Thermodynamics lecture 1

W.A.L.T.   (we are learning today)

Basic concepts and terminology

Quantum mechanics, General relativity,

Details of structure: particles, forces, fields

Thermodynamics

Things are made of "stuff"; we reason in terms of energy and entropy

Many thermodynamic concepts (e.g. energy) are strictly accurate at any scale, but some (e.g. temperature) become precise only in the **thermodynamic limit**, which is the limit of large systems (more precisely, those with a large number of internal degrees of freedom such as particle- or field- positions and momenta).
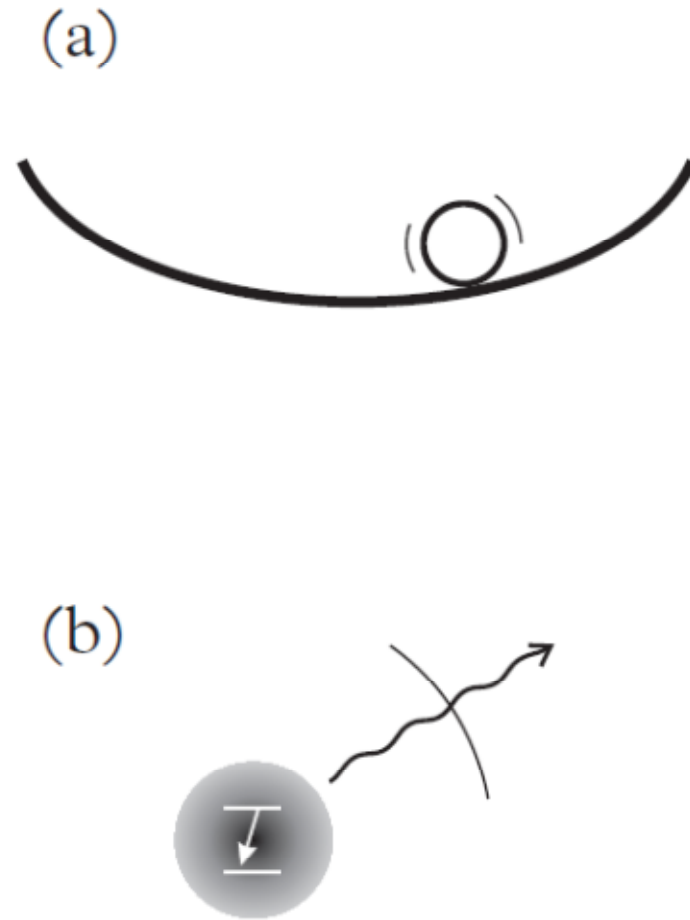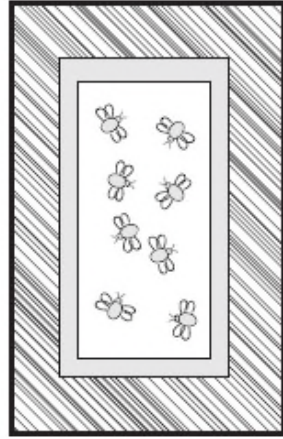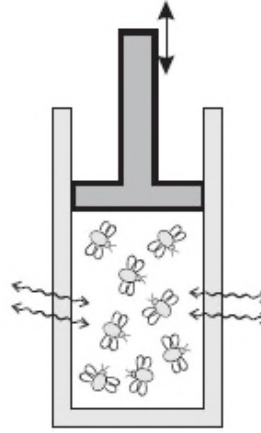
Direction of physical processes

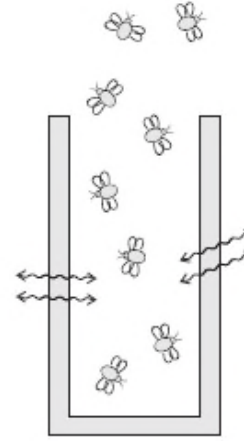**Fig. 3.1** *(a) A ball rolls in a curved bowl; (b) an atom emits a photon.*

Isolated   **Closed**   **Open**

Thermodynamic system		Conserved
Type	Definition and examples	quantities
Isolated	Not influenced at all by other things	U, N, V
	e.g.　　　a gas in a rigid, insulated chamber	
	a swarm of bees in such a chamber	
Closed	Cannot exchange matter with surroundings	N
	e.g.　　　a gas in a cylinder with movable piston	
	a swarm of bees in a thin flexible bag	
Open	Can exchange matter with surroundings	–
	e.g.　　　a pool of water in the open air	
	a swarm of bees flying freely	

