Lecture 8

The Second Law of Thermodynamics; Energy Exchange

- The second law of thermodynamics
- Statistics of energy exchange
- General definition of temperature
- Why heat flows from hot to cold

Reading for this Lecture:
Elements Ch 7

Reading for Lecture 10:
Elements Ch 8

Last Time

- Counting microstates of combined systems
- Volume exchange between systems
- Definition of Entropy and its role in equilibrium

Quick Review: The Scope of Thermodynamics

- When an isolated system can explore some number, Ω, of microstates the microstates are equally likely.
- The probability that you observe macrostate A is: $P_A = \Omega_A/\Omega_{All}$, *i.e.*, the fraction of all the microstates that look like A.

Entropy:

- The entropy of a system is $\ln(\Omega)$, where Ω counts all possible states. Therefore, P_A is proportional to e^{σ_A}, since $\sigma_A = \ln(\Omega_A)$.
- For a big system, the entropy of the most likely macrostate, σ_A, is not much less than the total entropy, σ_{All}.

Example: 10^6 spins:

$$\sigma_{All} = \ln(2^{10^6}) = 10^6 \ln(2) = 693147$$

$$\sigma_{5\times10^5\text{ up}} = \ln(10^6! \,/\, 5\times10^5!\; 5\times10^5!) = 693140$$

Thermodynamics applies to systems that are big enough so that this is true.

Question: What is the probability that in a system of 10^6 spins, exactly 5×10^5 will be pointing up?

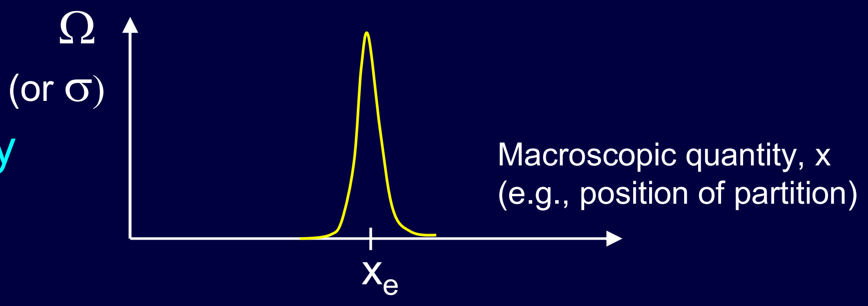
The Second Law of Thermodynamics

The Entropy of an isolated system can only increase (or remain constant) as a function of time.

$$\boxed{\frac{d\sigma}{dt} \geq 0}$$

This is a consequence of probability.

- Macroscopic systems have very sharply peaked probability distributions (much sharper than shown here).



- If x is initially far from its most likely position, x_e , then it will evolve towards x_e (where most of the microstates are). $\frac{d\sigma}{dt} > 0$
- If x is initially near its most likely position, x_e , then it will remain there. σ has its maximum value. $\frac{d\sigma}{dt} = 0$
- All available microstates are equally likely, but in big systems the vast majority of them correspond to very similar macrostates (*e.g.*, about 50% spin up).

Lessons from Volume Exchange

You learned last lecture:

When the system consists of independent parts:

The number of states of the whole was the product of the number of states of the parts.

$$\Omega_{TOT} = \Omega_1 \Omega_2$$

We define entropy to be the ln(# microstates).

$$\sigma \equiv \ln(\Omega)$$

For a big system in equilibrium we almost certainly see the macrostate that maximizes Ω_{TOT} (or σ_{TOT}).

$$\sigma_{TOT} = \sigma_1 + \sigma_2$$

To determine equilibrium, maximize the total entropy by maximizing the sum of the entropies of the parts.

If the parts can exchange volume:

In equilibrium each part must have the same derivative of its entropy with respect to its volume.

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

holding other properties fixed.

This argument doesn't rely on the parts being the same (or even similar).

Now use the same principle for systems that exchange ENERGY

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

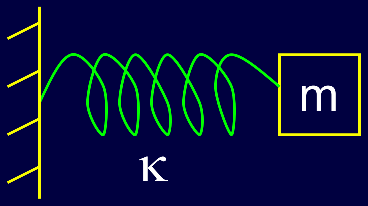
holding other properties fixed.

