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 $kT = \frac{1}{40}$eV The root-mean-square velocity is

$$v_{\text{rms}} = \sqrt{\bar{v}^2} = \sqrt{\frac{3kT}{m}} \tag{1.2}$$

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

$$U = Nf\frac{1}{2}kT \tag{1.3}$$

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.

-
$$dU = \text{d}Q + \text{d}W \tag{1.4}$$

  is just a statement of the law of conservation of energy, but it's still called **first law of thermodynamics**.

- Note that the dQ and dW are *inexact differentials.* There are no such as $Q(P,V)$ and $W(P,V)$ that depend only on the state of the system; they are path-dependent.

- 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 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.

- $W = -P\Delta V$ for quasistatic.

- If P is not constant,
$$W = -\int_{V_i}^{V_f} P(V)\,dV \tag{1.5}$$

- **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

$$W = -\int_{V_i}^{V_f} P(V)\, dV = NkT \ln \frac{V_i}{V_f} \tag{1.6}$$

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

$$Q = \Delta U - W = \underbrace{\Delta(\tfrac{1}{2}NfkT)}_{0} - W = NkT \ln \frac{V_f}{V_i} \tag{1.7}$$

- adiabatic process

  – In the PV plot the change is from one isotherm to another.

  – There should be no trasfer of heat so

  $$\Delta U = Q + W = W \tag{1.8}$$

  – 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 (1.5)

  $$\frac{f}{2}Nk\, dT = -P\, dV \tag{1.9}$$

  Using the ideal gas law for P and integrate

  $$\frac{f}{2}\ln \frac{T_f}{T_i} = -\frac{V_f}{V_i} \quad \text{or} \quad V_f T_f^{f/2} = V_i T_i^{f/2} = \text{const.} \tag{1.10}$$

  – 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

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

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

$$c \equiv \frac{C}{m} \tag{1.12}$$

- Note (1.12) is ambiguous, plug in the first law

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T} \tag{1.13}$$

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 (1.13) The **heat capacity at constant volume**, denoted C_V

$$C_V = \left(\frac{\Delta U}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{1.14}$$

- From (1.13) and (1.5) the **heat capacity at constant pressure**, denoted C_P

$$C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{1.15}$$

for solid last term is almost negligible.

- So for ideal gases we can write

$$C_P = C_v + Nk \tag{1.16}$$

- At a **phase transformation**, you add heat in a system without increasing its temperature; such as melting or 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

$$l \equiv \frac{L}{m} = \frac{Q}{m} \tag{1.17}$$

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

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

$$H = U + PV \tag{1.18}$$

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

- Also at constant pressure

$$\Delta H = Q + W_{\text{other}} \tag{1.19}$$

that is, the change in enthalpy is caused by heat and other type of work, *not* by compression-expansion work.

- We can think of C_P as the enthalpy capacity

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{1.20}$$

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 ideal 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 ideal 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** $\Delta S_{\text{total}} = 2Nk \ln 2$

- Process that creates new entropy is said to be **irreversible**.

- A process that leaves the total entropy of the universe unchanged is called **reversible**.

- The sudden expansion of gas created new entropy, but if it's slow enough, its entropy is unchanged.

- They can be explained by the quantum adiabatic process, where very slow squeeze of gas, takes the a molecule from the nth level to the nth level in the new volume.

Chapter 3

Interactions and Implications

We saw that when two systems interact, they will evolve toward a macrostate with the highest entropy. Which is the statement of the second law of thermodynamics. This isn't built into the fundamental laws of nature, it arises from the probabilistic law. From now on, we treat it as a fundamental law.

3.1 Temperature

- when two objects are in thermal equilibrium, their entropy has reached the minimum as well as their temperature are the same.
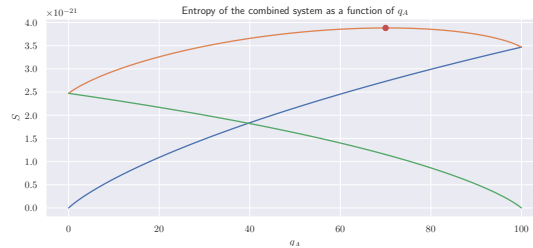

Figure 3.1: Entropies of two systems

- We see that it reached equilibrium when

$$\frac{\partial S_t}{\partial q_A} = 0 \quad \text{or} \quad \frac{\partial S_t}{\partial U_A} = 0 \tag{3.1}$$

  where the energy U_A is just q_A times a constant.

