213 Midterm coming up...

Monday Nov 12 @ 7 pm (conflict exam @ 5:15pm)

Covers:

Lectures 1-12 (not including thermal radiation)

HW 1-4

Discussion 1-4

Labs 1-2

Review Session

Sunday Nov 11, 3-5 PM, 141 Loomis

HW 4 is not due until Thursday, Nov 15 at 8 am, but some of the problems are relevant for the exam.

Lecture 9
Examples and Problems

- Counting microstates of combined systems

- Volume exchange between systems

- Definition of Entropy and its role in equilibrium

- The second law of thermodynamics

- Statistics of energy exchange

- General definition of temperature

- Why heat flows from hot to cold

Exercise: Microstates and Entropy

Pretend we are playing a coin-tossing game. We will toss 100 pennies (all distinguishable) into the air, and there is an equal chance they will land on the table or on the floor.

What is the probability that all 100 pennies will land on the table?

What is the dimensionless entropy associated with the situation that 70 pennies land on the table, and 30 land on the floor (accounting for the fact that each penny can land heads or tails, but ignoring the various places on the table or floor that each penny can land)?

Exercise: Microstates and Entropy

Pretend we are playing a coin-tossing game. We will toss 100 pennies (all distinguishable) into the air, and there is an equal chance they will land on the table or on the floor.

What is the probability that all 100 pennies will land on the table?

$$P(100 \text{ on table}) = 0.5^{100} = 7.9 \times 10^{-31}$$

What is the dimensionless entropy associated with the situation that 70 pennies land on the table, and 30 land on the floor (accounting for the fact that each penny can land heads or tails, but ignoring the various places on the table or floor that each penny can land)?

This is one macrostate, and we want to know how many microstates correspond to it. There are three parts:
1. how many ways to have a 70/30 split: $100!/(70!30!)$
2. how many ways for the 70 to be configured: 2^{70}
3. how many ways for the 30 to be configured: 2^{30}

Therefore: $\Omega(70 \text{ on table}) = 100!/(70!30!)\ 2^{70}\ 2^{30} = 100!/(70!30!)\ 2^{100}$

$\sigma = \ln\Omega = \ln[100!/(70!30!)\ 2^{100}] = 100 \ln 2 + \ln(100!) - \ln(70!) - \ln(30!)$
{We'll see later that $\ln x! \approx x \ln x - x$} $\rightarrow \sigma = 130$

Summary of Bin Counting

Number of microstates for N objects in M bins:

	Unlimited occupancy	Single occupancy	N << M Dilute gas
Distinguishable	M^N	$\dfrac{M!}{(M-N)!}$	M^N
Identical	$\dfrac{(N+M-1)!}{(M-1)!\,N!}$	$\dfrac{M!}{(M-N)!\,N!}$	$\dfrac{M^N}{N!}$

Needed at high densities
(liquids and solids)
OK for gases, too.

OK at low densities
(gases only)

Exercise: Microstates and Entropy

When the numbers are small, and the whole distribution matters,
the average and the most likely may not be very close.

Consider 3 particles (A, B, C) in a system with 6 multiple occupancy cells
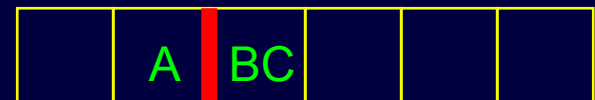partitioned by a movable barrier:

Some possible microstates:
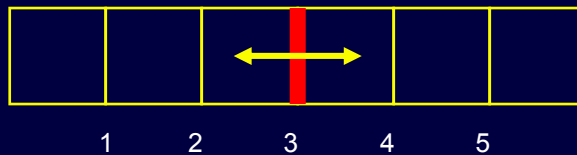
Take N_L=1 (particle A) and N_R=2 (particles B and C).

1) Calculate the entropy for each partition position.

2) What are the most likely and average partition positions?

Note: We are interested in the volume on the left and right, V_L and V_R,
so we'll express our answers in terms of them. $V_L + V_R = 6$.

