_2)_{max} = g_1(0) g_2(0) \exp\left(-\frac{2s^2}{N}\right)$$

Sharpness of maximum $g_1 g_2$

Let's investigate the sharpness of maximum $g_1 g_2$. We introduce δ which represent the deviation from the maximum

$$s_1 = \widehat{s_1} + \delta \quad and \;\; s_2 = s - (\widehat{s_1} + \delta) = \widehat{s_2} - \delta$$

$$g_1(N_1, s_1) g_2(N_2, s_2) = g_1(0) g_2(0) \exp\left(-\frac{2(\widehat{s_1} + \delta)^2}{N_1} - \frac{2(\widehat{s_2} - \delta)^2}{N_2}\right)$$

$$= g_1(0) g_2(0) \exp\left(-\frac{2\,\widehat{s_1}^{\,2}}{N_1} - \frac{2\,\widehat{s_2}^{\,2}}{N_2} - \frac{4\,\widehat{s_1}\delta}{N_1} - \frac{2\delta^2}{N_1} + \frac{4\,\widehat{s_2}\delta}{N_2} - \frac{2\delta^2}{N_2}\right)$$

$$= (g_1 g_2)_{max} \exp\left(-\frac{4\,\widehat{s_1}\delta}{N_1} - \frac{2\delta^2}{N_1} + \frac{4\,\widehat{s_2}\delta}{N_2} - \frac{2\delta^2}{N_2}\right)$$

Where

$$(g_1 g_2)_{max} = g_1(0) g_2(0) \exp\left(-\frac{2\,\widehat{s_1}}{N_1} - \frac{2(\widehat{s_2})^2}{N_2}\right)$$

Sharpness of maximum $g_1 g_2$

$$g_1(N_1, s_1) g_2(N_2, s_2) = (g_1 g_2)_{max} \exp\left(-4\delta\left(\frac{\hat{s_1}}{N_1}\right) - \frac{2\delta^2}{N_1} + 4\delta\left(\frac{\hat{s_2}}{N_2}\right) - \frac{2\delta^2}{N_2}\right)$$

here $\frac{\hat{s_1}}{N_1} = \frac{\hat{s_2}}{N_2}$

$$g_1(N_1, \hat{s_1} + \delta) g_2(N_2, \hat{s_2} - \delta) = (g_1 g_2)_{max} \exp\left(-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}\right)$$

We can see that the fractional deviation from equilibrium is very small numerically.

Let consider $N_1 = N_2 = 10^{23}$ and $\delta = 10^{12}$, then $\frac{\delta}{N_1} = 10^{-10}$ and $\frac{2\delta^2}{N_1} = 200$ and product of $g_1 g_2$ becomes $e^{-400} \approx 10^{-174}$ of its maximum value, which is extremely large drop.

The configuration for which maximum of $g_1 g_2$ is called the **most probable configuration**, which is:

$$g_1(N_1, \hat{s_1}) g_2(N_2, s - \hat{s_1})$$

Thermal Equilibrium

Let's consider two model spin systems is in thermal contact with contact total energy $U = U_1 + U_2$. S_1 and S_2 are in thermal contact so the energies of the sub-systems, U_1 and U_2 will not remain constant.

$$U = U_1 + U_2 = U_1' + U_2' = U'$$

The multiplicity $g(N, U)$ of the combined systems is

$$g(N, U) = \sum_{U_1} g_1(N_1, U_1) g_2(N_2, U - U_1)$$

Accessible states in a configuration if the product $g_1(N_1, U_1) g_2(N_2, U - U_1)$ and the sum of all configuration gives $g(N, U)$

Thermal Equilibrium Condition from Multiplicity

At equilibrium, the multiplicity is maximum, so:

$$dg = 0$$

Taking the differential:

$$dg = d\big(g_1(U_1, N_1)g_2(U_2, N_2)\big) = \left(\frac{\partial g_1}{\partial U_1}\right)_{N1} . g_2 dU_1 + \left(\frac{\partial g_2}{\partial U_2}\right)_{N2} . g_1 dU_2 = 0$$