Model System for Energy Exchange:

Simple Harmonic Oscillator (SHO)

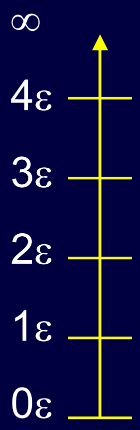
To make the mathematics simple we use a system with discrete, equally-spaced energy levels, $E_n = n \cdot \varepsilon$, where n = 1,2,3 … (quantum #)

These are the energy levels for a mass on a spring:



$$f = \frac{1}{2\pi}\sqrt{\frac{\kappa}{m}}$$

$\varepsilon = hf$, where h is Planck's constant



This system was studied in P214. All you need to know is the energy level formula ($E_n = n\varepsilon$).

Note to 214 folks: We drop the 0.5 ε for convenience, since only energy differences matter.

The SHO is an exact description of photons, and a very good description of vibrations of atoms in solids (= “phonons”).

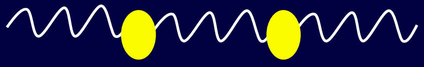
Our notation convention:

E = energy of a single oscillator

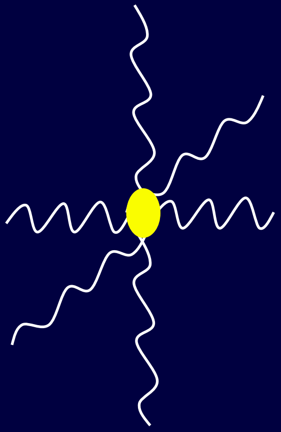
U = internal energy of a multi-oscillator system

Terminology for HW, Lab, etc.

1-D Einstein Solid:
A collection of N oscillators in 1 dimension.



3-D Einstein Solid:
A collection of N atoms each oscillating in
3 dimensions: 3N oscillators



We'll assume that each oscillator has the same frequency

(i.e., we ignore the frequency dependence of the "normal modes").

ACT 1: Energy Exchange

Two oscillators exchange energy. The total energy is $U = 4\varepsilon$.

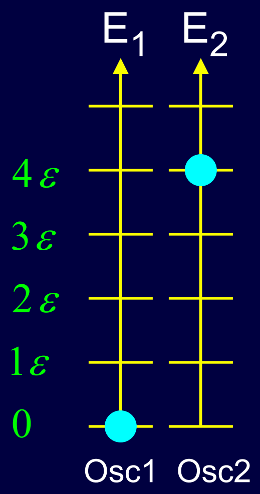
That is: $E_1 = n_1\varepsilon$, $E_2 = n_2\,\varepsilon$, where $n_1+n_2 = 4$.

What is the total number of microstates?

In general we say $U = q\varepsilon$, where q is the number of energy quanta.

A) 4 B) 5 C) 6 D) 7 E) 8

$q = 4$



Here’s one microstate.

Solution

Two oscillators exchange energy. The total energy is $U = 4\varepsilon$.

That is: $E_1 = n_1\,\varepsilon$, $E_2 = n_2\,\varepsilon$, where $n_1+n_2 = 4$.

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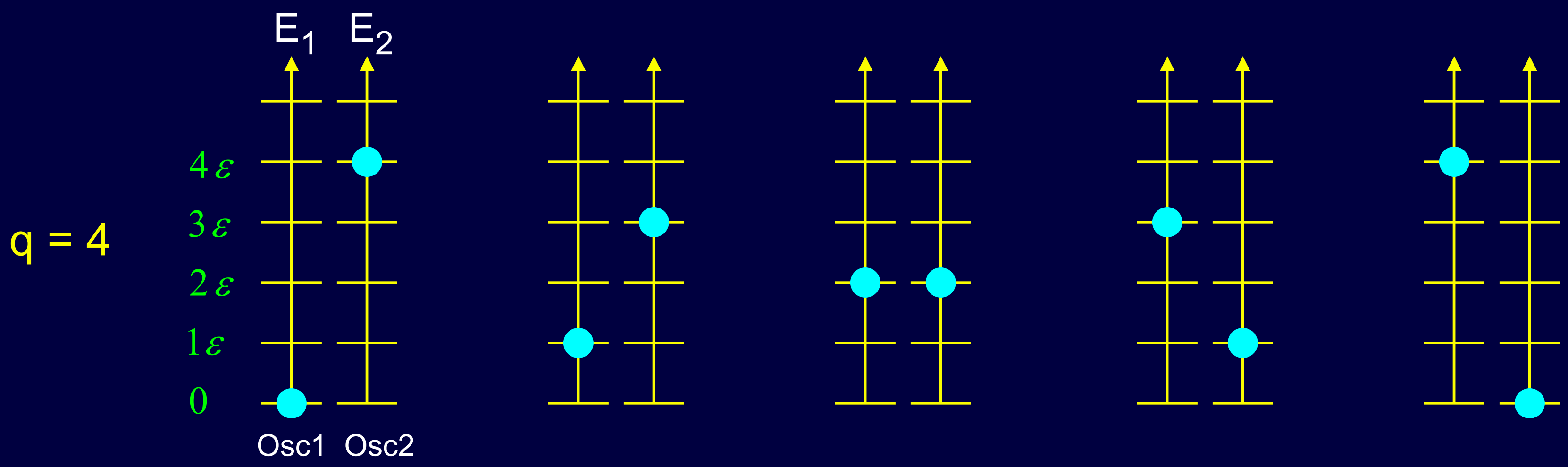
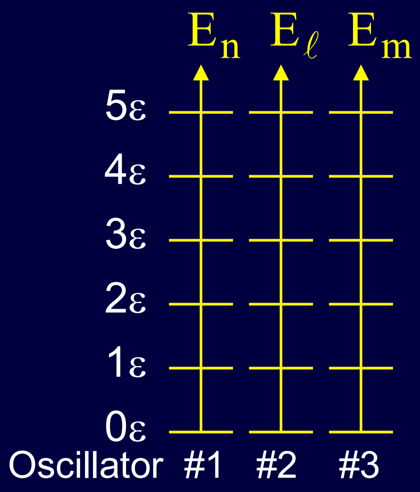
A) 4 [✓ B) 5] C) 6 D) 7 E) 8



