# Thermodynamics

**Thermo** : heat
**dynamics** : motion
Thermodynamics is the study of motion of heat.

- Time and Causality
- Engines
- Properties of matter

# The only subject it makes sense to learn

$$m_\alpha \ddot{\mathbf{x}}_\alpha = \mathbf{f}_\alpha \quad \text{with} \quad \mathbf{f}_\alpha = -\sum_{\beta=1,\beta\neq\alpha}^{\mathcal{N}} \frac{\partial \Phi_{\beta\alpha}}{\partial \mathbf{x}_\alpha} .$$

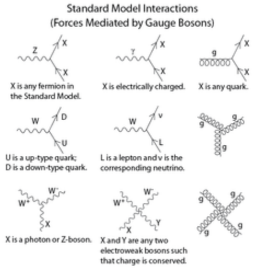
$$i\hbar\gamma^\mu\partial_\mu = mc\psi E^2 = p^2c^2 + m^2c^4 \quad \left[\frac{-\hbar^2}{2m}\nabla^2 + V\right]\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

$$\nabla \cdot \mathbf{D} = \rho$$
$$\nabla \cdot \mathbf{B} = 0$$
$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$
$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}$$

Time Dilation $\quad T_0 = \left[1 - \frac{v^2}{c^2}\right]^{1/2} T$

Length Contraction $\quad L = \left[1 - \frac{v^2}{c^2}\right]^{1/2} L_0$

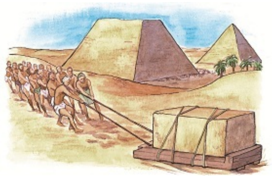
Relativistic Mass Increase $\quad m(v) = \left[1 - \frac{v^2}{c^2}\right]^{-1/2} m_0$



# Thermodynamics allows you to learn


Only thermodynamics breaks time-reversal symmetry.
(strictly CPT(i) )

# How physics came to rule the world



After DIY, work was achieved through military/politics

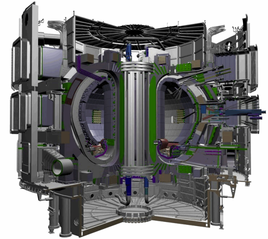
With help from physics.

Then the biologists got going.

# How physics came to rule the world


Chemists too,

Thermodynamics drove the modern world

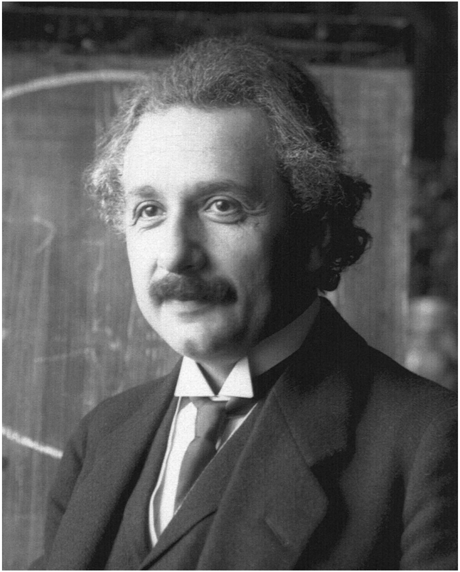


And physics is the future.

# A short list of things you already know

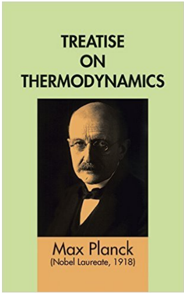
- Phases of matter: solids, liquids and gasses
- Ideal gases. Kinetic theory; Maxwell-Boltzmann velocity distributions; degrees of freedom and equipartition theorem.
- Non-ideal gases. Lennard-Jones type interaction; van der Waals; phase coexistence.
- Liquid phase. vapour pressure; surface tension.
- Properties of materials: compressibility $\frac{1}{V}\frac{dV}{dP}$, heat capacity $\frac{dQ}{dT}$ , thermal expansivity $\frac{1}{V}\frac{dV}{dT}$ , latent heat
- Elasticity and deformations. Young's modulus; sound waves; bulk modulus;
- *Flow and transport phenomena. Bernoulli's equation; viscosity; Reynolds number; thermal and electrical conductivity.*