- But $S_t = S_A + S_B$, so

$$\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0 \quad \text{or} \quad \frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \tag{3.2}$$

  because $dU_A = -dU_B$

- From Figure 3.1, if small values, say $q_A = 10$, for a bit of energy passes from solid B to A, the entropy gained by A is greater than entropy lost by B. Then the overall entropy will increase, this happens spontaneously according to the second law.

- So energy flows from object with smaller slope into solid with larger slope. We know energy flows from object with larger *temperature* into object with a lower one.

- So we can define the temperature , with correct units and at constant volume and number of particles, as

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V} \tag{3.3}$$

3.2   Entropy and Heat

We saw how to calculate the temperature as a function of energy (and vice versa) for any system with explicit formula for the multiplicity. To have something experimental, we differentiate the function $U(T)$

- volume we have

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{3.4}$$

- For an Einstein solid with $q \gg N$e heat capacity is

$$C_V = \frac{\partial}{\partial T}(NkT) = Nk \tag{3.5}$$

and for a monoatomic ideal gas

$$C_V = \frac{\partial}{\partial T}\left(\frac{3}{2}NkT\right) = \frac{3}{2}Nk \tag{3.6}$$

- To measure the entropy, if you add a bit of heat to a system, its entropy will be

$$dS = \frac{dU}{T} = \frac{dQ}{T} \tag{3.7}$$

This is valid even for changing volume, but it must be quasistatic.

- But if the temperature is changing, we write in terms of heat capacity at constant volume

$$dS = \frac{C_V dT}{T} \qquad \text{then} \qquad \Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_V}{T} dT \tag{3.8}$$

- If we know the $C_V(T)$, then we find the *total* entropy of the system

$$S_f - S(0) = \int_0^{T_f} \frac{C_V}{T} dT \tag{3.9}$$

- At zero temperature a system should settle into its unique lowest-energy state, so $\Omega = 1$ and $S = 0$. This fact is the **third law of thermodynamics**.

- In practice $S(0)$ is nonzero. As in the water molecules, we say it has a frozen-in **residual entropy**.

- To prevent the integral form divergence at $T = 0$, we say

$$C_V \to 0 \qquad \text{as} \qquad T \to 0 \tag{3.10}$$

3.3 Paramagnetism

Consider the **two-state paramagnet**. It consists of N spin-1/2 particles, immersed in a constant magnetic field $\vec{B}$ pointing in the $+z$ direction. Assume no interaction between dipoles.

- The alignment is quantized, only two values are allowed, 'up' (parallel) and 'down' (anti-parallel).

- The energy is given by $U = -\vec{\mu} \cdot \vec{B}$. Energy required to flip one dipole to be down is $\mu B - (-\mu B) = 2\mu B$

- The *total* energy of the system is

$$U = \mu B(N_\downarrow - N_\uparrow) = \mu B(N - 2N_\uparrow) \tag{3.11}$$

- The **magnetization** is defined as the total magnetic moment of the whole system,

$$M = \mu(N_\uparrow - N_\downarrow) = -\frac{U}{B} \tag{3.12}$$

- We note from the graph that the largest multiplicity and largest entropy occur at $U = 0$ when exactly half of the dipoles point down and

- At $U = 0$, T is infinite, with a higher energy T becomes negative.