Exercise

Energy exchange between 3 oscillators

Three oscillators have total energy $U = 2\varepsilon$. ($q = 2$) Find Ω.



$$E_n = n\varepsilon$$

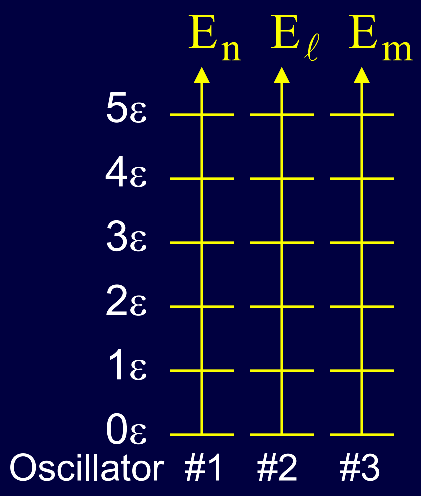
$$E_\ell = \ell\varepsilon$$

$$E_m = m\varepsilon$$

n, ℓ, m are integers ($n + \ell + m = 2$)

Solution

Three oscillators have total energy $U = 2\varepsilon$. ($q = 2$) Find Ω.



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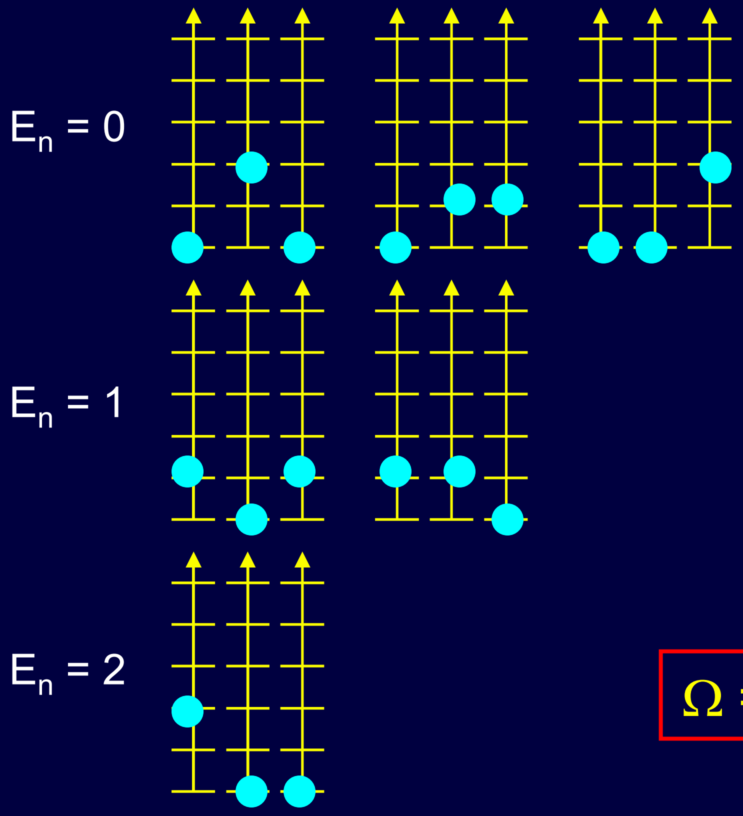


