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**Chursanova M.V.**

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Part 2: Molecular physics and thermodynamics. Electrostatics

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#### **Conspectus of lectures for the credit module "Physics 1: Mechanics. Molecular physics and thermodynamics. Electrostatics"**

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## CHAPTER 2. MOLECULAR PHYSICS AND THERMODYNAMICS

### Topic 2.1 Subject and method of molecular physics and thermodynamics.

#### Ideal gas

#### *Lecture 11*

**Molecular physics and thermodynamics** is the branch of science that studies physical properties of macroscopic systems and laws of energy transfer and transformation within such systems.

**Macroscopic system** (or **Thermodynamic system**) is the physical system consistent of a large number of particles (molecules, atoms, ions, electrons, etc.), which are in continuous random thermal motion.

While molecular physics considers **microscopic characteristics** of the particles of the system, such as their velocity and mechanical energy, thermodynamics studies the system as a whole without consideration of the molecular structure of the substance. Properties of the thermodynamic system can be described by **macroscopic characteristics** such as pressure, volume, and temperature.

The large number of particles in the system means that statistical arguments can be applied to its consideration, allowing to make relation between microscopic and macroscopic characteristics: the large-scale properties can be related to a description on a microscopic scale, where matter is treated as a collection of molecules. Applying Newton's laws of motion in a statistical manner to a collection of particles provides a reasonable description of thermodynamic processes.

To keep the mathematics relatively simple, we shall consider thermodynamic systems using the example of gases.

### ***2.1.1 Fundamentals of the kinetic theory of gases***

**Kinetic theory** is the *microscopic model* of an ideal gas. It describes a gas as a large number of submicroscopic particles (atoms or molecules), all of which are in constant rapid motion that has randomness arising from their many collisions with each other and with the walls of the container.

The kinetic theory for ideal gases makes the following assumptions:

1. The gas consists of very small particles known as molecules. The number of molecules in the gas is large, and the average separation between them is large compared with their dimensions. The size of molecules is negligible compared to the average separation between them, so we model the molecules as particles. The number of molecules in the gas is so large that statistical treatment can be applied. All the molecules are identical.
2. These molecules are in constant, random, and rapid motion. They obey Newton's laws of motion, but as a whole they move randomly. By "random" we mean that any molecule can move in any direction with any speed. Random motion of particles due to their thermal motion is called the **Brownian motion**. Brownian motion never stops.
3. The rapidly moving particles constantly collide among themselves and with the walls of the container. All these collisions are perfectly elastic. The molecules interact only by short-range forces during elastic collisions and exert no long-range forces on each other.

**Atomic mass unit** (unified atomic mass unit) is the standard unit for indicating mass on an atomic or molecular scale. It is defined as 1/12 of the mass of an unbound neutral atom of carbon  $^{12}\text{C}$ .

$$1 \text{ amu} = \frac{1}{12} m_c = 1.66 \cdot 10^{-27} \text{ kg}$$

**Relative molecular (atomic) mass** is the mass of a molecule/atom relative to the mass of  $^{12}\text{C}$ :

$$M_r = \frac{m_M}{\frac{1}{12}m_c}$$

**Amount of substance** ( $\nu$ ) is the number of particles (molecules, atoms) present in an ensemble relative to the number of particles in the 12 g of  $^{12}\text{C}$ . The SI unit for amount of substance is the mole (mol).

**Mole** is the amount of substance that contains as many particles (molecules, atoms) as there are atoms in 12 grams of carbon  $^{12}\text{C}$ .

**Avogadro constant** ( $N_A$ ) is the number of particles (molecules, atoms) that are contained in the amount of substance given by one mole:

$$N_A = 6.02 \cdot 10^{23} \text{ 1/mol.}$$

**Molar mass** ( $M$ ) is the mass of one mole of the substance:

$$M = M_r \cdot 10^{-3} \text{ kg/mol} = M_r \text{ g/mol, or } M = m_m \cdot N_A \text{ kg/mol.}$$

$$\text{Mass of the molecule of a substance: } m_M = \frac{M}{N_A}.$$

**Amount of substance:**

$$\nu = \frac{N}{N_A} = \frac{m}{M}, \tag{2.1}$$

where  $N$  is the number of molecules (atoms) in the substance;  $M$  is the mass of the substance.

**Concentration** of molecules is the number of molecules per unit volume.

$$n = \frac{N}{V}, \quad \text{where } N \text{ is the number of molecules contained in the volume } V.$$

**Diffusion** is a mutual penetration of molecules of one substance into another substance leading to the equalizing of their concentrations within the whole occupied volume. Therefore, diffusion is the net movement of molecules or atoms from a region of high concentration to a region of low concentration. This is also referred to as the movement of a substance down a concentration gradient.

**Standard conditions:** The standard pressure  $p_o = 1.0131 \cdot 10^5$  Pa;

The standard temperature  $t_o = 0$  °C, or  $T_o = 273$  K.

The molar volume, occupied by one mole of any gas at standard conditions is

$$V_M = 22.4 \cdot 10^{-3} \text{ m}^3 = 22.4 \cdot \text{liter}.$$

### ***2.1.2 Temperature***

**Temperature** of the thermodynamic system is a quantity characterizing its thermodynamic equilibrium. Usually, by default, a thermodynamic system is taken to be in its own internal state of **thermodynamic equilibrium**. A thermodynamic state of internal equilibrium is a state in which no changes occur within the system, and there are no macroscopic flows of matter or of energy within it. All the macroscopic state characteristics are equivalent in all the points of the system.

However, when two different systems are put into thermal contact with each other, the energy exchange begins between them. The two systems, which have been at different initial temperatures, eventually reach some intermediate temperature and the state of equilibrium. Thermal equilibrium is a situation in which two systems would not exchange energy by heat or electromagnetic radiation if they were placed in thermal contact. Two systems in thermal equilibrium with each other are at the same temperature.

#### **The zeroth law of thermodynamics (the law of equilibrium):**

If objects A and B are separately in thermal equilibrium with a third object C, then A and B are in thermal equilibrium with each other.

**Thermodynamic temperature** is the absolute measure of temperature. The International System of Units specifies the Kelvin scale for measurement of the thermodynamic temperature, where the triple point of water at 273.16 K is taken as the fundamental fixing point. Zero thermodynamic temperature is called the **absolute zero**: it is the lowest limit of the thermodynamic temperature scale, when the particle constituents of matter have minimal motion and can become no colder.

### 2.1.3 Ideal gas

**Ideal gas** is a theoretical gas composed of a large number of randomly moving point particles that do not interact except when they collide elastically.

- The size of the molecules is negligible, so they are considered as material points;
- The long-range interaction between the molecules is absent.

**State of ideal gas** is characterized by pressure  $p$ , volume  $V$  and absolute temperature  $T$ . **Equation of state** of the gas is the equation that interrelates these quantities. In general, the equation of state is very complicated, but for the ideal gas it is quite simple and can be determined from experimental results. We can use the ideal gas model to make predictions that are adequate to describe the behavior of real gases at low pressures.

**Thermodynamic process** is a passage of a thermodynamic system from one state to another.

Let's find out how the quantities volume  $V$ , pressure  $p$ , and temperature  $T$  are related for a sample of gas of mass  $m$ . Suppose an ideal gas is confined to a cylindrical container whose volume can be varied by means of a movable piston. The cylinder does not leak, so the mass (or the number of moles) of the gas remains constant. For such a system, experiments provide the following information for different thermodynamic processes (see Figure 2.1):

- When the gas is kept at a constant temperature, its pressure is inversely proportional to the volume. (**Boyle's law**.)

**Isothermal process** is a thermodynamic process during which the temperature of the closed system undergoing such a process remains constant.

$$pV = \text{const} \quad (T = \text{const}); \quad p_1V_1 = p_2V_2 \quad (2.2)$$

- When the pressure of the gas is kept constant, the volume is directly proportional to the temperature. (**Gay-Lussac's law**.)

**Isobaric process** is a thermodynamic process during which the pressure of the closed system undergoing such a process remains constant.



$$\frac{V}{T} = \text{const} \quad (p = \text{const}); \quad \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (2.3)$$

- When the volume of the gas is kept constant, the pressure is directly proportional to the temperature. (**Charles's law**.)

**Isochoric process** is a thermodynamic process during which the volume of the closed system undergoing such a process remains constant.

$$\frac{p}{T} = \text{const} \quad (V = \text{const}); \quad \frac{p_1}{T_1} = \frac{p_2}{T_2} \quad (2.4)$$

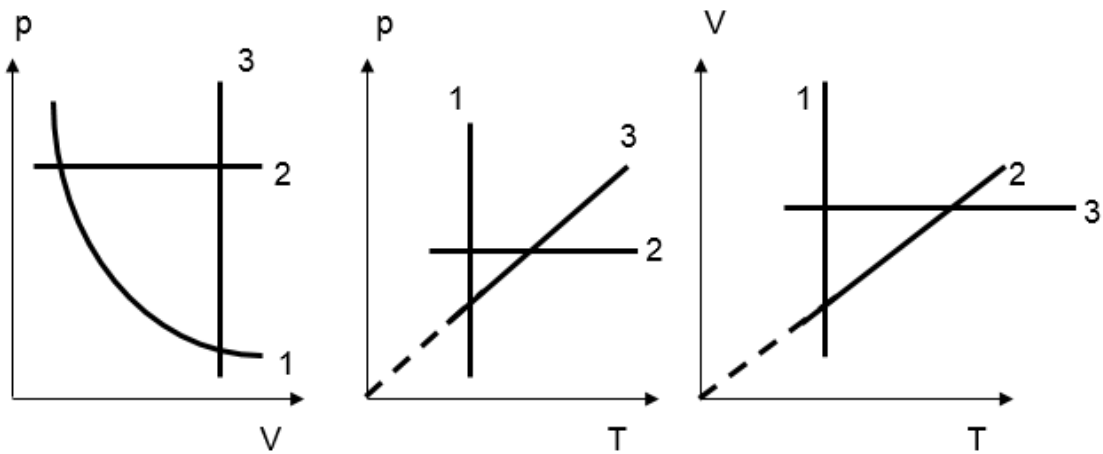


Figure 2.1 Diagrams of the thermodynamic processes:

- 1 - isothermal process  $T = \text{const}$ ;  $p = \frac{\text{const}}{V}$ ;
- 2 - isobaric process  $p = \text{const}$ ;  $V = \text{const} \cdot T$ ;
- 3 - isochoric process  $V = \text{const}$ ;  $p = \text{const} \cdot T$ .

These observations are summarized by the **equation of state for an ideal gas** (**Mendeleev – Clapeyron law**):

$$pV = \nu RT, \quad \text{or} \quad pV = Nk_B T, \quad \text{or} \quad \frac{pV}{T} = \text{const}, \quad (2.5)$$

where  $v$  is the number of moles of gas in the sample;  $R$  is the **universal gas constant**,  $R = 8.31 \text{ J/mol}\cdot\text{K}$ ;  $N$  is the total number of molecules;  $k_B$  is the **Boltzmann constant**,

$$k_B = \frac{R}{N_A} = 1.38 \cdot 10^{-23} \text{ J/K}.$$

### 2.1.4 Basic equation of the kinetic theory for ideal gases

**Basic equation of the kinetic theory** relates pressure, a macroscopic property of gas, to the average (translational) kinetic energy per molecule, root-mean-square speed, microscopic properties of the gas:

$$p = \frac{2}{3}n\bar{E}, \quad \text{or} \quad p = nk_B T, \quad \text{or} \quad p = \frac{1}{3}\rho\bar{v}_{rms}^2, \quad (2.6)$$

where  $n = N/V$  is the concentration of the molecules,  $\bar{E}$  is the average translational kinetic energy,  $\rho$  is density of the gas,  $\bar{v}_{rms}$  is the root-mean-square speed of the molecules of gas.

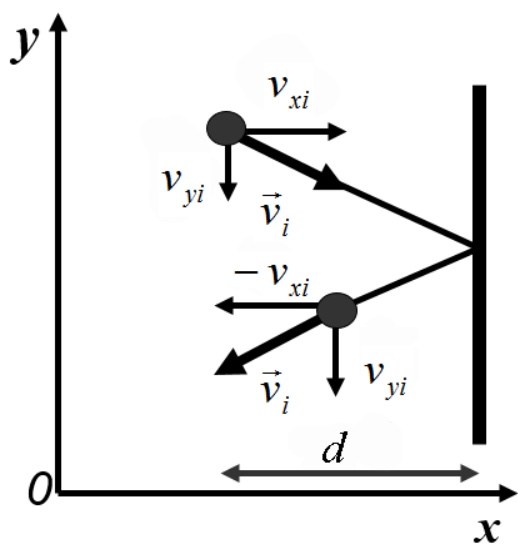


Figure 2.2.

Let's show that microscopic collisions of molecules with the walls of the container lead to the macroscopic pressure on the walls. Consider a collection of  $N$  molecules of an ideal gas in the container of volume  $V$ . The container is a cube with edges of length  $d$ . Let's focus our attention on the  $i$ -th molecules of mass  $m_0$  and assume it is moving so that its component of velocity in the  $x$  direction is  $v_{xi}$  (Figure 2.2).

As the molecule collides elastically with any wall, its velocity component perpendicular to the wall is reversed because the mass of the wall is far greater than the mass of the molecule. The molecule is modeled as a nonisolated system for which the impulse from the wall causes a change in the molecule's momentum:

$$\Delta p_{xi} = -m_0 v_{xi} - (m_0 v_{xi}) = -2m_0 v_{xi}.$$

Because the molecules obey Newton's laws, we can apply the impulse-momentum theorem to the molecule to give  $F_{xi}\Delta t = -2m_0v_{xi}$ , where  $F_{xi}$  is the  $x$  component of the average force the wall exerts on the molecule during the collision and  $\Delta t$  is the duration of the collision. For the molecule to make another collision with the same wall after this first collision, it must travel a distance of  $2d$  in the  $x$  direction (across the container and back). Therefore, the time interval between two collisions with the same wall is  $\Delta t = \frac{2d}{v_{xi}}$ . We can average the force over the time interval  $\Delta t$  for

the molecule to move across the cube and back. Sometime during this time interval the collision occurs, and exactly one collision occurs for each such time interval, so the change in momentum for this time interval is the same as that for the short duration of the collision. We obtain  $\langle F_{xi} \rangle = -\frac{2m_0v_{xi}}{\Delta t} = -\frac{m_0v_{xi}^2}{d}$ . By Newton's third law, the  $x$

component of the average force exerted by the molecule on the wall is equal in magnitude and opposite in direction. Now, the total average force exerted by the gas on the wall is found as sum of the average forces exerted by the individual molecules:

$$\langle F_x \rangle = \frac{m_0}{d} \sum_{i=1}^N v_{xi}^2.$$

For a very large number of molecules such as Avogadro's number variations in force with time (nonzero during the short interval of a collision and zero when no molecule happens to be hitting the wall) are smoothed out so that the average force can be considered as the constant force  $F$ .

The average value of the square of the  $x$  component of the velocity for  $N$  molecules is called the **root-mean square** value of the  $v_x$ :

$$v_{x\_rms}^2 = \frac{\sum_{i=1}^N v_{xi}^2}{N}; \quad v_{x\_rms} = \sqrt{\frac{\sum_{i=1}^N v_{xi}^2}{N}}. \quad (2.7)$$

$$\text{We obtain } F = \frac{m_0}{d} N v_{x\_rms}^2.$$

Now let's focus again on the  $i$ -th molecule with velocity components  $v_{xi}, v_{yi}, v_{zi}$ . The square of the speed of the molecule is the sum of the squares of the velocity components:  $v_i^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2$ . Hence, the root-mean square speed for all the molecules in the container  $v_{rms}^2 = v_{x\_rms}^2 + v_{y\_rms}^2 + v_{z\_rms}^2$ . Because the motion is completely random, the  $x$ ,  $y$  and  $z$  components are equal to one another:  $v_{rms}^2 = 3v_{x\_rms}^2$ .

Therefore, the total force exerted on the wall is  $F = \frac{Nm_0}{d} \frac{v_{rms}^2}{3}$ . The total pressure exerted on the wall is  $p = \frac{F}{S} = \frac{F}{d^2} = \frac{Nm_0 v_{rms}^2}{3d^3} = \frac{1}{3} \left( \frac{N}{V} \right) m_0 v_{rms}^2$ , where  $V = d^3$  is the volume of the cube, concentration of the molecules  $n = N/V$ . Thus, we have obtained the **basic equation of the kinetic theory**:

$$p = \frac{1}{3} n m_0 v_{rms}^2. \quad (2.8)$$

Besides,  $p = \frac{2}{3} n \frac{m_0 v_{rms}^2}{2} = \frac{2}{3} n \bar{E}$ , where  $\bar{E} = \frac{m_0 v_{rms}^2}{2}$  is the average translational kinetic energy of molecules.

