

# Lecture Notes 1

## 1. Basic concepts

To completely describe a macroscopic material one has to know the position vector and velocity vector of a huge number of molecules/atoms.

**Example:** 1 liter of water  $\text{H}_2\text{O}$  has a mass of 1kg. The number of molecules is:  $N = 1\text{kg}/(18 \times 1.66 \times 10^{-27}\text{kg}) = 3.3 \times 10^{25}$  molecules. Alternative calculation uses the Avogadro number which is the number of molecules in 1 mole of material:  $N_A = 6.02 \times 10^{23}\text{mole}^{-1}$ . One mole of water has a mass of 18g. Then the number of moles in 1kg of water is  $(1/18 \times 10^{-3}) = 55.6$  moles. Then the number of molecules is number of moles times the Avogadro number:  $55.6 \times 6.02 \times 10^{23} = 3.3 \times 10^{25}$  molecules.

Clearly a complete description of a system with so many degrees of freedom is not feasible. Fortunately, the time scale for our measurements is much larger than the time scale for molecular processes. The same is true with respect to spatial scales.

**Example:** Time scale for molecular processes can be estimated using the Heisenberg uncertainty principle:  $t \sim \hbar/E = 6.63 \times 10^{-34}/(13.6 \times 1.6 \times 10^{-19}) = 3 \times 10^{-16}\text{s}$ . I used for energy the ionization energy of Hydrogen 13.6eV. The time scale from a camera shutter is about  $10^{-3}$  s which is much longer. The length scale for atomic processes is  $10^{-10}$  m which is much shorter than measurement scale  $10^{-7}$  m (visible light wavelength). As a result, the measurements provide an average of many atomic configurations. Thermodynamics deals with those averages of various quantities. A complete determination of positions and velocities of all molecules represents a microstate. Many microstates correspond to a macrostate which could be out of equilibrium or in equilibrium. There is no apparent, macroscopic, motion in equilibrium. However, at the microscopic level molecules move and thus there are many microstates corresponding to the equilibrium macrostate. Our course focuses on equilibrium thermodynamics.

The time it takes for a particular system to reach an equilibrium state is called the relaxation time. For example, by moving the piston to the left increases the density of gas molecules in the immediate neighborhood of the piston. After a time of the order of:  $l/v = 1\text{m}/(300\text{m/s}) = 0.003\text{s}$  the molecules rearrange themselves so that the distribution is uniform. Here I took the length of the piston  $l \sim 1\text{m}$  and sound velocity  $v \sim 300\text{m/s}$ . The evolution towards the quiescent equilibrium state can be relatively fast, as in the example above, or in some cases, such as for glassy materials, very slow.

An equilibrium state is characterized by a few extensive quantities in contrast with the huge number of degrees of freedom needed to specify a microstate. The extensive variable, that are proportional to the size of the thermodynamic system, are: the energy  $U$ , the volume  $V$ , the number of molecules of species #1  $N_1$ , the number of molecules of species #2  $N_2$ , etc. and the entropy  $S$ . The entropy quantifies the complexity of that macrostate as it depends on the number of microstates.

## 2. Work, Pressure, Volume

The gas molecules in the cylinder move in hit the piston thus acting with some force  $F$ . The area of the piston is  $A$ . The pressure is  $P = F/A$ . The SI unit of pressure is called Pascal:  $\text{Pa} = \text{N}/\text{m}^2$ .

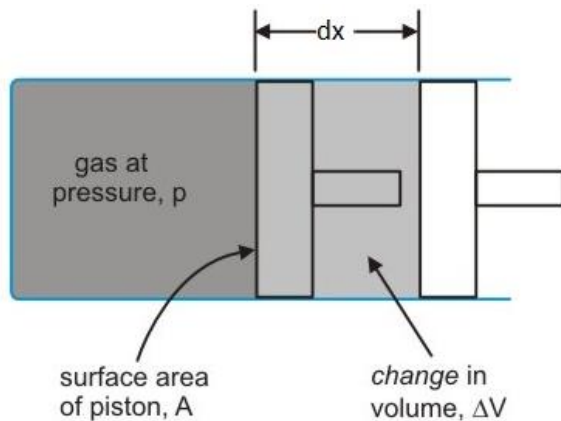


Figure 1: Work done on gas by piston on the gas:  $dW = -Fdx = -pAdx = -pdV$

In figure 1 we move the piston with force  $F$  to the left. The work we do on the gas is  $F(-dx)$  since  $dx < 0$ . Assuming to be in equilibrium during the time it takes to move the piston, the force is related to the pressure exerted by the gas molecules on the piston  $F = pA$ . Since the change in volume is  $dV = Adx$ , it follows that the work on the gas is:

$$dW = -pdV \quad (1)$$

## 3. Hydrostatic Equilibrium

Consider a fluid (liquid or gas) in equilibrium in the presence of gravity. The force exerted by the fluid above the slab is  $(p+dp)A$ . The force from fluid below the slab is  $pA$ , and the slab

weight is  $\rho Adzg$ . Here we denote the mass density by  $\rho$ .