Extensive, intensive
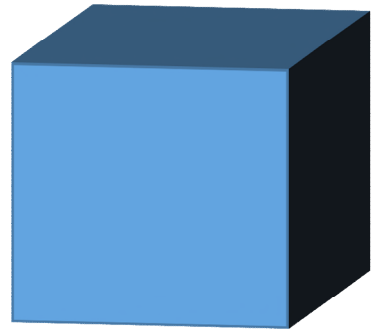
A system with given properties
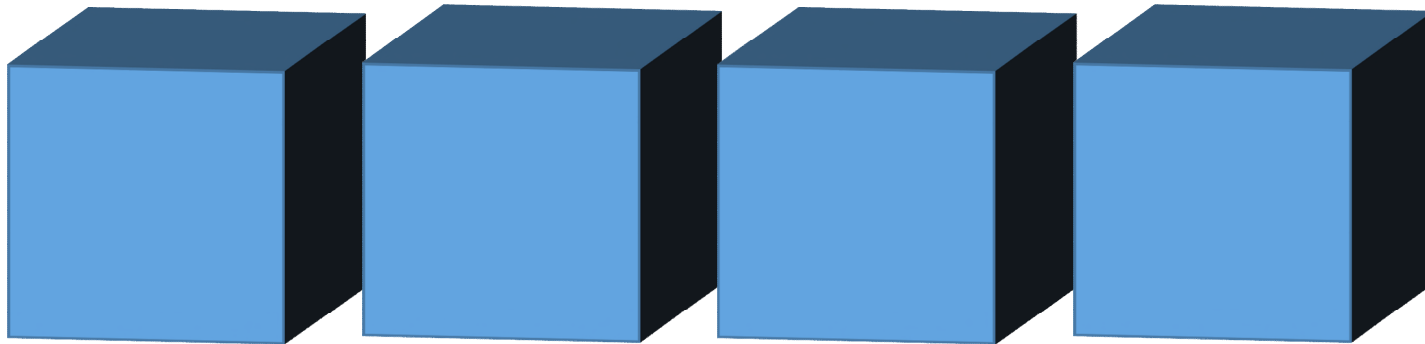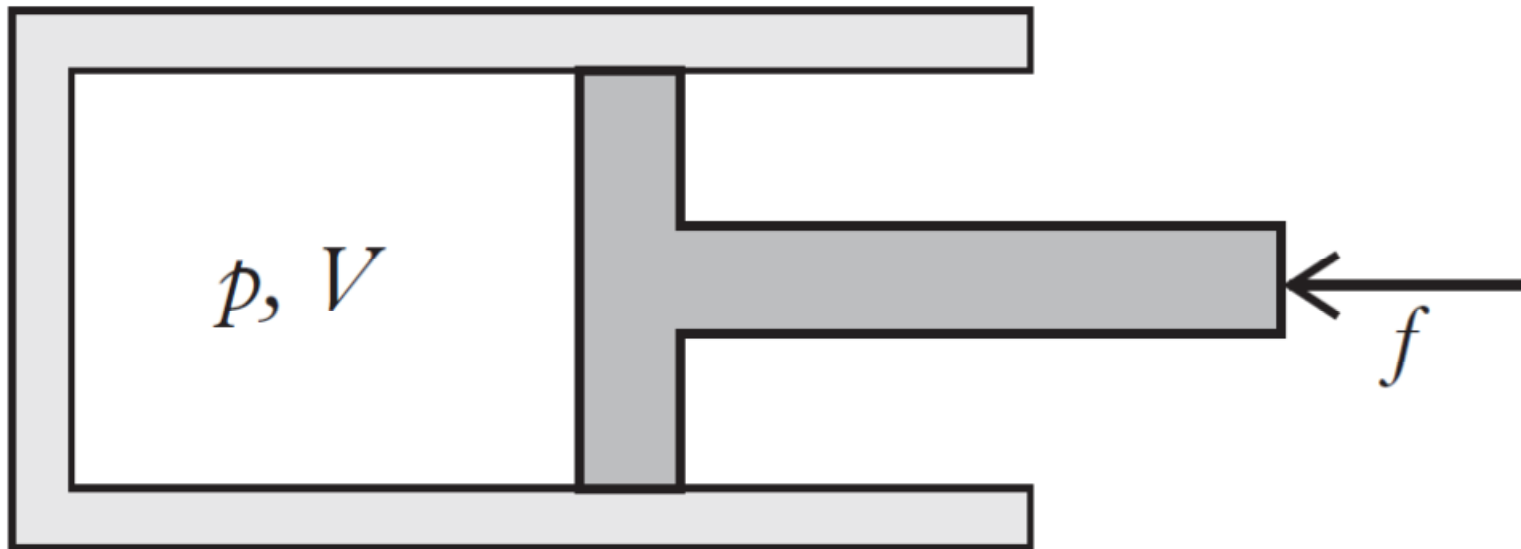
Make N copies and join them together.

Property unchanged (e.g. pressure, temperature) → **intensive**
Increased by factor N (e.g. total energy, volume, mass) → **extensive**
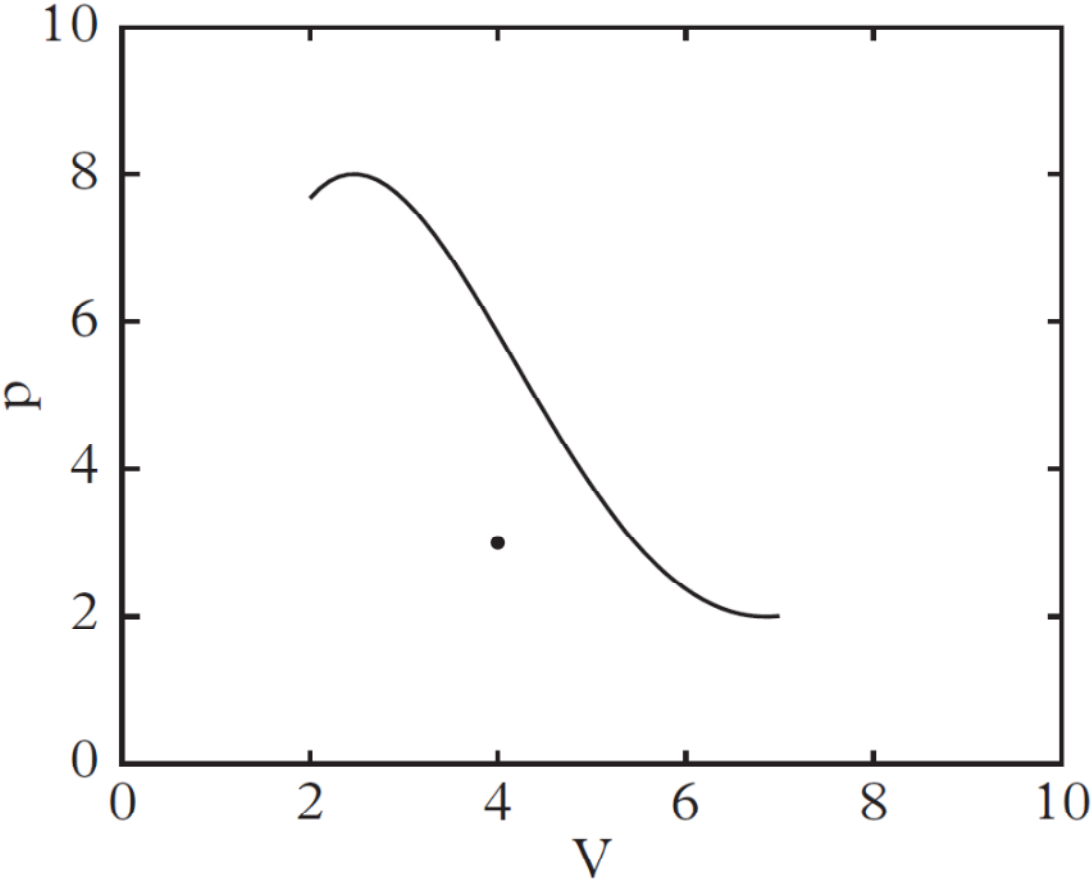Changed by some other factor → neither intensive nor extensive

Simple compressible system:

- It can be compressed
- Just two quantities (e.g. pressure, volume) are sufficient to define the state

p, V

f

Indicator diagram

Function of state

A quantity F is a function of state if and only if the change ΔF, when a system passes between any given pair of states, depends only on the initial and final states, not on the path.
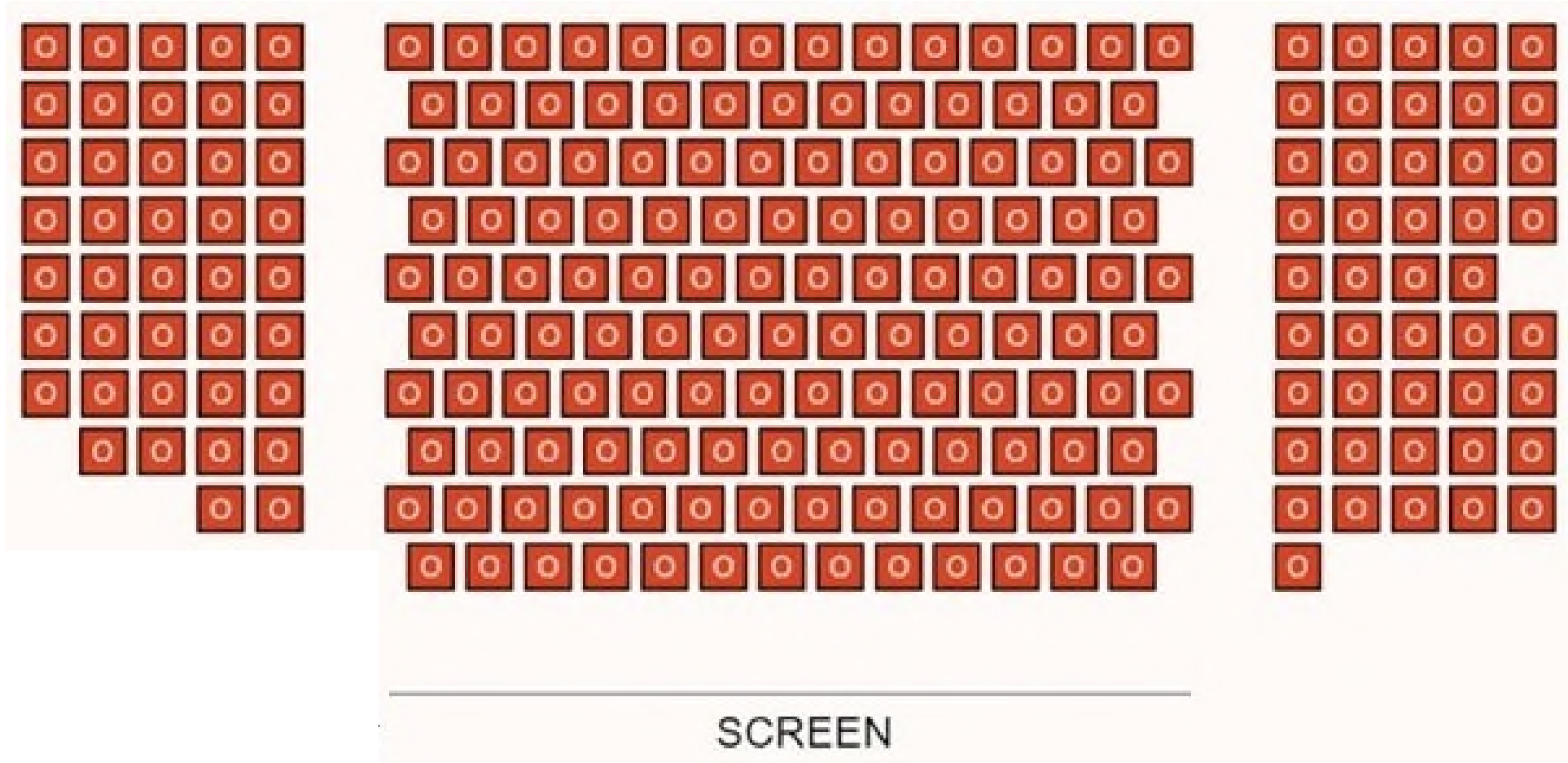
e.g. volume, pressure, temperature, heat capacity, compressibility, …