Now, let's consider another macroscopic variable, the temperature  $T$  of the gas, and compare this expression with the equation of state for an ideal gas:

$$pV = \frac{2}{3} N \bar{E} \quad \text{and} \quad pV = N k_B T.$$

Recall that the equation of state is based on experimental facts concerning the macroscopic behavior of gases. Equating the right sides of these expressions gives

$$T = \frac{2}{3 k_B} \bar{E}, \quad (2.9)$$

that is *temperature of the gas is a direct measure of average kinetic energy of its molecules*.

The **average kinetic energy per molecule** is

$$\bar{E} = \frac{m_0 v_{rms}^2}{2} = \frac{3}{2} k_B T. \quad (2.10)$$

As far as  $v_{rms}^2 = 3v_{x\_rms}^2$ , the  $x$  component of the average translational kinetic energy  $\frac{m_0 v_{x\_rms}^2}{2} = \frac{k_B T}{2}$ , and  $y$  and  $z$  components are the same. Therefore, each translational degree of freedom contributes an equal amount of energy,  $\frac{k_B T}{2}$ , to the gas (**degree of freedom** refers to an independent means by which a molecule can possess energy.)

A generalization of this result is the **theorem of equipartition of energy**:

Each degree of freedom contributes  $\frac{k_B T}{2}$  to the energy of a system, where possible degrees of freedom are those associated with translation, rotation, and vibration of molecules.

The total translational kinetic energy of  $N$  molecules of gas is the  $N$  times the average energy per molecule:

$$K_{tot} = N \frac{m_0 v_{rms}^2}{2} = \frac{3}{2} N k_B T = \frac{3}{2} \nu R T, \text{ where } \nu = \frac{N}{N_A} \text{ is the number of moles of gas.}$$

**Root-mean-square (rms) speed** of the molecules (atoms) can be found as

$$v_{rms} = \sqrt{\frac{3k_B T}{m_0}} = \sqrt{\frac{3RT}{M}}. \quad (2.11)$$

### ***Questions for self-control***

1. Statistical (microscopic) and thermodynamic (macroscopic) physical quantities.
2. Macroscopic parameters and their microscopic interpretation.
3. Postulates of the kinetic theory of gases
4. Temperature. Thermodynamic equilibrium. Zeroth law of thermodynamics
5. Definition of the ideal gas. Equation of state for an ideal gas.
6. Basic equation of the kinetic theory of gases.
7. Theorem of equipartition of energy

## Topic 2.2. The first law of thermodynamics

### Lecture 12

#### 2.2.1 Internal energy

Thermodynamic systems are characterized by the internal energy along with the mechanical energy.

**Internal energy** of the system is the sum of all kinds of kinetic and potential energy of the microscopic components within the system, but excluding the kinetic and potential energy of the system as a whole

Internal energy includes kinetic energy of random translational, rotational, and vibrational motion of molecules (atoms); vibrational potential energy associated with forces between atoms in molecules; and electric potential energy associated with forces between molecules, kinetic and potential energy of electrons in atoms.

$$U = \frac{i}{2} \nu RT = \frac{i}{2} pV, \quad (2.12)$$

where  $i$  is the **number of degrees of freedom** of the gas molecule (“number of degrees of freedom” is the number of independent parameters which characterize the molecule energy due to its translation, rotation and vibration.

$i = 3$  for a monoatomic molecule;

$i = 5$  for a diatomic molecule;

$i = 6$  for a many-atomic molecule.

In three-dimensional space, for a single particle we need 3 coordinates to specify its position during motion. For a molecule consisting of 2 particles the center of mass of the molecule can translate in 3 directions. In addition, the molecule can rotate about the two axes perpendicular to the line joining these particles,  $1 - 1$  and  $2 - 2$  (see Figure 2.3), and 2 rotational degrees of freedom

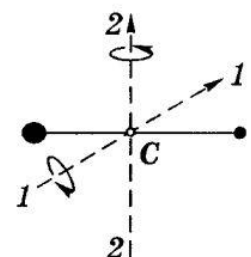


Figure 2.3.

are added. The total number of degrees of freedom is 5. For a general (non-linear) molecule with many atoms, all 3 rotational degrees of freedom are considered, and the total number of degrees of freedom is 6. As we know from the theorem of equipartition of energy, each degree of freedom contributes  $\frac{k_B T}{2}$  to the energy of a system, and after multiplying this quantity by the total number of molecules and by the number of degrees of freedom of the single molecule, we obtain the total internal energy of the gas  $U$ . The internal energy of an ideal gas depends only on its temperature.

### 2.2.2 Heat

**Heat**  $Q$  is the energy transferred across the boundary of a system due to a temperature difference between the system and its surroundings. It is the way of changing the energy of a system.

**Heat capacity** ( $C$ ) is the amount of heat  $Q$  needed to change the temperature of the system by 1K.

$$C = \frac{\delta Q}{dT}, \quad (2.13)$$

where  $\delta Q$  is elementary amount of heat;

$$Q = C\Delta T. \quad (2.14)$$

Both heat and heat capacity are **functions of the process** – they depend on the process through which the energy was transferred.

**Molar heat capacity** (the heat capacity per one mole of the substance):  $C_v = \frac{C}{\nu}$ .

**Specific heat capacity** (the heat capacity per unit mass):  $c = \frac{C}{m}$ .

Specific heat is essentially a measure of how thermally insensitive a substance is to the addition of energy. The greater a material's specific heat, the more energy must be added to a given mass of the material to cause a particular temperature change.

Heat  $Q$  transferred between a body of mass  $m$  and its surroundings to a temperature change  $\Delta T$ :

$$Q = mc\Delta T.$$

Besides, transfer of energy by heat can result not in change in temperature of the system, but in phase change of the system. **Phase change** of a thermodynamic system is the change of state of matter when the physical characteristics of the substance change from one form to another.

Two common phase changes are from solid to liquid (melting) and from liquid to gas (boiling); another is a change in the crystalline structure of a solid. All such phase changes involve a change in the system's internal energy but no change in its temperature. The increase in internal energy in boiling, for example, is represented by the breaking of bonds between molecules in the liquid state; this bond breaking allows the molecules to move farther apart in the gaseous state, with a corresponding increase in intermolecular potential energy.

Heat transferred to a substance of mass  $m$  during a **phase change**:

$Q = rm$ , where  $r$  is the **latent heat of vaporization** – the term used when the phase change is from liquid to gas;

$Q = \lambda m$ , where  $\lambda$  is the **latent heat of fusion** – the term used when the phase change is from solid to liquid (to fuse means “to combine by melting”).

This parameter is called **latent heat** (literally, the “hidden” heat) because this added or removed energy does not result in a temperature change.

When two bodies are in contact, the energy transfer by heat always takes place from the high-temperature body to the low-temperature body.

**Equation of the heat balance**: the amount of energy  $Q_{hot}$  that leaves the hot part of the system equal the amount of energy  $Q_{cold}$  that enters the cold part of the system.

$$Q_{hot} = Q_{cold} \tag{2.15}$$



### 2.2.3 Work

The work done on a deformable system, a gas, is another important mechanism of energy transfer in thermodynamic systems.

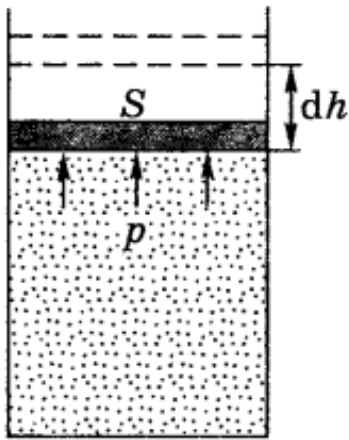


Figure 2.4.

Consider a gas contained in a cylinder fitted with a movable piston of negligible mass (Figure 2.4). At equilibrium, the gas occupies a volume  $V$  and exerts a uniform pressure  $p$  on the cylinder's walls and on the piston. If the piston has a cross-sectional area  $S$ , the force exerted by the gas on the piston is  $F = pS$ . Now let's assume we push the piston and compress the gas **quasi-statically**, that is, slowly enough to allow the system to

remain essentially in internal thermal equilibrium at all times. As the piston is pushed downward by a vertically directed external force  $F$  through a displacement of  $dh$ , the elementary work done on the gas is

$$\delta A = Fdh = -pSdh = -pdV.$$

If the gas is compressed,  $dV$  is negative and the work done on the gas is positive. If the gas expands,  $dV$  is positive and the work done on the gas is negative (they say that the gas does work on its surroundings). If the volume remains constant, the work done on the gas is zero.

#### The work done on the gas

$$\delta A = -pdV; \quad A = -\int_{V_i}^{V_f} pdV. \quad (2.16)$$

In general, the pressure depends on the volume and temperature of the gas, and the process through which the gas is progressing can be plotted on a graphical representation called a **PV diagram** (Figure 2.5).

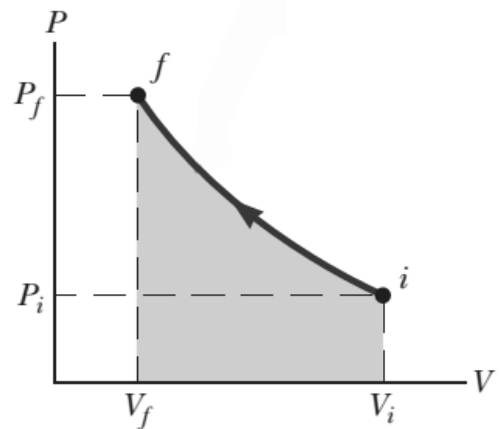


Figure 2.5.

Pressure volume diagram is the visualization of the  $p(V)$  dependence during the process. The curve on a PV diagram is called the **path** taken between the initial and final states.

The **work done on a gas** in a quasi-static process that takes the gas from an initial state to a final state is the negative of the area under the curve on a PV diagram, evaluated between the initial and final states.

The work done depends on the particular path taken between the initial and final states.

### ***2.2.4 First law of thermodynamics***

The **first law of thermodynamics** is a special case of the law of conservation of energy.

The change in the internal energy of an isolated thermodynamic system is equal to the sum of heat supplied to the system and the amount of work done on the system:

$$\Delta U = Q + A_{on\_gas}, \quad (2.17a)$$

or,

the heat supplied to the isolated thermodynamic system converts into the change in internal energy of the system and work done by the system on its surroundings:

$$Q = \Delta U + A_{by\_gas}, \quad (2.17b)$$

where  $Q$  is the heat supplied to the system;  $\Delta U$  is the change in internal energy of the system;  $A_{on\_gas}$  is the work done on the system and  $A_{by\_gas}$  is the work done by the system on its surroundings,  $A_{by\_gas} = -A_{on\_gas}$ .

Equivalently, perpetual motion machines of the first kind (which produce more work than the input of energy) are impossible.

The **first law of thermodynamics in the differential form:**

$$\delta Q = dU + \delta A_{by\_gas}, \quad (2.18)$$

where  $\delta Q$ ,  $\delta A_{by\_gas}$  are elementary amounts of heat and work,  $dU$  is the change in the internal energy.

The zeroth law of thermodynamics involves the concept of temperature, and the first law involves the concept of internal energy. Temperature and internal energy are both **state variables**; that is, the value of each depends only on the thermodynamic state of a system, not on the process that brought it to that state. On the contrary, heat, heat capacity and work are **process variables**; that is, the value of each depends on the process that brings the system into new state.

As the heat capacity of the gas is the function of process, let's find it for different thermodynamic processes. By substituting the expressions for heat, internal energy and work into the first law of thermodynamics and considering the heat capacity of one

mole of gas, we obtain  $CdT = \frac{i}{2}RdT + pdV$  ;

$$C = \frac{i}{2}R + \frac{pdV}{dT} . \quad (2.19)$$

**The first law of thermodynamics for different thermodynamic processes:**

***1) isochoric process.***

A process that takes place at constant volume is called an **isochoric (isovolumetric) process**. Because the volume of the gas does not change in such a process, the work done by the gas is zero:

$$A = 0.$$

Hence, from the first law we see that

$$Q = \Delta U , \text{ where } \Delta U = \frac{i}{2}\nu R(T_2 - T_1) = \frac{i}{2}V(p_2 - p_1) .$$

If energy is added by heat to a system kept at constant volume, all the transferred energy remains in the system as an increase in its internal energy.

Let's find the heat capacity of the gas in this process. Using the expression  $C = \frac{i}{2}R + \frac{pdV}{dT}$  and recalling that  $V = \text{const}$  and  $dV = 0$  in the isochoric process, we obtain:

$$C_V = \frac{i}{2}R, \quad (2.20)$$

where  $C_V$  is the molar **heat capacity at constant volume**.

### 2) isobaric process.

A process that occurs at constant pressure is called an **isobaric process**. In such a process, the values of the heat and the work are both usually nonzero.

$$Q = \Delta U + A,$$

where  $\Delta U = U_2 - U_1 = \frac{i}{2}\nu R(T_2 - T_1) = \frac{i}{2}p(V_2 - V_1)$ ; the work done by the gas in the isobaric process is simply  $A = p(V_2 - V_1)$  where  $p$  is the constant pressure of the gas during the process.

Let's find the heat capacity of the gas in this process. Using the expression for heat capacity we obtain  $C = \frac{i}{2}R + \frac{pdV}{dT} = C_V + \frac{pdV}{dT}$ . If we differentiate the equation of state for an ideal gas,  $d(pV) = d(RT)$ , we see that  $pdV = RdT$  when  $p = \text{const}$ .

Then,  $C = C_V + \frac{RdT}{dT} = C_V + R$ . Thus,

$$C_p = C_V + R = \frac{i+2}{2}R, \quad (2.21)$$

where  $C_p$  is the molar **heat capacity at constant pressure**.

### 3) isothermal process

A process that occurs at constant temperature is called an **isothermal process**.

$T = \text{const}$  and  $dT = 0$ , hence in an isothermal process involving an ideal gas  $\Delta U = 0$ ;

$$Q = A.$$

For an isothermal process, the energy transfer  $Q$  must be equal to the work done by the gas. Any energy that enters the system by heat is transferred out of the system by work; as a result, no change in the internal energy of the system occurs in an isothermal process.

Heat capacity of the gas in the isothermal process is infinity.

Suppose an ideal gas is allowed to expand quasi-statically at constant temperature. Let's calculate the work done by the gas in the expansion from state  $i$  to state  $f$ .

$$A = \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \frac{\nu RT}{V} dV = \nu RT \int_{V_i}^{V_f} \frac{dV}{V} = \nu RT \ln \frac{V_f}{V_i}. \quad (2.22)$$

### 2.2.5 Adiabatic process

**Adiabatic process** is one that occurs without transfer of heat between the thermodynamic system and its surroundings. Energy is transferred only as work.

$$\delta Q = 0 \text{ and } \delta A = -dU.$$

Let's find equation describing adiabatic process. From the first law of thermodynamics  $p dV + \frac{i}{2} \nu R dT = 0$ . Taking the total differential of the equation of state of an ideal gas,  $d(pV) = d(RT)$ , gives  $p dV + V dp = \nu R dT$ . Then,

$$p dV + \frac{i}{2} (p dV + V dp) = 0; \quad \frac{i+2}{2} p dV + \frac{i}{2} V dp = 0; \quad C_P p dV + C_V V dp = 0;$$

$$\frac{dp}{p} + \frac{C_P}{C_V} \frac{dV}{V} = 0.$$

Let's denote  $\gamma = \frac{C_P}{C_V} = \frac{i+2}{i}$  the

ratio of specific heats at constant pressure and at constant volume. Now we can write the previous equation as

$$d(\ln p) + \gamma d(\ln V) = d(\ln pV^\gamma) = 0,$$

which gives as the **equation for the adiabatic process** (Figure 2.6):

$$pV^\gamma = \text{const}. \quad (2.23)$$

### 2.2.6 Polytropic process

A **polytropic process** is a thermodynamic process that obeys the relation:

$$pV^n = \text{const}, \quad (2.24)$$

where  $n$  is the polytropic index (a real number).