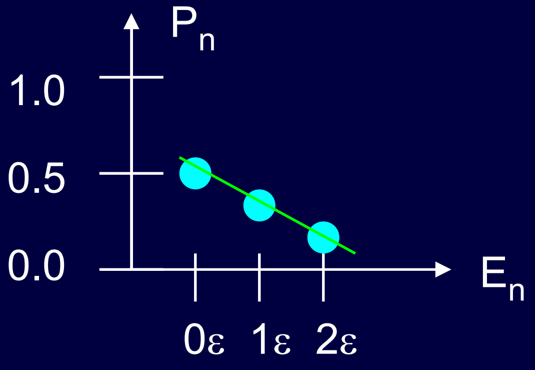
$$\boxed{\Omega = 6}$$

Probability of observing energy E_n

What is the probability that oscillator #1 has energy 0, ε, or 2ε?

Look at the solution to the exercise.

Probability that oscillator #1 has energy 0ε: $P_0 = 3/6 = 1/2$
Probability that oscillator #1 has energy 1ε: $P_1 = 2/6 = 1/3$
Probability that oscillator #1 has energy 2ε: $P_2 = 1/6$



Why does P_n decrease as E_n increases?

This is an important general feature of energy distributions in thermal equilibrium.

We'll discuss it more next week.

ACT 2: Average energies

In an example with 2ε in 3 SHOs, what would be the average thermal energy U_1 in the first SHO?

A) 0 B) $\varepsilon/3$ C) $2\varepsilon/3$ D) ε E) 2ε

Solution

In an example with 2ε in 3 SHOs, what would be the average thermal energy U_1 in the first SHO?

A) 0   B) $\varepsilon/3$ $\boxed{\text{C) } 2\varepsilon/3}$ D) ε E) 2ε

We can calculate it using the probabilities:

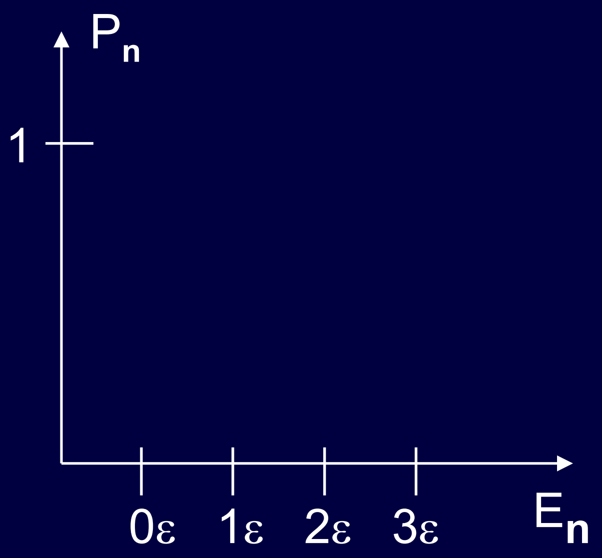
$$\begin{aligned} \langle U_1 \rangle &= P(E_0)E_0 + P(E_1)E_1 + P(E_2)E_2 \\ &= \tfrac{1}{2} * 0 \quad + 1/3 * \varepsilon \quad + 1/6 * 2\varepsilon = 2/3\varepsilon \end{aligned}$$

Of course, there's an easier way:
All three oscillators are the same, so they each must have, on average 1/3 of the total energy.

As in the previous example, the most likely energy (0) is not the average energy.

Home Exercise

For a system of 3 oscillators with $U = 3\varepsilon$,
Plot P_n, the probability that oscillator #1 has energy $E_n = n\varepsilon$.



Can you state in words why P_n decreases with increasing E_n?
It is very important that you understand this.

Relief from Counting

The general formula for the number of microstates in a system of N oscillators sharing q energy quanta:

$$\boxed{\Omega = \frac{(q+N-1)!}{(N-1)!(q)!}}$$

We'll call it the "q-formula".

This is the same as the formula for N identical particles in M bins.*

Particles		Energy
N particles	⟷	q energy quanta
M bins	⟷	N oscillators

Beware !!!
N means different things in the two situations.
(sorry for the notation)

The q energy quanta are identical (indistinguishable) "particles".
The N oscillators are multiple-occupancy "bins" for those quanta.

*See the derivation in last lecture's Appendix.