But not

heat delivered, work done, time taken to perform a change, …

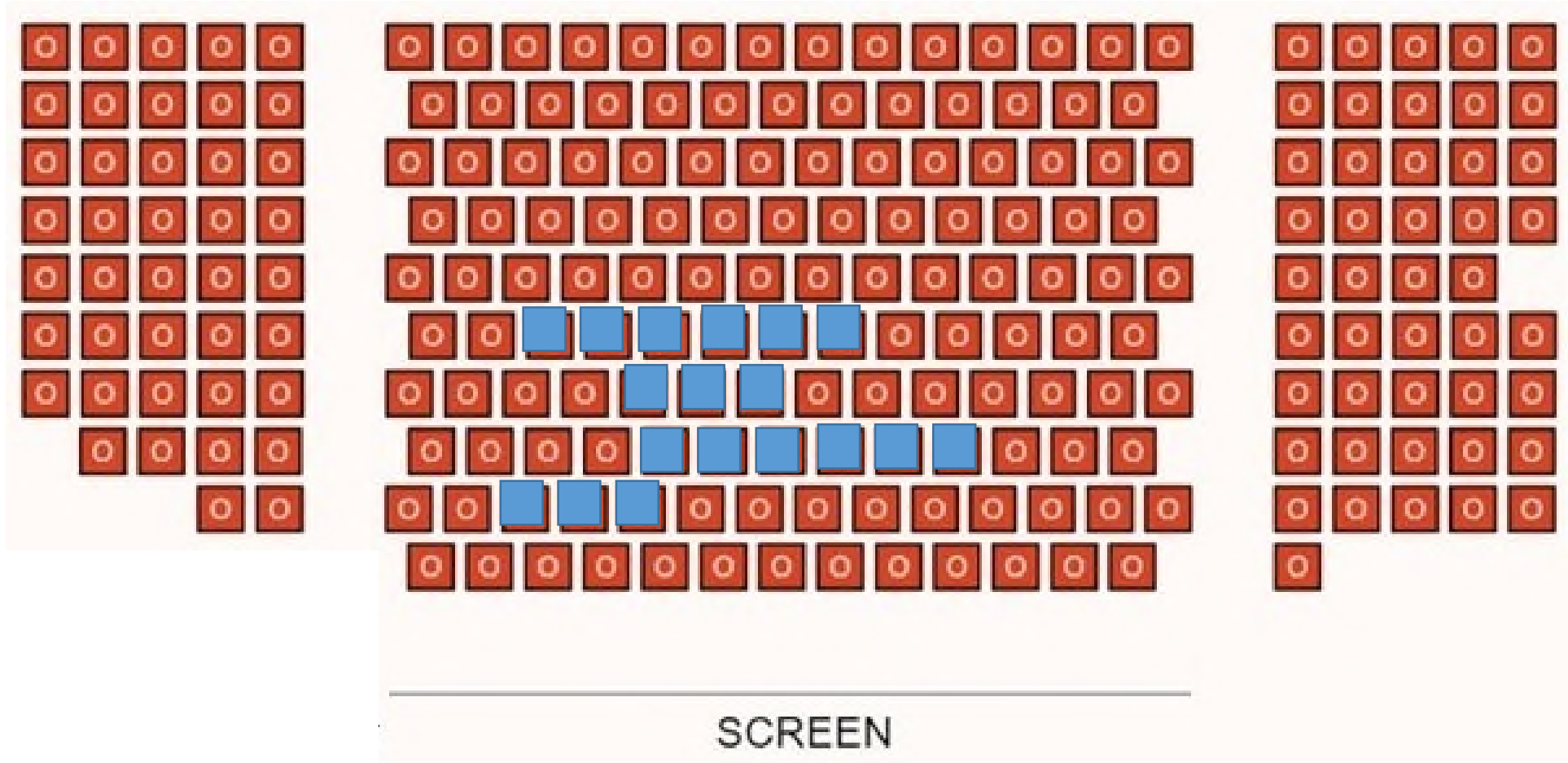Left door

Right door

SCREEN

Left door

Right door