Worksheet for this problem

1 particle on left
2 (distinguishable on right) multiple-occupancy bins

		Ω_L	Ω_R	$\Omega = \Omega_L \Omega_R$	$\sigma = \ln(\Omega)$
$V_L = 1$		1	$5^2 = 25$	25	3.22
$V_L = 2$					
$V_L = 3$					
$V_L = 4$					
$V_L = 5$					

Solution

1 particle on left
2 (distinguishable on right)
multiple-occupancy bins

	Ω_L	Ω_R	$\Omega = \Omega_L \Omega_R$	$\sigma = \ln(\Omega)$
$V_L = 1$	1	$5^2 = 25$	25	3.22
$V_L = 2$	2	$4^2 = 16$	32	3.47
$V_L = 3$	3	$3^2 = 9$	27	3.30
$V_L = 4$	4	$2^2 = 4$	16	2.77
$V_L = 5$	5	$1^2 = 1$	5	1.61

$\Omega_{tot} = 105$

The most likely $V_L = 2$.
The average $<V_L> = (1*25 + 2*32 + 3*27 + 4*16 + 5*5) / 105$
$= 259/105 = 2.47$
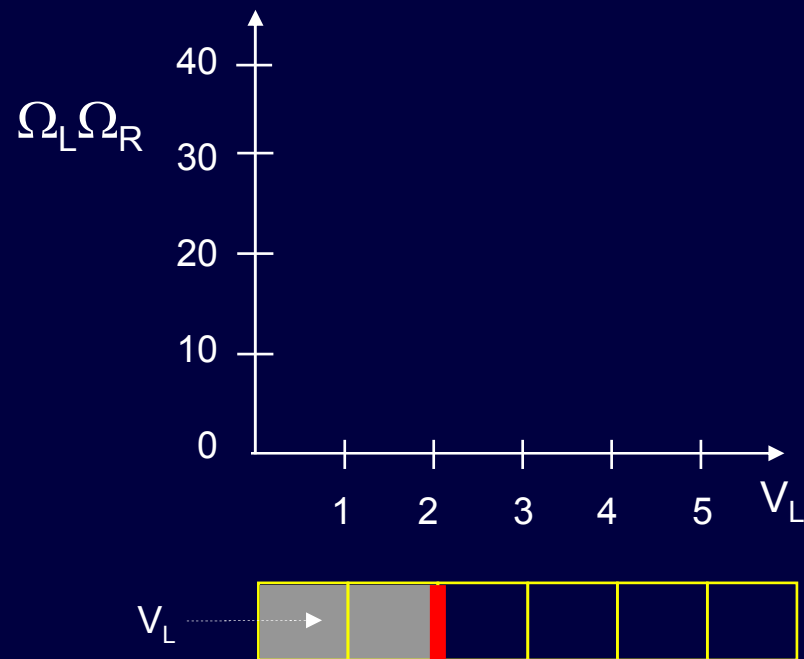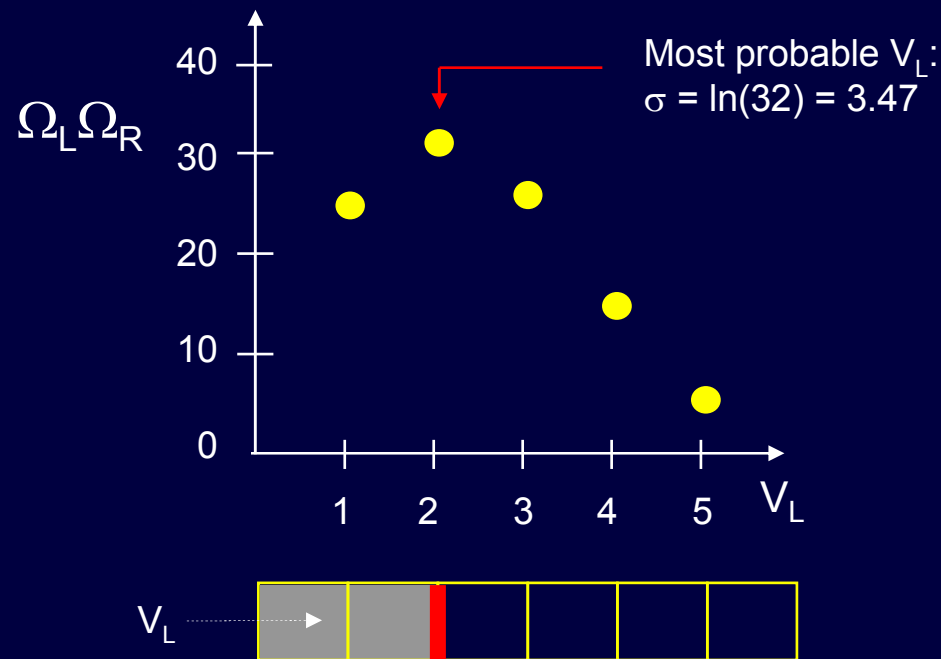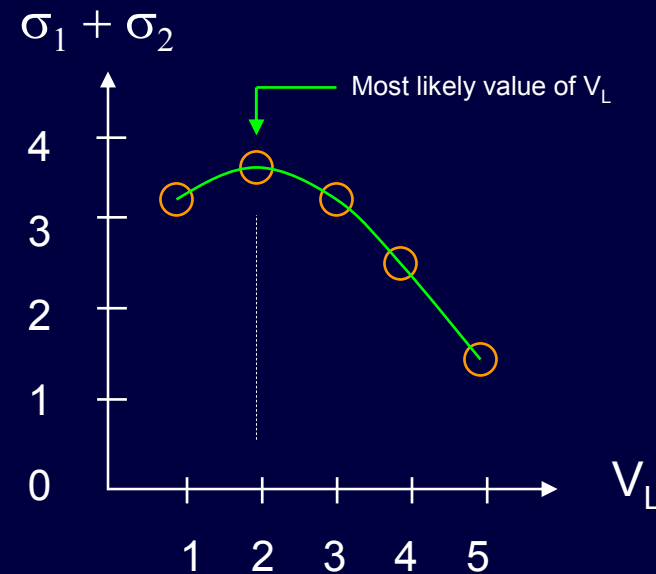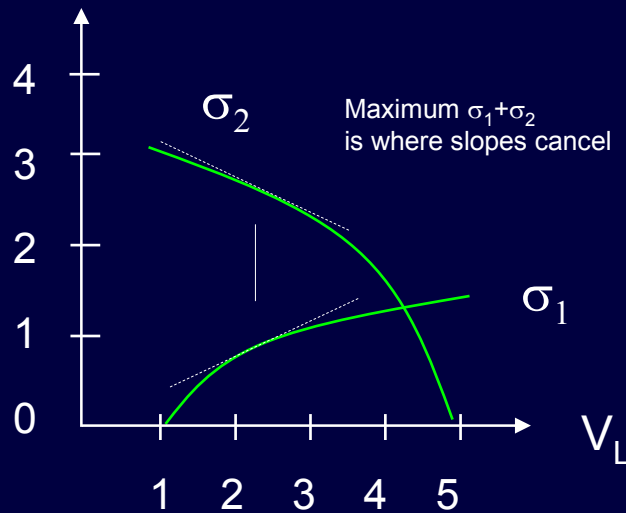
Graph the Results