- Analytical solution, the entropy is

$$\frac{S}{k} = \ln N! - \ln N_\uparrow! - \ln (N - N_\uparrow)! \tag{3.13}$$

$$\approx N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln (N - N_\uparrow) \tag{3.14}$$

- Using the temperature definition (3.3), we get

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,B} = \frac{\partial N_\uparrow}{\partial U} \frac{\partial S}{\partial N_\uparrow} = -\frac{1}{2\mu B} \frac{\partial S}{\partial N_\uparrow} \tag{3.15}$$

- Now putting (3.13) in (3.15) gives

$$\frac{1}{T} = \frac{k}{2\mu B} \ln \left(\frac{N - U/\mu B}{N + U/\mu B}\right) \tag{3.16}$$

- Solving for U gives

$$U = -N\mu B \tanh \left(\frac{\mu B}{kT}\right) \tag{3.17}$$

3.4 Mechanical Equilibrium and Pressure

To consider systems that can change their volume as they interact.

- exchange of volume between systems is governed by their pressures. So there should be a relation between pressure and entropy, analogous to (3.3).

- The total entropy is a function of two variables, U_A and V_A. So the equilibrium point is where S_{total} is maximum,

$$\frac{\partial S_t}{\partial U_A} = 0, \qquad \frac{\partial S_t}{\partial V_A} = 0. \tag{3.18}$$

- We've saw the first condition, but for the second one, we have

$$\frac{\partial S_t}{\partial V_A} = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} \tag{3.19}$$

- Knowing that the volume is conserved, $dV_A = -dV_B$, we have at equilibrium

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \tag{3.20}$$

- Since, at equilibrium they have the same T, we can find a relation for pressure as

$$P = T \left(\frac{\partial S}{\partial V}\right)_{U,N} \tag{3.21}$$

- We can derive (1.1) by using (2.17), then substitute it in the above equation.

- Consider a two-step process where we change the energy while the volume is fixed then change the volume while the energy is fixed, the entropy is

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV \tag{3.22}$$

- The **thermodynamic identity** is

$$dU = T \, dS - P \, dV \tag{3.23}$$

- If the change in volume takes place quasistatically, no other forms of work are done, and no other relevant variables are changing, then we know

$$W = -P \, dV \quad \text{and} \quad Q = T \, dS \tag{3.24}$$

- So even if the volume is changing we know the entropy is Q/T.

- As an special case of an adiabatic process ($Q = 0$) and quasistatic, the entropy is unchanged; it is called **isentropic**.

3.5   Diffusive Equilibrium and Chemical Potential

We saw when two system are in *thermal* equilibrium their temperatures are equal. When they're in *mechanical* equilibrium their pressures are equal. Now what about if they're *diffusive* equilibrium ? Consider two systems A and B, that can exchange both energy and particle, but of the same species.

- As previous section, if the total energy and total number of particles are fixed, the total entropy is a function of U_A and N_A.

- At equilibrium, the total entropy is maximized, so

$$\left(\frac{\partial S_t}{\partial U_A}\right)_{N_A,V_A} = 0 \quad \text{and} \quad \left(\frac{\partial S_t}{\partial N_A}\right)_{U_A,V_A} = 0 \tag{3.25}$$

- So we get

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \tag{3.26}$$

- After multiplying each side with $-T$, since they are in thermal equilibrium, we define the **chemical potential**.

$$\mu \equiv -T \left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{3.27}$$

this is the quantity that's the same for both systems when they're in *diffusive* equilibrium.

- The system with larger $\partial S/\partial N$ tends to gain particles. So Particles tend to flow form the system with higher μ into the system with lower μ.

- To generalize the thermodynamic identity,

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN \tag{3.28}$$

so it becomes

$$dU = T\,dS - P\,dV + \mu\,dN \tag{3.29}$$

- It helps in remembering the partial-derivative formulas for T, P, and μ.

- Note there are four variables changing, U, S, V, and N. By fixing any two you get different formula.

Chapter 4

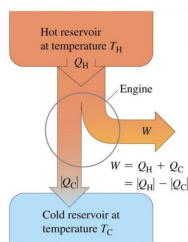# Engines and Refrigerators

4.1 Heat Engines

Figure 4.1:

- A **heat engine** is any device that absorbs heat and converts part of it into work.