Some specific values of  $n$  correspond to particular cases:

- $n = 0$  is an isobaric process,
- $n \rightarrow +\infty$  is an isochoric process,
- $n = 1$  is an isothermal process,
- $n = \gamma$  is an adiabatic process.

A process is polytropic if and only if the heat capacity in this process is kept constant:

$$C_n = \text{const}$$

Let's find the heat capacity of the gas in the polytropic process using the expression for heat capacity  $C = C_V + \frac{pdV}{dT}$ . If we differentiate the equation of the

polytropic process,  $d(pV^n) = 0$ ;  $V^n dp + pnV^{n-1}dV = 0$ ;  $V^n dp + nV^{n-1}pdV = 0$ .

The total differential of the equation of state of an ideal gas gives (for one mole) is

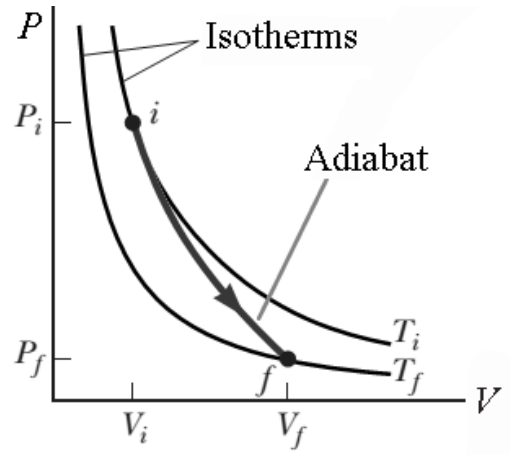


Figure 2.6.

$pdV + Vdp = RdT$ . By substituting  $Vdp = RdT - pdV$  into the previous equation we obtain  $V^{n-1}(RdT - pdV) + nV^{n-1}pdV = 0$ ;  $V^{n-1}RdT + (n-1)V^{n-1}pdV = 0$ ;

$$\frac{pdV}{dT} = -\frac{R}{n-1}, \text{ and } C = C_V + \frac{pdV}{dT} = C_V - \frac{R}{n-1}. \text{ Finally,}$$

$$C_n = C_V - \frac{R}{n-1} = \frac{R}{\gamma-1} - \frac{R}{n-1}, \quad (2.25)$$

that is **heat capacity of the gas in the polytropic process**  $C_n$  is constant.

Let's calculate the work done by the gas in the polytropic process. Using the first law of thermodynamics,  $A = Q - \Delta U = C_n \Delta T - C_V \Delta T = (C_n - C_V) \Delta T$ . For the  $\nu$  moles

of ideal gas,  $C_n - C_V = -\frac{\nu R}{n-1}$ , and

$$A = \frac{\nu R(T_1 - T_2)}{n-1} = \frac{p_1 V_1 - p_2 V_2}{n-1}. \quad (2.26)$$

### ***Questions for self-control***

1. What is the internal energy of the thermodynamic system?
2. Number of degrees of freedom
3. What is heat?
4. Latent heat
5. Equation of the heat balance
6. Work done on a gas
7. What is a quasi-static process?
8. The first law of thermodynamics.
9. State variables and process variables
10. Application of the first law of thermodynamics for the thermodynamic processes. Heat capacity of gases at constant pressure and at constant volume.
11. Equation for the adiabatic process
12. Equation for the polytropic processes.
13. Heat capacity of the gas in the polytropic process

## Topic 2.3. The second law of thermodynamics. Nernst theorem

### Lecture 13

#### 2.3.1 Cyclic processes

**Thermodynamic cycle** is a linked sequence of thermodynamic processes that involve transfer of heat and work into and out of the system, and that eventually returns the system to its initial state.

The cycle can convert heat from a warm source  $Q_1$  into useful work  $A$ , and dispose of the remaining heat  $Q_2$  to a cold sink returning to the initial state, thereby acting as a heat engine.

The useful work generated during the cycle  $A = Q_1 - Q_2$ .

**The heat engine** is a system that converts heat or thermal energy to mechanical energy, which can then be used to do mechanical work. It takes in energy by heat and, operating in a cyclic process, expels a fraction of that energy by means of work.

A heat engine carries some working substance through a cyclic process during which (1) the working substance absorbs energy by heat from a high-temperature energy reservoir, (2) work is done by the engine, and (3) energy is expelled by heat to a lower-temperature reservoir. Thus, the heat engine consists of 3 elements: a heat "source" that generates thermal energy, a "working body" (gas) that generates work while transferring heat to the colder "sink".

The **efficiency of a heat engine**:

$$\eta = \frac{A}{Q_1} = \frac{Q_1 - Q_2}{Q_1}. \quad (2.27)$$

Equation for the thermal efficiency shows that a heat engine has 100% efficiency only if  $Q_2 = 0$ , that is, if no energy is expelled to the cold reservoir. In other words, a heat engine with perfect efficiency would have to expel all the input energy by work.



Because efficiencies of real engines are well below 100%, the Kelvin–Planck form of the **second law of thermodynamics** states the following:

It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the input of energy by heat from a reservoir and the performance of an equal amount of work.

This statement of the second law means that during the operation of a heat engine, the useful work  $A$  can never be equal to  $Q_1$  or, alternatively, that some energy  $Q_2$  must be rejected to the environment. Every heat engine must have some energy exhaust.

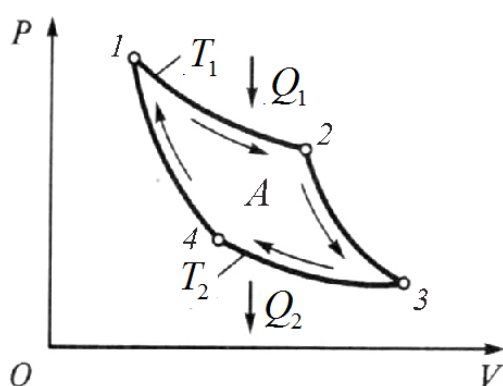


Figure 2.7.

An upper limit of the efficiency that any classical thermodynamic engine can achieve during the conversion of heat into work is provided by the **Carnot cycle**, which consists of two adiabats and two isotherms (see Figure 2.7).

A Carnot heat engine undergoing the Carnot cycle, is a "perfect" engine, but it is only a theoretical construct.

The thermal efficiency of a Carnot engine is

$$\eta_{\max} = \frac{T_1 - T_2}{T_1}, \quad (2.28)$$

where  $T_1$  is the absolute temperature of the source;  $T_2$  is the absolute temperature of the sink.

### **Carnot's theorem:**

No real heat engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

### 2.3.2 Clausius theorem

Another formulation of the **second law of thermodynamics**, stated by Clausius, is following:

Heat can never spontaneously pass from a colder to a warmer body without external work being performed on the system.

The second law of thermodynamics is concerned with the direction of natural processes: it asserts that a natural process runs only in one direction and is irreversible, unless external work is performed on the system.

The **Clausius theorem** ("**Inequality of Clausius**") is a mathematical explanation of the Second law of thermodynamics:

For a system exchanging heat with external reservoirs and undergoing a cyclic process, the amount of heat absorbed by the system from the reservoir divided by the temperature of that reservoir at a particular instant is not positive:

$$\oint \frac{\delta Q}{T} \leq 0. \quad (2.29a)$$

If the process is quasi-static (throughout the entire process the system is assumed to be in thermodynamic equilibrium with its surroundings), the process is reversible, and the absorbed amount of heat is defined only by the initial and final states of the system and is independent of the actual path followed. In this case

$$\oint \frac{\delta Q}{T} = 0. \quad (2.29b)$$

If the process is irreversible,  $\oint \frac{\delta Q}{T} < 0$ .

### 2.3.3 Entropy

The Clausius theorem allows to introduce a new state variable for the thermodynamic system called the entropy.

**Entropy**  $S$  is a function of state of a thermodynamic system that determines the measure of irreversible energy dissipation.

In the reversible process, an infinitesimal increment in the entropy  $dS$  of a system is defined to result from an infinitesimal transfer of heat  $\delta Q$  to a closed system divided by the temperature at that instant:

$$dS = \frac{\delta Q}{T} \text{ (reversible process).} \quad (2.30a)$$

For an actually possible irreversible infinitesimal process, the second law requires that the increment in system entropy must be greater than that:

$$dS > \frac{\delta Q}{T} \text{ (irreversible process).} \quad (2.30b)$$

Because entropy is a state variable, the change in entropy during a process depends only on the endpoints and therefore is independent of the actual path followed. The change in entropy for a finite reversible process

$$\Delta S = \int_i^f \frac{\delta Q}{T}. \quad (2.31)$$

The transferred energy is to be measured along a reversible path. The finite change in entropy of a system depends only on the properties of the initial and final equilibrium states. Therefore, we are free to choose a particular reversible path over which to evaluate the entropy in place of the actual path as long as the initial and final states are the same for both paths. To calculate changes in entropy for real (irreversible) processes between two equilibrium states we can consider a reversible process (or series of reversible processes) between the same two states.

Besides, for any reversible closed cycle initial and final states coincide and  $\Delta S = 0$ ,

$$\oint \frac{\delta Q}{T} = 0 \text{ (reversible closed cycle).} \quad (2.32)$$

Let's now consider a system consisting of a hot reservoir and a cold reservoir that are in thermal contact with each other and isolated from the rest of the Universe. The energy  $Q$  is transferred by heat from the hot reservoir to the cold reservoir. We can replace the real process for each reservoir with a reversible, isothermal process in

which the same amount of energy is transferred by heat. Because the cold reservoir absorbs energy  $Q$ , its entropy increases by  $Q/T_{cold}$ . At the same time, the hot reservoir loses energy  $Q$ , so its entropy change is  $-Q/T_{hot}$ .

When the heat transfer between the hot and cold parts of the system occurs, the increase in entropy of the cold reservoir is greater than the decrease in entropy of the hot reservoir:  $\frac{Q}{T_{hot}} < \frac{Q}{T_{cold}}$  because  $T_{hot} > T_{cold}$ . Therefore, the change in entropy of the

system (and of the Universe) is greater than zero:  $\Delta S = \frac{Q}{T_{cold}} - \frac{Q}{T_{hot}} > 0$ . We can

formulate the **entropy statement of the second law of thermodynamics**:

The total entropy of an isolated system can only increase over time  $\Delta S \geq 0$ . It can remain constant in ideal cases where the system is in a steady state (equilibrium) or undergoing a reversible process. The increase in entropy accounts for the irreversibility of natural processes, and the asymmetry between future and past.

Let's find change in entropy for one mole of the ideal gas in a quasi-static process. Using the first law of thermodynamics,  $dS = \frac{\delta Q}{T} = \frac{dU + \delta A}{T} = \frac{C_v dT + p dV}{T}$ ;

$dS = C_v \frac{dT}{T} + R \frac{dV}{V}$ . Taking the total differential of the logarithm of the equation of state of an ideal gas,  $d(\ln(pV)) = d(\ln(RT))$ ,  $d(\ln p) + d(\ln V) = d(\ln T)$ , gives

$\frac{dp}{p} + \frac{dV}{V} = \frac{dT}{T}$ . Then  $dS = C_v \frac{dp}{p} + C_p \frac{dV}{V}$ , and

$$\Delta S = C_v \ln \frac{p_f}{p_i} + C_p \ln \frac{V_f}{V_i}. \quad (2.33)$$

The change in entropy for any finite polytropic process

$$\Delta S = \int_i^f \frac{C_n dT}{T} = C_n \ln \frac{T_f}{T_i}. \quad (2.34)$$

The change in entropy in adiabatic process is zero because there is no energy transfer.

### 2.3.4 Entropy on a microscopic scale

Entropy can also be treated from a microscopic viewpoint through statistical analysis of molecular motions.

Let's use a microscopic model of the free expansion of an ideal gas, which was discussed from a macroscopic point of view before. In the kinetic theory of gases, gas molecules are represented as particles moving randomly. For a given uniform distribution of gas in the volume, there are a large number of equivalent microstates, and the entropy of the gas can be related to the number of microstates corresponding to a given macrostate. Let's count the number of microstates by considering the variety of molecular locations available to the molecules. Let's assume each molecule occupies some microscopic volume  $V_m$ . The total number of possible locations of a single molecule in a macroscopic initial volume  $V_i$  is the ratio  $w_i = V_i/V_m$ , which is the number of ways the molecule can be placed in the initial volume or, in other words, the number of microstates. We assume the probabilities of a molecule occupying any of these locations are equal.

As more molecules are added to the system, the number of possible ways the molecules can be positioned in the volume multiplies. For example, if you consider two molecules, there are  $w_i$  ways of locating the first molecule, and for each way, there are  $w_i$  ways of locating the second molecule. The total number of ways of locating the two molecules is  $(w_i)^2$ . Then, the number of ways of locating  $N$  molecules in the volume becomes  $\Omega_i = w_i^N = (V_i/V_m)^N$ . Similarly, when the volume is increased to  $V_f$ , the number of ways of locating  $N$  molecules increases to  $\Omega_f = w_f^N = (V_f/V_m)^N$ . The ratio of the number of ways of placing the molecules in the volume for the initial and final configurations is  $\frac{\Omega_f}{\Omega_i} = \left(\frac{V_f}{V_i}\right)^N$ . Taking the natural logarithm of this equation and multiplying by Boltzmann's constant gives

$$k_B \ln \Omega_f - k_B \ln \Omega_i = k_B \ln \left(\frac{V_f}{V_i}\right)^N = k_B N \ln \left(\frac{V_f}{V_i}\right) = \nu R \ln \left(\frac{V_f}{V_i}\right).$$

When a gas undergoes a free expansion from  $V_i$  to  $V_f$ , we can find the change in its entropy choosing any reversible path between the initial and final state. Let's take the isothermal path. Then  $Q = A = \nu RT \ln \frac{V_f}{V_i}$ , and the change in the entropy is

$$S_f - S_i = \nu R \ln \left( \frac{V_f}{V_i} \right). \text{ Notice that the right sides of obtained equations are identical.}$$

Therefore, from the left sides, we make the following important connection between entropy and the number of microstates  $\Omega$  for a given macrostate:

$$S = k_B \ln \Omega \tag{2.35}$$

This formula is the **microscopic definition of entropy**:

Entropy is defined by the number of microscopic configurations  $\Omega$  that a thermodynamic system can have when in a state specified by some macroscopic variables. The more microstates there are that correspond to a given macrostate, the greater the entropy of that macrostate. Entropy is a measure of disorder of the system.

### ***2.3.5 Nernst theorem.***

The **Nernst theorem** (the **third law of thermodynamics**) says that as temperature of a system approaches absolute zero, the entropy change for this macrosystem also approaches zero:

$$\lim_{T \rightarrow 0} \Delta S = 0. \tag{2.36}$$

Now we can calculate the absolute value of the entropy as

$$S = \int_0^T \frac{C(T)dT}{T}. \tag{2.37}$$

Heat capacity  $C$  of a macrosystem must approach zero as temperature of the system approaches absolute zero.

As entropy is related to the number of microstates, for a system consisting of many particles there is only one unique state (called the ground state) with minimum

energy. At absolute zero, the system must be in a state with the minimum possible energy.

Another formulation of the third law of thermodynamics is following:

The entropy change associated with any condensed system undergoing a reversible isothermal process approaches zero as the temperature at which it is performed approaches 0 K.

### *Questions for self-control*

1. What is a thermodynamic cycle?
2. What is a heat engine?
3. Efficiency of the heat engine
4. Carnot cycle and its efficiency.
5. The second law of thermodynamics
6. Clausius inequality.
7. Reversible and irreversible processes
8. What is entropy?
9. Entropy statement of the second law of thermodynamics
10. Microscopic definition of entropy
11. The third law of thermodynamics. Nernst theorem.

## Topic 2.4. Statistical distribution

### Lecture 14

The motion of the gas molecules is extremely chaotic. Gas consists of billions of molecule and any individual molecule collides with others billion times per second. Each collision results in a change in the speed and direction of motion of each of the participant molecules. Statistical distribution allows us to find out what is the relative number of molecules that possess some characteristic such as energy or speed within a certain range.

#### 2.4.1 The Maxwell distribution

Let's consider a container of gas at a constant temperature. We know that the rms velocity of the gas molecules is determined by the gas temperature. However, not all the molecules of the gas at a certain temperature move at the same velocity; actually velocities of gas molecules vary widely. Thus, it is necessary to determine the velocity distribution of the molecules, so that the number of molecules having a speed in a certain range can be determined. We expect this distribution to have its peak in the vicinity of the rms speed.