Notice that the most likely position occurs when:

$$\frac{N_L}{V_L} = \frac{N_R}{V_R} \left(= \frac{1}{2} \text{ in this example} \right)$$

What is the probability, $P(2)$, that $V_L = 2$?

Graph the Results

$\Omega_L \Omega_R$

Most probable V_L:
$\sigma = \ln(32) = 3.47$

V_L

Notice that the most likely position occurs when:

$$\frac{N_L}{V_L} = \frac{N_R}{V_R} \left(= \frac{1}{2} \right) \text{ in this example}$$

What is the probability, P(2), that $V_L = 2$?

$$P(2) = \frac{32}{105} = 30.5\%$$

Maximizing the Total Entropy

If the partition is allowed to move freely, the most likely macrostate occurs at maximum total entropy, $\sigma_{tot} = \sigma_L + \sigma_R$. This is equivalent to maximizing Ω.

This corresponds to $\dfrac{\partial \sigma_1}{\partial V_1} = \dfrac{\partial \sigma_2}{\partial V_2}$ not $\sigma_1 = \sigma_2$.

Entropy will be more convenient to calculate than Ω.

Summary

- The total entropy of an isolated system is maximum in equilibrium.
- So if two parts (1 and 2) can exchange V, equilibrium requires:

$$\frac{\partial \sigma_1}{\partial V_1} = \frac{\partial \sigma_2}{\partial V_2}$$

This is a general equilibrium condition.
A similar relation holds for any
exchanged quantity.

Entropy of an ideal gas:

For N distinguishable particles in volume V: $\Omega \propto V^N \Rightarrow \sigma = N\ln V + \text{const}$

You can't calculate the constant (that requires quantum mechanics),
but it drops out of problems where one only needs the entropy change.
For example, if the temperature is constant:

$$\sigma_f - \sigma_i = N\ln V_f - N\ln V_i = N\ln(V_f/V_i)$$

Act 1: Isothermal Expansion

We isothermally compress 1 mole of O_2 from 2 liters to 1 liter.