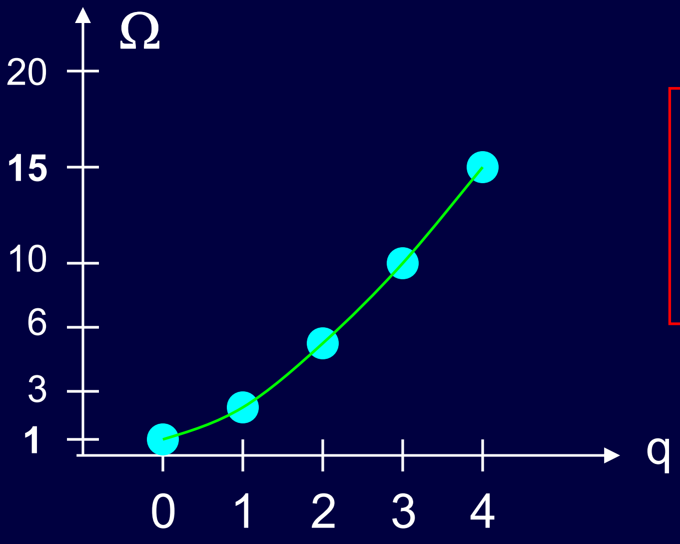
How Ω depends on U

Use the q-formula:

- For a 2-SHO system, $N=2$, $\Omega = q+1$.
- For $N=3$, here's Ω for q = 0, 1, 2, 3, 4:

Remember:
$U = q\varepsilon$

q	Ω
0	1
1	3
2	6
3	10
4	15



For N=3:

$$\Omega = (q+2)(q+1)/2$$

$$\propto q^2 \quad \text{when q is large.}$$

In general, $\Omega \propto U^{N-1}$ for N oscillators when $q \gg N$ (or, $U \gg N\varepsilon$).

Note: This happens when the average energy per oscillator, U/N, is much larger than the energy spacing, ε.

Thermal Equilibrium between 2 large hot systems

Assume the systems are large (N >> 1), so that we can take derivatives.

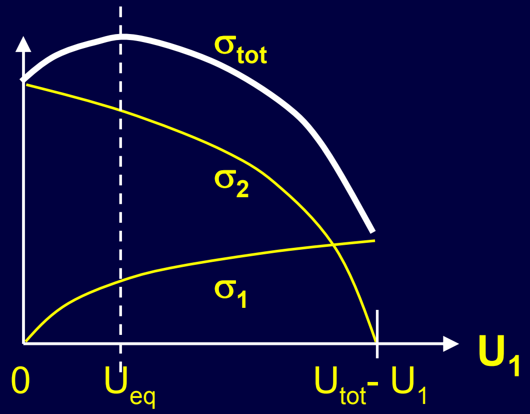
Calculate U_{eq} by maximizing σ_{tot} as we vary U_1: (keeping $U_1+U_2 = U_{tot}$)

$$\frac{d\sigma_{tot}}{dU_1} = \frac{\partial\sigma_1}{\partial U_1} + \frac{dU_2}{dU_1}\frac{\partial\sigma_2}{\partial U_2} = 0$$

We know: $dU_1 = -dU_2$

$$\frac{\partial\sigma_1}{\partial U_1} - \frac{\partial\sigma_2}{\partial U_2} = 0$$

$$\boxed{\frac{\partial\sigma_1}{\partial U_1} = \frac{\partial\sigma_2}{\partial U_2}}$$



This expression for thermal equilibrium was obtained by maximizing the entropy subject to a constraint.
The result is very similar to the one for volume exchange (see last lecture's summary slide).
Its form results from the sharing of some quantity among systems. We'll see other examples.

Note:
We are holding V constant.
That's the reason for the partial derivative.
σ is a function of both U and V.

General Definition of Temperature

Let’s use the energy sharing result to write a more general definition of temperature that does not assume equipartition which (as we’ll see soon) is not always valid. Recall that equipartition is needed for the ideal gas law, $pV = NkT$, so the new definition will free us from relying on ideal gases to measure temperature.

