Lecture 2: Energy

ERD: Chapter 2 (Z Chs 5 and 9)

Key points of the today’s lecture

- Matter and Energy are conserved in any process.

- Energy exchange

- Work (Energy transfer as work)
  1. Work in a gravitational field
  2. Work extending a spring
  3. Work in an electric field
  4. Photons and blackbody radiation (Energy transfer as heat)
  5. Pressure-Volume work

- Work Done By a gas and On a gas.
Key points of the last lecture

- Thermodynamics describes macroscopic properties of equilibrium systems

- 4 laws: (So far the zeroth and the first laws)
  - Temperature and Kinetic Energy Are related
  - Definition of temperature: 0th law of thermodynamics
  - Defining a temperature scale
  - Energy is conserved (as work or heat) in any process

- Definitions: system, surroundings, boundary, state variables, extensive, intensive properties

- Ideal and Real gases (and mixtures of gasses)
Thermodynamics \rightarrow \text{Energy exchange} \\
\downarrow \\
\text{work and heat} \\

Physics classes taught that there is an energy change to a system if work is done on the system:

$$\Delta \left( K.E. \right) = w$$

What is incomplete about this statement?

Different types of energies:

Potential
Kinetic
Chemical
Mechanical
Nuclear
Etc…

Different types of energies are transferred either as work or heat
Work

transfer of energy from system to surroundings and vice versa.

+ work $\rightarrow$ work done on the system or transferred into the system as Energy increases.

- work $\rightarrow$ work done by the system or transferred from the system to the surroundings. Energy of the system decreases.

From classical mechanics, we know that:

$$\left|\text{work}\right| = \left|\text{force} \cdot \text{displacement}\right| = \left|\int_{x_1}^{x_2} \text{force} \cdot dx\right|$$

(absolute value brackets remind us about the sign convention)
Work in a gravitational field

\[ F = ma = \frac{d(mv)}{dt} = \frac{dp}{dt} \quad \text{with} \quad F_{\text{earth's gravity}} = mg \]

\[ w = \int_{x_i}^{x_f} \text{force} \cdot dx = \int_{x_i}^{x_f} mg \, dx = mg \left( x_f - x_i \right) = mg \Delta h \]

If we do work and lift an object then the work is positive and the energy in the mass (as potential energy) goes up. The work done by us (i.e. the environment) just overcoming gravity to lift an object (no kinetic energy or motion) is transferred into the object, so its energy increases:

\[ \Delta E = w = mg \Delta h = \Delta V \quad \Phi_g = \Delta \Phi = g \Delta h \]

Where does the force to do work come from? The change in potential energy of the object (or system).

\[ F = - \frac{\Delta V}{\Delta x} = - \frac{dV}{dx} \]

Let an object fall in a gravitational field. Show that the kinetic energy and potential are exchanged but the total energy of the particle (system) is conserved, i.e. does not change.
Potential Energy in the Earth's Gravitational Field

\[
\Delta V = V(h) - V(h=0) = ghm
\]

\[
V = -g \left( \frac{r_o^2}{r_o + h} \right) m \approx -g \left( r_o \left( 1 - \frac{h}{r_o} \right) \right) m
\]

\[
V = -\frac{G \cdot M}{r} m = -\frac{G \cdot M}{r_0 + h} m = -g \frac{r_o^2}{r_o + h} m
\]

\[
g = \frac{G \cdot M}{r_o^2} = \frac{6.67 \cdot 10^{-11} \cdot 5.97 \cdot 10^{24}}{(6.37 \cdot 10^6)^2} = 9.8 \text{ m/sec}^2
\]
Change in Energy

A 10 g mass falls 10 meters. What is the change in potential, kinetic and total energy?

\[ \Delta V = mgh = 0.01 \cdot 9.8 \cdot (-10) = -0.98 \text{ J} \]

\[ F = m \frac{dv}{dt} = - \frac{dV}{dx} = -mg \]

\[ v = -gt \quad \text{Integrating} \quad h = -\frac{1}{2} gt^2 \quad v^2 = 2|h|g \]

\[ \Delta K.E. = \frac{1}{2} mv^2 = mg |h| = -\Delta V \]

\[ \Delta E = \Delta K.E. + \Delta V = 0 \]

What is the work done and how much work done?