1. How much does the (dimensionless) entropy of the <u>gas</u> change?

A) 0
B) 6×10^{23} ln(2)
C) -6×10^{23} ln(2)

2. How much does the (dimensionless) entropy of the <u>environment</u> change?

A) 0
B) 6×10^{23} ln(2)
C) -6×10^{23} ln(2)

Solution

We isothermally compress 1 mole of O_2 from 2 liters to 1 liter.

1. How much does the (dimensionless) entropy of the <u>gas</u> change?

A) 0

B) $6 \times 10^{23} \ln(2)$

C) $-6 \times 10^{23} \ln(2)$

There are half as many places for each gas particle:

$$\Omega_i \propto V^N \rightarrow \Omega_f \propto (V/2)^N$$

$$\sigma_f - \sigma_i = (N\ln V_f + \text{const}) - (N\ln V_i + \text{const}) = N\ln(V_f/V_i)$$

$$= N_A \ln(1/2) = -6 \times 10^{23} \ln 2)$$

2. How much does the (dimensionless) entropy of the <u>environment</u> change?

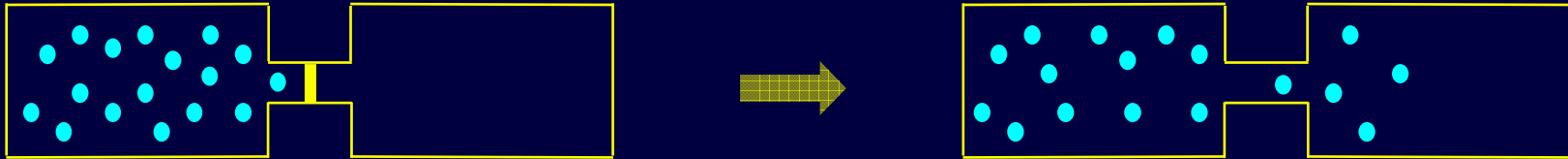A) 0

B) $6 \times 10^{23} \ln(2)$

C) $-6 \times 10^{23} \ln(2)$

According to the 2nd Law, the entropy of an isolated system must stay the same or increase. Considering the (gas + environment) as the 'system', the reduction in σ_{gas} must be matched by an increase in σ_{env}. We will see later that for isothermal processes, $\Delta\sigma_{total} = 0$ (i.e., they are reversible!).

Act 2: Free Expansion
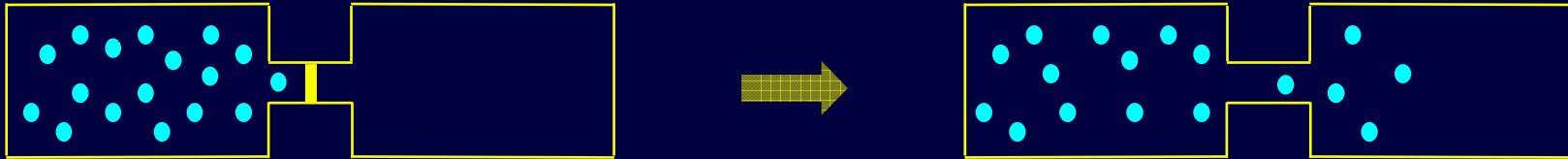
Now we let the gas 'free' expand back to 2 liters.

How much does the <u>total</u> entropy change?

A) 0
B) 6×10^{23} ln(2)
C) -6×10^{23} ln(2)

Solution

Now we let the gas 'free' expand back to 2 liters.

How much does the <u>total</u> entropy change?

A) 0
B) $6 \times 10^{23} \ln(2)$
C) $-6 \times 10^{23} \ln(2)$

There are twice as many places for each gas particle:

$$\Omega_i \propto V^N \rightarrow \Omega_f \propto (2V)^N$$

$$\sigma_f - \sigma_i = (N \ln V_f + \text{const}) - (N \ln V_i + \text{const}) = N \ln(V_f / V_i)$$

$$= N_A \ln(2) = 6 \times 10^{23} \ln 2)$$

This *is* an isothermal process (why?), but not quasi-static, i.e., the gas is not in equilibrium throughout the expansion. In fact, the gas does not interact with the enviroment at all, so σ_{env} doesn't change.

Because this is an irreversible expansion (the particles will never randomly all go back into the 1-liter box!), σ_{tot} increases.