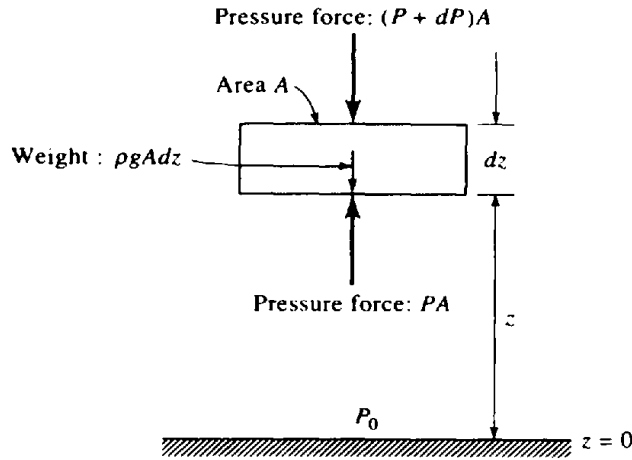


Figure 2: Hydrostatic equilibrium: The force from fluid above  $(p+dp)A$  and the slab weight  $\rho Adzg$  are balanced by the force from fluid below  $pA$   
 $(p+dp)A + \rho Adzg = pA$  where  $g$  is gravitational acceleration.

It follows that:

$$\frac{dp}{dz} = -\rho g \quad (2)$$

#### 4. Application: Incompressible Fluid, Buoyancy Force

Most liquids, have a constant density  $\rho$ , independent of  $z$ . They are incompressible fluids.

By integrating equation (2) above we get:

$$p = p_0 - \rho g z \quad (3)$$

where  $p_0$  is pressure at  $z = 0$ .

If a solid of height  $h$  is immersed inside a liquid there is a net force due to the pressure difference

$\Delta p = \rho g h$  which is pointing upwards. It is equal to:

$$F_{\text{buoyancy}} = \Delta p A = g \rho h A = g \rho V, \quad (4)$$

where  $V$  is volume of the immersed solid and  $\rho$  is the fluid density.

Hence Eq. (4) states that the buoyancy force is equal to the weight of the fluid displaced by the solid.

This is Archimedes' principle. This was discovered by the Greek physicist Archimedes (287BC – 212 BC).



Figure 3: Sculpture of Archimedes in bathtub demonstrating the buoyance force. At the discovery moment he yelled Eureka (I found it). The Israel Science Museum in Haifa.

### Exercise

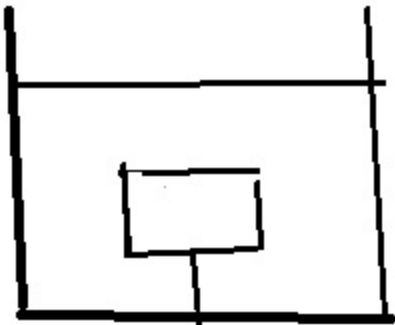


Figure 4: Cork immersed in water and tied to vessel bottom

A small piece of cork of density  $\rho_{\text{cork}} = 200\text{kg/m}^3$  is submerged in water of density  $\rho_{\text{water}} = 1000\text{kg/m}^3$ .

The cork volume is  $3\text{cm}^3$  and it is tied to the bottom of the vessel with a string.

(a) What is tension in the string. (b) If the string is cut what is the cork's acceleration?

(a)  $T + V \rho_{\text{cork}}g = V \rho_{\text{water}}g$

$$T = V(\rho_{\text{water}} - \rho_{\text{cork}})g = 0.0235\text{N}$$

(b) Newton's 2'nd law

$$F_{\text{buoyancy}} - mg = ma$$

$$V\rho_{\text{water}}g - V\rho_{\text{cork}}g = V\rho_{\text{cork}}a$$

$$a = g(\rho_{\text{water}}/\rho_{\text{cork}} - 1) = 39.24\text{m/s}^2$$

## 5. Atmospheric Pressure, Torricelli barometer

Evangelista Torricelli, a collaborator of Galileo, has measured the atmospheric pressure. Here is the principle of this experiment.

