

# PHYS430 - Thermal Physics

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# Chapter 1

## Energy in Thermal Physics

### 1.1 Thermal Equilibrium

- After two objects have been in contact long enough, we say that they are in **thermal equilibrium**.
- The time required for a system to come to thermal equilibrium is called the **relaxation time**.
- **Temperature** is a measure of the tendency of an object to spontaneously give up energy to its surroundings.
- The flow of energy is from the object with a higher temperature to the lower one.
- For low-density gas at constant pressure, the volume should go to *zero* at approximately  $-273^\circ\text{C}$ . which defines the **absolute zero**, in the **absolute temperature scale**, in K (kelvin).

### 1.2 The Ideal Gas

$$PV = nRT; \quad R = 8.31 \text{ J/mol K} \quad (1.1)$$

- A **mole** of molecules is Avogadro's number of them,  $6.02 \times 10^{23}$ .
- Number of molecules is  $N = n \times N_A$
- Ideal gas law becomes  $PV = NkT$ , where  $k$  is Boltzmann's constant.
- The average transnational kinetic energy is  $\bar{K}_{\text{trans}} = \frac{3}{2}kT$ , where  $kT = \frac{1}{40}\text{eV}$

### 1.3 Equipartition of Energy

**Equipartition theorem** At a temperature  $T$ , the average energy of any quadratic degree of freedom is  $\frac{1}{2}kT$ .

For a system of  $N$  molecules, each with  $f$  degree of freedom, and there are no other (non-quadratic) temperature-dependent forms of energy, then its **total thermal energy** is

$$U = Nf\frac{1}{2}kT \quad (1.2)$$

Note, This is the *average* total thermal energy, but for large  $N$ , fluctuations become negligible.

## 1.4 Heat and Work

- Total amount of energy in the universe never changes, **Conservation of energy**
- **Heat** any spontaneous flow of energy from one object to another, caused by difference in temperature.
- **Work**, in thermodynamics, is any other transfer of energy into or out of a system.
- Work and heat refer to energy *in transit*.
- The total energy in a system is determined, but not the work nor the heat, it's meaningless.
- We ask about how much heat *entered* a system and how much work *was done on* a system.
- $\Delta U = Q + W$  is just a statement of the law of conservation of energy, but it's still called **first law of thermodynamics**.
- Processes of heat transfer: Conduction, Convection, and Radiation.

## 1.5 Compression Work

- From classical mechanics work is  $W = \vec{F} \cdot d\vec{r}$
- Consider compressing gas with a piston of area  $A$  a distance  $\Delta x$ , the change in volume is  $\Delta V = -A\Delta x$
- Volume change should be quasistatic, meaning very slow so that the pressure defined is uniform. then  $W = P\Delta V$ , but  $\Delta x = -\Delta V/A$ ; minus since the volume decreases.
- $W = -P\Delta V$  - quasistatic.
- If  $P$  is not constant,

$$W = - \int_{V_i}^{V_f} P(V) dV \quad (1.3)$$

- **isothermal compression** is slow that the temperature doesn't raise.
- **adiabatic compression** is so fast that no heat escapes from the gas.
- Isothermal process
  - the change will be along an **isotherm** line, with  $P = NkT/V$ .
  - The work done is

$$W = - \int_{V_i}^{V_f} P(V) dV = NkT \ln \frac{V_i}{V_f} \quad (1.4)$$

- The heat enters the system, from the first law, is

$$Q = \Delta U - W = \underbrace{\Delta \left( \frac{1}{2} N f k T \right)}_0 - W = NkT \ln \frac{V_f}{V_i} \quad (1.5)$$

- adiabatic process

- In the PV plot the change is from one isotherm to another.
- There should be no transfer of heat so

$$\Delta U = Q + W = W \quad (1.6)$$

- If it's *ideal* gas,  $U$  is proportional to  $T$ , so the temperature increases.
- By the equipartition theorem  $U = \frac{f}{2}NkT$ , so  $dU = \frac{f}{2}Nk dT$ , then from (1.3)

$$\frac{f}{2}Nk dT = -P dV \quad (1.7)$$

Using the ideal gas law for  $P$  and integrate

$$\frac{f}{2} \ln \frac{T_f}{T_i} = -\frac{V_f}{V_i} \quad \text{or} \quad V_f T_f^{f/2} = V_i T_i^{f/2} = \text{const.} \quad (1.8)$$

- Using the ideal gas law to eliminate  $T$ ,  $V^\gamma P = \text{const.}$ ,  $\gamma$  is the **adiabatic exponent**.

## 1.6 Heat Capacities

- **Heat capacity** of an object is the amount of heat needed to raise its temperature, per degree change

$$C = \frac{Q}{\Delta T} \quad (1.9)$$

- The more matter you have the larger the heat capacity, by factoring out the mass  $m$  we get **specific heat**

$$c \equiv \frac{C}{m} \quad (1.10)$$

- Note (1.10) is ambiguous, plug in the first law

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T} \quad (1.11)$$

Even if the energy of an object is a well-defined function of its temperature alone, the work  $W$  done on the object is not; it depends on the process path on PV plot.

- From (1.11) The **heat capacity at constant volume**, denoted  $C_V$

$$C_V = \left( \frac{\Delta U}{\Delta T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V \quad (1.12)$$

- From (1.11) and (1.3) the **heat capacity at constant pressure**, denoted  $C_P$

$$C_P = \left( \frac{\Delta U - (-P\Delta V)}{\Delta T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P \quad (1.13)$$

for solid last term is almost negligible.