Start with the energy sharing result: In thermal equilibrium: $\frac{\partial\sigma_1}{\partial U_1} = \frac{\partial\sigma_2}{\partial U_2}$

Define the absolute temperature T: $\boxed{\frac{1}{kT} \equiv \left(\frac{\partial\sigma}{\partial U}\right)_V}$

By definition, $T_1 = T_2$ in equilibrium. That’s nice, but to be useful it must give other results that we all know and love. For example:

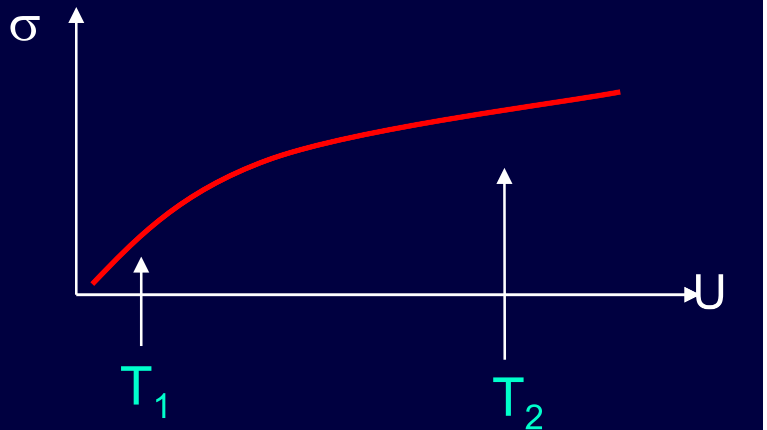
- Out of equilibrium, heat flows from hot to cold.
- Under everyday conditions (large objects, not near absolute zero) we have equipartition of energy: $U = \frac{1}{2}kT$ for each energy mode.

Act 2: σ and T

We previously saw that for a large collection of harmonic oscillators, $\Omega \propto U^{N-1} \sim U^N$, so that $\sigma = N\ln U + \text{const.}$, as shown here.

Which point corresponds to a higher temperature?

A) $T_1 > T_2$
B) $T_1 = T_2$
C) $T_1 < T_2$



Solution

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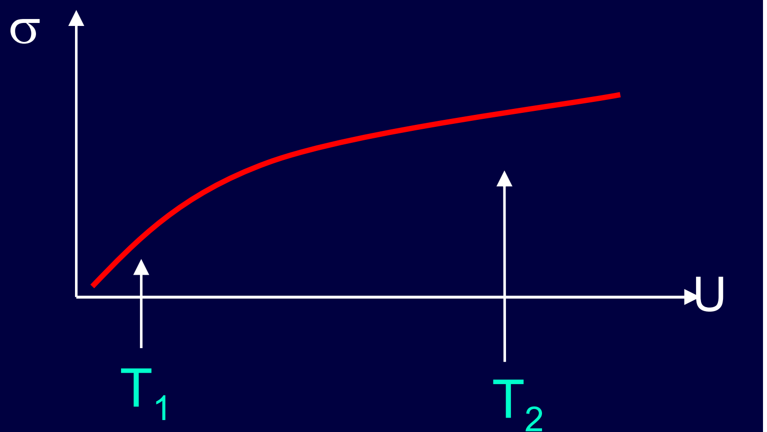
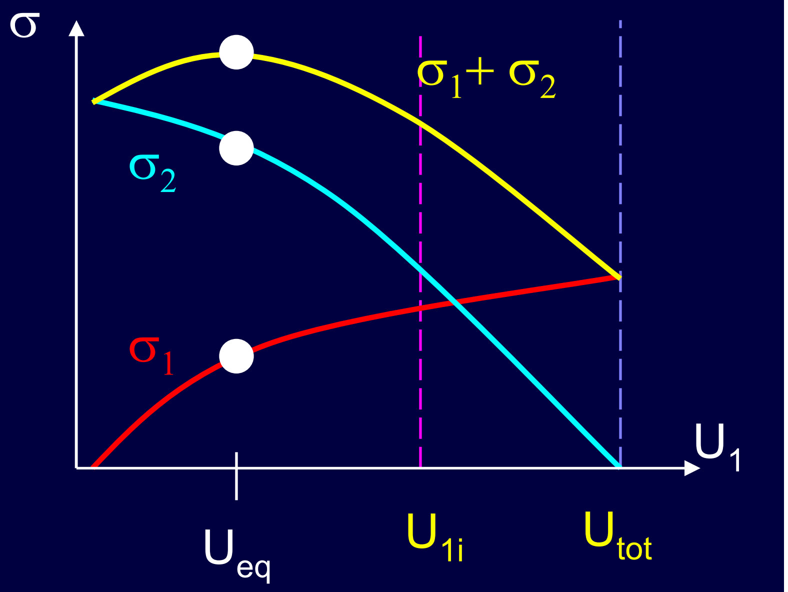
[✓ C) $T_1 < T_2$]



By definition, $\frac{1}{kT} \equiv \left(\frac{\partial\sigma}{\partial U}\right)_V$ so whereever the slope is biggest, the temperature must be *smallest*. This makes sense: if we add energy to a system that is at very low temperature (e.g., T_1), it will have a much bigger effect on the entropy than if the system is at a higher temperature (and already quite disordered).