What happens when the mass hits the earth’s surface?
A simple manometer, a device for measuring the pressure of a gas in a container.

\[
\Delta P \propto h = \Delta h < 0
\]

\[
\Delta P \propto h = \Delta h > 0
\]
Work in a gravitational field

\[ F = ma \quad F_{\text{earth's gravity}} = mg \]

What happens when mass is not constant with distance?

\[ m = \rho V \quad \rho = \text{density, } V = \text{volume} \]

\[ m = \int \rho dV \quad F_{\text{earth's gravity}} = gm = g \int \rho dV \]

For liquids the density is independent of force (or pressure). A manometer measures barometric pressure by pushing on a column of mercury. How much pressure (in Bars or Atmospheres) will raise a column of mercury 5cm? See Chem142/ZLC5a and manometer diagram:

\[ F_{\text{earth's gravity}} = gm = g \int \rho dV = g \rho A \Delta h \]

\[ \Delta P = \frac{F}{A} = g \rho \Delta h = 9.8 \cdot \left(13.6 \cdot 10^3 \frac{kg}{m^3}\right) 0.05 Pa \]

\[ \Delta P = 6.6 \cdot 10^3 Pa = 0.066 \text{ Bar} \]
Let us consider the effects of gravity on pressure and assume that $\rho$ is dependent on pressure, as in the case of a gas.

$$\Delta P = \frac{\Delta F}{A} = \int \frac{\rho g dV}{A} = \int \frac{\rho g A dx}{A} = \int \rho(x) g dx$$

Suppose the column of air were at a constant temperature. The density of the air is related to the atmospheric pressure.

The force of gravity causes the density to be highest at the surface of the earth and decrease as the altitude increases.

$$\rho = \rho_o e^{-\frac{Mgh}{RT}} \quad P = \rho \frac{RT}{M}$$

Show that this exponential decrease in density is consistent with the Ideal Gas expression

$$P_o = g \int_{x=0}^{\infty} \rho(x) dx = \rho_o g \int_{x=0}^{\infty} e^{-\frac{Mgx}{RT}} dx = \rho_o \frac{RT}{M}$$

If the atmosphere were of uniform density how high would it be to have a pressure of 1Atm? (Answer: ~10 km or ~6 miles). What fraction of the atmosphere is above 10 km? (Ans ~ 1/3).
Work done in extending a spring

\[ F_{spring} = k_{spring} (x - x_0) \]

Hooke’s Law, where \( k \) is the spring constant and \( x_0 \) is the equilibrium position of the spring

\[
W = \int_{x_1}^{x_2} k_{spring} (x - x_0) \, dx = \frac{k_s}{2} \left[ (x_2 - x_0)^2 - (x_1 - x_0)^2 \right]
\]

If spring is stretched, then work is done on system (blue mass) and work is positive and this increased the energy of the system by increasing the potential energy. Energy transferred into the system (work) becomes potential energy.

\[ \Delta E = w > 0 \]
Measuring the force from a single molecule with optical tweezers pulling a bead attached to the molecule
Individual molecules may behave like springs over some distance scale. How would you test if this is true?
Work done in an electric field

\[ V_{elec} = \frac{qQ}{r} \quad V_{grav} = -G \frac{mM}{r} = m\Phi_g \]

| Work | \[ |\text{work}| = QV \]

Charge (Coulombs) |
Analogous to mass |
Voltage (Volts) |
Electrical Potential |

\[ Q = It \]

Current (Amperes) | time (s)

Calculate the work done by a 12 V storage battery that discharges 0.1 A for 1 hour. A Volt is a Joule per Coulomb.

\[ w = VIt \quad \text{Power} = V \cdot I \text{ Watts} \]

\[ = (12 \text{ V})(0.1 \text{ A})(3600 \text{ s}) \]

\[ \text{work} = -4.32 \times 10^3 \text{ J} = -4.32 \text{ kJ} = -1.2 \times 10^{-3} \text{ kW-hr} \]

Why is the work negative, none of V, I, t, is negative?
A typical current in ion channels is 1 nA and the time it remains open is 1 ms. How many $K^+$ ions go through the channel when it is open?

\[
\text{# of ions} = \frac{\text{total charge}}{\text{charge of one ion}}
\]

\[
= \frac{(1 \times 10^{-9} \text{ A})(1 \times 10^{-3} \text{ s})}{(1.6 \times 10^{-19} \text{ C})} = 6 \times 10^6 \text{ ions}
\]
Pressure-Volume work

\[ \text{work} = \int_{x_i}^{x_f} \text{force} \cdot dx \]

\[ = \int_{V_i}^{V_f} PAdx = \int_{V_i}^{V_f} PdV \]

Work done by surroundings

Work done on system (transferred to system)

\[ \text{work} = w = -\int_{V_i}^{V_f} P_{ext} \, dV \]

In some cases, P is a function of V

Convince yourself that the sign makes sense!

When a gas is compressed, the energy of the gas increases and energy is transferred (via work) from surroundings to system.
Photons and blackbody radiation

\[ E_{\text{photon}} = h\nu \quad c = \lambda \nu \]

\[ E_{\text{radiation}} = Nh\nu \]

- # of photons
- Plank’s constant
- frequency

The transfer of light is an energy transfer from surroundings to system. However, this form of energy is really a heat transfer, not a work transfer.

