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 $-273°\text{C}$. which defines the **absolute zero**, in the **absolute temperature scale**, in K (kelvin).

1.2 The Ideal Gas

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

- 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

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

- 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 pahse 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