- Only *part* of the energy absorbed as heat can be converted to work by a heat engine. This is because as the heat flows in it brings along entropy, which must get rid of it.

- The absorbed heat of an engine comes from a **hot reservoir** with a temperature of T_h and the waste heat goes into **cold reservoir** with a temperature of T_c.

- Q_h is the heat absorbed form the host reservoir, and Q_c is for the heat expelled to the cold reservoir, all in given time interval.

- W is the net work done by the engine during this time.

- The benegit of heat engine is the ratio of the benfit (work) to the cost (heat of hot reservoir),

$$e \equiv \frac{W}{Q_h} \tag{4.1}$$

- For given values of T_h and T_c, what is the maximum possible efficiency?

- We need the first and second laws of thermodynamics, plus the assumption the engine is operating in cycles

- First law tells us the energy is conserved, since the state of the engine must be unchanged at the end of each cycle. So

$$Q_h = Q_c + W \tag{4.2}$$

- Substitute this into the efficiency formula

$$e = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} \tag{4.3}$$

- Second law tells us the entropy of the engine plus its surroundings must increase. since the state must be unchanged, the entropy it expels must be at least as much as the entropy it absorbs. so

$$\frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \quad \text{or} \quad \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h} \tag{4.4}$$

putting it back to the efficiency

$$e \leq 1 - \frac{T_c}{T_h} \tag{4.5}$$

- **Carnot cycle**

  - The first law tells us that e cannot bet greater than 1. That is, you can't produce work more than heat put in. The second law just make impossible to get $e = 1$.
  - To make engine with max e. Suppose we have gas as working substance, which is the matterial that absorbs heat, expels waste heat, and does work.
  - First we want the gas absorb heat Q_h form the hot reservoir. The entropy of the reservoir drops by Q_h/T_h, and the entropy of the gas increases by Q_h/T_{gas}.
  - But heat won't transfer to the gas unless gas' temperature is less than the reservoir, meaning creating new entropy. To avoid that we assume T_{gas} is very small than the reservoir and we keep it constant by letting it expand, so we can say $T_h = T_{gas}$. But this is an isothermal process.
  - And the same goes for dumping the waste heat into cold reservoir, by having T_c infinitesimal larger than T_{gas}
  - For the intermediate, T_h to T_c steps we don't the gas to lose heat, so it should be adiabatic.

4.2   Refrigerators

- To define the efficiency, we care about the ratio benefit/cost, to avoid confusion this formula is called **coefficient of performance**

$$\frac{Q_h}{T_h} \geq \frac{Q_c}{T_c} \quad \text{or} \quad \frac{Q_h}{Q_c} \geq \frac{T_h}{T_c} \tag{4.6}$$

- Plugging this result into COP

$$\text{COP} \leq \frac{1}{T_h/T_c - 1} = \frac{T_c}{T_h - T_c} \tag{4.7}$$

4.3 Real Heat Engines

- **Otto cycle** explains the internal combustion engines.

- Note that there is not such hot reservoirs, but the heat is produces internally by burning the fuel.

- The efficiency of a gasoline engine is the net work produces during the cycle divided by the heat absorbled during the ignition step. Which is given by

$$e = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma - 1} \tag{4.8}$$

- Knowing $TV^{\gamma - 1}$ si constant, we can requite the previous formula as

$$e = 1 - \frac{T_1}{T_2} = 1 - \frac{T_4}{T_3} \tag{4.9}$$

- In steam engine the cycle is called **Rankine cycle**.

- Recall that the enthalpy is $H = U + PV$ under constant-pressure process. So the change in enthalpy is the heat absorbed under constant-pressure conditions, where no other work is done.

- in Rankine cycle, heat is absorbed at constant pressure in the boiler and expelled at

- constant pressure in the condenser, so we can write the efficiency as

$$e = 1 - \frac{Q_c}{Q_h} = \frac{H_4 - H_1}{H_3 - H_2} \approx 1 - \frac{H_4 - H_1}{H_3 - H_1} \tag{4.10}$$

- Where $H_2 \approx H_1$ is good, because the term PV is negligible for liquids.