Since the total energy U is fixed,

$$0 = dU = dU_1 + dU_2 \rightarrow dU_1 = -dU_2$$

$$\left(\frac{\partial g_1}{\partial U_1}\right)_{N1} . g_2 dU_1 = \left(\frac{\partial g_2}{\partial U_2}\right)_{N2} . g_1 dU_1$$

$$\frac{1}{g_1}\left(\frac{\partial g_1}{\partial U_1}\right)_{N1} = \frac{1}{g_2}\left(\frac{\partial g_2}{\partial U_2}\right)_{N2}$$

Condition for Most Probable Energy Distribution

Using $\frac{1}{f}\frac{\partial f}{\partial x} = \frac{\partial Log(f)}{\partial x}$

$$\left(\frac{\partial Ln(g_1)}{\partial U_1}\right)_{N1} = \left(\frac{\partial Ln(g_2)}{\partial U_2}\right)_{N2}$$

- This condition determines how the total energy is distributed between the two systems.
- The corresponding values of U_1 and U_2 define the most probable configuration.

We define the quantity σ, called **entropy**, by

$$\sigma(N, U) \equiv Ln\ g(N, U)$$

Ludwig Boltzmann, Austrian Physicist, was the first introduced this expression. Helps us understanding the connection entropy and disorder.

Ludwig Boltzmann, the definition of entropy S in terms of the logarithm of accessible states is engraved in his tomb.

Condition for Most Probable Energy Distribution

In thermodynamics, entropy is written as:

$$S = k_B \ln g$$

Where k_B is the Boltzmann constant.

Physical Insight

- Entropy measures the number of accessible microscopic configurations.
- Systems naturally evolve toward states with maximum multiplicity (maximum entropy).
- This provides a statistical interpretation of "disorder", though entropy is more precisely a measure of state multiplicity.

Ludwig Boltzmann, the definition of entropy S in terms of the logarithm of accessible states is engraved in his tomb.

From Entropy to Temperature

Rewriting using entropy.

$$\left(\frac{\partial \ln g_1}{\partial U_1}\right)_{N1} = \left(\frac{\partial \ln g_2}{\partial U_2}\right)_{N2}$$

Using the definition of entropy

$$S = k_B \ln g$$

We can rewrite the condition as

$$\left(\frac{\partial S_1}{\partial U_1}\right)_{N1} = \left(\frac{\partial S_2}{\partial U_2}\right)_{N2}$$

S_1 and S_2 are in thermal equilibrium, $T_1 = T_2$. We define temperature through entropy as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$$

From Entropy to Temperature

Physical Interpretation

- Temperature measures how entropy changes with energy.
- Systems in thermal contact exchange energy until entropy is maximized.
- Equilibrium occurs when both systems have the same temperature.

Note

Temperature is not a fundamental input — it emerges naturally from the statistical definition of entropy.

Entropy

Instead of the thermodynamic quantities S and T, the textbook uses σ and τ. S and σ are connected by a scale factor:

$$S = k_B \sigma$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N \Rightarrow \frac{k_B}{T} = \left(\frac{\partial (k_B S)}{\partial U}\right)_N$$

$$\frac{1}{\tau} = \left(\frac{d\sigma}{dU}\right)_N$$

Where τ is fundamental temperature, which is differs from Kelvin temperature and τ has the dimensions of energy. It defines as,