SCREEN

Left door
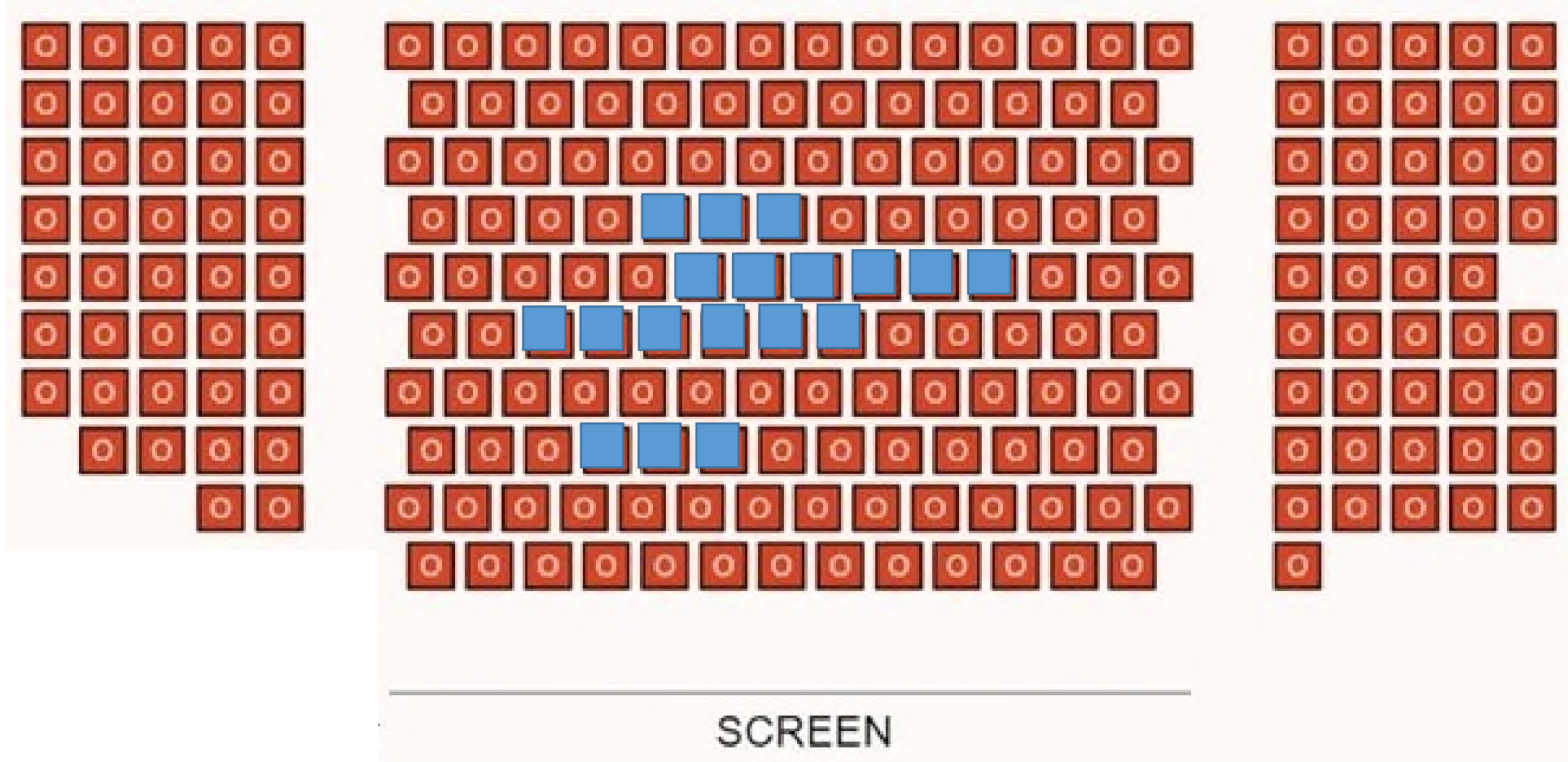
Right door

SCREEN

Left door

Right door

SCREEN

Heat

Work

Internal energy

SCREEN