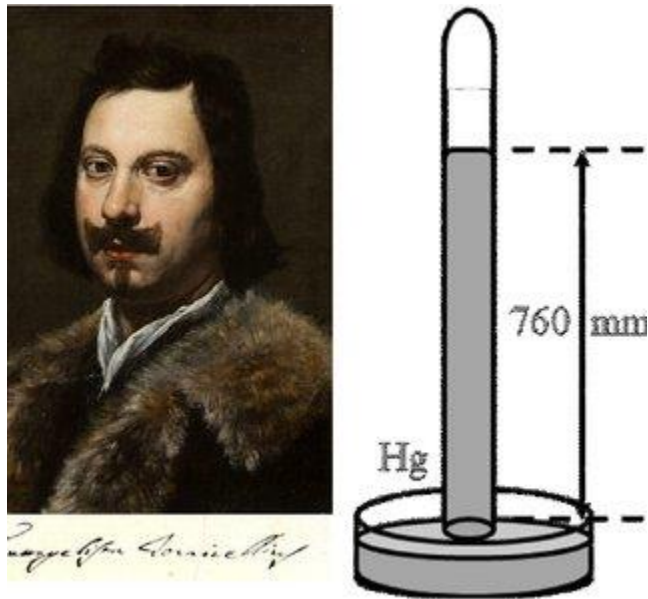


Figure 5: Evangelista Torricelli (1608-1647) and his barometer.

In an inverted test tube in a dish of mercury the mercury rises to a height of 0.76m.

The atmospheric pressure is balanced by the pressure from the weight of mercury in the tube.

$$p_{\text{atm}} = \rho_{\text{Hg}}gh = 13.6 \cdot 10^3 \cdot 9.8 \cdot 0.76 = 1.01 \cdot 10^5 \text{ Pa}$$

1atm is atmospheric pressure at sea level. Other unit for pressure is torr: 1atm = 760torr =  $1.01 \cdot 10^5$  Pa.

## 6. Fluid Dynamics

Consider a liquids flowing in a tube. The mass conservation is expressed in the continuity equation.

The mass flowing per unit time, mass rate flow, is:

$$\frac{\Delta m}{\Delta t} = Av\rho$$

Assuming the mass flow rate to be constant and also assuming an incompressible fluid, constant density, it follows:

$$Av = \text{constant} \quad (4)$$

The conservation of energy per unit volume in an incompressible and inviscid flow (the absence of heat losses due to viscosity) is expressed in the equation stated by Daniel Bernoulli,



Figure 6a: Daniel Bernoulli (1700-1782)  
Swiss physicist, mathematician.

$$\rho v^2 / 2 + \rho gh + p = \text{constant} \quad (5)$$

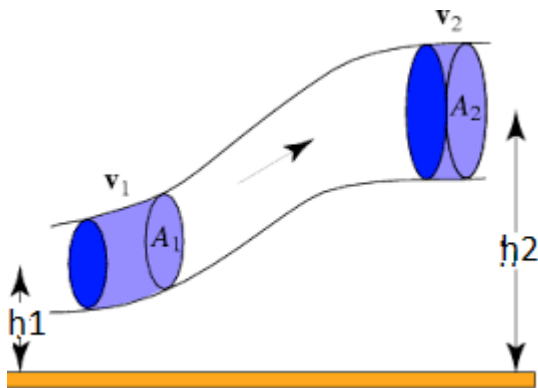


Figure 7b

The first term in the Bernoulli equation (5) is the kinetic energy per unit volume. The second term is the gravitational potential energy per unit volume. The last term represents the work per unit volume (see Eq.(1)) to push the fluid through the pipe.

## 7. Heat, Temperature, Entropy

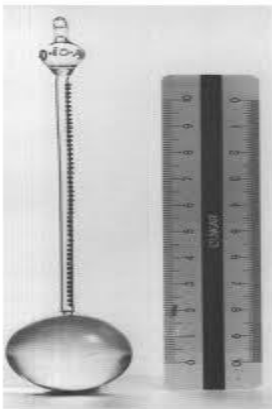
Heat is a form of energy, denoted by  $Q$ . For example, by running a current  $I$  through a wire of resistance  $R$  during a time  $t$  we generate an amount of heat  $Q = RI^2t$ .

