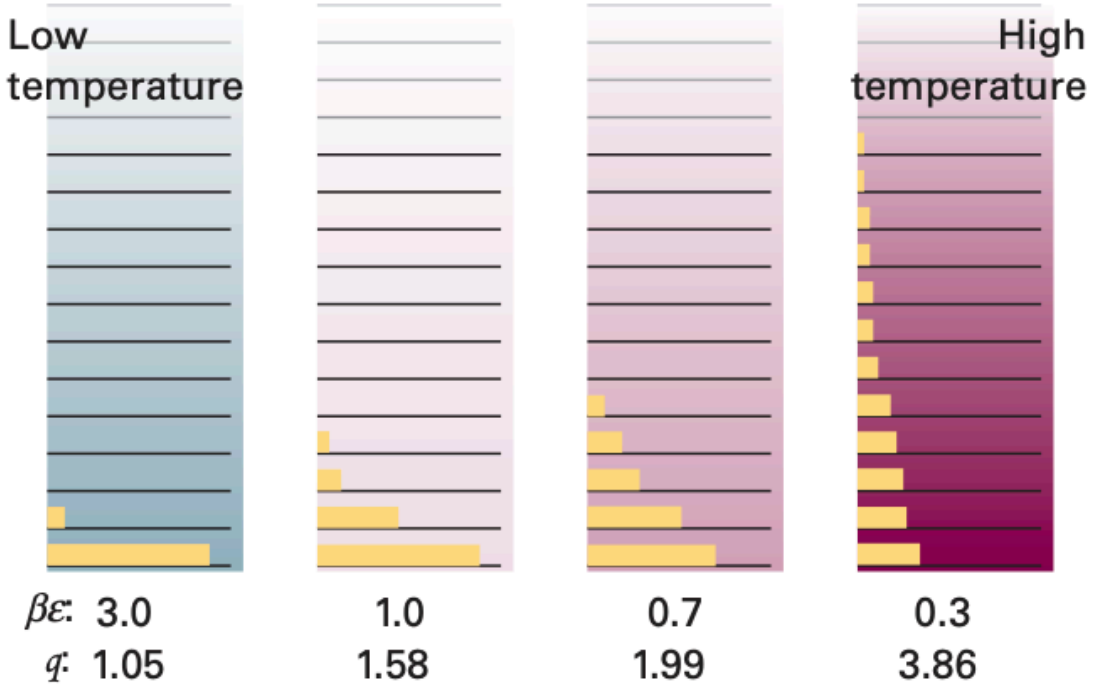
Thermodynamics, Part 1

Last time	Today	Next time
Temperature	Energy	Entropy
Partition functions	First law of thermodynamics	Second law of thermodynamics

Last time

- Temperature is a property of the most probable configuration
- Statistical definition $T = 1/k\beta$ agrees with some of our intuitions
- Partition function is, roughly, the number of thermally accessible states



Today: Thermodynamics

Statistical mechanics provides a microscopic picture of the world

Thermodynamics looks at the macroscopic scale, where systems are described in terms of bulk properties like volume, pressure, and temperature

Today, we will revisit the laws of classical thermodynamics and see how they can be derived from the microscopic statistical picture

The four laws of thermodynamics

0. If two systems are each in thermal equilibrium with a third, they are in thermal equilibrium with each other.
1. Energy is conserved.
2. The entropy of an isolated system always increases.
3. The entropy of a system approaches a constant value as the temperature goes to zero.

Zeroth law

If two systems are each in thermal equilibrium with a third, they are in thermal equilibrium with each other.

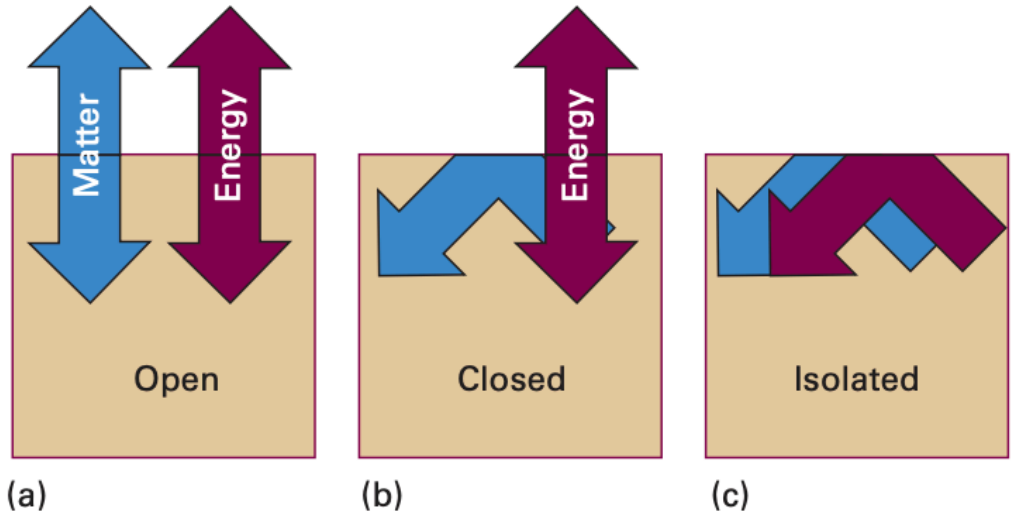
The zeroth law defines thermal equilibrium.