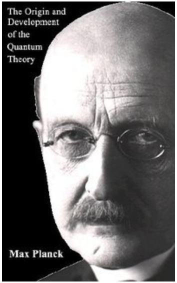
# Einstein's Opinion



*Thermodynamics is the only physical theory of universal content which I am convinced, within the areas of applicability of its basic concepts, will never be overthrown.*
A. Einstein 1949

# How Planck discovered his law of black-body radiation



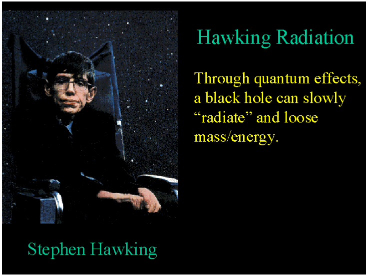

*I had no alternative but to tackle the problem again ... from the side of thermodynamics. In fact, my previous studies of the Second Law of Thermodynamics came to stand me in good stead now, for at the very outset I hit upon the idea of correlating not the temperature of the oscillator but its entropy with the energy... While a host of outstanding physicists worked on the problem of the spectral energy distribution both from the experimental and theoretical aspect, every one of them directed his efforts solely towards exhibiting the dependence of the intensity of radiation on the temperature. On the other hand, I suspected that the fundamental connection lies in the dependence of entropy with the energy ... Nobody paid any attention to the method which I adopted and I could work out by calculations completely at my leisure, with absolute thoroughness, without fear of interference or competition.*

Using thermodynamics, Hawking showed that black holes with mass, charge, angular momentum have *entropy* and *temperature*.

Entropy is proportional to the surface area of the event horizon.

Temperature is inversely proportional to mass.

Temperature means they give off black-body radiation. Field theory calculations are consistent with this idea.




*"Just outside the event horizon there will be virtual pairs of particles, one with negative energy and one positive. The negative energy particle can tunnel into the hole, while the positive energy one escapes to infinity."*

# Main postulate of EQUILIBRIUM thermodynamics

Isolated systems settle into **equilibrium states** having uniform **macroscopic** properties (in the absence of potentials)*,
e.g. uniform pressure, temperature, density, magnetisation etc.

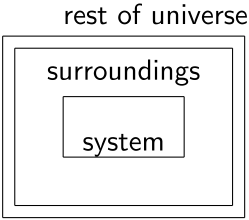
> *An equilibrium state is one in which all the bulk physical properties do not change with time and are uniform throughout the system*.*

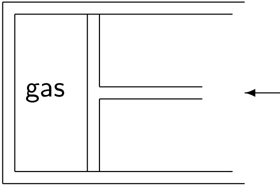
* for the special case where there is phase separation the system comprises homogeneous portions, with uniform properties in each portion.
**Note** Surroundings and system need not be in equilibrium with each other.

# Definitions

Sample of interest = the **system**,
interacts with **surroundings**,

- System and surroundings are separated by some kind of **boundary** wall.
- The **boundary** defines what is held constant in the system.
- e.g. a moving piston means *volume* is not constant
- A well insulated piston means no heat flow - *adiabatic*
- Slow compression with no insulation means the temperature in constant - *isothermal*
- In a thermodynamic process, how *system* variables change depends on *surroundings*