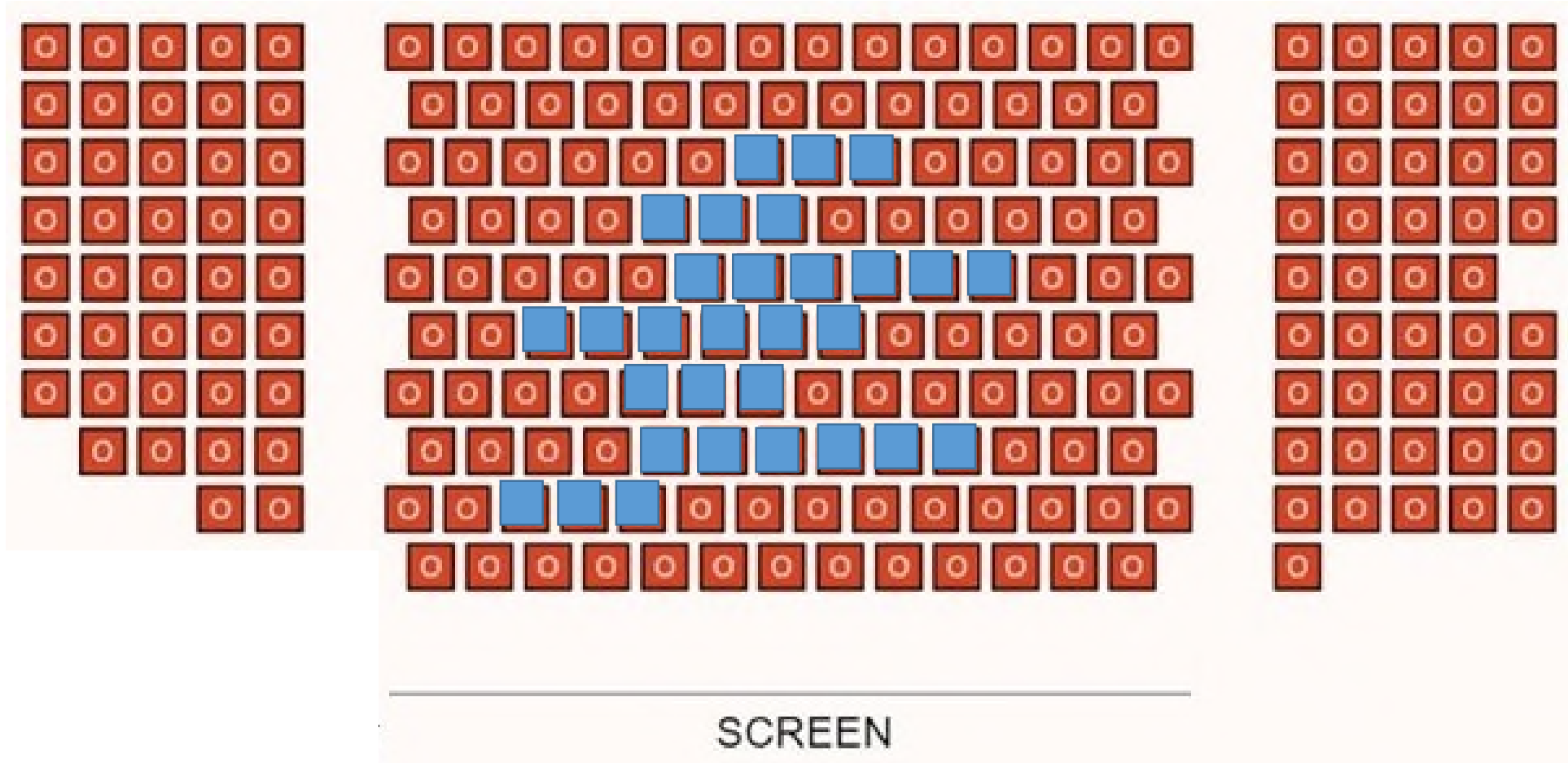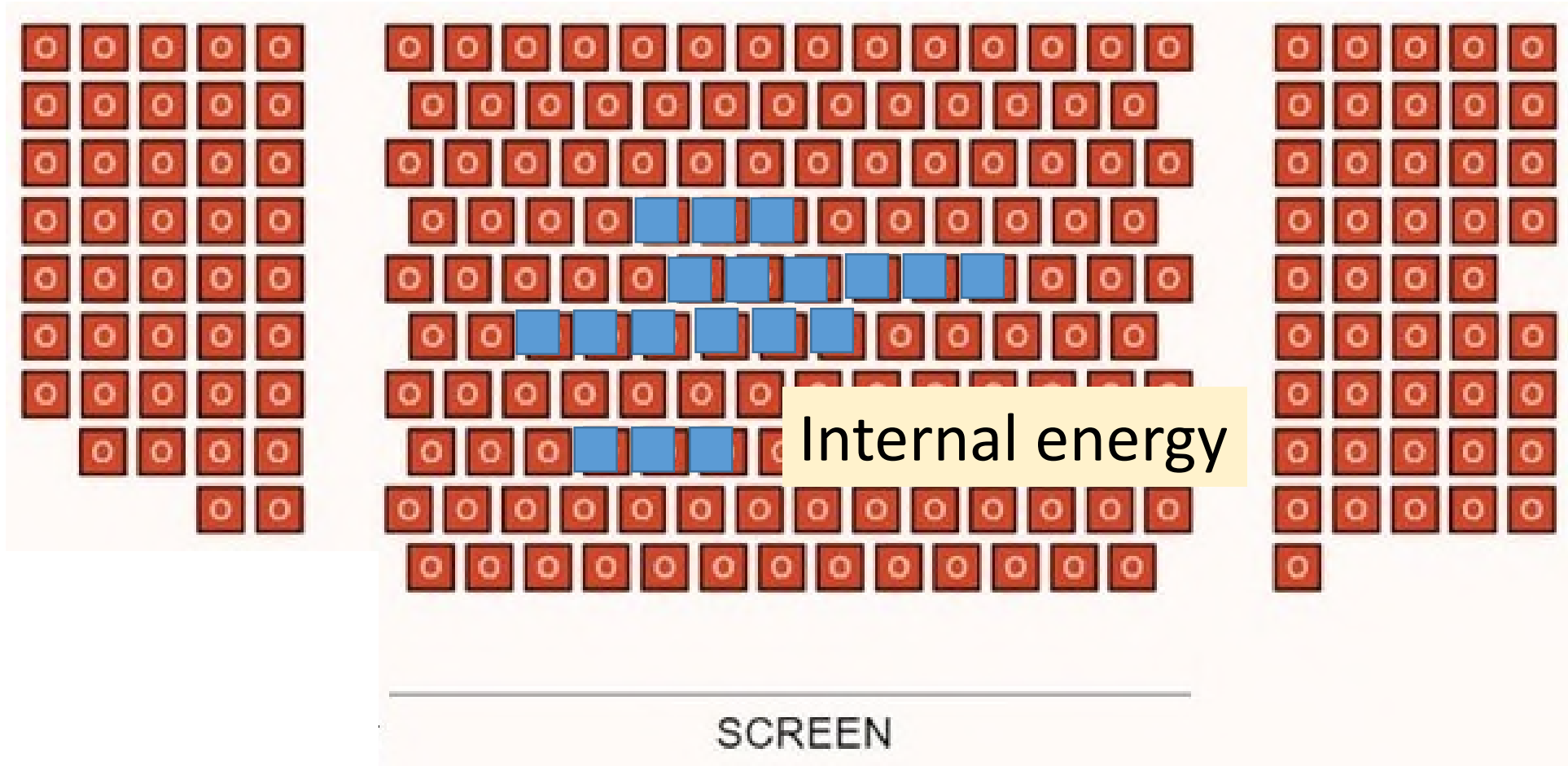
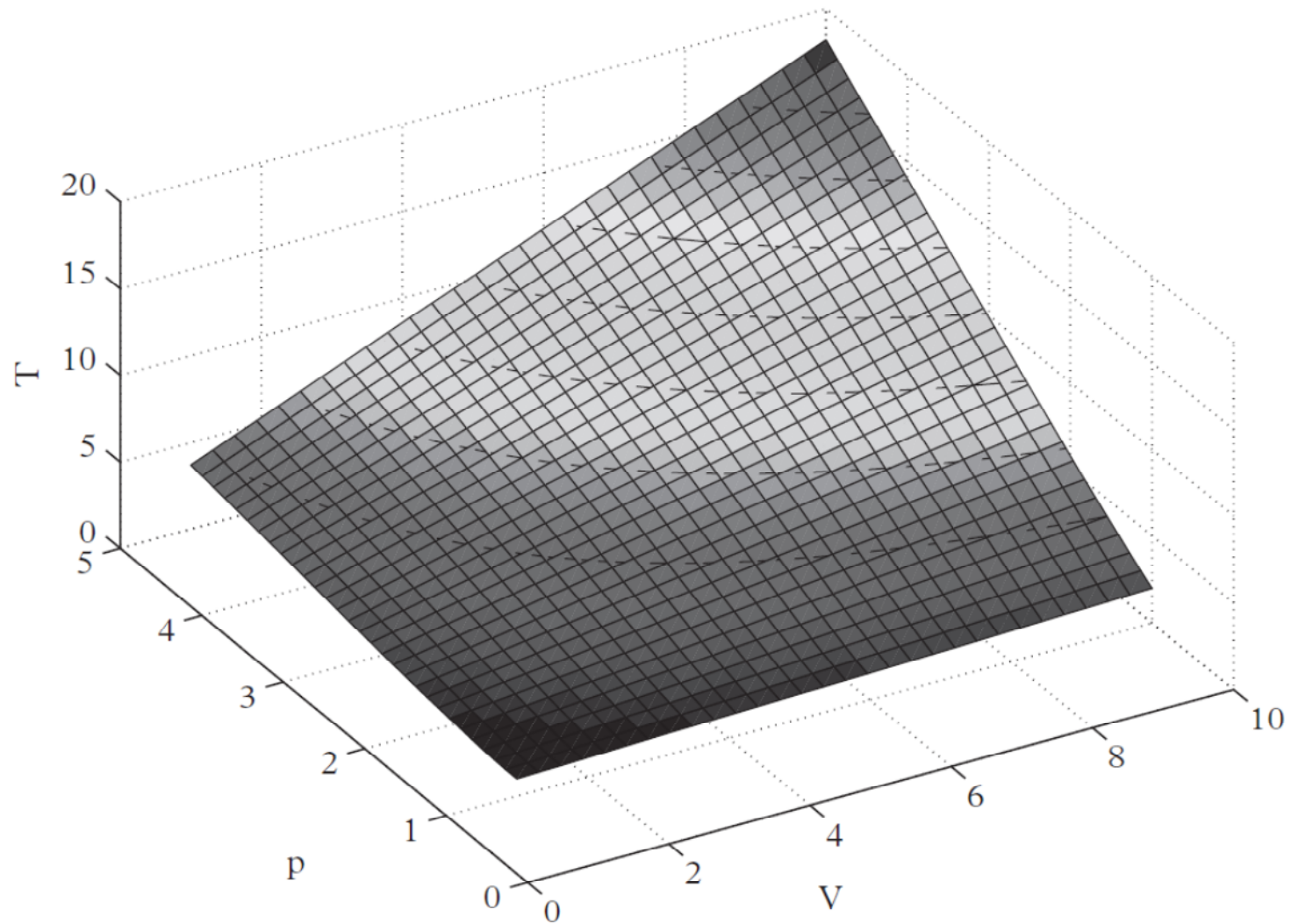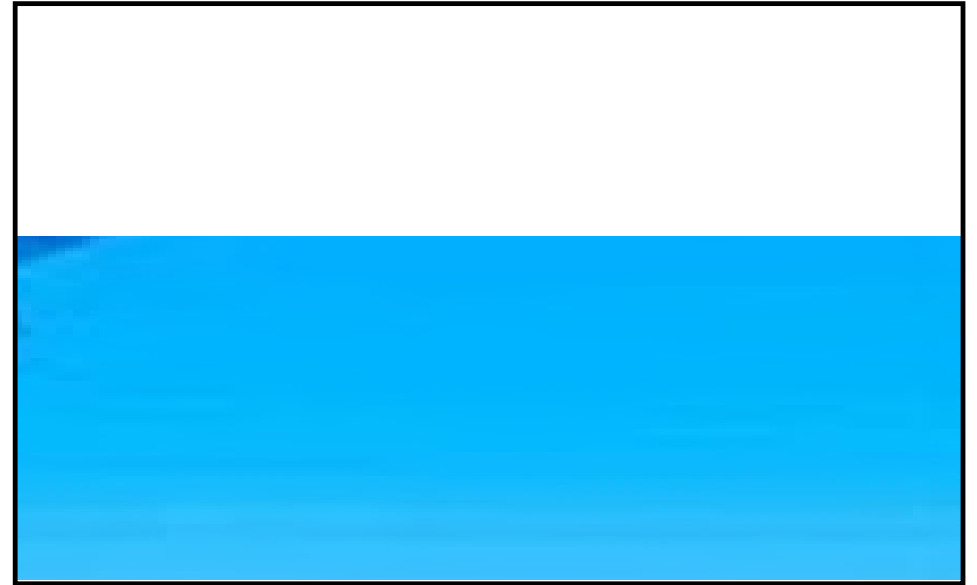# Function of state