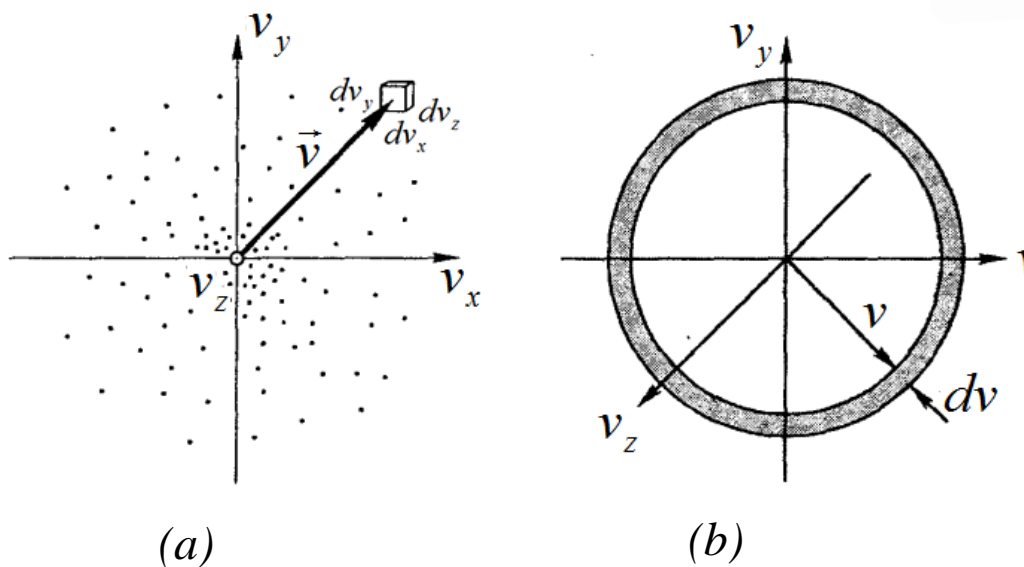


Figure 2.8.



Let us imagine a velocity space with pair-wise perpendicular coordinate axes  $v_x, v_y, v_z$  (Figure 2.8, a). Then the instantaneous velocity vector  $\vec{v}$  of each molecule can be represented as a point with coordinates  $v_x, v_y, v_z$  in this velocity space. Though coordinates of the point corresponding to a single molecule vary with time, for a very large number of molecules these variations are smoothed out, so that the overall distribution of points remains constant in the state of thermodynamic equilibrium. Moreover, because the motion is completely random, all the directions are equally probable, and distribution of points in the velocity space must have spherical symmetry (Figure 2.8, b). That's why distribution of points depends on the speed  $v$  of molecules. Let's introduce a **distribution function**  $\varphi(v)$ , also called a **probability density function**, so that  $\varphi(v)dV$  is the number of molecules per unit volume  $dV$  in the velocity space with speeds between  $v$  and  $v + dv$ .

Let the total number of molecules in the gas be  $N$ . The number of molecules whose speeds lie between  $v$  and  $v + dv$  would be represented by the spherical strip of thickness  $dv$ , and be denoted by  $dN_v$ . Let  $dN_{v_x}$  represent the number of molecules whose  $x$ -component velocities lie between  $v_x$  and  $v_x + dv_x$ . The ratio of the number of molecules that have the desired characteristic to the total number of molecules is the probability that a particular molecule has that characteristic. Then the probability of an arbitrary molecule having  $x$ -component of velocity within the interval  $(v_x ; v_x + dv_x)$  is

$dp_{v_x} = \frac{dN_{v_x}}{N} = \varphi(v_x)dv_x$ , where  $\varphi(v_x)$  is the distribution function for  $x$ -component of velocity. Similarly, for  $y$ - and  $z$ - components of velocity,  $dp_{v_y} = \frac{dN_{v_y}}{N} = \varphi(v_y)dv_y$  and

$$dp_{v_z} = \frac{dN_{v_z}}{N} = \varphi(v_z)dv_z.$$

Probabilities that the molecule has components of velocity within intervals  $(v_x ; v_x + dv_x)$  and  $(v_y ; v_y + dv_y)$  and  $(v_z ; v_z + dv_z)$  are independent, so

$$dp_{v_x, v_y, v_z} = dp_{v_x} dp_{v_y} dp_{v_z} = \varphi(v_x)\varphi(v_y)\varphi(v_z)dv_x dv_y dv_z. \quad (2.38)$$

On the other hand,  $dp_v = \varphi(v)dV$ , that is the number of representative points per unit volume, or the density of point in velocity space is

$$\varphi(v) = \varphi(v_x)\varphi(v_y)\varphi(v_z). \quad (2.39)$$

Since the velocity distribution is isotropic in the state of thermodynamic equilibrium, the probability density is the same in any volume element, so that

$$\varphi(v) = \varphi(v_x)\varphi(v_y)\varphi(v_z) = \text{const} \text{ and } d(\varphi(v)) = 0.$$

Let's find this differential:

$$\varphi'(v_x)\varphi(v_y)\varphi(v_z)dv_x + \varphi(v_x)\varphi'(v_y)\varphi(v_z)dv_y + \varphi(v_x)\varphi(v_y)\varphi'(v_z)dv_z = 0;$$

$$\frac{\varphi'(v_x)}{\varphi(v_x)}dv_x + \frac{\varphi'(v_y)}{\varphi(v_y)}dv_y + \frac{\varphi'(v_z)}{\varphi(v_z)}dv_z = 0.$$

As far as distribution of points in the velocity space has spherical symmetry, while the velocity components  $v_x, v_y, v_z$  vary in the result of molecule collisions, the total speed remains constant:

$$v^2 = v_x^2 + v_y^2 + v_z^2 = \text{const}.$$

If we differentiate this expression,

$$v_x dv_x + v_y dv_y + v_z dv_z = 0.$$

Let's apply the Lagrange's method and multiply the last expression by undetermined multiplier  $\lambda$  and add it to the expression for the distribution function:

$$\left( \frac{\varphi'(v_x)}{\varphi(v_x)} + \lambda v_x \right) dv_x + \left( \frac{\varphi'(v_y)}{\varphi(v_y)} + \lambda v_y \right) dv_y + \left( \frac{\varphi'(v_z)}{\varphi(v_z)} + \lambda v_z \right) dv_z = 0.$$

Since  $v_x, v_y, v_z$  are now independent variables, the coefficients of  $dv_x, dv_y, dv_z$  are individually equated to zero:

$$\frac{\varphi'(v_x)}{\varphi(v_x)} + \lambda v_x = 0; \quad \frac{\varphi'(v_y)}{\varphi(v_y)} + \lambda v_y = 0; \quad \frac{\varphi'(v_z)}{\varphi(v_z)} + \lambda v_z = 0. \quad (2.40)$$

Integrating these equations, we obtain

$$\ln \varphi(v_x) = -\lambda \frac{v_x^2}{2} + \text{const}, \text{ or } \varphi(v_x) = \text{const} \cdot e^{-(\lambda v_x^2)/2}.$$

$$\text{Similarly, } \varphi(v_y) = \text{const} \cdot e^{-(\lambda v_y^2)/2}, \varphi(v_z) = \text{const} \cdot e^{-(\lambda v_z^2)/2}.$$

The symmetry provides the same integration constant for all the three equations. According to the condition for normalization of the probability density, for all possible values of  $v_x$  between  $-\infty$  and  $+\infty$ ,

$$p_{v_x} = \int_{-\infty}^{+\infty} \varphi(v_x) dv_x = 1; \quad \int_{-\infty}^{+\infty} \text{const} \cdot e^{-(\lambda v_x^2)/2} dv_x = 1. \quad (2.41)$$

It is known that  $\int_{-\infty}^{+\infty} e^{-(\lambda v_x^2)/2} dv_x = \sqrt{\frac{2\pi}{\lambda}}$ , then the constant  $\text{const} = \sqrt{\frac{\lambda}{2\pi}}$ . We obtain:

$$\varphi(v_x) = \sqrt{\frac{\lambda}{2\pi}} \cdot e^{-(\lambda v_x^2)/2}; \quad \varphi(v_y) = \sqrt{\frac{\lambda}{2\pi}} \cdot e^{-(\lambda v_y^2)/2}; \quad \varphi(v_z) = \sqrt{\frac{\lambda}{2\pi}} \cdot e^{-(\lambda v_z^2)/2}, \text{ and}$$

$$dp_v = \left(\frac{\lambda}{2\pi}\right)^{3/2} \cdot e^{-\frac{\lambda}{2}(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z = \left(\frac{\lambda}{2\pi}\right)^{3/2} \cdot e^{-\frac{\lambda}{2}v^2} dv_x dv_y dv_z. \quad (2.42)$$

The probability density is found to be a function of speed  $v$  only. To calculate the probability that molecules have speeds between  $v$  and  $v + dv$ , the volume of the spherical shell of thickness  $dv$  at a distance  $v$  from the origin must be considered:

$$dV = 4\pi v^2 dv = dv_x dv_y dv_z. \text{ Then,}$$

$$dp_v = \left(\frac{\lambda}{2\pi}\right)^{3/2} \cdot e^{-\frac{\lambda}{2}v^2} 4\pi v^2 dv = 4\pi \left(\frac{\lambda}{2\pi}\right)^{3/2} \cdot e^{-\frac{\lambda}{2}v^2} v^2 dv; \quad (2.43)$$

$$\varphi(v) = 4\pi \left(\frac{\lambda}{2\pi}\right)^{3/2} \cdot v^2 e^{-\frac{\lambda}{2}v^2}. \quad (2.44)$$

The **most probable speed**  $v_{mp}$  is the speed at which the distribution curve reaches a peak. Using the condition that the derivative of the distribution function equals zero  $d\varphi(v)/dv = 0$  when  $v = v_{mp}$ , we find that  $\lambda = \frac{2}{v_{mp}^2}$ .

Using the law of conservation of energy we can state that  $\frac{m_0 v_{mp}^2}{2} = k_B T$ , where  $m_0$  is the mass of the gas molecule. Then,  $v_{mp} = \sqrt{\frac{2k_B T}{m_0}}$ , and we obtain the final form of the distribution function:

$$\varphi(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m_0}{2k_B T}\right)^{3/2} \cdot v^2 e^{-\frac{m_0 v^2}{2k_B T}}. \quad (2.45)$$

This is the **Maxwell distribution**: the probability that molecules have speeds between  $v$  and  $v + dv$  is

$$dp_v = \frac{dN_v}{N} = \frac{4}{\sqrt{\pi}} \left(\frac{m_0}{2k_B T}\right)^{3/2} \cdot v^2 e^{-\frac{m_0 v^2}{2k_B T}} dv. \quad (2.46)$$

By denoting a relative speed  $u = \frac{v}{v_{mp}}$ , we can obtain a simpler form of the Maxwell distribution, which is independent of the gas nature and temperature:

$$dp_u = \frac{4}{\sqrt{\pi}} \cdot u^2 e^{-u^2} du. \quad (2.47)$$

Knowing the distribution function, we can find the average speed of the molecules as  $v_{avg} = \int_0^{\infty} v\varphi(v)dv = \int_0^{\infty} \frac{4}{\sqrt{\pi}} \left( \frac{m_0}{2k_B T} \right)^{3/2} \cdot v^3 e^{-\frac{m_0 v^2}{2k_B T}} dv$ . Calculating this integral gives

$$v_{avg} = \sqrt{\frac{8k_B T}{\pi m_0}}. \quad (2.48)$$

We see that  $v_{rms} > v_{avg} > v_{mp}$ .

Having obtained the speed distribution, now we can obtain the energy distribution of the gas molecules. Kinetic energy of a molecule is  $E = \frac{m_0 v^2}{2}$ . Now let's denote  $\Phi(E)$  the energy distribution function, such that  $\Phi(E)dE$  is the probability that molecules have energy between  $E$  and  $E + dE$ . Then, let's express accordance between energy and speed distributions:  $\Phi(E)dE = \varphi(v)dv$ . Take into account that

$$dE = d\left(\frac{m_0 v^2}{2}\right) = m_0 v dv; \quad \frac{dE}{dv} = \sqrt{2m_0 E}.$$

$$\begin{aligned} \text{So, } \Phi(E) &= \varphi(v) \frac{dv}{dE} = \frac{4}{\sqrt{\pi}} \left( \frac{m_0}{2k_B T} \right)^{3/2} \cdot v^2 e^{-\frac{m_0 v^2}{2k_B T}} \cdot \frac{1}{\sqrt{2m_0 E}} = \\ &= \frac{4}{\sqrt{\pi}} \left( \frac{m_0}{2k_B T} \right)^{3/2} \cdot \frac{2E}{m_0} e^{-\frac{E}{k_B T}} \cdot \frac{1}{\sqrt{2m_0 E}} = \frac{2}{\sqrt{\pi}} \left( \frac{1}{k_B T} \right)^{3/2} \sqrt{E} e^{-\frac{E}{k_B T}}. \text{ Finally,} \end{aligned}$$

$$\Phi(E) = \frac{2}{\sqrt{\pi}} \left( \frac{1}{k_B T} \right)^{3/2} \sqrt{E} e^{-\frac{E}{k_B T}}, \quad (2.49)$$

which is the expression for the function of the **Maxwell energy distribution**. The probability of finding the molecules in a particular energy state varies exponentially as the negative of the energy divided by  $k_B T$ .

The most probable energy can be found from the condition of maximum for this function:  $E_{mp} = \frac{k_B T}{2}$ .

### 2.4.2 Barometric formula and Boltzmann distribution

The Maxwell distribution law is obtained for an ideal gas in the state of thermodynamic equilibrium with no external forces acting on it. Now let's consider a gas in the gravitational field of the Earth. All the molecules would fall onto the Earth surface under the action of gravitational force unless the thermal agitation at a temperature  $T$  did not excite them to thermal motion. Distribution of the gas molecules in the atmosphere of the Earth is the result of collective influence of the thermal motion and gravitational field. Consequently, density of the gas as well as its pressure depend on the height above the Earth surface.

**Barometric formula** is a formula used to model how the pressure (or density) of the air changes with altitude.

Suppose we have a horizontal slab of air with thickness  $dh$  at the altitude  $h$  above the sea level (Figure 2.9). The density of air  $\rho$  is a function of height  $h$ , but within the thin slab it may be considered as constant. The pressure of the air at height  $h$  must be equal to the pressure of the air above it plus the weight of the air in the slab. In other words, the change in pressure as we go from height  $h$  to  $h + dh$  is

$$dp = -\rho g dh,$$

where  $g$  is the acceleration of gravity. The minus sign accounts for the fact that pressure decreases as we go higher.

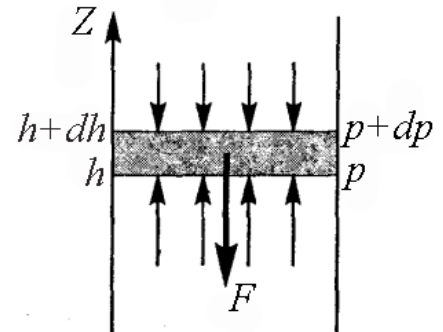


Figure 2.9.

According to the basic equation of the kinetic theory for gases,  $p = nk_B T$ .

Concentration of molecules  $n = \frac{N}{V} = \frac{Nm_0}{Vm_0} = \frac{m}{Vm_0} = \frac{\rho}{m_0}$ , where  $N$  is the total number of

molecules,  $m_0$  is the mass of the single molecule. Then,  $\rho = m_0 n = m_0 \frac{p}{k_B T}$ . We obtain

$$dp = -m_0 g \frac{p}{k_B T} dh; \quad \frac{dp}{p} = -\frac{m_0 g}{k_B T} dh.$$

Considering  $g$  and  $T$  as constants since the atmosphere's thickness isn't really large enough to affect  $g$  and the gas is in the state of thermodynamic equilibrium, we can integrate the equation to get

$$p = p(0) e^{-\frac{m_0 g}{k_B T} h} \quad (2.50)$$

So, we have obtained the **barometric formula** showing that the pressure decreases exponentially with altitude.