- At a **phase transformation**, you add heat in a system without increasing its temperature; such as melting of boiling water. Then  $C = \frac{Q}{\Delta T} = \infty$
- The amount of heat needed to do this phase transformation is called **latent heat**  $L$ , and the **specific latent heat** is

$$l \equiv \frac{L}{m} = \frac{Q}{m} \quad (1.14)$$

It's ambiguous, but we assume the pressure is constant, and no other work done.

- Adding  $PV$  onto the energy gives the **enthalpy**

$$H = U + PV \quad (1.15)$$

it's the *total* energy you would need to create the system out of nothing.

# Chapter 2

## The Second Law

### 2.1 Two-State system

- Irreversible processes are not *inevitable*, they are just overwhelmingly *probable*.
- A **microstate** is an outcome.
- A **macrostate** is saying number of particle for each state, e.g., two heads.
- **multiplicity** of a macrostate is the number of microstates for a given macrostate.
- Total multiplicity of all macrostates is the total number of microstates. Then the probability of a macrostate is

$$p = \frac{\Omega(n)}{\Omega(\text{all})} \quad (2.1)$$

- Number of different ways of choosing  $n$  items out of  $N$ , or the *combination* of  $n$  chosen from  $N$ .

$$\Omega(N, n) = \frac{N!}{n!(N-n)!} = \binom{N}{n} \quad (2.2)$$

### 2.2 The Einstein Model of a Solid

Consider a collection of microscopic system that can each store any number of energy ‘units’ Equal-size energy units as in quantum harmonic oscillator.

- In three-dimensional solid, each atom can oscillate in three independent directions, for  $N$  oscillators there are  $N/3$  atoms.
- The multiplicity of an Einstein solid with  $N$  oscillators and  $q$  energy units is

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!} \quad (2.3)$$

## 2.3 Interacting Systems

To understand the heat flow and irreversible processes, consider two Einstein solids that can share energy back and forth

- Assume the two solids are **weakly coupled**; the exchange of energy between them is slower than the exchange of energy among atoms within each solid.
- Then the individual energies of solids,  $U_A$  and  $U_B$ , will change slowly; over short time they are fixed.
- On longer time scales the values of  $U_A$  and  $U_B$  will change, so we consider  $U_{\text{total}} = U_A + U_B$ .
- The total multiplicity for independent system is just the product of  $\Omega_A$  and  $\Omega_B$ .
- **Fundamental assumption of statistical mechanics** In an isolated system in thermal equilibrium, all accessible microstates are equally probable.
- Invoking this principle on the two Einstein solids, we conclude that, while all the *microstates* are equally probable, some *macrostates* are more probable than others.
- The *heat*, then, is a probabilistic phenomenon; if system started *initially* with all the energy in solid  $B$  and wait for a while, it's more certain to find that the energy has flowed from  $B$  to  $A$ .
- The tendency of increasing multiplicity is the **second law of thermodynamics**.

## 2.4 Large Systems

- There are three categories of numbers here:
  - **small numbers**, 12, 43
  - **large numbers**, in order of Avogadro's number  $10^{23}$
  - **very large numbers**, exponentiating of large numbers.
- Adding a small number to a large number doesn't change. Multiplying a large number by a very large number.
- Using Stirling's approximation for factorial of a large number

$$N! \approx N^N e^{-N} \sqrt{2\pi N}; \quad N \gg 1 \quad (2.4)$$

- The approximated multiplicity is

$$\Omega(N, q) \approx \left(\frac{eq}{N}\right)^N; \quad q \gg N \quad (2.5)$$

within the high-temperature limit.

- Multiplicity of two Einstein interacting solids with  $N$  oscillators and total  $q$  energy units is

$$\Omega = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N \quad (2.6)$$

- Taking  $\Omega = \Omega(q_A)$ , it has a peak at  $q_A = q/2$  with a very large number value of

$$\Omega_{\text{max}} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N} \quad (2.7)$$



- Around this maximum,  $\Omega$  is a **Gaussian** as

$$\Omega = \Omega_{\max} e^{-N(2x/q)^2} \quad (2.8)$$

- $\Omega = \Omega_{\max}/e$  when

$$x = \frac{q}{2\sqrt{N}}$$

the width is  $q/\sqrt{N}$

## 2.5 The Ideal Gas

For ideal gas the states are proportional to the ‘volume’ of available **momentum space**.

$$\Omega_1 \propto V \cdot V_p$$

To have a finite number of microstates we invoke quantum mechanics principles of wavefunction, which is spread in both position and momentum spaces; it adheres to the *Heidenberg*

The molecule’s kinetic energy equals  $U$ ,

$$U = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \quad \text{or} \quad p_x^2 + p_y^2 + p_z^2 = 2mU \quad (2.9)$$

which is the surface of a *sphere* in momentum space with radius  $\sqrt{2mU}$

Multiplicity of an ideal gas of two *distinguishable* molecules is

$$\Omega_2 = \frac{V^2}{h^6} A \quad (2.10)$$

Where  $A$  is area of momentum hypersphere.

Multiplicity of an ideal gas of two *indistinguishable* is less by a foactor of 2

$$\Omega_2 = \frac{1}{2} \frac{V^2}{h^6} A \quad (2.11)$$

For an ideal gas of  $N$  indistinguishable molecules

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \times A \quad (2.12)$$

where  $A$  is surface area of a  $3N$ -dimnensional hypersphere whose radius  $\sqrt{2mU}$ .

Surface area of hypersphere in  $d$ -dimensional is

$$A = \frac{2\pi^{d/2}}{(\frac{d}{2} - 1)!} r^{d-1} \quad (2.13)$$

Then, having that  $d = 3N$  and  $r = \sqrt{2mU}$ ,

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} (\sqrt{2mU})^{3N-1} \approx \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2})!} (\sqrt{2mU})^{3N} \quad (2.14)$$