Related to heat, as pressure is to work, is the temperature  $T$ . The analog of volume in equation (1) is the entropy  $S$ .

$$dQ = TdS. \quad (6)$$

Temperature, like pressure, is an intensive quantity. By putting in contact two objects of different temperatures after a while the two temperatures become equal to each other. The entropy on the other hand is extensive as the volume is also. The entropy provides a quantification of the degree of disorder. This abstract concept will be further explored in the Statistical Physics course.

Devices that measure temperatures are called thermometers. One of the simplest is the Florentine thermometer that uses the thermal expansion of a fluid like alcohol or mercury. Other thermometers are: electric resistance thermometer uses the temperature dependence of Ohmic resistance and constant volume gas thermometer uses the fact that pressure is proportional to temperature in a process that keeps the gas volume constant.



*Figure 7: Florentine thermometer*

Temperature scale used in this course are:

1. Celsius scale. Temperature is  $100^{\circ}\text{C}$  when water boils and it is  $0^{\circ}\text{C}$  when water freezes.
2. Fahrenheit scale related to Celsius scale through:  $T_{\text{F}} = (9/5)T_{\text{C}} + 32$ .
3. Kelvin or absolute scale:  $T = T_{\text{C}} + 273$ .

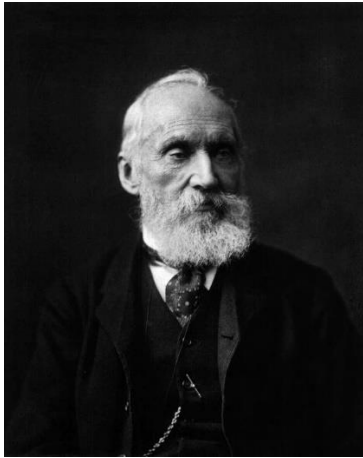
The SI (international system) unit for temperature is the Kelvin. The temperature  $T$  in Kelvins is for most thermodynamic systems positive. In Statistical Physics course we will discuss a special system of nuclear spins that exhibits negative absolute temperatures.

### Exercise

Under atmospheric pressure water freezes at  $0^{\circ}\text{C}$  and boils at  $100^{\circ}\text{C}$ . Compute those temperatures in degrees Fahrenheit and in Kelvins.

Freezing  $T_{\text{F}} = 32^{\circ}\text{F}$ ,  $T = 273\text{K}$ .

Boiling  $T_{\text{F}} = [(9/5)*100 + 32]^{\circ}\text{F} = 212^{\circ}\text{F}$ ,  $T = 373\text{K}$ .



*Figure 8: Lord Kelvin, William Thomson, published in Philosophical Magazine in 1848 the article On an Absolute Thermometric Scale.*

## 8. Ideal Gas

An ideal gas is a low density gas. The typical distance between molecules is much larger than the range of interactions. As a result, the whole energy is the kinetic energy associated with the molecular motion.



The equation of state relates pressure,  $p$ , volume,  $V$ , and temperature,  $T$ . It was discovered experimentally in the seventeenth century.



$\frac{1}{2}$

*Figure 9a: Robert Boyle (1627 – 1691) was an English chemist, physicist.*



*Figure 9b: Edme Mariotte, (1620 -1684), was a French physicist, plant physiologist.*

The Boyle-Mariotte law states that for a fixed amount of gas undergoing an isothermal process:  
 $pV = \text{constant}$ .

Gay-Lussac law states that for a fixed amount of gas undergoing an isochoric process:  $p/T = \text{constant}$ .



Figure 10: Joseph Louis Gay-Lussac (1778 - 1850), French physicist, chemist.



Figure 11: Jacques Charles (1746 – 1823) was a French physicist.

Charles` law states that for a fixed amount of gas undergoing an isobaric process:

$$V/T = \text{constant.}$$

Those three empirical laws are included in the equation of state of ideal gases:

$$pV = Nk_B T \quad (7)$$

N is the number of molecules.  $k_B$  is a fundamental constant of nature called the Boltzmann constant.  $k_B = 1.381 \cdot 10^{-23} \text{ J/K}$ .



*Figure 12a: Ludwig Boltzmann (1844 – 1906) was an Austrian physicist who discovered Statistical Mechanics.*



*Figure 12b: Amedeo Avogadro (1776 – 1856) was an Italian physicist.*

Since 1 mole of material contains Avogadro number of molecules  $N_A = 6.02 \cdot 10^{23} \text{mole}^{-1}$  it follows that for  $\mathcal{N}$  moles the number of molecules is  $N = \mathcal{N}N_A$ . The equation of state Eq (7) becomes:

$$pV = \mathcal{N}RT \quad (8)$$

where  $R = N_A \cdot k_B = 8.31 \text{J}/(\text{K} \cdot \text{mol})$  is called the universal gas constant.