Now we can obtain the law of molecules distribution in the gravitational field. Since  $p = nk_B T$ ,

$$n = n(0) e^{-\frac{m_0 g}{k_B T} h}. \quad (2.51)$$

The obtained distribution is universal, it is valid for any macroscopic system of particles located in the potential field of external forces. In terms of potential energy, this law can be written as the **Boltzmann distribution**:

$$n = n(0) e^{-\frac{U(h)}{k_B T}}, \quad (2.52)$$

where  $U(h)$  is the potential energy. Also, the number of molecules located inside the elementary volume can be found as  $dN = n(0) e^{-\frac{U}{k_B T}} dV$ .

Maxwell and Boltzmann distributions can be united into the **Maxwell – Boltzmann distribution law**. The number of molecules whose coordinates and components of velocity lie within intervals  $(x; x + dx)$ ,  $(y; y + dy)$ ,  $(z; z + dz)$ ,  $(v_x; v_x + dv_x)$ ,  $(v_y; v_y + dv_y)$ ,  $(v_z; v_z + dv_z)$  is

$$dN_{x,y,z,v_x,v_y,v_z} = \text{const} \cdot e^{-\frac{U}{k_B T}} e^{-\frac{m_0 v^2}{2k_B T}} dx dy dz dv_x dv_y dv_z, \text{ or}$$

$$dN_{x,y,z,v_x,v_y,v_z} = \text{const} \cdot \exp\left(-\frac{m_0 v^2 / 2 + U}{k_B T}\right) dx dy dz dv_x dv_y dv_z, \quad (2.53)$$

where the constant  $\text{const} = n(0) \left(\frac{m_0}{2\pi k_B T}\right)^{3/2}$ ;  $v^2 = v_x^2 + v_y^2 + v_z^2$ ; the potential energy is

the function of molecule coordinates  $U = U(x, y, z)$ .

### ***Questions for self-control***

1. What is the velocity space?
2. What is the distribution function?
3. Maxwell speed distribution
4. The most probable speed
5. Maxwell energy distribution
6. Boltzmann distribution
7. Barometric formula
8. Maxwell-Boltzmann distributions.



## Lecture 15

### 2.4.3 Transport phenomena in gases

Whenever a thermodynamic system is brought out of the state of thermodynamic equilibrium, it will attempt to achieve the equilibrium state again. But the entropy of the system increases, so the process is irreversible. Disturbance of equilibrium is always accompanied by physical phenomena where particles, energy, or other physical quantities are transferred inside a system due to two mechanisms: diffusion and convection. These irreversible processes are called **transport phenomena**.

Though speed of thermal motion of gas molecules is very high, macroscopic distances covered by molecules are small due to many collisions between them. Every collision modifies direction of motion or energy or other molecule properties.

The **mean free path**  $\langle l \rangle$  of a particle (a gas molecule) is the average distance the particle travels between successive collisions with other moving particles.

Consider a gas molecule as an absolutely elastic sphere of diameter  $d$  (the **effective diameter of a molecule**). Then in unit time the molecule travels a distance  $\langle v \rangle$  and collides with all the molecule within a cylinder of volume  $\pi d^2 \langle v \rangle$ . The mean number of collisions equals to the number of molecules inside this cylinder  $\pi d^2 n \langle v \rangle$ , where  $n$  is concentration of molecules in the gas. Instead of absolute velocity of the molecule it is more convenient to consider its relative velocity with respect to other molecules participating in collisions. According to the Maxwell speed distribution,  $\langle v \rangle_{rel} = \sqrt{2} \langle v \rangle$ . Then the mean number of collisions in unit time is

$$\langle z \rangle = \sqrt{2} \pi d^2 n \langle v \rangle, \quad (2.54)$$

and the mean free path is  $\langle l \rangle = \frac{\langle v \rangle t}{\langle z \rangle t}$ ,

$$\langle l \rangle = \frac{1}{\sqrt{2} \pi d^2 n} = \frac{1}{\sqrt{2} \sigma n}. \quad (2.55)$$

The quantity  $\sigma = \pi d^2$  is called the **effective cross-sectional area of collision**, while the molecules in the gas are treated as hard spheres of effective diameter  $d$  that interact by direct contact.

Using the basic equation of kinetic theory of gases, we obtain

$$\langle l \rangle = \frac{k_B T}{\sqrt{2} \sigma p}. \quad (2.56)$$

#### ***2.4.4 Diffusion***

**Diffusion** is the mutual penetration of molecules of contacting substances due to their thermal motion. It is spontaneous net motion of particles down their concentration gradient (from a region of high concentration to a region of low concentration).

**Molecular diffusion** is the thermal motion of all particles at temperatures above absolute zero. The rate of this movement is a function of temperature, viscosity of the fluid and the size (mass) of the particles. Diffusion explains the net flux of molecules from a region of higher concentration (density) to one of lower concentration (density). Once the concentrations are equal the molecules continue to move, but since there is no concentration gradient the process of molecular diffusion has ceased and is instead governed by the process of **self-diffusion**, originating from the random motion of the molecules. The result of diffusion is a gradual mixing of material such that the distribution of molecules is uniform. Since the molecules are still in motion, but an equilibrium has been established, the end result of molecular diffusion is called a "**dynamic equilibrium**".

In diffusion, we are interested in the movement of molecular concentration. It is described by the Fick's laws.

**Fick's law** of diffusion relates the diffusive flux to the concentration under the assumption of steady state. It postulates that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient (spatial derivative).

Transport of material (a “mass flux”) in solute will move across a concentration gradient, and in one (spatial) dimension, the law is:

$$j_m = -D \frac{d\rho}{dx}, \quad (2.57)$$

where  $j_m$  is the "**diffusion flux**," or the mass flux density,  $j_m = \frac{\Delta m}{\Delta S \Delta t}$ , (kg/s·m<sup>2</sup>), which measures the amount of substance that will flow through a unit area during a unit time interval;

$D$  is the **diffusion coefficient** or diffusivity, which depends on the temperature, viscosity of the fluid and the size of the particles;

$\rho$  is the concentration, or density, that is the amount of substance per unit volume;

$\frac{d\rho}{dx}$  is the density gradient.

In two or more dimensions we must use the gradient operator  $\nabla$ , which generalises the first derivative, obtaining

$$\vec{j}_m = -D \nabla \rho. \quad (2.58)$$

Let's obtain the Fick's law. Consider a self-diffusion in a thin slab of gas of cross-sectional area  $S$ . We divide the box in half so that the number of molecules on one side of the partition is  $N_1$  and on the other side is  $N_2$ . Assume that the whole box is at a constant temperature  $T$ . Since only half the molecules will, on average, be moving towards the partition in three dimensions of space, the number  $\Delta N_1$  of molecules that cross the partition in a time  $\Delta t$ , which is the time it takes a molecule to move distance of mean free path  $\langle l \rangle$ , is  $\Delta N_1 = \frac{1}{2 \cdot 3} (N_1 - N_2)$ . The same number of molecules cross the partition in the opposite direction  $\Delta N_2 = -\Delta N_1$ , and the net number of molecules  $\Delta N = 2\Delta N_1 = \frac{1}{3} (N_1 - N_2)$ .

If the gradient in molecule number is  $\frac{dN}{dx}$  then we have  $\Delta N = \frac{1}{3} \langle l \rangle \frac{dN}{dx}$ , and the net rate at which molecules cross the partition per unit area, that is the diffusion flux, is  $|j| = \frac{\Delta N}{S \Delta t} = \frac{1}{3} \frac{\langle l \rangle}{S \Delta t} \frac{dN}{dx} = \frac{1}{3} \frac{\langle v \rangle}{S} \frac{dN}{dx} = \frac{1}{3} \frac{\langle v \rangle \langle l \rangle}{V} \frac{dN}{dx} = \frac{1}{3} \langle l \rangle \langle v \rangle \frac{dn}{dx}$ , where volume  $V = S \langle l \rangle$  and molecular concentration  $n = N/V$ . The absolute value indicates that this is the magnitude of the flux. As the flux is in the opposite direction to the gradient, we will have

$$j = -\frac{\langle l \rangle \langle v \rangle}{3} \cdot \frac{dn}{dx}.$$

The quantity  $\frac{\langle l \rangle \langle v \rangle}{3}$  is an approximation for the diffusion constant  $D$  for an ideal gas, and we can write this equation as the Fick's law for the flux of concentration:

$$j = -D \cdot \frac{dn}{dx}. \quad (2.60)$$

It is easy to obtain now the Fick's law for the mass flux

$$j_m = -D \cdot \frac{d\rho}{dx}, \text{ where } \rho \text{ is the mass density.}$$

### ***2.4.5 Internal friction in gases***

Internal friction appears when random thermal motion of the gas molecules is superposed with the ordered motion, that is, when the gas flow occurs.

Let's consider two horizontal, parallel flat plates with a gas sandwiched between them. If one plate moves parallel to the other, the gas between the plates exerts a drag force inhibiting the motion of the plates. In the reference frame with the lower plate at rest and the upper plate moving at some speed  $u_x$  to the right, we'd expect the fluid between the plates to be moving at a speed that increases from zero next to the lower plate up to  $u_x$  next to the upper plate.

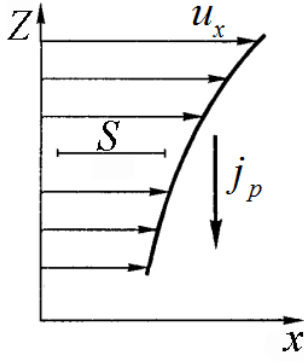


Figure 2.10.

The speed  $u_x$  of the fluid flow is directed along the  $x$  axis and depends only on the coordinate  $z$  between the plates (see Figure 2.10). This gradient in speed is the result of *momentum transfer* between adjacent layers in the fluid. Because of Newton's law of equal action and reaction, the horizontal drag force exerted on each plate is equal and opposite to the force on the fluid layer directly adjacent to the plate.

The force on each plate is proportional to the area  $S$  of the plate and to the relative speed of the upper and lower plates  $u_{x\_top} - u_{x\_bottom}$ , and inversely proportional to the distance  $\Delta z$  between the plates. The last two assumptions are equivalent to saying that the force is proportional to the velocity gradient  $du_x / dz$ . That is

$$\frac{F_x}{S} = \eta \frac{du_x}{dz}, \quad (2.61)$$

where  $\eta$  is the **coefficient of viscosity** or just the viscosity.

$$\text{The force of internal friction } F_x = \eta S \frac{du_x}{dz}.$$

On the other hand, from the Newton's second law,  $\frac{F_x}{S} = \frac{\Delta p_x}{S \Delta t} = j_p$ , and deriving the Fick's law for the transfer of momentum,

$$j_p = \frac{\Delta p_x}{S \Delta t} = \frac{1}{3} \frac{\langle l \rangle}{S \Delta t} \frac{dp_x}{dz} = \frac{1}{3} \frac{\langle v \rangle}{S} \frac{m}{dz} \frac{du_x}{dz} = \frac{1}{3} \frac{\langle v \rangle \langle l \rangle}{V} \frac{m}{dz} \frac{du_x}{dz} = \frac{1}{3} \langle l \rangle \langle v \rangle \rho \frac{du_x}{dz},$$

we obtain

$$j_p = -\frac{\langle l \rangle \langle v \rangle \rho}{3} \cdot \frac{du_x}{dz} = -\eta \frac{du_x}{dz}, \quad (2.62)$$

where  $\Delta p_x$  is the transferred momentum,  $p_x = mu_x$  is the momentum,  $m$  is the total mass of gas in a slab of area  $S$  and thickness  $\langle l \rangle$ ,  $\rho = m/V$  is density of the gas.

$$\text{Thus, viscosity } \eta = \frac{\langle l \rangle \langle v \rangle \rho}{3}. \quad (2.63)$$

### 2.4.6 Thermal conductivity of gases

Thermal conductivity is the transfer of heat in the material across the temperature gradient.

Consider a box of molecules with a temperature gradient in the  $x$  direction. The flux of thermal energy is  $j_Q = \frac{\Delta Q}{S \Delta t}$ . Deriving the Fick's law for the transfer of energy

similarly to the previous cases, the net heat transfer  $\Delta Q = -\frac{1}{3} \Delta U$ , where

$U = \nu N_A \cdot \frac{i}{2} k_B T = \frac{i}{2} \nu R T = C_V T$  is the internal thermal energy of the gas. Then,

$j_Q = -\frac{1}{3} C_V \frac{\Delta T}{S \Delta t}$ . Assuming a linear temperature gradient,  $\Delta T = \langle l \rangle \frac{dT}{dx}$ , we obtain

$$j_Q = -\frac{1}{3} C_V \frac{\langle l \rangle \langle v \rangle \rho}{3} \cdot \frac{dT}{dx} = -\kappa \frac{dT}{dx}. \quad (2.64)$$

The quantity  $\kappa = \frac{1}{3} C_V \frac{\langle l \rangle \langle v \rangle \rho}{3}$  is called **thermal conductance**. Recalling

the formula for the average speed  $\langle v \rangle$ , we see that the thermal conductance  $\kappa \propto \sqrt{T}$ .

### Questions for self-control

1. What are the transport phenomena?
2. What is a mean free path?
3. What is diffusion?
4. What is self-diffusion?
5. The Fick's law
6. Internal friction in gases. Viscosity.
7. Thermal conductivity of gases.

## Topic 2.5. Real gases

### Lecture 16

#### 2.5.1 The van der Waals equation of state

For most applications, the ideal gas approximation can be used with reasonable accuracy. But in real life gases are not ideal. They are made up of atoms and molecules that actually take up some finite volume, and interact with each other through intermolecular forces. The real-gas models have to be used near the condensation point of gases, near critical points, at very high pressures or low temperatures.

**Real gases** are non-hypothetical gases whose molecules occupy space and have interactions.

The **van der Waals equation** is the equation of state for real gases. The van der Waals model of a substance is able to predict (qualitatively) the existence of the liquid-gas phase transition and the critical point (where there is no clear distinction between the liquid and gas phases). The model is a refinement of the ideal gas equation of state,  $pV = \nu RT$ , which looks like this:

$$\left( p + \frac{a}{V_m^2} \right) (V_m - b) = RT, \quad \text{or} \quad \left( p + \frac{a\nu^2}{V^2} \right) (V - \nu b) = \nu RT, \quad (2.65)$$

where  $V_m$  is the molar volume,  $a$  and  $b$  are constants whose values depend on the particular substance we're describing.

The correction to the volume term is due to the fact that in a real substance, it is not possible to reduce the volume to zero since the molecules have a size below which they cannot be compressed further. Thus the minimum volume of an amount of substance containing  $\nu$  moles is  $\nu b$ , where  $b$  depends on the nature of the substance.

The correction to the pressure in the ideal gas law accounts for the fact that gas molecules do in fact attract each other and that real gases are therefore more compressible than ideal gases. Due to electric interactions, all molecules exhibit a long

term attraction to each other. This causes the additional pressure called the internal pressure  $p_i = \frac{av^2}{V^2}$ , where  $a$  depends on the nature of the substance.

When the molar volume  $V_m$  is large,  $b$  becomes negligible in comparison with  $V_m$ ,  $a/V_m^2$  becomes negligible with respect to  $p$ , and the van der Waals equation reduces to the ideal gas law.

### 2.5.2 Energy of the van der Waals gas

Internal energy of the van der Waals gas is the sum of the kinetic energy of random thermal motion of molecules and the net potential energy of the intermolecular interaction:  $U = K + U_{int}$ .

The work by interaction forces equals to the negative of potential energy:  $dA = -dU_{int}$ . The potential energy is negative since we're dealing with an attractive interaction. Thus two molecules separated by some finite distance require positive work done on them to pull them apart to an infinite distance, at which point the potential energy is zero. That is, the work is required to pull them out of a potential well, so their potential energy is negative.

The attractive forces are characterized by the internal pressure  $p_i = \frac{a}{V_m^2}$ . Then the elementary work by these forces is  $\delta A = -p_i dV_m$  (during gas expansion the work done on the gas is negative, that is, the gas does work on its surroundings). We obtain

$$\delta A = -\frac{a}{V_m^2} dV_m = -d\left(-\frac{a}{V_m}\right). \quad (2.66)$$

We can make a conclusion that potential energy of the intermolecular interaction  $U_{int} = -\frac{a}{V_m}$ . The total kinetic energy due to thermal motion of molecules is

$$K = \frac{i}{2} RT = C_v T.$$

Thus, the internal energy of one mole of the van der Waals gas is



$$U_m = C_v T - \frac{a}{V_m}. \quad (2.67)$$

### 2.5.3 The van der Waals isotherms

From the van der Waals equation,

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}, \quad (2.68)$$

$$\text{or } pV_m^3 - (bp + RT)V_m^2 + aV_m - ab = 0.$$

This is a cubic equation, and depending on the values of  $p$  and  $T$  it can have different roots.