Act 2: Heat Flow

Consider the entropies of two systems in thermal contact. System 1 starts with internal energy $U_{1i} > U_{eq}$.



1. Which direction will energy flow?

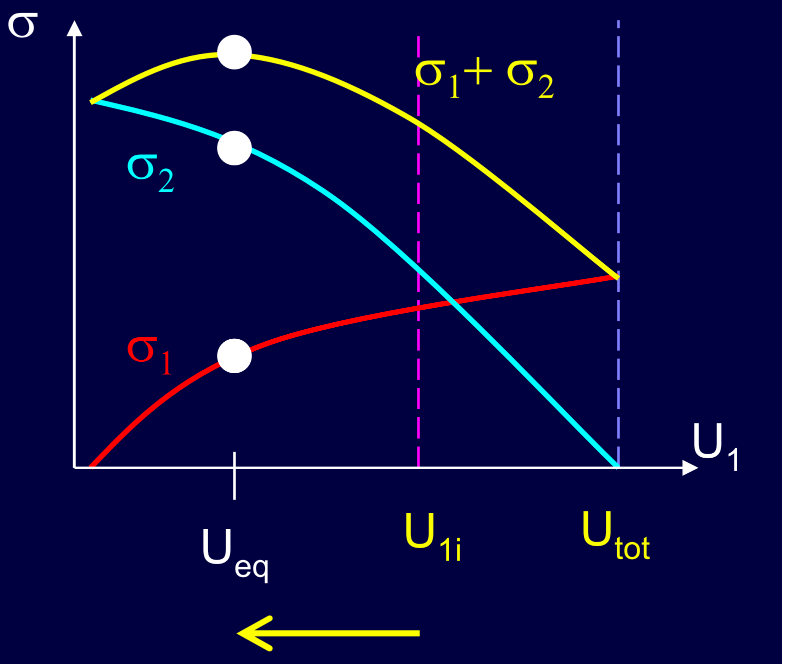
A) From 1 to 2
B) From 2 to 1
C) Neither (no flow)

2. Which system has a higher initial temperature?

A) System 1
B) System 2
C) Neither (equal temperatures)

Solution

Consider the entropies of two systems in thermal contact. System 1 starts with internal energy $U_{1i} > U_{eq}$.



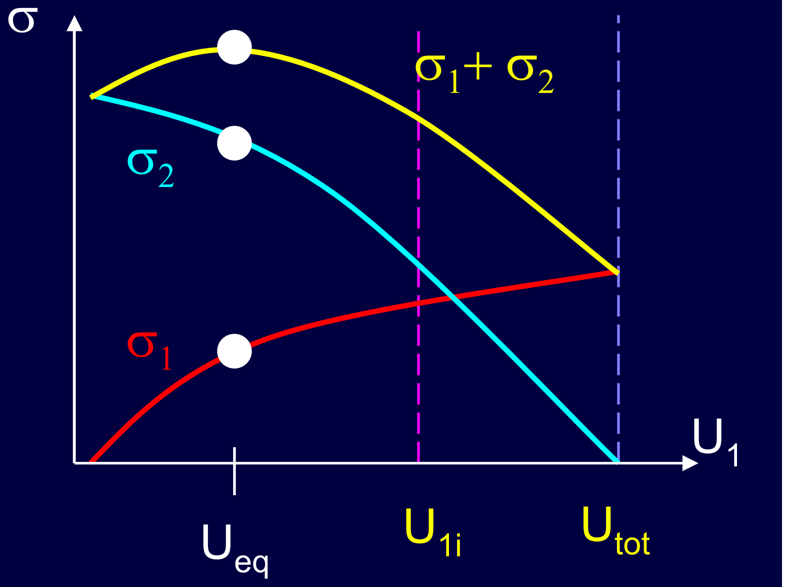
1. Which direction will energy flow?

A) From 1 to 2
B) From 2 to 1
C) Neither (no flow)

The two systems will evolve toward the white dots, as shown. U_1 decreases. Heat flows until $\sigma_1 + \sigma_2$ is a maximum.

Solution

Consider the entropies of two systems in thermal contact. System 1 starts with internal energy $U_{1i} > U_{eq}$.