Act 3
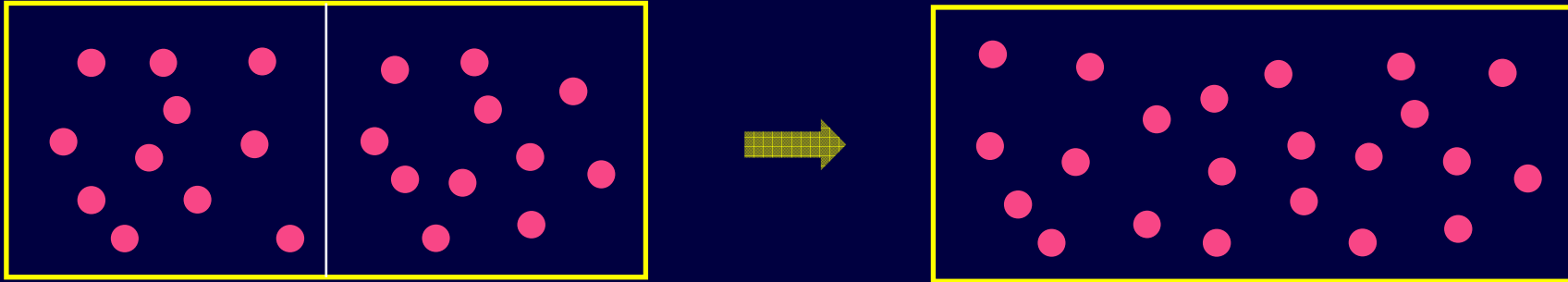
A partition separates two equal halves of a container, each containing N atoms of He. What is the change in the dimensionless entropy after the partition is removed?

A) $\Delta\sigma = 0$

B) $\Delta\sigma = N \ln 2$

C) $\Delta\sigma = 2N \ln 2$

Solution (Gibbs Paradox)
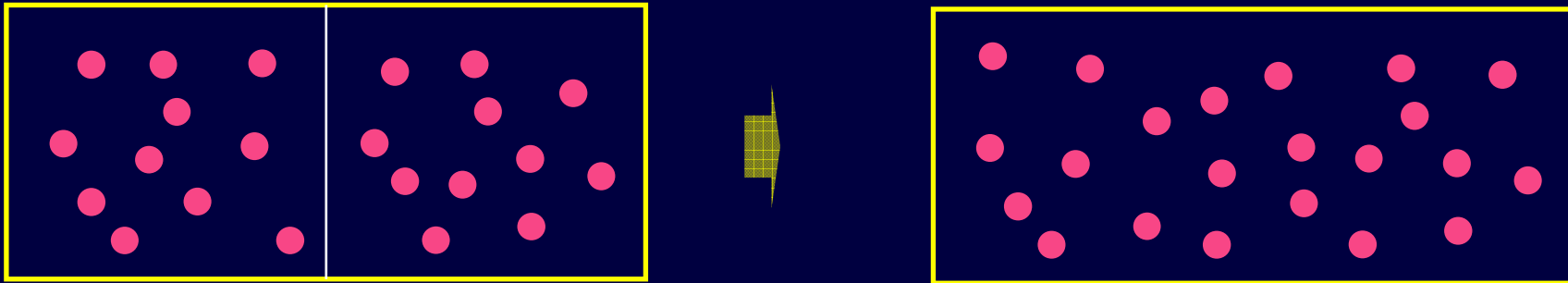

A partition separates two equal halves of a container, each containing N atoms of He. What is the change in the dimensionless entropy after the partition is removed?

- The system before removing the partition is physically identical to the system after removing the partition, i.e., the number of microstates does not change.

A) $\Delta\sigma = 0$

B) $\Delta\sigma = N \ln 2$

- Therefore, $\Delta\sigma = 0$. Let's calculate it.

C) $\Delta\sigma = 2N \ln 2$

Initial entropy

$$\Omega_L = \Omega_R = (n_T V)^N$$

$$\sigma_i = \sigma_L + \sigma_R$$

$$\sigma_i = 2N \ln(V) + 2N \ln(n_T)$$

final entropy

$$\Omega_f = (2n_T V)^{2N}$$

$$\sigma_f = 2N \ln(2V) + 2N \ln(n_T)$$

$$\Delta\sigma = \sigma_f - \sigma_i = 2N \ln(2)$$

What did we do wrong?

Gibbs Paradox (2)

- So far we have dealt with situations where the number of particles in each subsystem is fixed. Here, after the partition is removed, particles can move freely between the two halves.