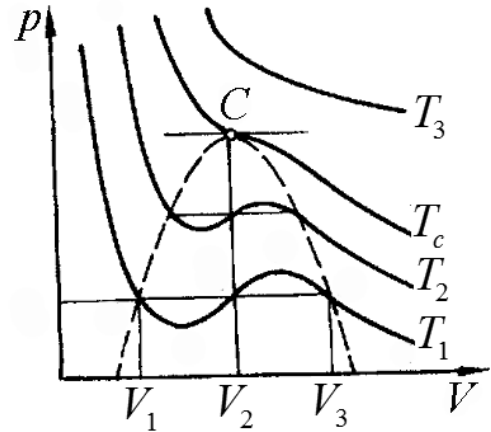


Figure 2.11.

We can plot van der Waals isotherms on a PV diagram (Figure 2.11). As we see, there is a critical temperature  $T_c$  when all the three roots of the equation are equal. At the critical temperature  $T = T_c$  the minimum in the pressure curve becomes an inflection point, where both  $\frac{dp}{dV}$  and  $\frac{d^2p}{dV^2}$  are zero (this is a point like that in the graph of  $y = x^3$  at  $x = 0$ ). This point is called a critical point. At the temperatures higher than the critical  $T > T_c$  the minimum in the pressure disappears (it corresponds to one real and two imaginary roots of the cubic equation) and we are left with a curve that gets closer to that for an ideal gas, where  $p = vRT/V$  (which is a hyperbola), see Figure 2.11, temperature  $T_3$ . At the temperatures lower than the critical  $T < T_c$  the equation has three real roots and the curve shows a minimum pressure as we reduce the volume, which seems to indicate that as we compress the substance, its pressure actually decreases, see Figure 2.11, temperatures  $T_1, T_2$ . Actually, such behavior indicates transition from the gas phase to the liquid phase.

At the critical point where the three roots are equal we can rewrite the van der Waals equation in the form

$$p_c(V_m - V_c)^3 = 0;$$

$$p_c V_m^3 - 3p_c V_c V_m^2 + 3p_c V_c^2 V_m - p_c V_c^3 = 0,$$

and comparing the multiples of corresponding terms, we obtain that  $p_c V_c^3 = ab$ ,  $3p_c V_c^2 = a$ ,  $3p_c V_c = bp_c + RT_c$ . Then,

$$p_c = \frac{a}{27b^2}; \quad V_c = 3b; \quad T_c = \frac{8a}{27Rb}.$$

However, experimental isotherms for real gases show that for temperatures lower than the critical there is a region where  $p$  is a constant function of  $V$  at given temperatures (region CD at Figure 2.12). This pressure is called a **vapor pressure**, that is, a pressure of vapor in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature. This region corresponds to the **liquefaction of gases** when the liquid phase and the gas phase are in equilibrium. The van der Waals equation fails to accurately model observed experimental behavior in regions near the critical point.

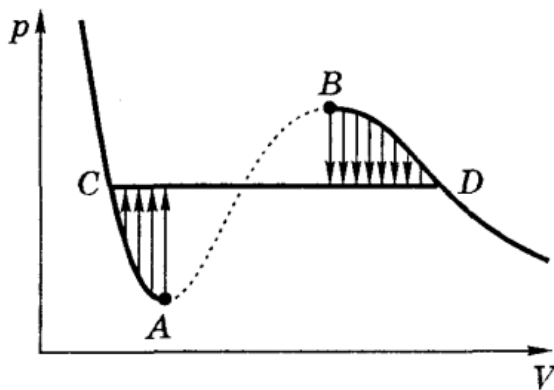


Figure 2.12.

Region CA corresponds to the **superheated liquid**, while region BD corresponds to **supersaturated vapor**.

Superheating is the phenomenon in which a liquid is heated to a temperature higher than its boiling point, without boiling. Superheating is achieved by heating a homogeneous substance in a clean container, free of nucleation sites, which are centers of initiating phase transition.

Supersaturated vapor has pressure higher than the vapor pressure at given temperature, but without condensation. It can be achieved by increasing the pressure of gas in a clean container, free of condensation sites.

The **Clausius–Clapeyron relation** characterizes behavior of a closed system during a phase change, during which temperature and pressure are constant.

It is a way of characterizing a discontinuous phase transition between two phases of matter of a single constituent. Two phases coexist in equilibrium only at the certain pressure depending on the temperature. On a pressure–temperature (P–T) diagram, the line separating the two phases is called a coexistence curve. The Clausius–Clapeyron relation gives the slope of the tangents to this curve. Mathematically,

$$\frac{dp}{dT} = \frac{L}{T\Delta V_s} = \frac{\Delta S_s}{\Delta V_s}, \quad (2.69)$$

where  $\frac{dp}{dT}$  is the slope of the tangent to the coexistence curve at any point,  $L$  is the specific latent heat,  $T$  is the temperature,  $\Delta V_s$  is the specific volume change of the phase transition, and  $\Delta S_s$  is the specific entropy change of the phase transition.

### ***Questions for self-control***

1. The difference between the real gas and the ideal gas.
2. Van der Waals equation.
3. Internal energy of the real gas.
4. Isotherms of real gases.
5. Critical temperature
6. Phase transition
7. Difference between the theoretical and experimental van der Waals isotherms
8. Metastable states
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10. Clausius–Clapeyron relation

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## CHAPTER 3. ELECTROSTATICS

### Topic 3.1. Electrostatic field in vacuum

#### *Lecture 17*

#### *3.1.1. Electrostatic force*

**Electrostatics** is a branch of physics that deals with the phenomena and properties of stationary electric charges.

**Electric charge** is the physical property of matter that causes it to experience a force when interacting with other charged objects. There are two types of electric charges: positive and negative. Charges of the same sign repel one another and charges with opposite signs attract one another.

**Point charge** is a charged particle of zero size.

**Elementary charge** ( $e$ ) is the smallest electric charge existing for isolatable particles. It is the electric charge carried by a single proton (or by a single electron,  $-e$ ). The value of the elementary charge  $e = 1.6 \cdot 10^{-19}$  C

**Charge quantization** is the principle that the charge of any object is an integer multiple of the elementary charge. That is, electric charge exists as discrete value:

$q = +Ne$ , where  $N$  is some integer.

#### **Electric charge conservation law:**

In an isolated system the algebraic sum of electric charges is always conserved:

$$q_1 + q_2 + \dots + q_n = \text{const} \quad (3.1)$$

That is, when the object is electrified, charge is not created in the process. The electrified state is due to a transfer of charge from one object to the other. The electrified state appears when one object gains some amount of negative charge while the other gains an equal amount of positive charge.

The electric force is one of the fundamental forces in nature. Experimental observations carried out by Charles Coulomb have allowed to generalize the properties of the electric force between two stationary charged particles.

The magnitude of the **electric force** (sometimes called the **Coulomb force**) between two point charges is given by **Coulomb's law**:

$$F = k \frac{|q_1| \cdot |q_2|}{\epsilon_r r^2}, \quad (3.2)$$

where  $|q_1|$  and  $|q_2|$  are the magnitudes of the charges; the scalar  $r$  is the distance

between the charges;  $k$  is the Coulomb constant:  $k = \frac{1}{4\pi\epsilon_0} = 9 \cdot 10^9 \text{ Nm}^2/\text{C}^2$ ;

$\epsilon_0 = 8.85 \cdot 10^{-12} \text{ C}^2/\text{Nm}^2$  is **electric constant** (also called as the permittivity of free space or vacuum permittivity);  $\epsilon_r$  is the **relative permittivity** of the medium (in vacuum or

in the air  $\epsilon_r = 1$ );  $\epsilon_r = \frac{F_0}{F}$ , where  $F_0$  is the force between charges in vacuum;  $F$  is the force between charges in the medium.

Coulomb's law expressed in vector form for the electric force exerted by a charge  $q_1$  on a second charge  $q_2$ , is

$$\vec{F}_{12} = k \frac{q_1 \cdot q_2}{\epsilon_r r^2} \cdot \vec{e}_r, \quad (3.3)$$

where  $\vec{e}_r = \frac{\vec{r}}{|\vec{r}|}$  is a unit vector directed from  $q_1$  toward  $q_2$ , (see Figure 3.1).

According to the Newton's third law, the electric force exerted by  $q_2$  on  $q_1$ , is equal in magnitude to the force exerted by  $q_1$  on  $q_2$ , and in the opposite direction  $\vec{F}_{12} = -\vec{F}_{21}$ . The electric force vector is directed along the line joining the two charges.

Finally, if  $q_1$  and  $q_2$  have the same sign (Figure 3.1a), the product  $q_1 q_2$  is positive and the electric force on one particle is directed away from the other particle. If  $q_1$  and

$q_2$  are of opposite sign (Figure 3.1b), the product  $q_1q_2$  is negative and the electric force on one particle is directed toward the other particle.

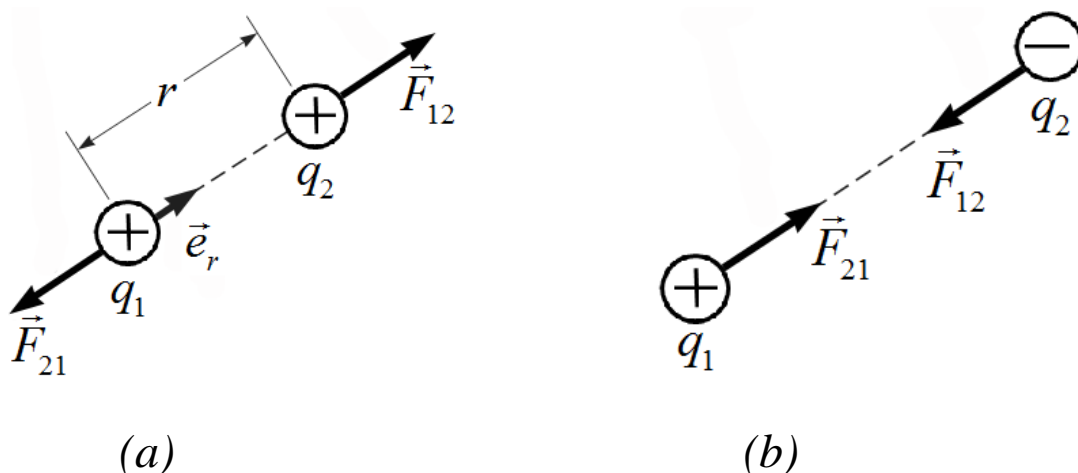


Figure 3.1 Electric force on the charged particles.

When more than two charges are present, the resultant force on any one of them equals the vector sum of the forces exerted by the other individual charges:

$$\vec{F} = \vec{F}_1 + \vec{F}_2 + \dots + \vec{F}_n.$$

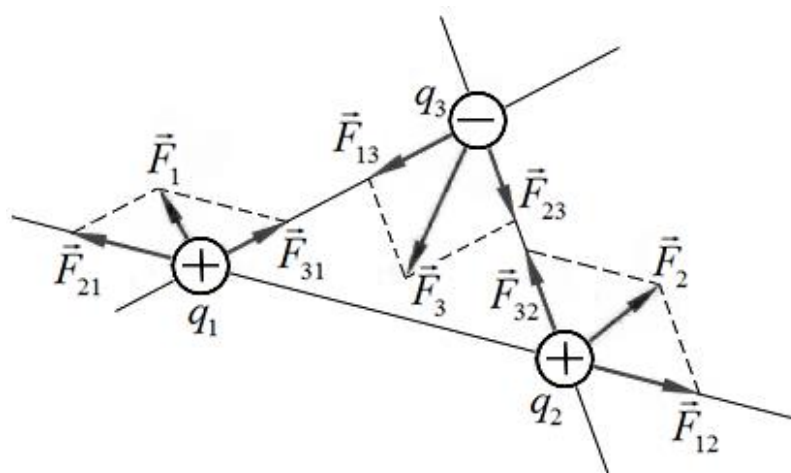


Figure 3.2.

For example, for the system of 3 charges (Figure 3.2):

– Electric force on  $q_1$

$$\vec{F}_1 = \vec{F}_{21} + \vec{F}_{31};$$

– Electric force on  $q_2$

$$\vec{F}_2 = \vec{F}_{12} + \vec{F}_{32};$$

– Electric force on  $q_3$

$$\vec{F}_3 = \vec{F}_{13} + \vec{F}_{23};$$

### 3.1.2. Electrostatic field

Electric charges or charged objects are the source of electric field. When another charged object — the test charge — enters this electric field, an electric force acts on it. The existence of an electric field is a property of its source; the test charge just serves as a detector of the electric field presence. The field forces can act through space, producing an effect even when no physical contact occurs between interacting objects.

**The electric field vector**  $\vec{E}$  is the electric force  $\vec{F}$  acting on a test charge  $q$  divided by the magnitude of this charge:

$$\vec{E} = \frac{\vec{F}}{q}. \quad (3.4)$$

The electric field vector at a given point in space has the same direction as the electric force that would act on a positive test charge placed at that point.

Hence, the **electric force** experienced by a point charge  $q$  in the electric field

$$\vec{F} = q\vec{E}. \quad (3.5)$$

If  $q$  is positive, the force is in the same direction as the field; if  $q$  is negative, the force is in the opposite direction as the field.

**Electric field lines** are the visualization of the electric field in a region of space (Figure 3.3):

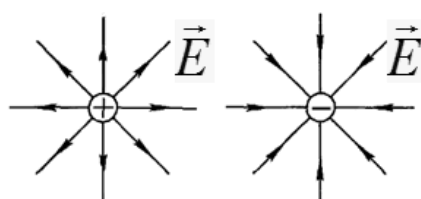


Figure 3.3.

- The electric field vector is tangent to the electric field line at each point.
- The number of lines per unit area is proportional to the magnitude of the electric field in that region.
- The lines begin on a positive charge and terminate on a negative charge.

If the electric field vector is constant at every point in space then the electric field is called **uniform**.

**Superposition principle:** at any point in space, the total electric field due to a group of source charges equals the vector sum of the electric fields of all the charges.

$$\vec{E} = \vec{E}_1 + \vec{E}_2 + \dots + \vec{E}_n. \quad (3.6)$$

This superposition principle applied to fields follows directly from the vector addition of electric forces.



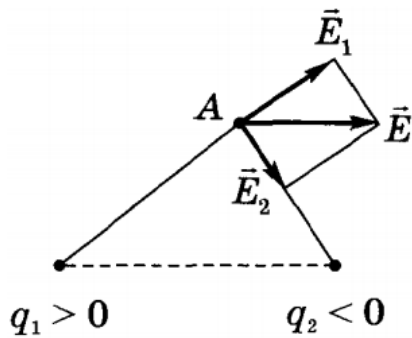


Figure 3.4.

For example, for the system of two charges (Figure 3.4):

$$\vec{E} = \vec{E}_1 + \vec{E}_2.$$

**Electric field due to a point charge**  $q$  at a distance  $r$  away from it (Figure 3.5):

$$\vec{E} = k \frac{q}{\epsilon r^2} \cdot \frac{\vec{r}}{|\vec{r}|}$$

(3.7)

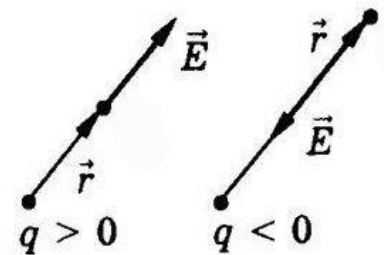


Figure 3.5.

### 3.1.3 Electric field due to a continuous distributed charge

The system of closely spaced charges is equivalent to a total charge that is continuously distributed along some line, over some surface, or throughout some volume.

- If a charge  $q$  is uniformly distributed throughout a volume  $V$ , the volume charge density  $\rho$  is defined by  $\rho = \frac{dq}{dV}$ ;
- If a charge  $q$  is uniformly distributed on a surface of area  $S$ , the surface charge density  $\sigma$  is defined by  $\sigma = \frac{dq}{dS}$ ;
- If a charge  $q$  is uniformly distributed along a line of length  $l$ , the linear charge density  $\lambda$  is defined by  $\lambda = \frac{dq}{dl}$ .