Application:

Compute the volume of 1mole of ideal gas under standard conditions: temperature  $0^\circ\text{C}$  and pressure  $1 \text{atm} = 1.01 \cdot 10^5 \text{Pa}$ .

$$V = \mathcal{N}RT/p = 1 \cdot 8.31 \cdot 273 / (1.01 \cdot 10^5) = 22 \cdot 10^{-3} \text{m}^3 = 22 \text{liters}.$$

## 9. Barometric Formula

Determines the drop in atmospheric pressure,  $p$ , with altitude,  $h$ . We assume the atmosphere to be in hydrostatic equilibrium. We further assume to be described by the ideal gas equation of state. Hence:

$$\frac{dp}{dh} = -\rho g \quad (9)$$

The density is mass/volume:

$$\rho = \frac{NM}{V} = \frac{Mp}{RT} \quad (10)$$

$M$  stands for molar mass. To get the right hand side of eq. (10) I used the equation of state (8).

Combining (9) and (10) we find:

$$\frac{dp}{dh} = -\frac{Mg}{RT} p \quad (11)$$

We next assume the atmosphere to be isothermal. This is only an approximation. Departures from this assumption are discussed in computer labs 1, 7, 8. We now can integrate equation (11) by separating the variables:

$$\int_{p_0}^p \frac{dp}{p} = -\frac{Mg}{RT} h \quad (12)$$

The integral on the left hand side is equal to  $\ln(p/p_0)$ , where  $p$  is pressure at altitude  $h$  and  $p_0$  is pressure at  $h = 0$ . By exponentiating the two sides of equation (12) we get:

$$p = p_0 e^{-\frac{Mg}{RT} h} \quad (13)$$

Equation (13) is the barometric formula.

Application: The atmospheric pressure at sea level is  $p_0 = 1 \text{ atm} = 1.01 \cdot 10^5 \text{ Pa} = 760 \text{ torr}$ . Calculate the atmospheric pressure in Cleveland,  $h = 250 \text{ m}$ , and in Denver,  $h = 1600 \text{ m}$ .

The molar mass for air is  $M = 29 \text{ g/mol} = 29 \cdot 10^{-3} \text{ Kg/mol}$ ;  $g = 9.8 \cdot \text{m/s}^2$ ,  $T = 273 \text{ K}$ . Substitute numerical values in eq. (13).

For  $h = 250 \text{ m}$ ,  $p = 737 \text{ torr}$ . For  $h = 1600 \text{ m}$ ,  $p = 622 \text{ torr}$ .

## 10. Mechanical Equivalent of Heat

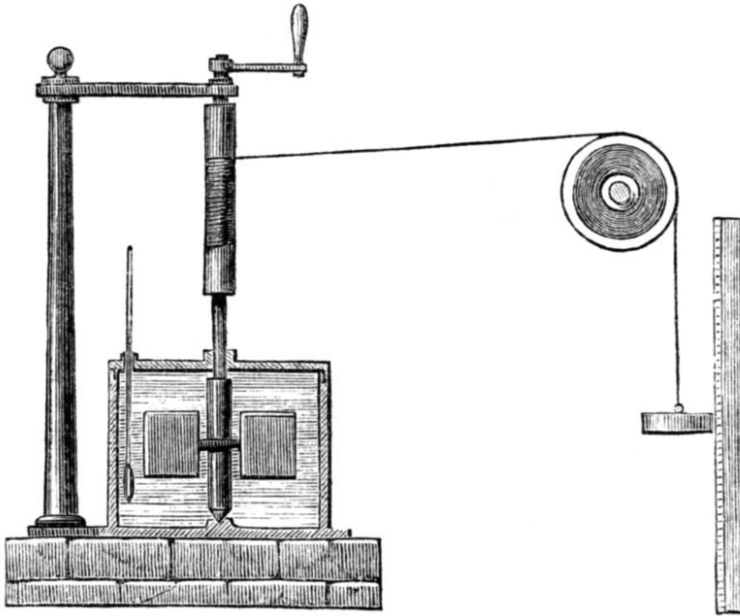


Figure 13. Joule's apparatus for measuring the mechanical equivalent of heat.

