On the menu today

09/14/2021

Lecture 4: chapters 11 and 12

Lecture 11. *Energy*

- In this unit we will learn about

  - Energy

  - First law of thermodynamics

What happens when energy is *transformed* from one form to another?

How much work can you get out of a quantity of heat?

https://www.miningreview.com/energy/

More definitions: thermal equilibrium

- In thermodynamics, we define a system to be whatever part of the Universe we select for study.

- Near the system are its surroundings.

- A system is in **thermal equilibrium** when its macroscopic observables (such as its pressure or its temperature) have ceased to change with time.

- For example, a system in thermal equilibrium having a particular set of macroscopic observables is said to be in a particular equilibrium state.

(a)

| hot T_1 | | cold T_2 |

(b)

flow of heat

| hot T_1 | → | cold T_2 |

(c)

| T_f | — | T_f |
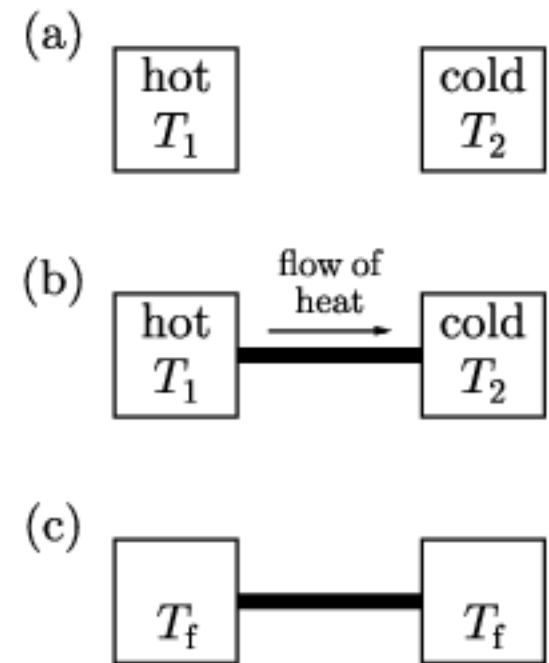
From lecture 4

More definitions: functions of state

- A system is in an equilibrium state if macroscopic observable properties have fixed, definite values, independent of "how they got there"

- These properties are **functions of state** (sometimes called **variables of state**).

  - **Definition: A function of state is any physical quantity that has a well defined value for each equilibrium state of the system.**

  - Examples are volume, pressure, temperature, and internal energy, etc

- **Examples of quantities that are not functions of state include**

    - the position of a specific particle,

    - the total work done on a system, and

    - the total heat put into the system.

Formal definition of a function of state

Let the state of a system be described by parameters $x = (x_1, x_2, \ldots)$ and let $f(x)$ be some function of state.

Functions of state are usually combinations of these "parameters". Then if the system parameters change from x_i to x_f, the change in f is

$$\Delta f = \int_{x_i}^{x_f} \mathrm{d}f = f(x_f) - f(x_i)$$

This only depends on the end points   and   .

The quantity   is an exact differential and functions of state have exact differentials. By contrast, a quantity that is represented by an inexact differential is not a function of state.

Example of an exact differential

Let a system be described by two parameters, x and y. Let $f = xy$ so that

$$\mathrm{d}f = \mathrm{d}(xy) = y\,\mathrm{d}x + x\,\mathrm{d}y$$

Then if   changes from (0,0) to (1,1), the change in   is given by

This answer is independent of the exact path taken because   is an exact differential.

Example of an inexact differential

Now consider $\bar{d}g = y\,\mathrm{d}x$

The change in g when (x, y) changes from (0,0) to (1,1) along the path shown in the figure is given by

$$\Delta g = \int_{(0,0)}^{(1,1)} y\mathrm{d}x = \int_0^1 x\mathrm{d}x = \frac{1}{2}$$

However when the integral is not carried out along the line   but along the path shown in the second figure it is given by

Functions of state can either be:

- **extensive (proportional to system size)**, *e.g.*, energy, volume, magnetization, mass,

  or

- **intensive (independent of system size)**, *e.g.*, temperature, pressure, magnetic field, density, energy density.

In general one can find an equation of state that connects functions of state: for a gas this takes the form $f(p, V, T) = 0$.