$$\tau = k_B T$$

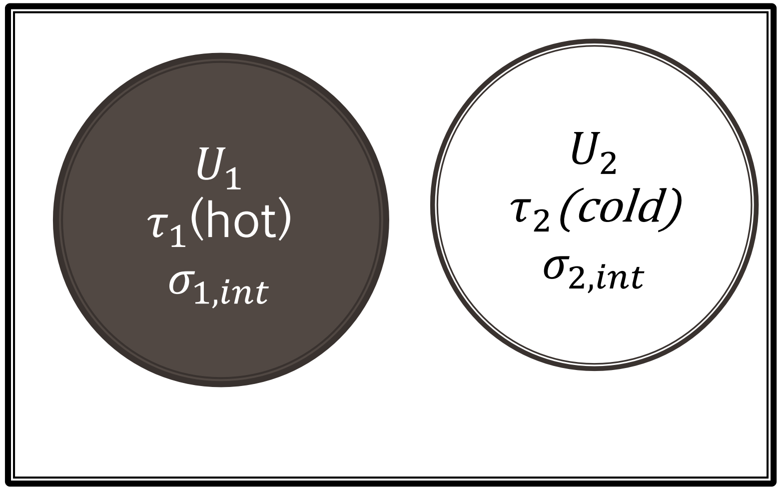
Note Boltzmann distribution, $\beta = \frac{1}{k_B T}$

Laws of Thermodynamics

i. **The Zeroth Law**: If two systems are independently in equilibrium with a third one, then they are in thermal equilibrium with each other.
ii. **The First Law of Thermodynamics**: "Heat is a form of energy; or "Energy is conserved in any process if heat is taken into account."
iii. **The Second Law of Thermodynamics**: "The entropy of a closed system either remains constant or increases."

Entropy

Let's consider what happen to entropy when two systems that are initially different temperature are brought into thermal contact

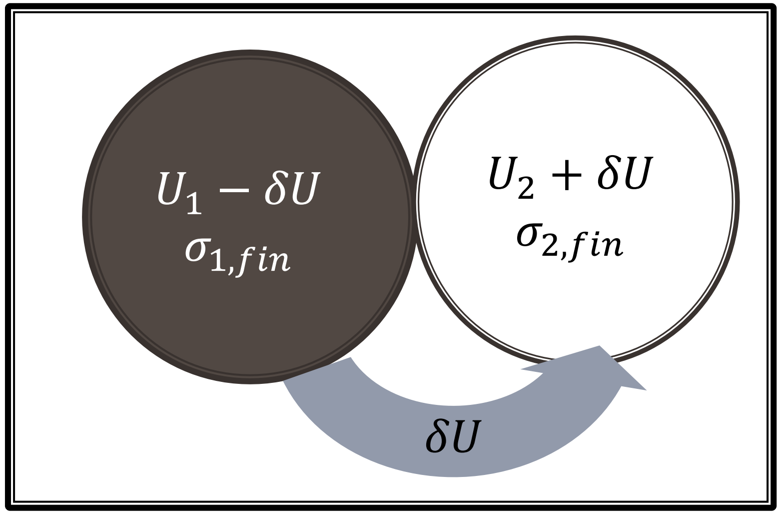


$$S = k_B \sigma$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N \Rightarrow \frac{1}{\tau} = \left(\frac{d\sigma}{dU}\right)_N$$

The temperatures are such that $\tau_1 > \tau_2$.

change in entropy that accompanies this process.



$$d\sigma = d\sigma_1 + d\sigma_2$$

$$d\sigma = \frac{\partial \sigma_1}{\partial U_1} dU_1 + \frac{\partial \sigma_2}{\partial U_2} dU_2$$

Entropy

U is constant, yields $dU_1 = -dU_2$

Since the temperature of system1 is higher (by assumption) we know that energy will flow *from* system 1 *into* system 2. So

$$dU_1 < 0, \qquad and \;\; dU_2 > 0$$

Let's call the magnitude of the change in energy in either system ΔU, so $dU_1 = -\Delta U$, and, $dU_2 = \Delta U$.

$$\Delta\sigma = -\frac{\partial\sigma_1}{\partial U_1}\Delta U + \frac{\partial\sigma_2}{\partial U_2}\Delta U$$

$$\Delta\sigma = -\frac{1}{\tau_1}\Delta U + \frac{1}{\tau_2}\Delta U = \Delta U\left(\frac{\tau_1 - \tau_2}{\tau_1\tau_2}\right) > 0$$

Since $\tau_1 > \tau_2$,

Entropy

Always thermally linking two systems at different temperature results in an increase in the entropy of the combined system.

