A statistical view of entropy

The **entropy** of a system can be defined in terms of the possible distributions of its molecules. For identical molecules, each possible distribution of molecules is called a **microstate of the system**. All equivalent microstates are grouped into a configuration of the system. The number of microstates in a configuration is the **multiplicity** W of the configuration.

For a system of N molecules that may be distributed between the two halves of a box, the multiplicity is given by

 $W = \frac{N!}{n_1! n_2!}$ (multiplicity of configuration).

Here n_1 is the number of molecules in one half of the box and n_2 is the number in the other half. A basic assumption of statistical mechanics is that all the microstates are equally probable. S= klow

A Statistical View of Entropy

In Chapter 19 we saw that the macroscopic properties of gases can be explained in terms of their microscopic, or molecular, behavior. Such explanations are part of a study called **statistical mechanics**. Here we shall focus our attention on a single problem, one involving the distribution of gas molecules between the two halves of an insulated box. This problem is reasonably simple to analyze, and it allows us to use statistical mechanics to calculate the entropy change for the free expansion of an ideal gas. You will see that statistical mechanics leads to the same entropy change as we would find using thermodynamics.

Figure 20-17 shows a box that contains six identical (and thus indistinguishable) molecules of a gas. At any instant, a given molecule will be in either the left or the right half of the box; because the two halves have equal volumes, the molecule has the same likelihood, or probability, of being in either half.



Figure 20-17

An insulated box contains six gas molecules. Each molecule has the same probability of being in the left half of the box as in the right half. The arrangement in (a) corresponds to configuration III in Table 20-1, and that in (b) corresponds to configuration IV.

Molecules are <u>distinguishable</u>

 $W = \frac{N!}{n_1! n_2!}$ (multiplicity of configuration).

the same probability of being

in the left half of the box as in the right half. The arrangement in

- (a) corresponds to configuration III in Table 20-1
- (b) corresponds to configuration IV.

An insulated box col

Table 20-1 Six Molecules in a Box Calculation Entropy 10^{-23} J/K Configuration Multiplicity W of W(number of microstates) Label (Eq. 20-20) (Eq. 20-21) n_1 n_2 $6!/(6! \ 0!) = 1$ 0 Ι 6 0 1 Π 5 1 6 6!/(5! 1!) = 62.47 III 2 15 6!/(4! 2!) = 153.74 4 IV 3 6!/(3! 3!) = 203 20 4.13 2 4 6!/(2! 4!) = 153.74 V 15 5 VI 1 6!/(1! 5!) = 62.47 6 VII 0 6 1 6!/(0! 6!) = 10 Total = 64

(a) Insulation

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All microstates are equally probable.

NI~ NNE-N S = k ln W $\omega = \frac{N!}{n! n_{z!}}$ $W_i = \frac{N!}{N!0!} = 1, S_i = 0$ $W_{f=} N!$ $\left(\frac{N}{N}\right)\left(\frac{N}{N}\right)$ $\Delta S = Nkln2$ The R = 2N $S_{f} = R \ln 2^{N} = f$

Probability and Entropy

The multiplicity *W* of a configuration of a system and the entropy *S* of the system in that configuration are related by **Boltzmann's entropy** equation:

 $S = k \ln W$ (Boltzmann's entropy equation).

Here $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant.

When *N* is very large (the usual case), we can approximate ln *N*! with **Stirling's approximation**:

 $\ln N! \approx N(\ln N) - N$ (Stirling's approximation).

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Chapter summary

Irreversible (one-way) Process

• If an irreversible process occurs in a closed system, the entropy of the system always increases.

Second Law of Thermodynamics

 If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes.

$$\Delta S \ge 0$$
 Eq. 20-5

Entropy Change

• The efficiency ε of any engine

 $\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_{\text{H}}|}$ Eq. 20-11

• Efficiency of Carnot engine

$$\varepsilon_C = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H}$$
 Eq. 20-12&13

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Entropy Change

• Entropy change for reversible process is given by

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} \quad \text{Eq. 20-1}$$

Chapter summary

Refrigerator

Coefficient of performance Entropy from Statistical Point of refrigerator:
 View

$$K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_{\rm L}|}{|W|}$$

Eq.
$$50^{-1}$$
 system of N molecul $W = \frac{N!}{n_1! n_2!}$ Eq. 20-20

Carnot Refrigerator

$$K_{C} = \frac{|Q_{\rm L}|}{|Q_{\rm H}| - |Q_{\rm L}|} = \frac{T_{\rm L}}{T_{\rm H} - T_{\rm L}}$$

• Boltzmann's entropy equati
$$S = k \ln W$$
, Eq. 20-21

• Stirling's approximati $\ln N! \approx N(\ln N) - N$ Eq. 20-22



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Learning Objectives

- **14.01** Distinguish fluids from solids.
- **14.02** When mass is uniformly distributed, relate density to mass and volume.
- **14.03** Apply the relationship between hydrostatic pressure, force, and the surface area over which that force acts.

$$S = \frac{m}{V} = \frac{\Delta m}{\Delta V} \frac{Rg/m}{V}$$

- Physics of fluids is the basis of hydraulic engineering
- A **fluid** is a substance that can flow, like water or air, and conform to a container
- This occurs because fluids cannot sustain a shearing force (tangential to the fluid surface)
- They can however apply a force perpendicular to the fluid surface
- Some materials (pitch) take a long time to conform to a container, but are still fluids
- The essential identifier is that fluids do not have a crystalline structure