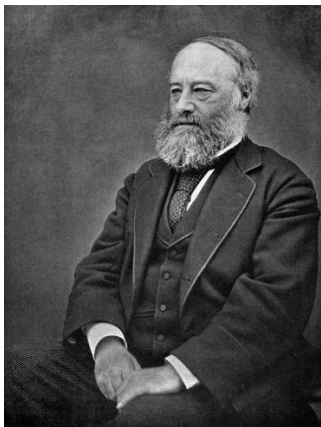


Figure 14. James Prescott Joule (1818-1889) English physicist.

Joule found experimentally that 4.187j of mechanical work are needed to raise the temperature of 1g of water by 1°C.

Heat unit: 1cal = 4.187j.

Heat Q applied to a material of mass m and specific heat c raises the temperature by  $\Delta T$ .

$$Q = mc \Delta T \quad (14)$$

Hence the specific heat of water is  $c = 4.187 \cdot 10^3 \text{ j}/(\text{Kg} \cdot ^\circ\text{C})$

Application: One BTU, British thermal unit, is the heat needed to raise the temperature of 1 pound of water by 1°F. Compute how many joules are in 1Btu.

$$m = 1\text{lb} = 0.454\text{kg}; \Delta T = 1^\circ\text{F} = 0.555^\circ\text{C}, c = 4.187 \cdot 10^3 \text{J}/(\text{Kg} \cdot ^\circ\text{C}).$$

$$Q = 0.454 \cdot 0.555 \cdot 4.187 \cdot 10^3 = 1055\text{J} = 1\text{BTU}.$$

## 11. Chemical Work, Chemical Potential, Number of Moles

The chemical work  $W_C$  stands for the energy change when changing the amount of material in the absence of heat exchange or mechanical work. By analogy with eqs. (1) and (6) for mechanical work and heat, we write:

$$dW_C = \mu dN \quad (15)$$

The chemical potential  $\mu$  is measured in J or in J/mole if  $N$  is expressed in moles. The chemical potential like temperature and pressure is an intensive variable. The number of molecules  $N$ , on the other hand is extensive as the entropy and the volume are also.

## 12. Mathematics for Thermodynamics

Consider a function of several variables:  $f(x, y)$

If we ask for the change in  $f$  when we change slightly the independent variables  $x, y$  we use the Taylor expansion:

$$f(x+dx, y+dy) = f(x, y) + df + (1/2)d^2f + \dots, \quad (16)$$

$df$  is the first differential. It is given by:

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \quad (17)$$

$d^2f$  is the second differential. It is given by:

$$d^2f = \frac{\partial^2 f}{\partial x^2} dx^2 + 2 \frac{\partial^2 f}{\partial x \partial y} dx dy + \frac{\partial^2 f}{\partial y^2} dy^2 \quad (18)$$

Note that for mixed derivatives the order of differentiation is not important.

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad (19)$$

This mathematical result translates in thermodynamics in the important Maxwell relations.

### READINGS:

Halliday, Resnick, Walker, Ch14: *Fluids*  
 Callen, Ch.1: *The problem and the postulates*  
 Problem Set 1

## Lecture Notes 2

### 1. Energy of Ideal Gas

An ideal gas has only kinetic energy as the molecules are so far apart one from the other that the interaction energy is neglected.

$$U = \Sigma mv^2/2$$

Assuming elastic collisions with the wall, a molecule hits surface  $\Delta A$  (in plane  $yz$ ) with a force  $2mv_x/\Delta t$ . Assuming also uniform distribution of molecules in the container of volume  $V$  the fraction of all molecules hitting the wall is:  $(1/2)\Delta x\Delta A/V$ . The  $1/2$  factor signifies that half of those molecules move away from the wall

$$\text{Then: } \Delta F = p\Delta A = \Sigma[(1/2)\Delta x\Delta A/V][2mv_x/\Delta t] = \Sigma mv_x^2[\Delta A/V] = (2/3)U[\Delta A/V]$$

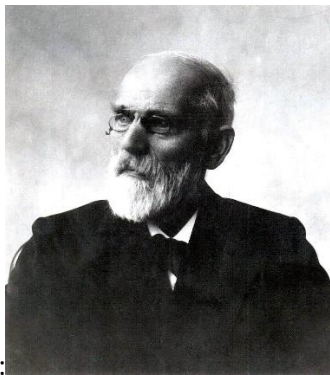
Here we also assumed isotropy, i.e. all directions equivalent. This explains the  $1/3$  factor.

