Equilibrium does <u>not</u> mean "no change" or "no motion"

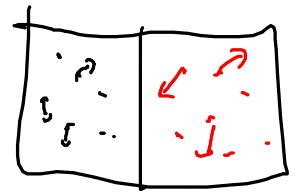
- there may be "flows" from one side to the other & vice versa! these flows will be equal at equilibrium
- fluctuations occur around equilibrium

$$\langle |\Delta N_L| \rangle \propto \sqrt{N}$$

as system size increases, fluctuations increase too

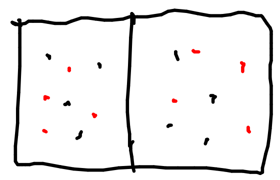
<u>but</u> relative fluctuations $\dfrac{\langle \Delta N \rangle}{N} \propto \dfrac{\sqrt{N}}{N} = \dfrac{1}{\sqrt{N}}$

Add faster particles on the right



lower KE higher KE

let them diffuse



KE's are equal

Energy has flowed from right to left due to mathematics!

Not due to forces or interactions

This flow of energy due to random processes is called heat

Flows of energy due to forces are called work.

Heat & work are processes, not properties.

A cup of coffee does not "have a lot of heat in it"

it has a lot of thermal energy.

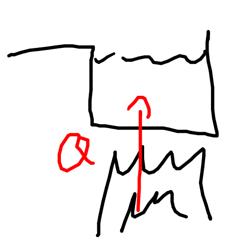
Two systems are in thermal equilibrium when they have the same temperature T.

When they are not in th. eq., heat Q flows from higher T to lower T always.

If an energy flow is not heat, it's work W.

e.g. rub hands together: work

pot on a stove



: heat

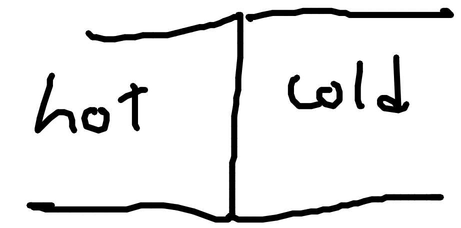
warm up soup in a microwave

- Work to warm up water molecules
- Heat flows into other parts of soup.