- To calculate the change in entropy, we must account for the fact that the particles are _identical_.

Initial entropy

$$\Omega_L = \Omega_R = (n_T V)^N / N!$$

$$\sigma_i = \sigma_L + \sigma_R$$
$$\sigma_i = 2N \ln(n_T V) - 2 \ln(N!)$$

final entropy

$$\Omega_f = (2n_T V)^{2N} / (2N)!$$

$$\sigma_f = 2N \ln(2n_T V) - \ln((2N)!)$$

Use: $\ln(N!) \approx N \ln N - N$

$$\Delta\sigma = \sigma_f - \sigma_i = 0$$

Exercise

Consider a ~1 liter container of N_2 at STP. What fractional increase in the volume of the box V will double the number of microstates?

1) What is N?

2) What is Ω?

3) What is Ω_f/Ω_i?

Exercise

Consider a ~1 liter container of N_2 at STP. What fractional increase in the volume of the box V will double the number of microstates?

1) What is N?

At STP, 1 mole of a gas occupies 22.4 liter. Therefore, in 1 liter there is $N = 1 \text{ liter} \times (6 \times 10^{23}/22.4 \text{ liter}) = 2.7 \times 10^{22}$

2) What is Ω?

$$\Omega = (n_T V)^N$$

3) What is Ω_f/Ω_i?

$$\Omega_f/\Omega_i = 2 = (n_T V_f)^N/(n_T V_i)^N = (V_f/V_i)^N$$

$(V_f/V_i) = 2^{1/N} = 2\char`^(3.7\times 10^{-23}) = 1.0$ according to my calculator.

$= 1 + 2.56 \times 10^{-23}$ according to Mathematica

The lesson: the number of microstates increases mind-bogglingly fast – that's why the gas fills the space.

Example: Exchanging Energy

Two oscillators, A and B ("solid 1") with energy level spacing ε share a total of 6 quanta. One possible microstate is shown in the figure below. They are brought into contact with four oscillators, C, D, E and F ("solid 2") which initially share no quanta.
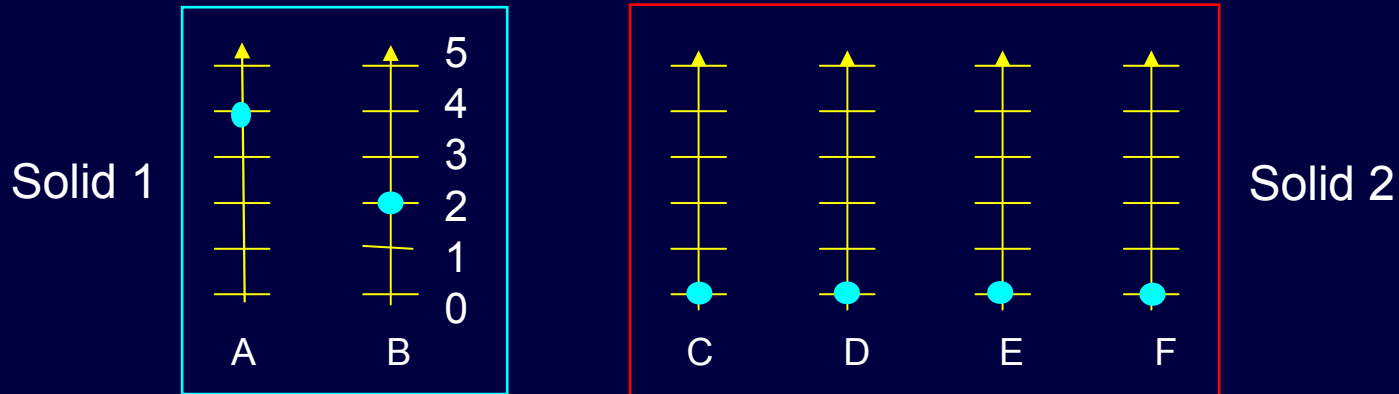
1) Initially, what is the entropy of solid 1? Solid 2?

2) If solid 2 is brought into contact with solid 1, what is the total entropy after equilibrium is reached?

3) What is the average energy in oscillator A, before and after?