It follows:  $U = (3/2)pV$ .

Here we considered an ideal gas of monatomic molecules. Diatomic and polyatomic ideal gases will be discussed in future lectures.

### 2. van der Waals Equation of State

The ideal gas equation of state works for low density gases so that the distance between molecules is much larger than the range of interactions. As a result, the ideal gas has only the kinetic energy of the molecules.



*Figure 1: Johannes Diderik van der Waals (1837-1923), Dutch physicist who discovered the equation of state of gases and liquids.*

This equation is a modification of the equation of state of ideal gases.

It accounts for the minimum volume obtained under large pressure by replacing in the ideal gas equation of state volume by  $V - \mathcal{N}b$ . Here  $\mathcal{N}$  is number of moles and  $b$  is volume of 1 mole under huge compression.

It also accounts for the attraction between molecules which reduces the pressure. So in the equation of state of ideal gases we replace the pressure by  $p + (\mathcal{N}/V)^2a$ . Here we estimated the number of pairs of molecules that interact  $\mathcal{N}(\mathcal{N}-1)/2 \simeq \mathcal{N}^2/2$  for large  $\mathcal{N}$ . The constant  $a$  which estimates the strength of the attraction incorporates the  $1/2$  factor.

The van der Waals equation of state is:

$$(p + (\mathcal{N}/V)^2a)(V - \mathcal{N}b) = \mathcal{N}RT$$

The constants  $a$  and  $b$  depend on which chemical we study. For example the values for water are:

$$a = 0.544\text{Pa}\cdot\text{m}^6/\text{mol}^2$$

$$b = 30.5\cdot 10^{-6}\text{m}^3/\text{mol}$$

Exercise: Compute pressure needed to apply to 1 mole of water vapor at  $27^\circ\text{C}$  to get a volume of 10l. Use the van der Waals and ideal gas equations of state.

$$p = \mathcal{N}RT/(V - \mathcal{N}b) - (\mathcal{N}/V)^2a = 8.31\cdot 300/(0.01 - 30.5\cdot 10^{-6}) - (1/0.01)^2\cdot 0.544$$

$$p = 2.45\cdot 10^5\text{Pa}$$

$$p_{\text{ideal}} = \mathcal{N}RT/V = 8.31\cdot 300/0.01 = 2.49\cdot 10^5\text{Pa}$$

### Reading

HRW Ch.19 Sec 4.

Callen Ch 3, Sec 5



## Lecture Notes 3

### 1. First Law of Thermodynamics

The internal energy of a material, denoted by  $U$ , is a state variable meaning that it depends solely on the state of the system and it is independent of the process that lead to that state. The entropy  $S$ , the volume  $V$ , the number of molecules  $N$  and are also state variables. The equation relating these variables is a fundamental equation, as it contains all the information about the considered material.

$$U = U(S, V, N) \quad (1)$$

The first law is the energy conservation law. It states that adding to the material heat  $dQ = TdS$ , doing mechanical work  $dW = -pdV$  on the material, and doing chemical work  $dW_c = \mu dN$  changes the energy of the material:

$$dU = dQ + dW + dW_c = TdS - pdV + \mu dN \quad (2)$$

On the other hand the differential of  $U$  is:

$$dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial N} dN \quad (3)$$

Comparing (2) and (3) we find:

$$T = \left( \frac{\partial U}{\partial S} \right)_{V,N} \quad (5)$$

$$p = - \left( \frac{\partial U}{\partial V} \right)_{N,S} \quad (6)$$

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} \quad (7)$$

### 2. Extensive and Intensive Variables

When the size of a system increases by a factor  $\lambda$  the extensive variables  $U$ ,  $S$ ,  $V$ ,  $N$  increase by the same factor  $\lambda$ :

$$U(\lambda S, \lambda V, \lambda N) = \lambda U \quad (8)$$

Equation (8) states that energy is a homogeneous function of first degree of entropy, volume and number of molecules. The temperature  $T$ , the pressure  $p$  and the chemical potential  $\mu$  are intensive variables as they do not change when the size of the system changes by the factor  $\lambda$ , see Eqs. 5, 6, 7.

### 3. Euler Equation

This relation characterizes homogeneous functions.