$$\text{state of system} \xrightarrow{\text{uniquely fixes}} \text{value of function of state}$$

Temperature is a function of state

Thermodynamic equilibrium:

the state which an undisturbed system tends to over time.

Thermal equilibrium: no heat flow

Mechanical equilibrium: no unbalanced forces

Chemical equilibrium: no movement of material between places or types

Thermal equilibrium and temperature
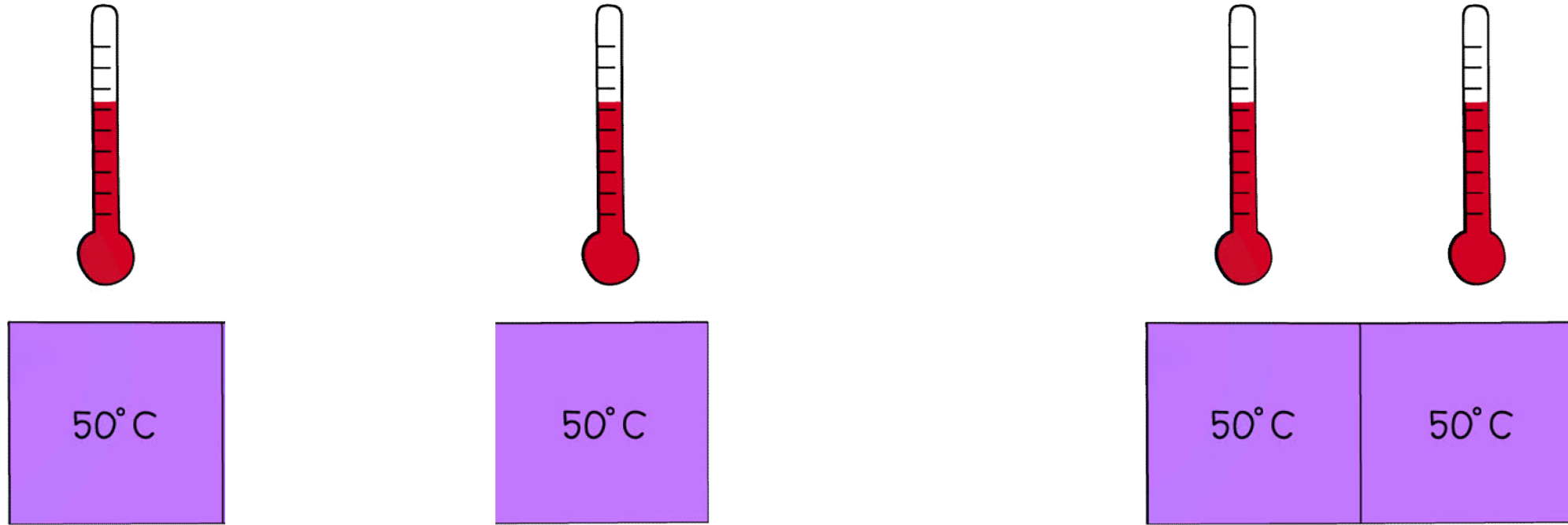
Temperature is defined as the property which indicates whether one body will be in thermal equilibrium with another. Two bodies which, if they were to be placed in thermal contact, would be found to be in thermal equilibrium with one another without any changes taking place, have, by definition, the same temperature.

Quasistatic

A process which can be considered, to sufficient approximation, as a sequence of equilibrium states.

Reversible

The direction can be reversed by an infinitesimal change;

the system can be returned to its initial state with no net change in the surroundings.

All reversible processes are quasistatic.

But not all quasistatic processes are reversible (e.g. toothpaste)
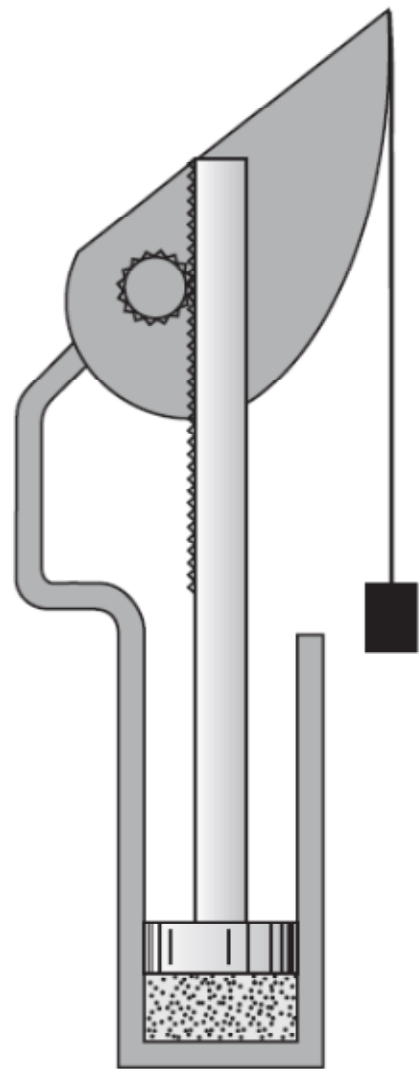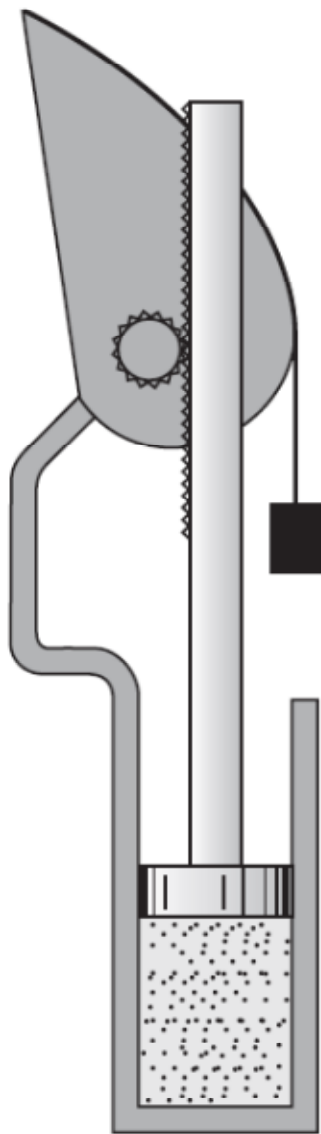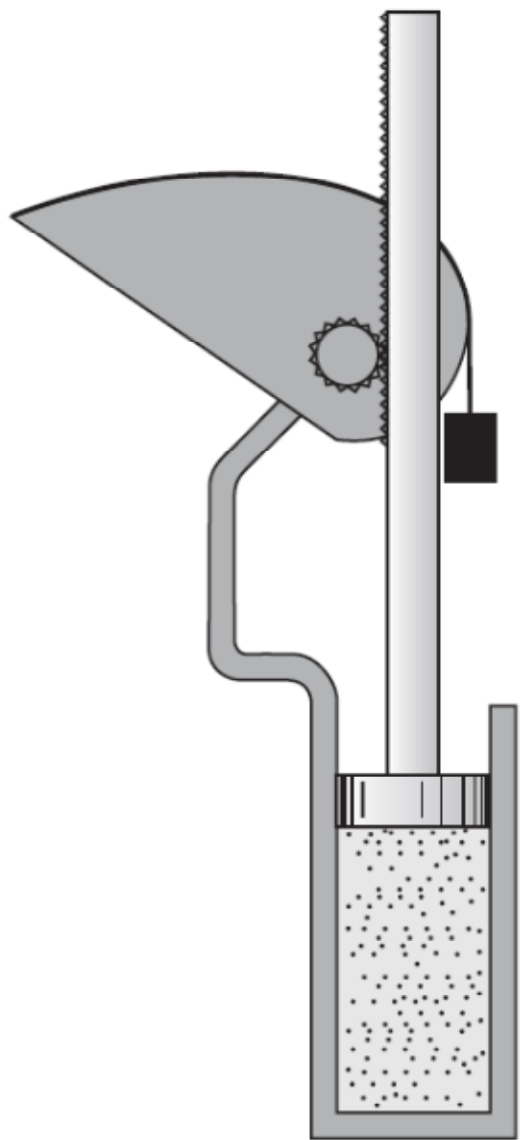
- Isothermal   = at constant temperature
  (and, N.B., there is usually heat flow)