1. Which direction will energy flow?

[✓ A) From 1 to 2]
B) From 2 to 1
C) Neither (no flow)

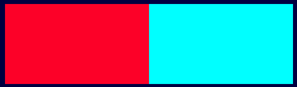
2. Which system has a higher initial temperature?

[✓ A) System 1]
B) System 2
C) Neither (equal temperatures)

The temperature is inversely proportional to the slope ($d\sigma/dU$). Therefore (look at the graph) $T_{1i} > T_{2i}$.

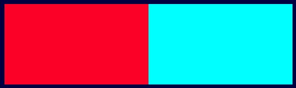
Why Heat Flow from Hot to Cold Is Irreversible

If we prepare an isolated system out of equilibrium,



$T_1 > T_2$

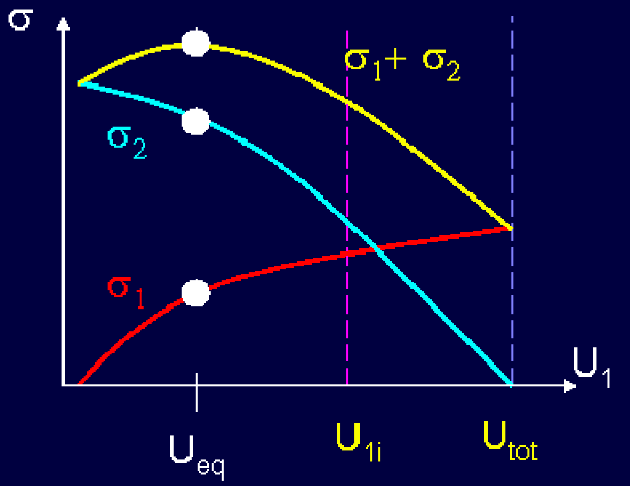
the system will irreversibly adjust itself to:



$T_1 = T_2$

Isolated systems evolve toward the macrostate that has maximum total entropy (maximum probability).

Almost all the probability is very near to the equilibrium macrostate, so once equilibrium is reached, it is very unlikely that the system will go anywhere else.



The age of the universe is short compared to how long you'd have to wait for the energy to re-separate!

What about Equipartition?

Equipartition holds for everyday phenomena. In this situation, U >> Nε. That is, each oscillator (atom, or something similar) has many energy quanta, because q = U/ε >> N.

Large objects also have N >> 1: N-1 ~ N.

(We don't actually *need* this approximation, but it makes the math simpler, since <U> = $U_{\text{most likely}}$.)

We want to verify that our new definition of temperature agrees with the usual one (which is based on the ideal gas law) in the everyday regime. In particular, we want to verify that equipartition holds, in which case the ideal gas formulas for specific heat, *etc*. will work out.

Let's consider harmonic oscillators, because we know how to do the calculation. Recall:

Using the above approximations

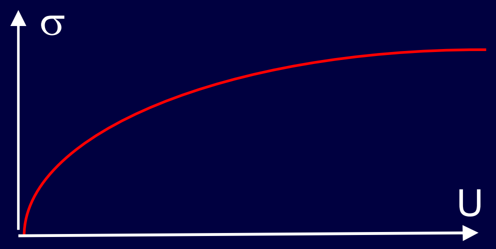
$$\Omega(N,q) = \frac{(q+N-1)!}{q!(N-1)!} \approx \frac{q^N}{N!}$$

Therefore:

$$\sigma = \ln(\Omega) \propto N\ln(q) + \text{const}$$

$$\boxed{\sigma \propto N\ln(U)} + \text{const}'$$

The constant contains (among other things) the volume dependence.



Equipartition (2)

Now calculate the temperature of N oscillators that have internal energy U:

$$\frac{1}{kT} = \frac{\partial \sigma}{\partial U} = \frac{\partial (N \ln(U) + const')}{\partial U} = \frac{N}{U}$$

The constant doesn't depend on U, so its partial derivative is zero.

Thus, U = NkT. Equipartition holds if q >> N.

Here's a more practical way to write the q >> N condition:

$U = q\varepsilon \gg N\varepsilon$, or $U/N \gg \varepsilon$. Therefore, $kT = U/N \gg \varepsilon$.

Equipartition holds if the thermal energy, kT, is much larger than the energy spacing, ε.

Equipartition fails at low temperatures.
We'll study this phenomenon later.

Entropy, T, and C_V

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

Our basic definition of T is then: → $$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_V$$

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

For fixed-V processes:

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

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).

Next Week

- The Boltzmann factor (and applications)
- What happens when equipartition fails?