An example is the equation of state for an ideal gas, $pV = nRT$, the ideal gas equation

First law of thermodynamics

- Joule:

  - **Equivalence between heat and energy**

- Mayer and Helmholtz:

  - **Energy is conserved and heat and work are both forms of energy**

Internal energy U

- System has **internal energy** U, which is the sum of the energy of all the internal degrees of freedom that the system possesses.

- U is a function of state because it is a well-defined value for each equilibrium state of the system

- **Heat (Q) and Work (W) are NOT functions of states, since they concern the manner in which energy is delivered or extracted from the system**

- Looking at U, one cannot tell if Q or W (and how much) was involved!

$$\Delta U = \Delta Q + \Delta W$$

Thermally isolated system

$$\Delta U = \Delta W$$

Differential changes

$$\Delta U = \Delta Q + \Delta W$$

Heat Capacity

- Adding and removing heat and how this changes the internal energy of a gas

- We know that $U = U(T, V)$, thus:

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p$$

$$c_V = \frac{C_V}{M}$$

$$c_p = \frac{C_p}{M}$$

Specific heat capacity: dividing by the mass of the material. expressed in JK⁻¹kg⁻¹

- In that case, U is just due to kinetic energy, $U = 3/2RT$ per mole

- Thus

- For one mole of gas: $pV = RT$

- Thus:

Definition: the adiabatic index

The ratio of C_p to C_V turns out to be a very useful quantity and therefore we give it a special name. We define the adiabatic index γ as

$$\gamma = \frac{C_p}{C_V}$$

Substance	Phase	Isobaric mass heat capacity c_p J·g⁻¹·K⁻¹	Isobaric molar heat capacity $c_{p,m}$ J·mol⁻¹·K⁻¹	Isochore molar heat capacity $c_{v,m}$ J·mol⁻¹·K⁻¹	Isochore atom-molar heat capacity in units of R $c_{v,am}$ atom-mol⁻¹	$C_{p,m}/C_{v,m}$
Air (Sea level, dry, 0 °C (273.15 K))	gas	1.0035	29.07	20.7643	~ 1.25 R	1.40
Air (typical room conditionsᴬ)	gas	1.012	29.19	20.85	~ 1.25 R	1.40
Argon	gas	0.5203	20.7862	12.4717	1.50 R	1.67
Carbon dioxide CO_2[B]	gas	0.839*	36.94	28.46	1.14 R	1.30
Methane at 2 °C	gas	2.191	35.69		0.85 R	
Nitrogen	gas	1.040	29.12	20.8	1.25 R	1.40
Neon	gas	1.0301	20.7862	12.4717	1.50 R	1.67
Oxygen	gas	0.918	29.38	21.0	1.26 R	1.40
Water at 100 °C (steam)	gas	**2.080**	**37.47**	**28.03**	1.12 R	1.34

$$\frac{C_p}{C_v} = \frac{5}{3}$$

Wikipedia

Important result for ideal gas

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

Internal energy per unit mass and per unit volume for an ideal gas

We know that $U = C_V T$ and also that $pV = Nk_B T$ with a density of $\rho = Nm/V$, it follows that

$$\frac{p}{\rho} = \frac{k_B T}{m}$$

Summary

- Functions of state have exact differentials.

- The first law of thermodynamics states that "energy is conserved and heat is a form of energy".

- $$\mathrm{d}U = \mathrm{d}W + \mathrm{d}Q$$

- For a reversible change,

-

-       and   for a mole of ideal gas.

- The adiabatic index is

Supplement: exact differential

- In these units we will review some basics of exact differentials

Partial Differentials

$$x = x(y, z) \qquad \mathrm{d}x = \left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y + \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z$$

$$z = z(x, y) \qquad \mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y$$

$$\mathrm{d}x = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left[\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x\right] \mathrm{d}y$$

$$\mathrm{d}x = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left[\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x\right]\mathrm{d}y$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

Reciprocal theorem

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Reciprocicty theorem

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

Exact differential

$$f(x,y) \longrightarrow \mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)\mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)\mathrm{d}y \longrightarrow \int_1^2 \mathrm{d}f = f(2) - f(1)$$