The second law of thermodynamics states that "**the entropy of a closed system will either remain constant, or it will increase**" (the latter, generally, if internal constraints are removed).

Law of Increase Entropy

To examine this further, consider a closed system, S, constituted by two sub-systems, S_1 and S_2. S_1 and S_2 have been maintained isolated from each other by some internal constraints. The constraints are removed. What happens with the entropy?

$$g_{init}(N,U) \ = \ g_{1,init}(N_1,U_1) \bullet \ g_{2,init}(N_2,U_2)$$

After thermal contact is established between S_1 and S_2 $g(N,U)$ becomes:

$$g_{final}(N,U) = \sum_{all\ U_1 \leq U} \mathrm{g}_1(\mathrm{N}_1,\mathrm{U}_1) \bullet \mathrm{g}_2(\mathrm{N}_2,\mathrm{U}-\mathrm{U}_1)$$

$$g_{final}(N,U) \geq g_{_{1init}}(N,U_1) \bullet \ g_{_{2init}}(N,U_2)$$

Law of Increase Entropy

We have also seen that $g(N, U)$ is a very sharply peaked function. This means that the sum:

$$g(N, U) = \sum_{all\ U_1 \leq U} g_1(N_1, U_1) \bullet g_2(N_2, U - U_1)$$

is approximately equal to the largest term in it: $g(N, U) \approx (g_1 g_2)_{max}$