To find the electric field due to the distributed charge, let's use the differentiation - integration procedure. First, divide the charge distribution into small elements, each of which contains a small charge  $dq$  as shown in Figure 3.6. Next, use equation for the

electric field due to a point charge to calculate the electric field due to one of these elements at a point  $P$ . Finally, evaluate the total electric field at  $P$  due to the charge distribution by summing the contributions of all the charge elements (that is, by applying the superposition principle).

The electric field at  $P$  due to one charge element carrying charge  $dq$  is

$$d\vec{E} = k \frac{dq}{r^2} \cdot \vec{e}_r, \quad (3.8)$$

where  $r$  is the distance from the charge element to point  $P$  and  $\vec{e}_r$  is a unit vector directed from the element toward  $P$ . The total electric field at  $P$  due to all elements in the charge distribution is

$$\vec{E} = k \int \frac{dq}{r^2} \cdot \vec{e}_r, \quad (3.9)$$

where the integration is over the entire charge distribution.

### 3.1.3.1 Electric field due to a uniformly charged rod

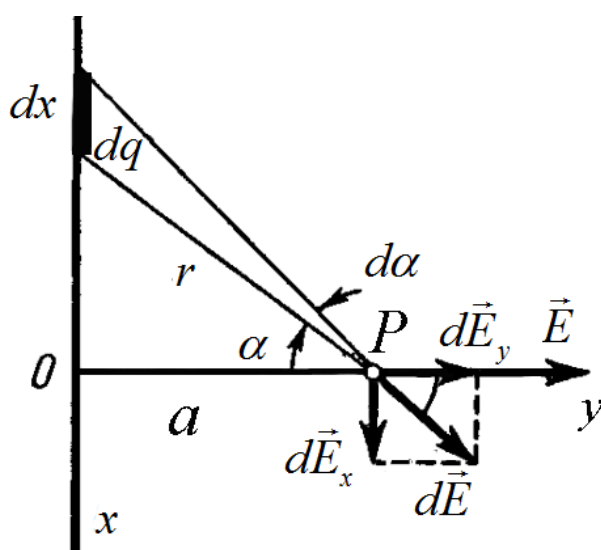


Figure 3.6.

The field  $d\vec{E}$  at  $P$  due to the elementary charge  $dq$  is

$$d\vec{E} = k \frac{dq}{r^2} \cdot \vec{e}_r = k \frac{\lambda dx}{r^2} \cdot \vec{e}_r.$$

In order to calculate the integral of  $d\vec{E}$  we need to make a substitution:

Let's calculate the electric field due to an infinitely long straight rod carrying a uniformly distributed positive charge of linear density  $\lambda$  at a point  $P$  at a distance  $a$  from the rod. Let's assume the rod is lying along the  $x$  axis,  $dx$  is the length of one small segment, and  $dq$  is the charge on that segment (see Figure 3.6).

$$r = \frac{a}{\cos \alpha}; \quad x = a \cdot \operatorname{tg} \alpha; \quad dx = \frac{a}{\cos^2 \alpha} \cdot d\alpha.$$

$$\text{Then, } d\vec{E} = k\lambda \frac{\cos^2 \alpha}{a^2} \cdot \frac{a}{\cos^2 \alpha} \cdot d\alpha \vec{e}_r = \frac{k\lambda}{a} d\alpha \vec{e}_r.$$

Now we need to consider  $x$  and  $y$  components of the vector quantity  $d\vec{E}$ :

$$dE_x = \frac{k\lambda}{a} \sin \alpha d\alpha; \quad dE_y = \frac{k\lambda}{a} \cos \alpha d\alpha.$$

Now we can obtain the  $x$  and  $y$  components of the total electric field  $\vec{E}$  by calculating the integrals:

$$E_x = \int_{-\pi/2}^{\pi/2} \frac{k\lambda}{a} \sin \alpha d\alpha = -\frac{k\lambda}{a} \cos \alpha \Big|_{-\pi/2}^{\pi/2} = 0;$$

$$E_y = \int_{-\pi/2}^{\pi/2} \frac{k\lambda}{a} \cos \alpha d\alpha = \frac{k\lambda}{a} \sin \alpha \Big|_{-\pi/2}^{\pi/2} = \frac{2k\lambda}{a}.$$

The resulting electric field is directed along the  $y$  axis and its magnitude is

$$E = \frac{2k\lambda}{a}. \quad (3.10)$$

### 3.1.3.2 Electric field due to a uniformly charged thin ring

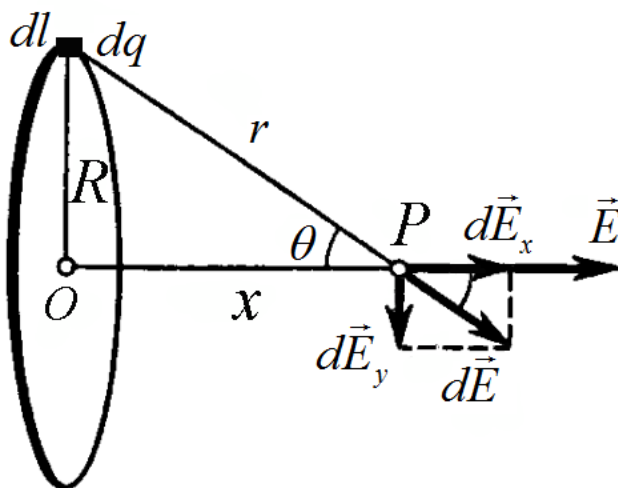


Figure 3.7.

Consider a ring of radius  $R$  carrying a uniformly distributed positive charge of linear density  $\lambda$ . Let's calculate the electric field due to the ring at a point  $P$  lying a distance  $x$  from its center along the central axis perpendicular to the plane of the ring (see Figure 3.7).

Let's consider an elementary segment of the ring of the length  $dl$  and charge  $dq$ . The field  $d\vec{E}$  at  $P$  due to the elementary charge  $dq$  is

$$d\vec{E} = k \frac{dq}{r^2} \cdot \vec{e}_r = k \frac{\lambda dl}{r^2} \cdot \vec{e}_r.$$

The distance  $r^2 = R^2 + x^2$  is the same for all the points on the ring. Now we have to consider the components of the field vector  $dE_x$  parallel to the axis of the ring and  $dE_{\perp}$  perpendicular to the axis. Because of the symmetry of the situation, the perpendicular components of the field cancel. That is, the resulting field is directed along the  $x$  axis and its magnitude

$$E = \int dE_x, \text{ where } dE_x = k \frac{\lambda dl}{r^2} \cdot \cos \theta; \cos \theta = \frac{x}{r} = \frac{x}{\sqrt{R^2 + x^2}}.$$

$$\text{Then, } E = \int_0^{2\pi R} k \frac{\lambda dl}{(R^2 + x^2)} \cdot \frac{x}{\sqrt{R^2 + x^2}} = 2\pi R \lambda k \frac{x}{(R^2 + x^2)^{3/2}}, \text{ or}$$

$$E = kq \frac{x}{(R^2 + x^2)^{3/2}}, \quad (3.11)$$

where  $q$  is the total charge of the ring.

### 3.1.4 Electric potential

When the test charge is moved in the field by some external agent, the work done by the field on the charge is equal to the negative of the work done by the external agent causing the displacement.

For an infinitesimal displacement  $d\vec{l}$  of a point charge  $q_0$  immersed in an electric field, the work done within the charge–field system by the electric field on the charge is  $A = \vec{F}_e d\vec{l} = q_0 \vec{E} d\vec{l}$ . As this amount of work is done by the field, the potential energy of the charge–field system is changed by an amount  $dW = -A = -q_0 \vec{E} d\vec{l}$ . The negative sign means that in a system consisting of a positive charge and an electric field, the electric potential energy of the system decreases when the charge moves in the direction of the field. Equivalently, an electric field does work on a positive charge when the charge moves in the direction of the electric field. For a finite displacement

of the charge from point 1 to point 2, the change in potential energy of the system  $\Delta W = W_2 - W_1$  is

$$\Delta W = -q_0 \int_1^2 \vec{E} d\vec{l} . \quad (3.12)$$

Because the electrostatic force  $q_0 \vec{E}$  is conservative, this line integral does not depend on the path taken from 1 to 2. Moreover, the integral over a closed path, called a **circulation** of the vector  $\vec{E}$  in the electrostatic field, equals zero:

$$\oint \vec{E} d\vec{l} = 0 . \quad (3.13)$$

For a given position of the test charge in the field, the charge–field system has a potential energy  $W$ . Dividing the potential energy by the test charge gives a physical quantity that depends only on the source charge distribution and has a value at every point in an electric field.

**Electric potential** is the amount of electric potential energy of a charged particle at any location divided by the charge of that particle.

$$\varphi = \frac{W}{q_0} . \quad (3.14)$$

Then, the potential difference is

$$d\varphi = -\vec{E} d\vec{l} ; \quad \Delta\varphi = -\int_1^2 \vec{E} d\vec{l} . \quad (3.15)$$

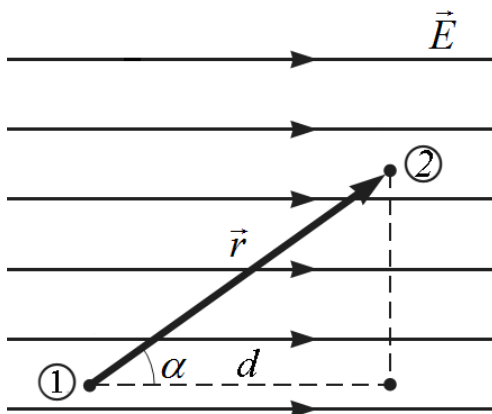


Figure 3.8.

The electric potential difference  $U = \Delta\varphi$  is called **voltage**. Potential difference between two points 1 and 2 separated by a distance  $d$  in a uniform electric field ( $E = const$ , Figure 3.8) will be

$$\Delta\varphi = -\int_1^2 \vec{E} d\vec{l} = -\int_1^2 E dl \cos \alpha = -Ed ,$$

where  $d$  is the distance between the two points projected onto the vector  $\vec{E}$ . The negative sign indicates that the electric potential at point 2 is lower than at point 1. Electric field lines always point in the direction of decreasing electric potential.

The electric potential at any point in space is equal to the **work done by the electric field** in carrying a unitary charge from that point to infinity without any acceleration. The work by the electric field in carrying the test charge  $q$  from point 1 to point 2 is

$$A = q(\varphi_1 - \varphi_2), \quad (3.16)$$

where  $\varphi_1 - \varphi_2$  is the potential difference between the two points.

The **equipotential surface** is the locus of points having the same electric potential (see Figure 3.9). Equipotential surfaces are always perpendicular to the net electric field lines passing through it. The work done to move a charge from any point on the equipotential surface to any other point on the same surface is zero since they are of the same potential.

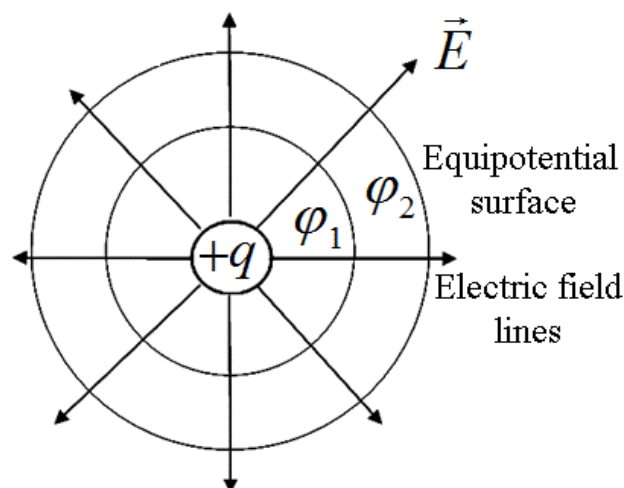


Figure 3.9.

### 3.1.4.1 Electric potential due to a point charge

To find the electric potential at a point located a distance  $r$  from the point charge  $q$ , let's begin with the general expression for potential difference,  $d\varphi = -\vec{E}d\vec{l}$ . Using the expression for the electric field due to the point charge, we obtain

$$d\varphi = -k \frac{q}{r^2} \cdot \vec{e}_r d\vec{l} = -k \frac{q}{r^2} \cdot d\vec{r} = -d \left( k \frac{q}{r} + const \right).$$

Now we see, that the potential due to the point charge is

$$\varphi = k \frac{q}{r}. \quad (3.17)$$

Electric potential is a scalar quantity, and its sign is given by the source electric charge.

The **total electric potential** due to a group of source charges at any point in space equals the algebraic sum of the electric potentials created by every individual charge at that point.

$$\varphi = \varphi_1 + \varphi_2 + \dots + \varphi_n. \quad (3.18)$$

For the case of continuously distributed charge,

$$\varphi = k \int \frac{dq}{r}. \quad (3.19)$$

### 3.1.5 Relation between the electric potential and the electric field vector

Let's find components of the vector  $\vec{E}$ . Considering displacement along the  $x$  axis,  $d\varphi = -\vec{E}d\vec{l} = -E_x dx$ . Then,  $E_x = -\frac{d\varphi}{dx}$ . Similarly,  $E_y = -\frac{d\varphi}{dy}$ ;  $E_z = -\frac{d\varphi}{dz}$ . Then, the vector  $\vec{E}$  is

$$\vec{E} = -\left( \frac{d\varphi}{dx} \vec{i} + \frac{d\varphi}{dy} \vec{j} + \frac{d\varphi}{dz} \vec{k} \right), \text{ or } \vec{E} = -grad(\varphi). \quad (3.20)$$

### 3.1.6 Electric dipole

**Electric dipole** is defined as a positive charge  $q$  and a negative charge  $-q$  separated by a fixed distance  $l$ . Neutral atoms and molecules behave as dipoles when placed in an external electric field.

Electric field due to the dipole is considered at a distance  $r$  from the dipole,  $r \gg l$ . Electric potential due to the electric dipole at point P

$$\varphi = k \left( \frac{q}{r_+} - \frac{q}{r_-} \right) = kq \frac{r_- - r_+}{r_+ r_-}.$$

As far as  $r \gg l$ ,  $r_- - r_+ \approx l \cos \theta$ ;  $r_- r_+ \approx r^2$  (see Figure 3.10). Then,

$$\varphi = k\rho \frac{\cos \theta}{r^2}, \quad (3.21)$$

where  $\rho = ql$  is the **electric dipole moment**. Actually, the electric dipole moment is a vector directed from the negative charge to the positive:

$$\vec{\rho} = q\vec{l}. \quad (3.22)$$

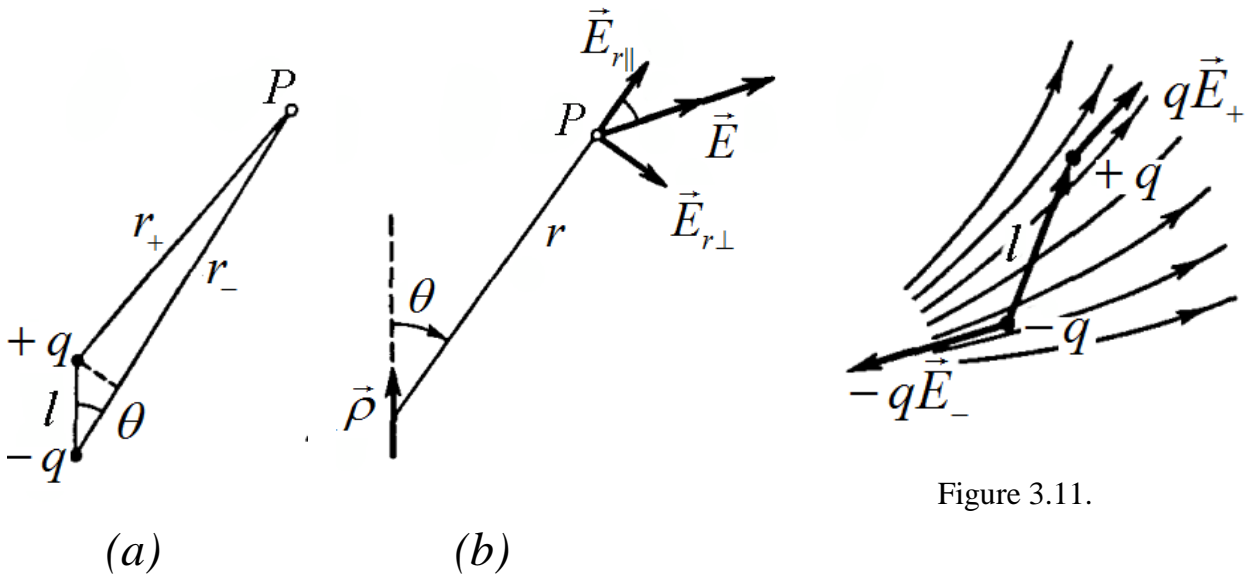


Figure 3.11.