Path independent

Gradient of f: $\quad F_1 = \left(\dfrac{\partial f}{\partial x}\right), \quad F_2 = \left(\dfrac{\partial f}{\partial y}\right) \longrightarrow F_1(x,y)\,\mathrm{d}x + F_2(x,y)\,\mathrm{d}y$

$$\int_1^2 F_1(x,y)\,\mathrm{d}x + F_2(x,y)\,\mathrm{d}y = \int_1^2 \boldsymbol{F}\cdot\mathrm{d}\boldsymbol{r} = \int_1^2 \mathrm{d}f = f(2) - f(1)$$

Exact differential

$$\int_1^2 \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{r} = \int_1^2 \mathrm{d}f = f(2) - f(1) \quad \longrightarrow \quad \nabla \times \boldsymbol{F} = 0$$

Stokes Theorem

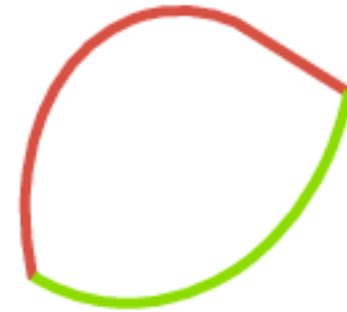$$\left(\frac{\partial F_2}{\partial x}\right) = \left(\frac{\partial F_1}{\partial y}\right)$$

Condition:

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right)$$

Inexact differential

For an inexact differential this is not true and knowledge of the initial and final states is not sufficient to evaluate the integral: you have to know which path was taken.
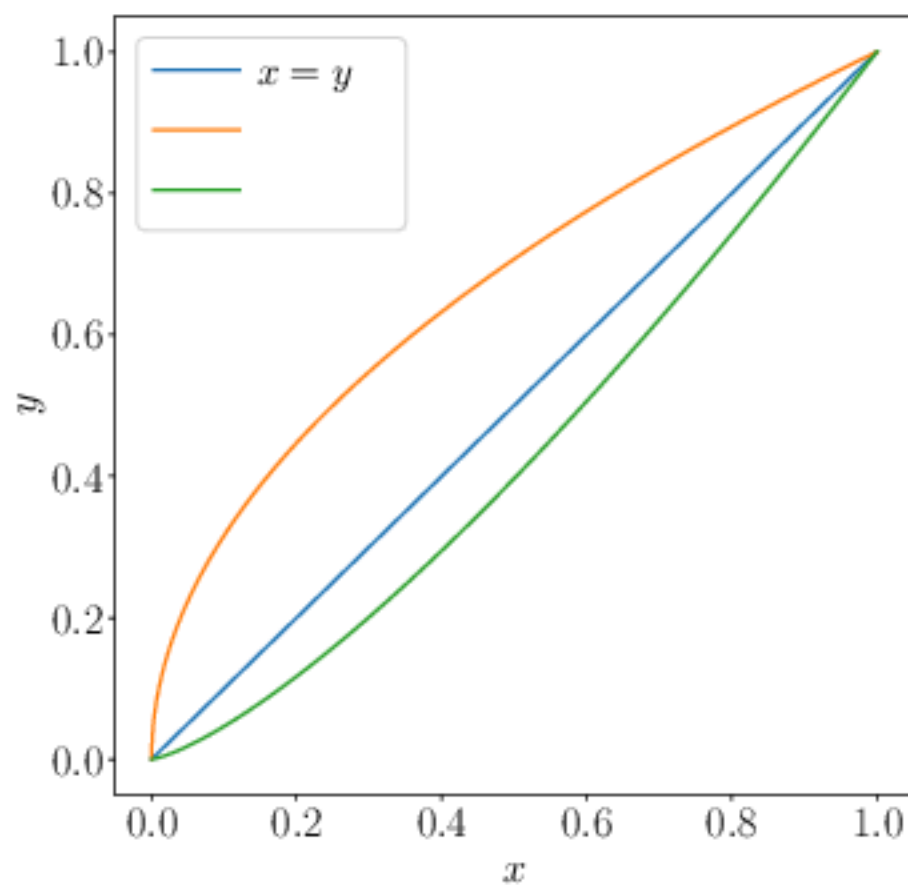
$$\int_1^2 \mathrm{d}f = f(2) - f(1)$$