Solution

Two oscillators, A and B ("solid 1") with energy level spacing ε share a total of 6 quanta. One possible microstate is shown in the figure below. They are brought into contact with four oscillators, C, D, E and F ("solid 2") which initially share no quanta.
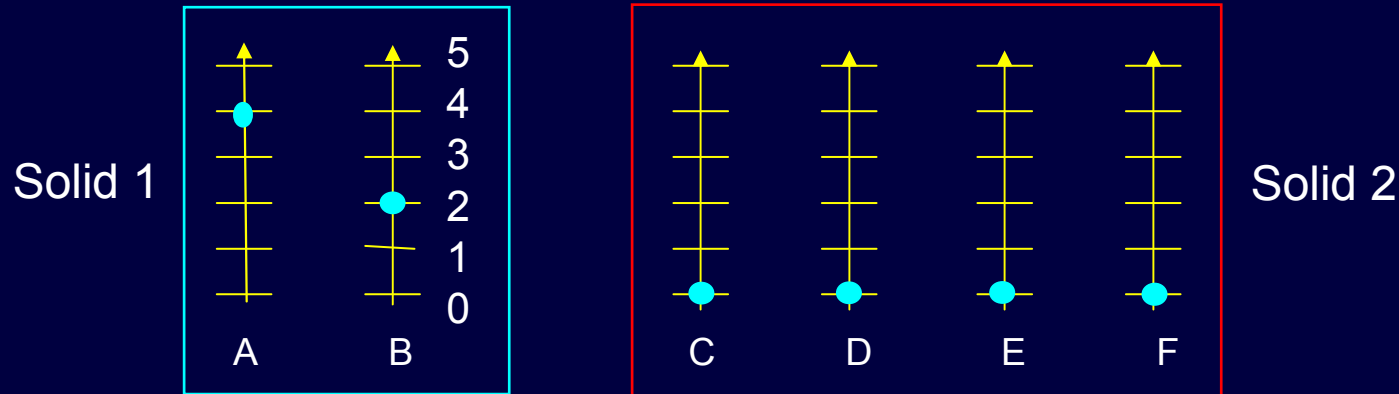
1) Initially, what is the entropy of solid 1? Solid 2?

$$\Omega_1 = \frac{(q_1 + N_1 - 1)!}{q_1!(N_1 - 1)!} = 7 \quad \Rightarrow \quad \sigma_1 = 1.95 \quad \sigma_2 = \ln(1) = 0$$

2) If solid 2 is brought into contact with solid 1, what is the total entropy after equilibrium is reached?

$$\Omega_{tot} = \frac{(q_{tot} + N_{tot} - 1)!}{q_{tot}!(N_{tot} - 1)!} = 462 \quad \Rightarrow \quad \sigma_{tot} = 6.14$$

3) What is the average energy in oscillator A, before and after?

Before: 2 oscillators share 6ε. $<U_{av}>$ = 3ε.
After: 6 oscillators share 6ε. $<U_{av}>$ = ε.

Entropy, T, and C_V

A conventional entropy, $S \equiv k\,\sigma$, is often used.

Our basic definition of T is then: $\longrightarrow$

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_V$$

S has dimensions energy/temperature (J/K).

For fixed-V processes:

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V \equiv \frac{C_V}{T}$$

So:

$$S(T_f) - S(T_0) = \int_{T_0}^{T_f} \frac{C_V(T')}{T'}\, dT'$$

Or:

$$\sigma(T_f) - \sigma(T_0) = \int_{T_0}^{T_f} \frac{C_V(T')}{kT'}\, dT'$$

One can use this to calculate absolute entropy (no arbitrary constants).

FYI: Absolute Entropy

There is a natural method to determine absolute entropy (no arbitrary constants).

- At T=0, an object in equilibrium has only one accessible state (maybe two) (the lowest energy level, or two if there is degeneracy).

  $\Rightarrow$ Entropy is ~0 at T=0.

- As T $\rightarrow$ 0, the entropy falls smoothly to that limit.
  This is sometimes called the "Third Law of Thermodynamics"

- So, the absolute S(T) can be calculated by setting S(0) = 0:

$$S(T) = \int_0^{T_F} \frac{C_v(T')}{T'} dT'$$

  This integral does not diverge, because $C_v \rightarrow 0$ as T $\rightarrow$ 0.

- Absolute entropies are computed for many substances.
  For example, S_{O2}(T=25° C, p=1Atm) = 205.04 J/mol.K

  http://www.egr.msu.edu/classes/me417/somerton/FCTables.pdf

Exercise:
A Large Collection of Oscillators

Consider 10^{24} oscillators at 300 K with ε << kT.

1) What's C_V?

2) If 1 J of U is added, how much does T go up?

3) How much does that 1 J make σ go up?