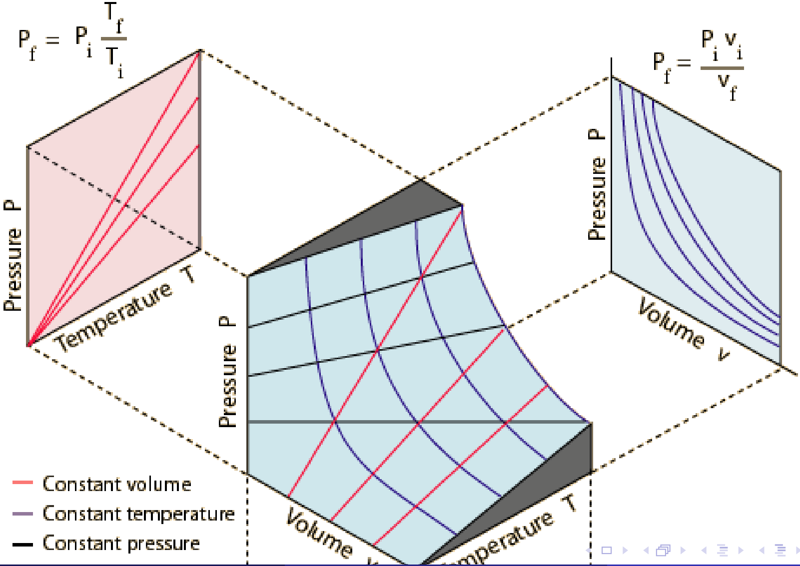


# State functions and state variables

- Thermodynamics is about MACROSCOPIC properties.
- The various properties that can be quantified without disturbing the system eg internal energy $U$ and $V$, $P$, $T$ are called *state functions* or *state properties*.
- Properties whose absolute values are easily measured eg. $V, P, T$ are also called state variables.
- Relations between state functions for a particular material are called the equation of state of the material.
- Ideal gas: PV=nRT

# Relationships between properties: Equation of state of Ideal Gas



# Experimentally observed Zeroth law of Thermodynamics.

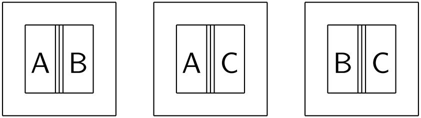
Consider two systems (A,B) in thermal contact.

**If** A and a third system C are brought into thermal equilibrium,

**and** this results in no change in the values of the state variables of A.

**then** it is observed that B and C, if put in thermal contact are also in thermal equilibrium with each other.

Diathermal, Movable walls:
Heat may flow, boundary may move.




Thermal and mechanical equilibrium.

This *observation* is the **Zeroth Law of Thermodynamics**:

# Zeroth Law of Thermodynamics

*Zeroth Law: If each of two systems is in thermal equilibrium with a third system they are in thermal equilibrium with each other.*

The argument can be repeated for fourth, fifth, ... systems (D, E, ...). If each is in thermal equilibrium with all the others, they must have the same value of some property that has a common value.

**This property is called thermodynamic temperature $T$.**

The direction of heat flow tells us which system is at higher temperature.

*Thermodynamic equilibrium temperature gives an ordering from cold to hot, and defines "equal temperature" but is not a numerical scale*

# Ideal Gas Temperature Scale

Empirical observation of Gas Laws leads to a temperature scale...

We choose: $T = T_{IG} = PV/nR$.

$T_{IG}$ has a value stated in "kelvin", denoted by the symbol K.

**Kinetic Theory Temperature Scale**

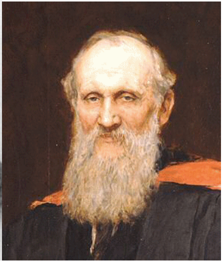
The kinetic theory connects empirical $T_{IG}$ to theoretical microscopic kinetic energy.

$$m\bar{v^2}/2 = (3/2)k_B T$$

introducing Boltzmann's Constant $k_B = R/N_A$

# A beardy equation

For each degree of freedom
Boltzmann's * Kelvins = Joules

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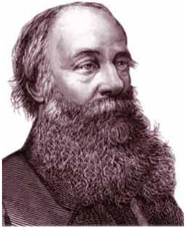

Thermodynamic equilibrium, ideal gas and kinetic energy "Temperatures" are *the same thing*

# Definition of temperature switched from water to sound ($k_B$)

Speed of sound in ideal gas is

$$
\begin{aligned}
c_0 &= \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_s} \\
&= \sqrt{\frac{\gamma P}{\rho}} \\
&= \sqrt{\frac{\gamma N_A k_B T}{M}}
\end{aligned}
$$

July 2013, NPL measured
$k_B = 1.38065156(98) \times 10^{23} J/K$
Using speed of sound in argon, by resonance of copper sphere whose diameter is known to 11.7nm (500 atoms)

More accurate than the measurement of the critical temperature of water.

http://iopscience.iop.org/0026-1394/50/4/354 Michael de Podesta et al 2013 Metrologia 50 354