**DNA photo-damage**

UVB: 320 nm – 280 nm
UVC: below 280 nm

Energy of 1 UVC photon @ 280 nm

\[ E_{\text{radiation}} = Nh\nu = Nh \frac{c}{\lambda} \]

\[ = (1 \text{ photon})(6.626 \times 10^{-34} \text{ Js}) \frac{(3 \times 10^8 \text{ ms}^{-1})}{(280 \times 10^{-9} \text{ m})} \]

\[ = 7 \times 10^{-19} \text{ J} \quad \text{Enough energy to knock loose an electron from DNA} \]
Different Scenarios for Pressure-Volume Work

\[ \text{work} = w = - \int_{V_i}^{V_f} P_{\text{ext}} \, dV \]

Free Expansion

\[ P = P_{\text{ext}} = 0 \quad \Rightarrow w = 0 \]

Constant Volume

\[ dV = 0 \quad \Rightarrow w = 0 \]

Constant external pressure

\[ P = P_{\text{ext}} = \frac{mg}{A} = \text{constant} \quad w = -P_{\text{ext}} \left( V_f - V_i \right) \]

Reversible volume change

\[ P_{\text{ext}} \approx P_{\text{int}} \neq \text{constant} \quad w = -\int_{V_i}^{V_f} P(V) \, dV \]

One step (Irreversible) expansion or compression

\[ P_{\text{ext}} \approx P_{\text{final}} = \text{constant} \quad w = -P_f \left( V_f - V_i \right) \]
isothermal volume change for an ideal gas (for a constant # of moles)

\[ w = -\int_{V_i}^{V_f} P_{ext}(V)\,dV \]
\[ P_{int} = P(V) = \frac{nRT}{V} \]

Reversible \( P_{ext} = P_{int}(V) \)

One Step \( P_{ext} = P_f(V) \)

\[ w = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} \]

\[ w = -P_f \left( V_f - V_i \right) \]

\[ w_{isoT}^{rev} = -nRT \ln \left( \frac{V_f}{V_i} \right) \]

\[ w_{isoT}^{1-stp} = -nRT \left( 1 - \frac{V_i}{V_f} \right) \]
Say we compress a gas from 2 L to 1 L with the final pressure equal to 1 atm in a reversible isothermal manner. What is the work done on the system?

How do you do this kind of work (compression)?

What will be the sign of the work?
Example: Ideal gas of \( n \) moles expands from 1 L to 4 L at a constant temperature, \( T \). What is the work done by the gas (i) in a 1-Step (irreversible) and (ii) in a reversible manner?

\[
w_{rev} = -nRT \ln \left( \frac{V_f}{V_i} \right) = -nRT \ln (4)
\]

\[
w_{1-Step} = -nRT \left( 1 - \frac{V_i}{V_f} \right) = -nRT \left( \frac{3}{4} \right)
\]

\[
\ln (4) = 1.38 > \frac{3}{4}
\]

\[
|w_{rev}| > |w_{irrev}|
\]

For the same system change, the system does more work following a reversible path than a 1-Step, or any other irreversible path.
Reversibility and Maximizing work

Example 1: isothermal compression of an ideal gas, with a constant # of moles

\[ V_f = 1.00 \text{ L}, \ V_i = 2.00 \text{ L}, \ P_i = 0.500 \times 10^5 \text{ Pa} \]

\[ V_{ii} = \frac{5}{3} \text{ L}, \ V_{iii} = \frac{4}{3} \text{ L} \]

\[ P_{vi} = 100 \ \text{J} = nRT \]

1 – step, irreversible compression

\[ w_{1-step} = 100 \ \text{J} \]

3 – step, irreversible compression

\[ w_{3-step} = 78.3 \ \text{J} \]

Infinite step, irreversible compression

\[ w_{inf-step} = 69.3 \ \text{J} \]

NB: The area under the curves (and the blue shaded regions) is the work.

When environment does work, the reversible path is the lowest work path
For the full cycle:

\[ W_{\text{total}} = W_{\text{compression}} + W_{\text{expansion}} \]

\[ = 100 + (-50) = 50 \text{ J (for irr, 1-step)} \]

\[ = 78.3 + (-61.7) = 16.6 \text{ J (for irr, 3-step)} \]

\[ = 69.30 + (-69.3) = 0 \text{ J (for reversible case)} \]

In what limit does a reversible reaction look like an irreversible reaction?

\[ \frac{V_i}{V_f} \sim 1 \quad \ln \left( \frac{V_i}{V_f} \right) \sim \left( \frac{V_i}{V_f} - 1 \right) \]

\[ nRT \ln \left( \frac{V_i}{V_f} \right) \rightarrow -nRT \left( 1 - \frac{V_i}{V_f} \right) \]
Key points of the today’s lecture

• Energy exchanges

• Forms of Work (and Heat)
  1. Work in a gravitational field
  2. Work extending a spring
  3. Work in an electric field
  4. Photons and blackbody radiation (heat not work)
  5. Pressure-Volume work

• Reversible and Irreversible Work
  (one step work and many step work)