Solution

Consider 10^{24} oscillators at 300 K with $\varepsilon \ll kT$.

1) What's C_V?

    Equipartition holds, so $C_V = Nk = 13.8$ J/K.

2) If 1 J of U is added, how much does T go up?

    $\Delta T = \Delta U / C_V = 0.07$ K

3) How much does that 1 J make σ go up?

    $d\sigma/dU = 1/kT$
    T is almost constant here, so:
    $\Delta\sigma = \Delta U/kT = 1 \text{ J} / (4.2\times10^{-21} \text{ J}) = 2.4\times10^{20}$

    $\Delta\Omega$ is the exponential of this, a gigantic number.

Note:
$\Delta S = k\Delta\sigma = \Delta U/T$
    = 14 J/K

Example: Energy Exchange

Consider this situation:

$N_1 = 3$, $N_2 = 4$

$q = q_1 + q_2 = 8$ (*i.e.*, $U = 8\varepsilon$)

What is the most likely energy for each of the two systems?

U_1	U_2

Solution

Consider this situation:

$N_1 = 3, \quad N_2 = 4$

$q = q_1 + q_2 = 8 \quad (i.e., U = 8\varepsilon)$

What is the most likely energy for each of the two systems?

U_1	U_2

I am not going to work it out in detail.
Here's a graph of the solution.
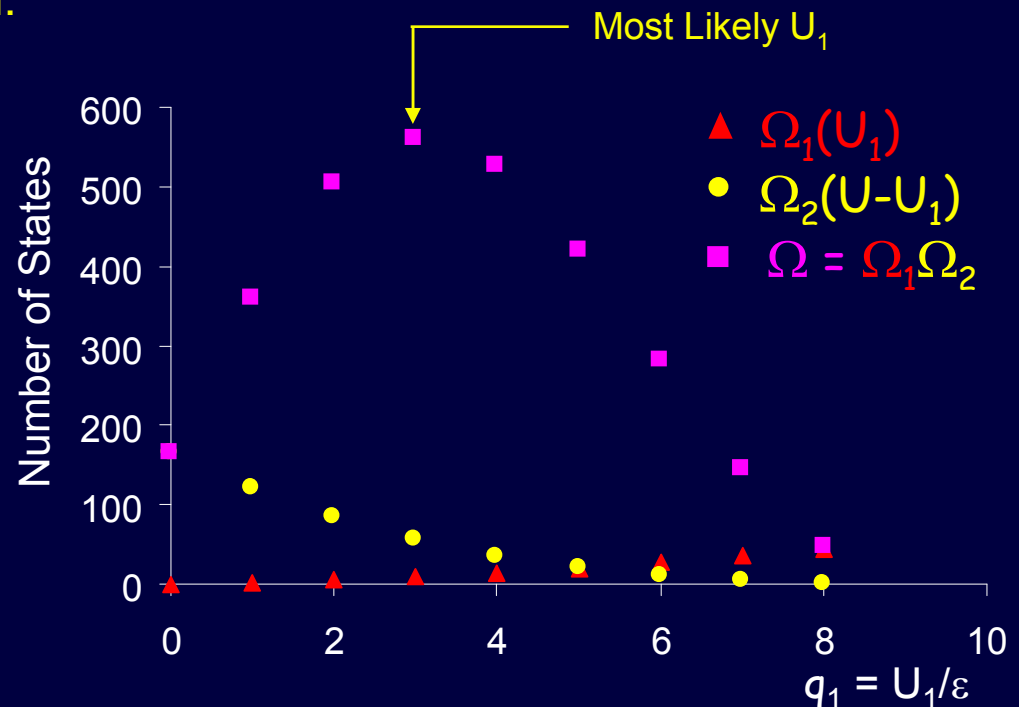
Sample calculation: $q_1=1$, $q_2 = 7$.

Use: $\Omega_i = \dfrac{(q_i + N_i - 1)!}{q_i!(N_i - 1)!}$

Then: $\Omega_1 = \dfrac{3!}{1!2!} = 3$

$\Omega_2 = \dfrac{10!}{7!3!} = 120$

$\Omega = 360$

Most Likely U_1

- ▲ $\Omega_1(U_1)$
- ● $\Omega_2(U-U_1)$
- ■ $\Omega = \Omega_1\Omega_2$

Number of States

$q_1 = U_1/\varepsilon$

Most likely macrostate: $U_1/N_1 = 3/3 \approx U_2/N_2 = 5/4$. ~ Equipartition. N is not large.