Types of Heat

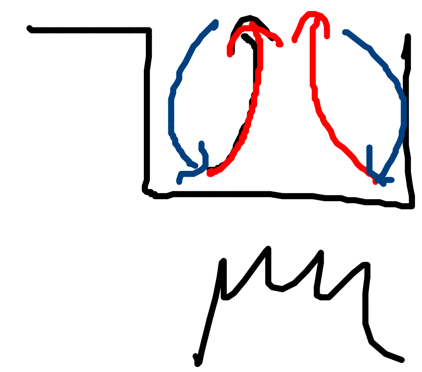
1) conduction: physical contact

heat is exchanged from atom to atom



2) convection: due to a flow of particles carrying thermal energy with them

only in fluids

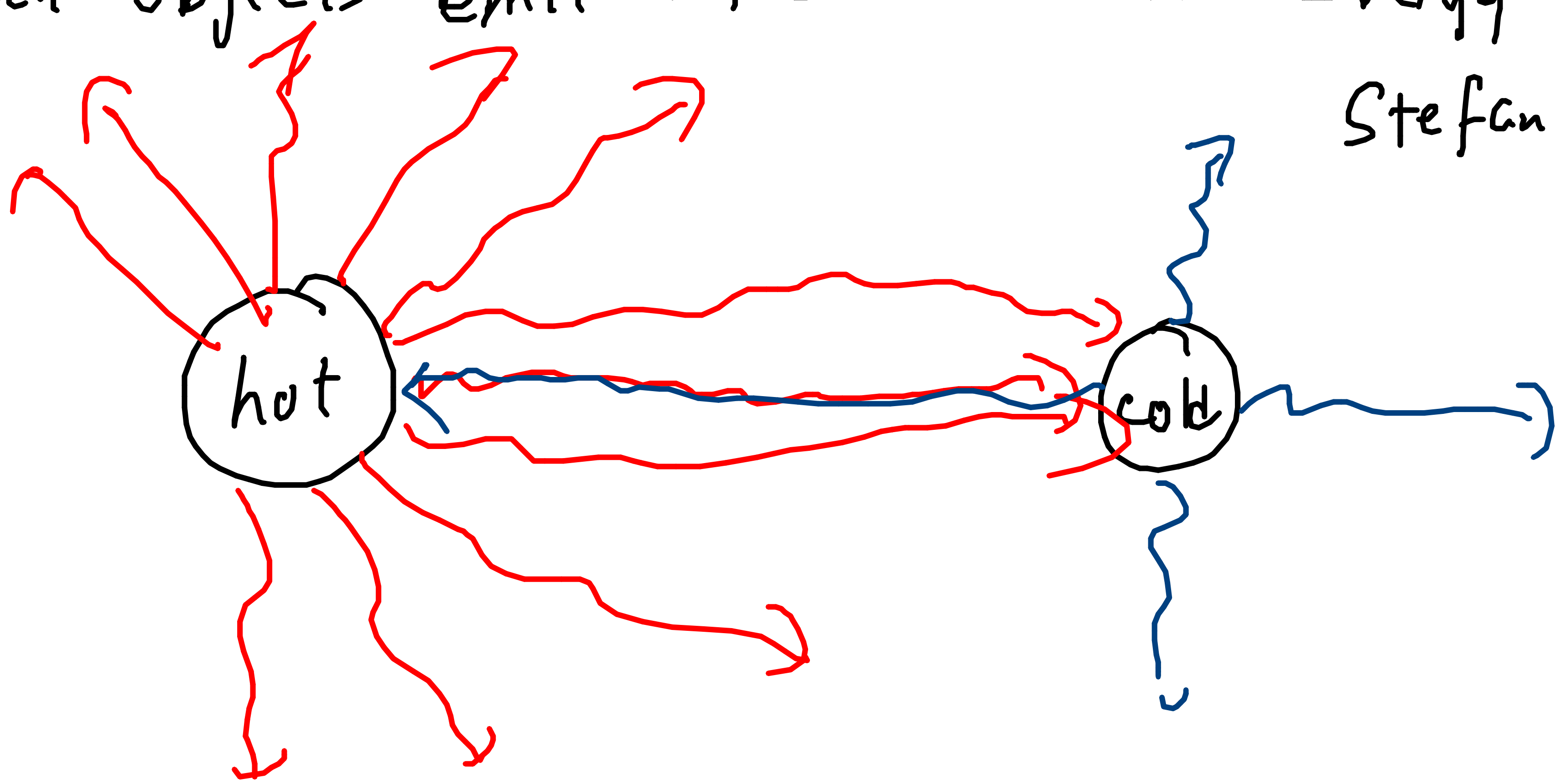


3) radiation: can occur in a vacuum

all objects emit EM radiation

Energy ~ T^4

Stefan's Law



net flow of radiated energy from hot to cold: heat

Objects possess thermal energy U

$$\Delta U = Q + W$$ 1st law of thermodynamics (conservation of energy)

$Q, W > 0$ when they flow into the system

For a system of point particles, thermal energy is due to their kinetic energy KE (relative to their Center-of-mass KE)

$$U = \sum_{i=1}^{N} KE_i = \frac{1}{2} m_1 |\vec{v}_1|^2 + \frac{1}{2} m_2 v_2^2 + \frac{1}{2} m_3 v_3^2 + \cdots$$

in 3D
$$= \left(\frac{1}{2} m_1 v_{1x}^2 + \frac{1}{2} m_1 v_{1y}^2 + \frac{1}{2} m_1 v_{1z}^2\right) + \cdots$$

Each of $v_{1x}, v_{1y}, v_{1z}, v_{2x}, \ldots$ is a <u>degree of freedom</u> (d.o.f.)

U is a function of these $3N$ variables

Each term in the sum above is a d.o.f. term $\frac{1}{2} m_1 v_{1x}^2, \frac{1}{2} m_5 v_{5z}^2, \ldots$

In general, each term is different at a given moment in time.

$\frac{1}{2} m_2 v_{2x}^2 = 1 J$
$\frac{1}{2} m_2 v_{2y}^2 = 8 J$

$\frac{1}{2} m_1 v_{1x}^2 = 5 J$
$\frac{1}{2} m_1 v_{1y}^2 = 0 J$

In equilibrium, the time average of each d.o.f. term is same: $\langle \frac{1}{2} m_1 v_{1x}^2 \rangle = \cdots = \frac{1}{2} k_B T$

k_B: Boltzmann constant 1.38×10^{-23} J/K

T: absolute temperature (in Kelvin)

<u>Equipartition Theorem</u>