• The **density**, ρ , is defined as:

$$ho = rac{\Delta m}{\Delta V}$$
. Eq. (14-1)

In theory the density at a point is the limit for an infinitesimal volume, but we assume a fluid sample is large relative to atomic dimensions and has uniform density. Then

$$ho=rac{m}{V}$$
 Eq. (14-2)

- Density is a scalar quantity
- Units kg/m³

• The **pressure**, force acting on an area, is defined as:

$$p = \frac{\Delta F}{\Delta A}$$
. Eq. (14-3)

• We could take the limit of this for infinitesimal area, but if the force is uniform over a flat area *A* we write

$$p = \frac{F}{A}$$
 Eq. (14-4)

 $\mathbf{\Gamma}$

• We can measure pressure with a sensor



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- We find by experiment that for a fluid at rest, pressure has the same value at a point regardless of sensor orientation
- Therefore static pressure is scalar, even though force is not
- Only the magnitude of the force is involved •
- Units: the pascal $(1 \text{ Pa} = 1 \text{ N/m}^2)$ the atmosphere (atm) the torr (1 torr = 1 mm Hg)the nound per square inch (nei)

 $1 \text{ atm} = 1.01 \times 10^5 \text{ Pa} = 760 \text{ torr} = 14.7 \text{ lb/in.}^2$.

Learning Objectives

- **14.04** Apply the relationship between the hydrostatic pressure, fluid density, and the height above or below a reference level.
- **14.05** Distinguish between total pressure (absolute pressure) and gauge pressure.

• *Hydrostatic* pressures are those caused by fluids at



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Figure 14-2

• Write the balance of forces:

$$F_2 = F_1 + mg.$$
 Eq. (14-5)

• Rewrite: forces with pressures, mass with density

$$p_2 A = p_1 A + \rho A g(y_1 - y_2)$$
$$p_2 = p_1 + \rho g(y_1 - y_2).$$
Eq. (14-7)

• For a depth *h* below the surface in a liquid this becomes: $p = p_0 + \rho gh$ Eq. (14-8)

The pressure at a point in a fluid in static equilibrium depends on the depth of that point but not on any horizontal dimension of the fluid or its container.

- The pressure in 14-8 is the absolute pressure
- Consists of p_0 , the pressure due to the atmosphere, and the additional pressure from the fluid
- The difference between absolute pressure and atmospheric pressure is called the **gauge pressure** because we use a gauge to measure this pressure difference
- The equation can be turned around to calculate the atmospheric pressure at a given height above ground:

$$p=p_0-\rho_{\rm air}gd.$$



Answer: All the pressures will be the same. All that matters is the distance *h*, from the surface to the location of interest, and *h* is the same in all cases.

Learning Objectives

14.06 Describe how a barometer can measure atmospheric pressure.

14.07 Describe how an opentube manometer can measure the gauge pressure of a gas.

- Figure 14-5 shows *mercury barometers*
- The height difference between the air-mercury interface and the mercury level is *h*:



- Only the height matters, not the cross-sectional area
- Height of mercury column is numerically equal to torr
 pressure only if:
 - Barometer is at a place where g has its standard value
 - Temperature of mercury is 0°C

Figure 14-6 shows an open-tube manometer



 The gauge pressure can be positive or negative, depending on whether the pressure being measured is greater or less than atmospheric pressure

Learning Objectives

14.08 Identify Pascal's principle.

14.09 For a hydraulic lift, apply the relationship between the input area and displacement and the output area and displacement.

 Pascal's principle governs the transmission of pressure through an incompressible fluid:

A change in the pressure applied to an enclosed incompressible fluid is transmitted undiminished to every portion of the fluid and to the walls of its container.

• Consider a cylinder of fluid (Figure 14-7) Lead shot • Increase p_{ext} , and p at any point must change $\Delta p = \Delta p_{ext}$. Eq. (14-12) • Independent of hFigure 14-7

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- Describes the basis for a hydraulic lever
- Input and output forces related by:

$$F_o = F_i \frac{A_o}{A_i}$$
. Eq. (14-13)

The distances of movement are related by:



Eq. (14-14)

 So the work done on the input piston equals the work output

$$W = F_o d_o = \left(F_i \frac{A_o}{A_i}\right) \left(d_i \frac{A_i}{A_o}\right) = F_i d_i, \quad \text{Eq. (14-15)}$$

• The advantage of the hydraulic lever is that:

With a hydraulic lever, a given force applied over a given distance can be transformed to a greater force applied over a smaller distance.

14-5 Archimedes' Principle

Learning Objectives

- **14.10** Describe Archimedes' principle.
- **14.11** Apply the relationship between the buoyant force on a body and the mass of the fluid displaced by the body.
- **14.12** For a floating body, relate the buoyant force to the gravitational force.

- **14.13** For a floating body, relate the gravitational force to the mass of the fluid displaced by the body.
- **14.14** Distinguish between apparent weight and actual weight.
- **14.15** Calculate the apparent weight of a body that is fully or partially submerged.

14-5 Archimedes' Principle

- The **buoyant force** is the net upward force **on** a submerged object **by** the fluid in which it is submerged
- This force opposes the weight of the object

It comes from the increase in pressure with depth



(a)

The buoyant force is due to the pressure of the surrounding water.





(c)

Figure 14-10

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