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 on.

- For low-density gas at constant pressure, the volume should go to *zero* at approximately $-273°$C. which defines the **absolute zero**, in the **absolute temperature scale**, in K (kelvin).

1.2 The Ideal Gas

$$PV = nRT; \qquad R = 8.31 \, \text{J/mol K} \tag{1.1}$$

- A **mole** of molecules is Avogadro's number of them, 6.02×10^{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

$$U = Nf\frac{1}{2}kT \tag{1.2}$$

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 form on e 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   Commpression Work

- From classical mmechanics work is $W = \vec{F} \cdot d\vec{r}$

- Consider compressing gas with a piston of area A a distance Δx, 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 $W = PA\Delta V$, but $\Delta x = -\Delta V$; minus since the volume decreases.

- $W = -PA\Delta V$ - quasistatic.

- If P is not constant,

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

- **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

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

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

$$Q = \Delta U - W = \underbrace{\Delta(\tfrac{1}{2}NfkT)}_{0} - W = NkT\,\ln\frac{V_f}{V_i} \tag{1.5}$$

- adiabatic process

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

$$\Delta U = Q + W = W \tag{1.6}$$

  - 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)

$$\frac{f}{2}Nk\,dT = -P\,dV \tag{1.7}$$

  Using the ideal gas law for P and integrate

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

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

$$C = \frac{Q}{\Delta T} \tag{1.9}$$

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

$$c \equiv \frac{C}{m} \tag{1.10}$$

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

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T} \tag{1.11}$$

  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

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

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

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

  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

$$l \equiv \frac{L}{m} = \frac{Q}{m} \tag{1.14}$$

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

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

$$H = U + PV \tag{1.15}$$

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.

- **multiplcity** 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

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

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

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

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

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

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 then the exchange of energy among atom 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 $U_{\text{total}} = U_A + U_A$

- The total multiplicity for independent system is just the product of Ω_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 *micro*states are equally probable, some *macro*states 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 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

$$N! \approx N^N e^{-N} \sqrt{2\pi N}; \qquad N \gg 1 \tag{2.4}$$

- Or for N is a large number, roughly

$$N! \approx \left(\frac{N}{e}\right)^N = N^N e^{-N} \tag{2.5}$$

- For *logarithm* of $N!$ from above result

$$\ln N! \approx N \ln N - N \tag{2.6}$$

- The approximated multiplicity is

$$\Omega(N, q) \approx \left(\frac{eq}{N}\right)^N; \qquad q \gg N \tag{2.7}$$

within the high-temperature limit.

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

$$\Omega = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N \tag{2.8}$$

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

$$\Omega_{\text{max}} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N} \tag{2.9}$$

- Around this maximum, Ω is a **Gaussian** as

$$\Omega = \Omega_{\text{max}} e^{-N(2x/q)^2} \tag{2.10}$$

- $\Omega = \Omega_{\text{max}}/e$ 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 wavefuntion, which is spread in both position and momentum spaces; it adheres to the *Heisenberg*

- The molecule's kinetic energy equals U,

$$U = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \quad \text{or} \quad p_x^2 + p_y^2 + p_z^2 = 2mU \tag{2.11}$$

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

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

$$\Omega_2 = \frac{V^2}{h^6} \times A \tag{2.12}$$

Where A is area of momentum hypersphere.

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

$$\Omega_2 = \frac{1}{2}\frac{V^2}{h^6} \times A \tag{2.13}$$

- For an ideal gas of N indistinguishable molecules

$$\Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}} \times A \tag{2.14}$$

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

- Surface area of hypersphere in d-dimensional is

$$A = \frac{2\pi^{d/2}}{(\frac{d}{2} - 1)!} r^{d-1} \tag{2.15}$$

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

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} (\sqrt{2mU})^{3N-1} \approx \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2})!} (\sqrt{2mU})^{3N} \tag{2.16}$$

  or to simplify the formula where, $f(N)$ is function of N

$$\Omega(U, V, N) = f(N) V^N U^{3N/2} \tag{2.17}$$

- Suppose *two* ideal gases separated by a partition that allows energy to flow, and if each gas has N molecules, the total multiplicity is

$$\Omega_{\text{total}} = [f(N)]^2 (V_A V_B)^N (U_A U_B)^{3N/2} \tag{2.18}$$

  with a peak-width of $\frac{U_{\text{total}}}{\sqrt{3N/2}}$

- Now allow gases to exchange volume with a movable partition, we'll have a width-peak of $\frac{V_{\text{total}}}{\sqrt{3N/2}}$

2.6   Entropy

- Any large systems in equilibrium will be found in the macrostate with the greatest multiplicity, a general statement for the **second law of thermodynamics**

- Or multiplicity tends to increase.

- To simplify dealing with very large number of Ω, we define the **entropy** as

$$S \equiv k \ln \Omega \quad [\text{J/K}] \tag{2.19}$$

- Entropy tends to increase.

- No matter what you do to decrease the entropy in one place, you're bound to create at least as much entropy somewhere else.

- Entropy for idea gas, with Stirling's approximation, is called **Sackur-Tetrode equation**

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \tag{2.20}$$

- Entropy of an ideal gas depends on its volume, energy, and number of particles.

- If the volume changes from V_i to V_f

$$\Delta S = Nk \ln \frac{V_f}{V_i} \qquad (U, N \text{ fixed}) \tag{2.21}$$

- In **free expansion** no work is done by gas nor heat $\Delta U = Q + W = 0 + 0 = 0$, however there's an increase in entropy by (2.21)

- Suppose two different monoatomic idea gases, A and B, each with the same energy, volume and # of particles. After mixing them, each gas will expand to twice its initial volume, so $\Delta S_A = Nk \ln 2$, then the total entropy is **Entropy of mixing** $\Delta S_{\text{total}} = 2Nk \ln 2$