We saw last time that there is a single parameter—the temperature—which determines the equilibrium distribution, implying that all systems with the same temperature are in equilibrium with each other.

First law

Version 1: **Energy is conserved.**

Version 2: **The internal energy of an isolated system is constant.**



$$\Delta U_{\text{total}} = \Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0$$

$$\Delta U_{\text{system}} = -\Delta U_{\text{surroundings}}$$

Internal energy

Microscopically, the internal energy is the total energy of the occupied microstates:

$$U = E = \sum_i n_i \varepsilon_i$$

First law

How can the internal energy change?

$$\Delta U = Q + W$$

The change in the internal energy of a system is equal to the heat Q *entering* the system plus the work W done *on* the system.

Both heat and work are transient; they describe energy flow, not static content. They are processes, not things.

Note: Some books (and Wikipedia) use the sign convention $\Delta U = Q - W$, where W is the work done *by* the system.

Work

$$\Delta U = Q + W$$

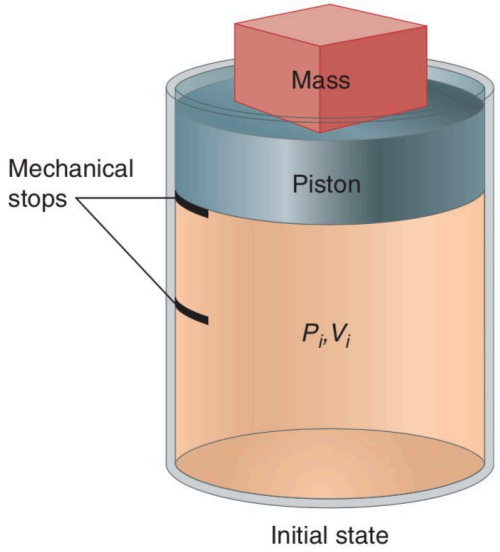
Work is done when a macroscopic force causes a displacement:

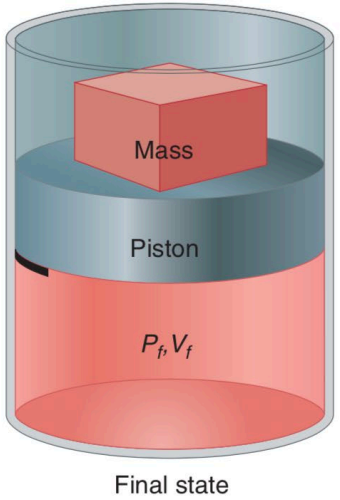
$$dW = \mathbf{F} \cdot d\mathbf{x}$$

Expansion work:

$$dW = -p_{\text{ext}} dV$$

Total expansion work: $$W = -\int_{V_i}^{V_f} p_{\text{ext}} dV$$





Mentimeter

Non-expansion work

More generally, work is done by a *generalised force* **F** acting through a *generalised displacement* d**x**

$$dW = \mathbf{F} \cdot d\mathbf{x}$$

Type of work	dw	Comment
Expansion	$-p_{ex}\,dV$	p_{ex} is the external pressure dV is the change in volume
Surface expansion	$\gamma d\sigma$	γ is the surface tension dσ is the change in area
Extension	$f dl$	f is the tension dl is the change in length
Electrical	ϕdQ	ϕ is the electric potential dQ is the change in charge

Mentimeter

Heat

$$\Delta U = Q + W$$

Heat is any energy flow into or out of a system that is **not** work.

It is the energy that flows across the boundary of a system due to a temperature difference with its surroundings.

Mentimeter

Microscopic picture of work and heat

$$U = \sum_i n_i \varepsilon_i$$

$$dU = \sum_i n_i \, d\varepsilon_i + \sum_i \varepsilon_i \, dn_i$$

Work Heat

Mentimeter

Summary

Key points:

- The four laws of thermodynamics are not fundamental, but can be derived from statistical mechanics
- First law: Energy is conserved
- Energy, heat, and work have microscopic interpretations

Next time

Next time, we will derive the remaining two laws of thermodynamics from statistical mechanics, including the most important one, the second law.

Reading:

E&R *Phys. Chem.* 32.4–32.5, 5.1, 5.3–5.8 **or**

E&R *Thermo.* 15.4–15.5, 5.1, 5.3–5.8