Here

$$g_f(N, U) \geq g_i(N, U)$$

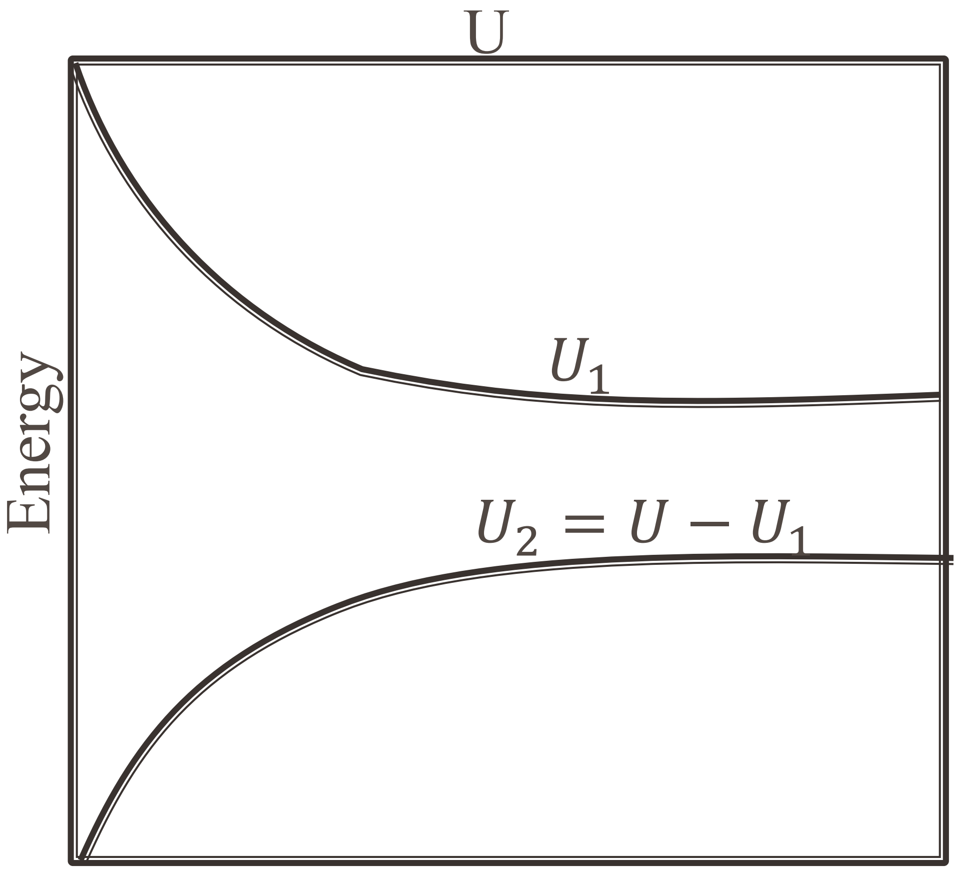
$$Ln[g_f(N, U)] \geq Ln\,[g_i(N, U)]$$

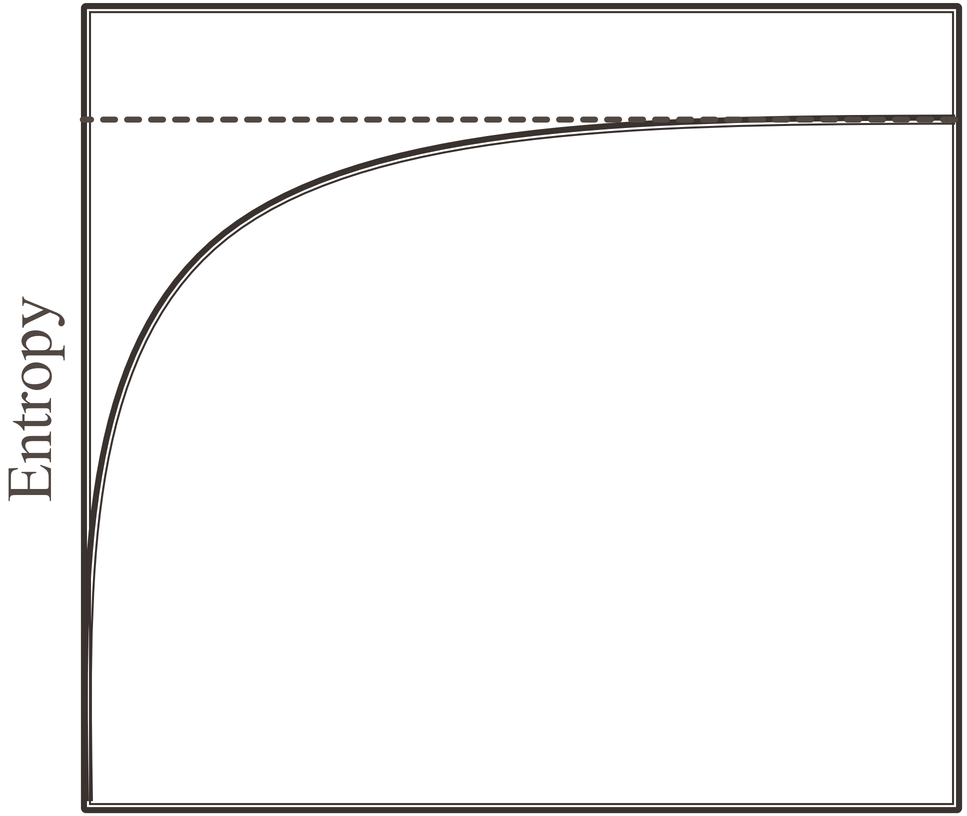
since the entropy is defined as

$$S = k_B Ln[g(N, U)])$$

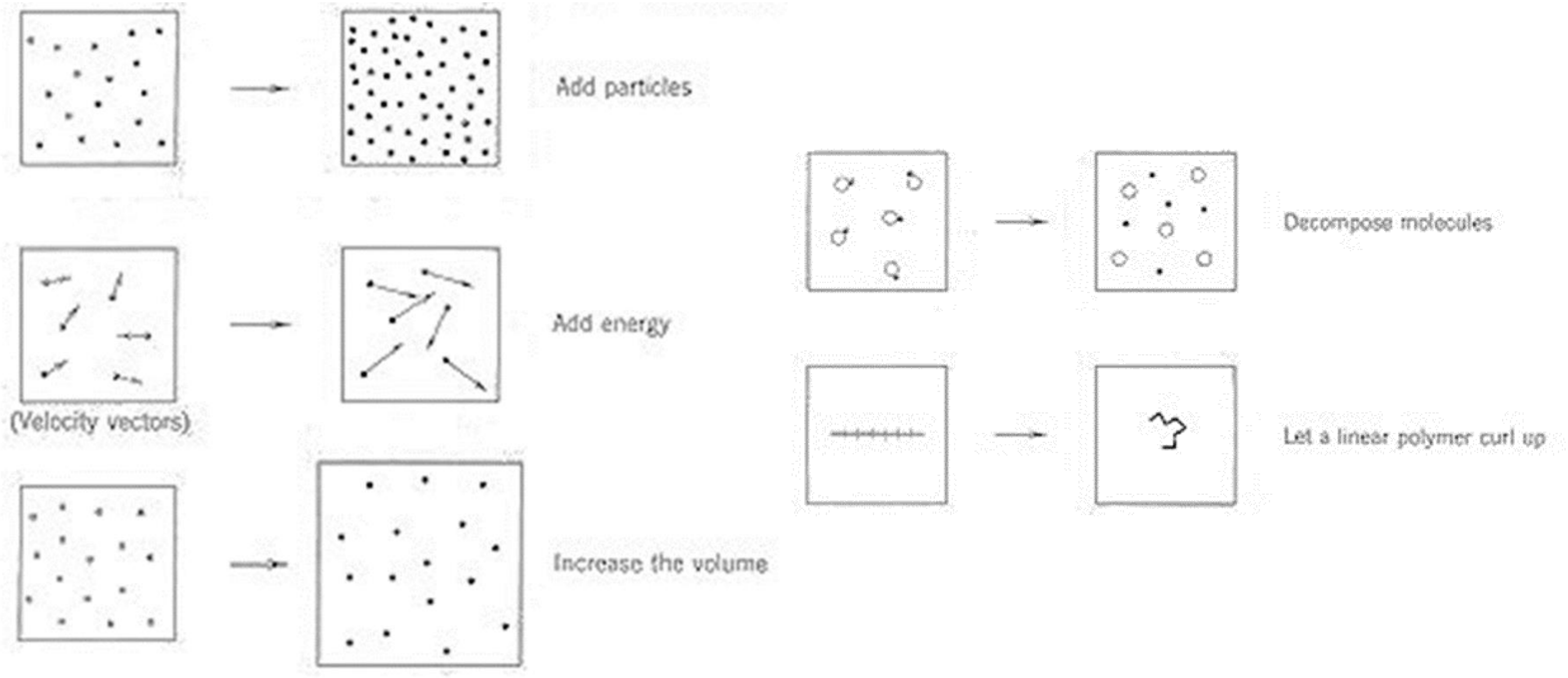
This provides us with a clear understanding of the law of increase of entropy, the second law of thermodynamics.

Law of Increase Entropy





Ways to Increase Entropy



Quiz:5-1

Consider a system of N spin- $\frac{1}{2}$ particles arranged in a row. Each spin can be either up (u) or down (d), and each distinct ordering represents a microstate.

a) For N=10, how many possible microstates (outcomes) are there?

b) What is the probability of obtaining the specific sequence $uduuddudud$?

c) What is the probability of obtaining 6 spins up and 4 spins down?

d) For $N = 6.02 \times 10^{23}$, Determine the multiplicity function $g(N, s)$ for equal numbers of spins up and down (s = 0)

Thank you very much for your attention