For thermal physics, a crucial point to remember is that functions of state have exact differentials.
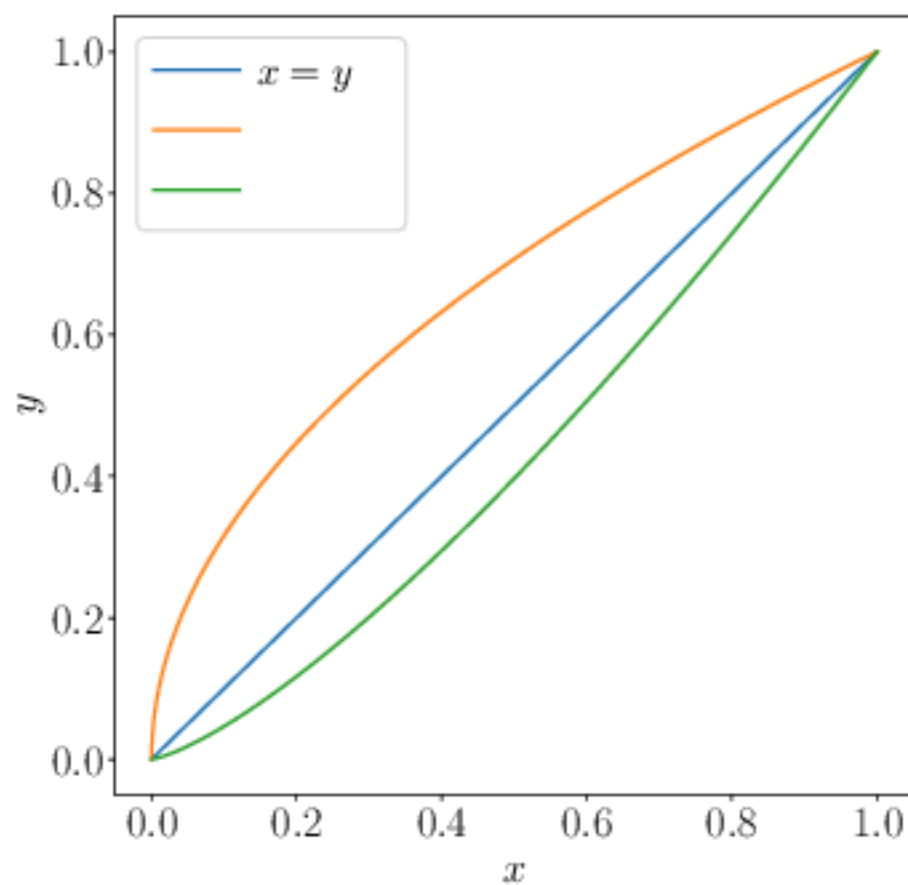
Example

Problem: integrate from (0,0) to (1,1)

Example

Problem: integrate from (0,0) to (1,1)

Lecture 12. *Isothermal and adiabatic processes*

- In this unit we will learn about

  - Consequences of 1st law

  - Reversibility

Reversibility

- In physics if one process is allowed, the time-reversed process is allowed as well.

- Many processes seem to be irreversible.

  - Laws of physics do not preclude them to happen, but

  - they are never actually observed

- Why is this the case? Most of the cases show release of heat to the environment and the reverse is unlikely to happen.

- **The reason has to do with the number of microstates and the many ways that entropy can be distributed as heat. Once again, we must focus on probability!**

Example: back to 100 coins

We assume that each of the 2^{100} possible configurations (the microstates) are equally likely to be found ($P \sim 10^{-30}$).

However, the measurement made is counting the number of heads and the number of tails (the macrostates), and the results of this measurement are not equally likely.

Imagine that you had in fact carefully prepared the coins so that they were lying heads up. Following a good shake, the coins will most probably be a mixture of heads and tails.

$$2^{100}$$

Statistical behavior of large systems

Statistical behavior of large systems seems to drive many systems in an irreversible direction

Reversible process?

- In the design of engines, in which you want to waste as little heat as possible to make your engine as efficient as possible.

- It was realized that when gases are expanded or compressed, it is **possible to convert energy irreversibly into heat, and this will generally occur when we perform the expansion or the compression very fast**, causing shock waves to be propagated through the gas.

Reversible process?

- However, it is possible to perform the expansion or compression reversibly if we do it sufficiently **slowly**

  - **so that the gas remains in equilibrium** throughout the entire process and

  - passes seamlessly from one equilibrium state to the next, each equilibrium state differing from the previous one by an infinitesimal change in the system parameters.