- Adiathermal   = without heat flow

- Isentropic   = reversible and adiathermal

- Adiabatic   used to mean adiathermal; is now often taken
  to mean isentropic; that is how we will use it

Name	Definition	Value for ideal gas
Isothermal compressibility	$\kappa_T = -\dfrac{1}{V}\left.\dfrac{\partial V}{\partial p}\right|_T$	$\dfrac{1}{p}$
Adiabatic compressibility	$\kappa_S = -\dfrac{1}{V}\left.\dfrac{\partial V}{\partial p}\right|_S$	$\dfrac{1}{\gamma p}$
Isobaric expansivity	$\alpha = \dfrac{1}{V}\left.\dfrac{\partial V}{\partial T}\right|_p$	$\dfrac{1}{T}$
Heat capacity at constant volume	$C_V = \dfrac{\text{đ}Q_V}{\mathrm{d}T}$	typically in the range $1.5\text{–}3Nk_B$
Heat capacity at constant pressure	$C_p = \dfrac{\text{đ}Q_p}{\mathrm{d}T}$	$C_V + Nk_B$
Isothermal bulk modulus	$B_T \equiv 1/\kappa_T$	p
Adiabatic bulk modulus	$B_S \equiv 1/\kappa_S$	γp

Thermal reservoir
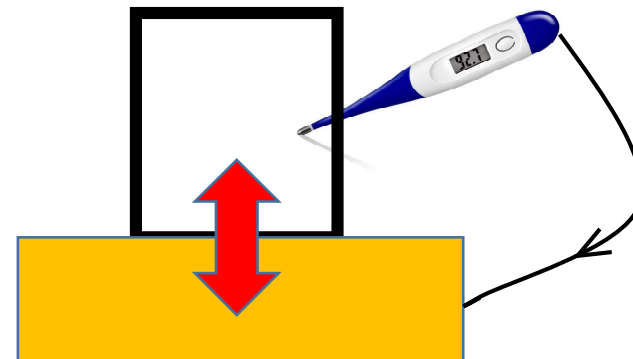## (a.k.a. "heat bath"):
a body in/out of which arbitrary amounts of heat can be transferred without affecting the temperature.
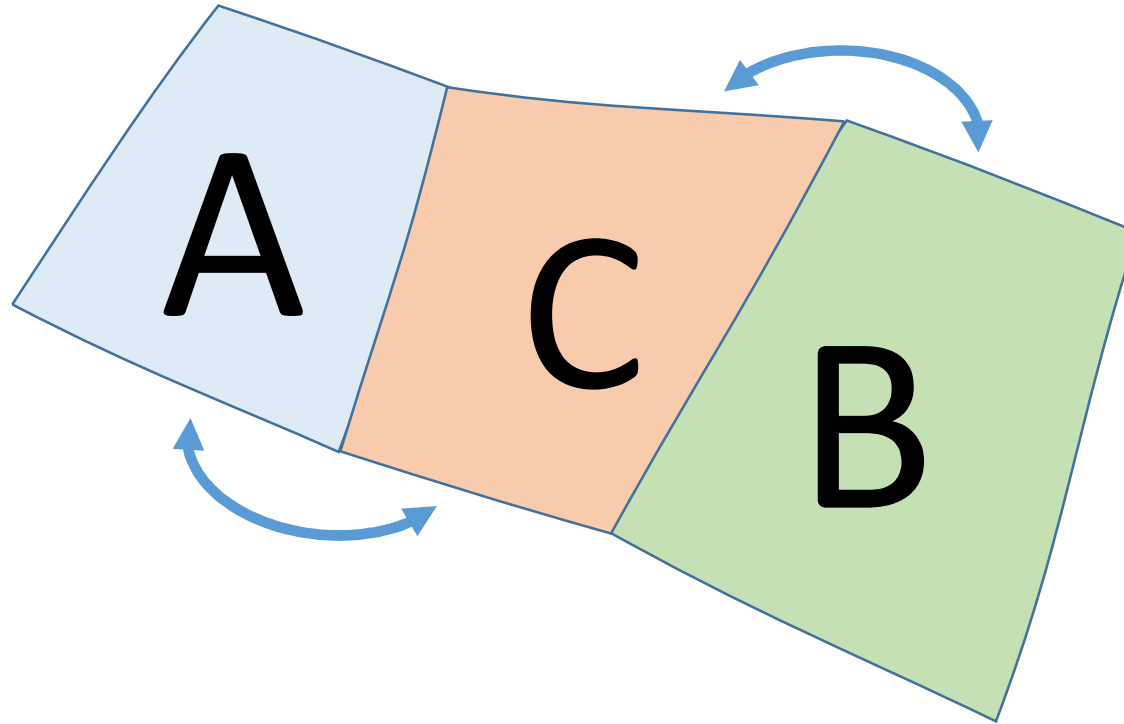
e.g.
1. The Pacific Ocean (approximately)

2. An apparatus with a thermostat (i.e. temperature sensor and heater/cooler in a feedback loop)

Zeroth law

If two bodies A and B are separately in a condition of thermal equilibrium with a third, then they must be in thermal equilibrium with one another.

First law

Energy is conserved.

The alternative statement is

The amount of work required to change the state of a thermally isolated system depends solely on the initial and final states.

The second law of thermodynamics

Clausius statement: No process is possible whose sole effect is the transfer of heat from a colder to a hotter body.

Kelvin statement: No process is possible whose sole effect is to extract heat from a single reservoir and convert it into an equivalent amount of work.

Carathéodory statement: In the neighbourhood of any state K of a thermally isolated system, there are states K' which are inaccessible from K.

Entropy statement: There exists an additive function of state known as the *equilibrium entropy* S, which can never decrease in a thermally isolated system.

Where we are heading

Zeroth law	$\rightarrow$	T (temperature)
First law	$\rightarrow$	U (energy)
Second law	$\rightarrow$	S (entropy)

The fundamental relation: $\qquad \mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$

Ratio of heats for a reversible engine: $\qquad \dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2}.$