*Figure 1: Leonard Euler (1707 – 1783) was a Swiss mathematician.*

Take derivative with respect to  $\lambda$  on both sides of Eq. (8). Then set  $\lambda = 1$ . In view of Eqs. 5, 6, 7, we get the Euler Equation:

$$TS - pV + \mu N = U \quad (9)$$

Equation (9) can be rewritten by using molecular energy  $u = U/N$ , molecular entropy  $s = S/N$ , and molecular volume  $v = V/N$ :

$$u = Ts - pv + \mu \quad (10)$$

### 4. Molecular Form of 1<sup>st</sup> Law

By substituting  $\lambda = 1/N$  in equation (8) we get  $u = u(s, v)$ , where  $u = U/N$ ,  $s = S/N$ ,  $v = V/N$ . We write the 1<sup>st</sup> law using the molecular energy, entropy and volume:

$$d(Nu) = Td(Ns) - pd(Nv) + \mu dN \quad (11)$$

$$Ndu + udN = TNds + TsdN - pNdv - pvdN + \mu dN \quad (12)$$

In view of Eq. (10) the terms having a factor  $dN$  cancel out. Then Eq. 12 reduces to:

$$du = Tds - pdv \quad (13)$$

Equation (13) is the molecular form of the 1<sup>st</sup> Law.

## 5. Gibbs – Duhem Equation



*Figure 2: Josiah Willard Gibbs (1839 – 1903) was an American physicist, professor at Yale. He developed the foundations of statistical mechanics.*

Substitute U, as given in Eq. 9, into the left hand side of the 1<sup>st</sup> Law, Eq.2:

$$d(TS - pV + \mu N) = TdS - pdV + \mu dN \quad (14)$$

Since:  $d(TS) = TdS + SdT$ ;  $d(pV) = pdV + Vdp$ ;  $d(\mu N) = \mu dN + Nd\mu$ ,

Eq. (14) reduces to the Gibbs-Duhem equation:

$$SdT - Vdp + Nd\mu = 0 \quad (15)$$

Solving for differential of chemical potential we get:

$$d\mu = -sdT + vdp \quad (16)$$

where  $s = S/N$  is molecular entropy and  $v = V/N$  is molecular volume.

The fundamental equation using only intensive variables is:

$$\mu = \mu(T, p)$$

and according to (16):

$$s = -\left(\frac{\partial \mu}{\partial T}\right)_p \quad (17)$$

$$v = \left(\frac{\partial \mu}{\partial p}\right)_T \quad (18)$$

## 6. Specific Heats, Compressibilities, Thermal Expansion

Heat capacity C measures the amount of heat needed to raise temperature by 1K.

$C = dQ/dT = TdS/dT$ . When we divide  $C$  by size of the system  $N$  we get the specific heat  $c = C/N$ . For gases it is important to specify whether the heating process is isobaric (constant pressure) or isochoric (constant volume).

$$c_p = T \left( \frac{\partial s}{\partial T} \right)_p \quad (19)$$

$$c_v = T \left( \frac{\partial s}{\partial T} \right)_v \quad (20)$$

The compressibility measures the fractional change in volume when we decrease pressure by one unit. For gases the compressibilities depend on the process: isothermal or adiabatic.

$$k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \quad (21)$$

$$k_s = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_s \quad (22)$$

The strength of solids and liquids are often characterized by the bulk modulus  $B = 1/k$ .

The thermal expansion measures the fractional change in volume when we raise isobarically the temperature by 1K.

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad (23)$$

Application:

For ideal gas we calculate the thermal expansion and isothermal compressibility. We use the equation of state:  $pV = Nk_B T$ .

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \left( \frac{\partial (Nk_B T/p)}{\partial T} \right)_p = \frac{Nk_B}{pV} = \frac{1}{T} \quad (24)$$

$$k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left( \frac{\partial \left( \frac{Nk_B T}{p} \right)}{\partial p} \right)_T = \frac{Nk_B T}{p^2 V} = \frac{1}{p} \quad (25)$$

For ideal gas we calculate the isochoric specific heat by using  $u = (3/2)pv = (3/2)k_B T$ . From the 1<sup>st</sup> Law in molecular form, Eq. 13,  $du = Tds - pdv = Tds$  since  $dv=0$  because  $v$  is constant.

Hence:

$$c_v = T \left( \frac{\partial s}{\partial T} \right)_v = \frac{du}{dT} = \frac{3}{2} k_B \quad (26)$$

This specific heat per molecule. The molar specific heat is:

$$c_v = \frac{3}{2} R \quad (27)$$

Reading

HRW Ch.19

Callen Ch. 2, Sec 1, 2; Ch. 3

Problem Set 2, 3