- Such a process is said to be **quasistatic**, since the process is almost in completely unchanging static equilibrium.

  - So heat can nevertheless be absorbed or emitted in the process, while still maintaining reversibility.

  - In contrast, for an irreversible process, a non-zero change (rather than a sequence of infinitesimal changes) is made to the system, and therefore the system is not in equilibrium throughout the process.

An important property of reversible processes is that you can run them in reverse.

It would take an infinite amount of time for a strictly reversible process to occur, **so most processes we term reversible are approximations**.

- **Isothermal**: at constant temperature

- For an ideal gas, we have $dU = C_V dT$

- So, for an isothermal change, we have $\Delta U = 0$

- Therefore:

- The work done by the gas on its surroundings as it expands is equal to the heat absorbed by the gas.

- For a reversible expansion:

Note: energy remains the same but energy density is reduced

The energy density is proportional to the pressure, this means that the pressure must have gone down.

$$\frac{p}{\gamma - 1}$$

Adiabatic expansion of an ideal gas

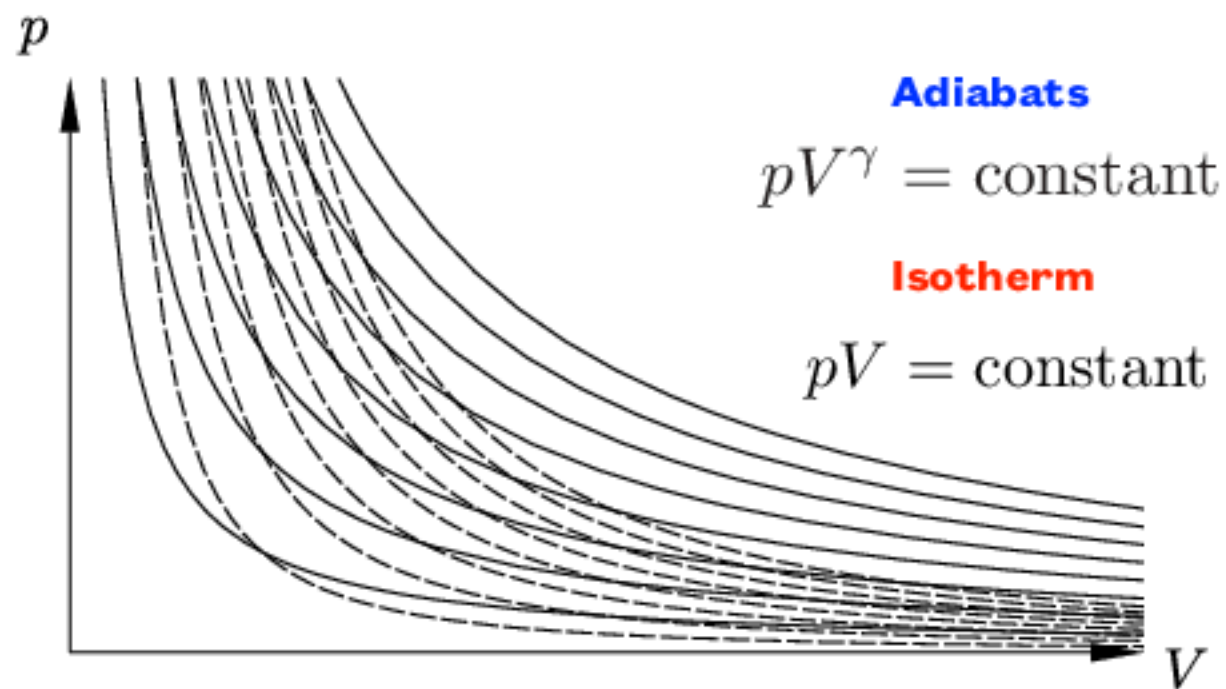- **Adiabatic change**: adiathermal (without flow of heat) and reversible

$\Longrightarrow$

Fig. 12.1 Isotherms (solid lines) and adiabats (dashed lines).

Lecture 13. *Heat Engines and the second law*

- In this unit we will learn about

  - Heat engines

  - Different statements of the second law

  - Carnot cycle

  - Most efficient engine