Now let's find the electric field due to the electric dipole (see Figure 3.10b). Component of the electric field parallel to the direction of radius vector

$E_{r\parallel} = -\frac{d\varphi}{dr} = k \frac{2\rho \cos \theta}{r^3}$ . Component of the electric field perpendicular to the direction

of radius vector  $E_{r\perp} = -\frac{d\varphi}{rd\theta} = k \frac{\rho \sin \theta}{r^3}$ . Then, the total electric field

$$E = \sqrt{E_{r\parallel}^2 + E_{r\perp}^2} = k \frac{\rho}{r^3} \sqrt{1 + 3\cos^2 \theta}. \quad (3.23)$$

In particular cases, when  $\theta = 0$  or  $\theta = \pi/2$ , we obtain expressions for the electric field on the dipole axis ( $E_{\parallel}$ ) and perpendicular to the dipole axis ( $E_{\perp}$ ):



$$E_{\parallel} = k \frac{2\rho}{r^3}; \quad E_{\perp} = k \frac{\rho}{r^3}. \quad (3.24)$$

### 3.1.6.1 Force on the electric dipole

Let's consider an electric dipole in nonuniform electric field (Figure 3.11). The electric field vector at the points of positive and negative charges of the dipole is  $\vec{E}_+$  and  $\vec{E}_-$ . Then, the net electric force on the dipole is  $\vec{F} = q(\vec{E}_+ - \vec{E}_-)$ . The quantity  $\Delta\vec{E} = \vec{E}_+ - \vec{E}_-$  is the change in the electric field over an infinitesimal distance  $l$ . So  $\Delta\vec{E} = \frac{d\vec{E}}{dl} l$ . Thus we obtain the **force on the electric dipole moment**  $\rho$ :

$$\vec{F} = \rho \frac{d\vec{E}}{dl}. \quad (3.25)$$

The force on the electric dipole is nonzero only in the nonuniform electric field.

### 3.1.6.2 Torque on the electric dipole

An object with an electric dipole moment is subject to a torque when placed in an external electric field. The net torque on the dipole  $\vec{M} = [\vec{r}_+, q\vec{E}_+] - [\vec{r}_-, q\vec{E}_-] \approx, \approx [\vec{r}_+ - \vec{r}_-, q\vec{E}] = [\vec{l}, q\vec{E}]$ , where  $\vec{E}_+ \approx \vec{E}_- \approx \vec{E}$  as far as the distance  $l$  between the positive and negative charges is small. Thus,

$$\vec{M} = [\vec{\rho}, \vec{E}]. \quad (3.26)$$

Now consider an electric dipole placed in a uniform external electric field  $\vec{E}$  making an angle  $\theta$  with the field as shown in Figure 3.12. The electric forces acting on the two charges are equal in magnitude ( $F_+ = F_- = qE$ ) and opposite in direction as shown in Figure 3.12. Therefore, the net force on the dipole is zero. However, the two forces produce a net torque on the dipole. As a result, the dipole rotates in the direction

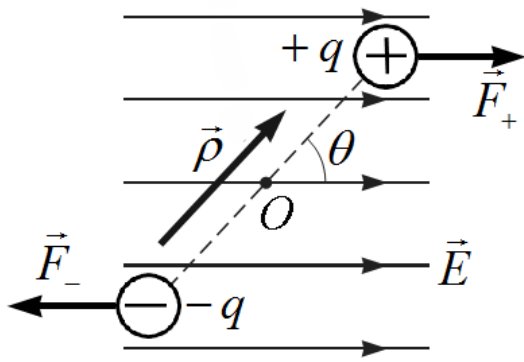


Figure 3.12.

that brings the dipole moment vector into greater alignment with the field. The torque due to the force on the positive charge about an axis through  $O$  in Figure 3.12 has magnitude  $qE \frac{l}{2} \sin \theta = \frac{\rho E}{2} \sin \theta$ . This force tends to produce a clockwise rotation. The torque about  $O$  on the negative charge has the

same magnitude and also tends to produce a clockwise rotation. Therefore, the magnitude of the net torque on the dipole in the uniform electric field is

$$M = \rho E \sin \theta. \quad (3.27)$$

### 3.1.6.3 Energy of the electric dipole in the electric field

The torque tends to align the dipole parallel with the electric field vector  $\vec{E}$  when  $\theta = 0$ . A dipole aligned parallel to the electric field has lower potential energy than a dipole making some angle with it. The work done by an external agent to rotate the dipole through the angle is then stored as potential energy in the system of the dipole and the external electric field.

As we know, potential energy of the point charge  $q$  in the external electric field is  $W = q\varphi$ , where  $\varphi$  is the electric potential at the point where the charge  $q$  is located. As far as electric dipole is a system of two point charges of opposite signs, its energy in the external electric field is  $W = q_+\varphi_+ + q_-\varphi_- = q(\varphi_+ + \varphi_-)$ , where  $\varphi_+$  and  $\varphi_-$  are potentials due to the external electric field at the points where the charges  $+q$  and  $-q$  are located;  $\varphi_+ + \varphi_- = \frac{d\varphi}{dl} l$ . But according to the relation between the electric field vector and electric potential,  $-\frac{d\varphi}{dl} = E_l$ , where  $E_l$  is projection of the vector  $\vec{E}$  on the

vector  $\vec{l}$ , which shows the direction of the electric dipole moment  $\vec{p} = q\vec{l}$ . Then,

$\varphi_+ + \varphi_- = \frac{d\varphi}{dl}l = -E_l l = -\vec{E}\vec{l}$ , and the electric potential energy of the dipole is

$$W = -q\vec{E}\vec{l} = -\vec{p}\vec{E}. \quad (3.28)$$

It is seen, that electric dipole has its minimum potential energy ( $W_{\min} = -pE \cos 0 = -pE$ ) when it is aligned parallel with the external electric field  $\vec{p} \uparrow \uparrow \vec{E}$ , which is the equilibrium orientation of the dipole. That's why electric dipoles tend to align with the field. If the change in the system is made, the dipole begins to rotate back toward the configuration in which it is aligned with the field.

### ***Questions for self-control***

1. What is the electrostatic field?
2. What is the point charge? Properties of the electric charges
3. Charge quantization law
4. Electric charge conservation law
5. Coulomb's law
6. What is the electric field vector
7. Superposition principle
8. Properties of the electric field lines
9. Uniform electric field
10. Electric field due to a point charge
11. Properties of the distributed electric charge
12. Calculation of the electric field due to the linearly distributed charge
13. Circulation of the electric field vector
14. Electric potential
15. What is the equipotential surface?
16. Electric potential due to a point charge
17. work done by the electric field
18. Relation between the electric potential and the electric field vector
19. Electric dipole. Dipole moment
20. Torque on the electric dipole

## Lecture 18

### 3.1.7 Electric flux

**Electric flux** is the measure of flow of the electric field through a given area. It is proportional to the number of electric field lines going through a normally perpendicular surface.

If the electric field is uniform, the electric flux passing through a surface of vector area  $\vec{S}$  (see Figure 3.13) is

$$\Phi = \vec{E}\vec{S} = ES \cos \alpha \quad (3.29)$$

where  $\vec{E}$  is the electric field,  $E$  is its magnitude,  $\vec{S}$  is the vector area, whose direction is defined to be perpendicular to the surface,  $S$  is magnitude of the area of the surface, and  $\alpha$  is the angle between the electric field lines and the perpendicular to the surface.

We see that the flux through a surface of fixed area has a maximum value when the surface is perpendicular to the field; the flux is zero when the surface is parallel to the field.

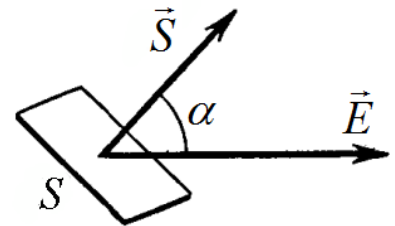


Figure 3.13.

For a non-uniform electric field, the electric flux  $d\Phi$  through a small surface area  $dS$  is given by

$$d\Phi = \vec{E}d\vec{S} = EdS \cos \alpha$$

The electric flux over a surface  $S$  is therefore given by the surface integral:

$$\Phi = \iint_S \vec{E}d\vec{S} = \iint_S EdS \cos \alpha. \quad (3.30)$$

We are often interested in evaluating the flux through a closed surface. Then vector  $d\vec{S}$  is a differential area on the closed surface  $S$  with an outward facing surface normal defining its direction.

### 3.1.8 Gauss's law

**Gauss's law** is a general relationship between the net electric flux through a closed surface (often called a **gaussian surface**) and the charge enclosed by the surface.

The electric flux through a closed surface is equal to the total electric charge enclosed within this surface divided by the electric constant:

$$\oint_S \vec{E} d\vec{S} = \frac{q}{\epsilon_0} \quad (3.31)$$

Consider a positive point charge  $q$  located at the center of a sphere of radius  $r$  and surface area  $S$  as shown in Figure 3.14. The magnitude of the electric field everywhere on the surface of the sphere is  $E = kq/r^2$ . The field lines are directed radially outward and hence are perpendicular to the surface at every point on the surface. Therefore, the electric flux through the surface element  $dS$  is

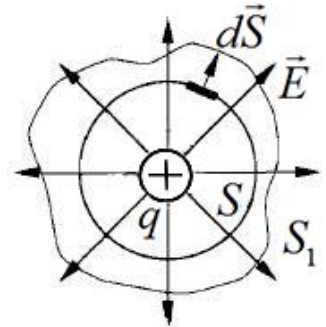


Figure 3.14.

$$d\Phi = \vec{E} d\vec{S} = \frac{kq}{r^2} dS = \frac{q}{4\pi\epsilon_0 r^2} dS .$$

Then we obtain the net flux through the gaussian surface by integrating  $\Phi = \oint_S \vec{E} d\vec{S} = \oint_S E dS = E \oint_S dS$ , where we have moved  $E$  outside of the integral because,

by symmetry,  $E$  is constant over the surface. As the surface is spherical,  $\oint_S dS = 4\pi r^2$ ,

and the net flux is  $\Phi = \frac{q}{4\pi\epsilon_0 r^2} \cdot 4\pi r^2 = \frac{q}{\epsilon_0}$ , so the Gauss' theorem is proved. The flux

is independent of the radius  $r$  because the area of the spherical surface is proportional to  $r^2$ , whereas the electric field is proportional to  $1/r^2$ .

By definition, flux is proportional to the number of electric field lines passing through a surface surrounding the charge  $q$ . But the number of lines through spherical surface is equal to the number of lines through the nonspherical surface (surface  $S_1$  in

Figure 3.14). Therefore, the net flux through any closed surface surrounding a point charge  $q$  is given by  $\frac{q}{\epsilon_0}$  and is independent of the shape of that surface.

Now consider a point charge located outside a closed surface of arbitrary shape as shown in Figure 3.15. As can be seen from this construction, any electric field line entering the surface leaves the surface at another point. The number of electric field lines entering the surface equals the number leaving the surface. Therefore, the net electric flux through a closed surface that surrounds no charge is zero.

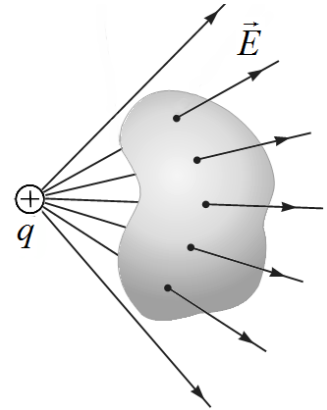


Figure 3.15.

Now let's generalize the Gauss' law for the electric flux due to many point charges and due to a continuous distribution of charge. Using the superposition principle, the flux through any closed surface can be expressed as

$$\oint_S \vec{E} d\vec{S} = \oint_S (\vec{E}_1 + \vec{E}_2 + \dots) d\vec{S} = \oint_S \vec{E}_1 d\vec{S} + \oint_S \vec{E}_2 d\vec{S} + \dots = \Phi_1 + \Phi_2 + \dots$$

We know that  $\oint_S \vec{E}_i d\vec{S} = \frac{q_i}{\epsilon_0}$  if the charge  $q_i$  is inside the surface, or  $\oint_S \vec{E}_i d\vec{S} = 0$  if

the charge is outside the surface. We obtain that

$$\oint_S \vec{E} d\vec{S} = \frac{1}{\epsilon_0} \sum_i q_i = \frac{q_{in}}{\epsilon_0}, \quad (3.32)$$

where  $q_{in}$  is the net charge inside the gaussian surface. For the continuous distribution of charge,  $q_{in} = \int_V \rho dV$ , where  $\rho$  is the volumetric charge density,  $V$  is the volume over

which the charge is distributed inside the Gaussian surface. So,

$$\oint_S \vec{E} d\vec{S} = \frac{1}{\epsilon_0} \int_V \rho dV. \quad (3.33)$$

### 3.1.9 Differential form of the Gauss' law

For the distributed electric charge, the Gauss' law can be written as  $\frac{1}{V} \oint_S \vec{E} d\vec{S} = \frac{\langle \rho \rangle}{\epsilon_0}$ , where  $\langle \rho \rangle$  is the average volumetric charge density throughout the volume  $V$ ,  $q_{in} = \langle \rho \rangle V$ .

**Divergence** of the electric field vector represents the volume density of the outward flux of a vector field from an infinitesimal volume around a given point:

$$div \vec{E} = \lim_{V \rightarrow 0} \frac{1}{V} \oint_S \vec{E} d\vec{S}. \quad (3.34)$$

For the Cartesian coordinate system we obtain

$$div \vec{E} = \vec{\nabla} \cdot \vec{E} = \frac{dE_x}{dx} + \frac{dE_y}{dy} + \frac{dE_z}{dz}. \quad (3.35)$$

**Divergence theorem**, also known as **Ostrogradsky's - Gauss's theorem**, states that the outward flux of a vector field through a closed surface is equal to the volume integral of the divergence over the region inside the surface:

$$\oint_S \vec{E} d\vec{S} = \int_V div \vec{E} dV. \quad (3.36)$$

By the combination of the Gauss law and the divergence theorem,  $\oint_S \vec{E} d\vec{S} = \frac{1}{\epsilon_0} \int_V \rho dV = \int_V div \vec{E} dV$ , the Gauss' law can alternatively be written in the **differential form**:

$$div \vec{E} = \frac{\rho}{\epsilon_0}. \quad (3.37)$$

### 3.1.10 Circulation and curl of the electric field vector

The **curl** of a vector field describes the infinitesimal rotation at every point in the field and is defined as the infinitesimal area density of the circulation of that field.

Consider a vector field  $\vec{E}$  and an infinitesimal area  $\Delta S$  enclosed by the path  $L$ . Let the unit vector  $\vec{n}$  be perpendicular to the plane of the area  $\Delta S$  and related with the

direction of circulation along the path  $L$  according to the right-hand rule (Figure 3.16).

Then, the curl of the vector field projected onto the  $\vec{n}$  is defined as

$$rot_n \vec{E} = \lim_{\Delta S \rightarrow 0} \frac{\oint_L \vec{E} d\vec{l}}{\Delta S}. \quad (3.38)$$

For the Cartesian coordinate system,

$$rot \vec{E} = [\vec{\nabla}, \vec{E}] = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{d}{dx} & \frac{d}{dy} & \frac{d}{dz} \\ E_x & E_y & E_z \end{vmatrix}. \quad (3.39)$$

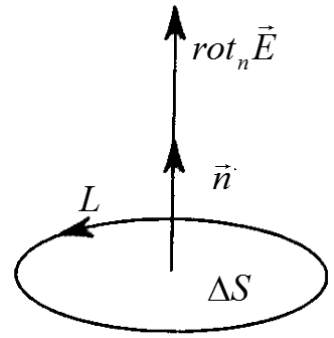


Figure 3.16.

The **Stokes theorem** relates the surface integral of the curl of a vector field  $\vec{E}$  over a surface  $S$  to the line integral of the vector field over its boundary  $L$ :

$$\int_S rot \vec{E} dS = \oint_L \vec{E} d\vec{l}. \quad (3.40)$$

As far as circulation of the vector  $\vec{E}$  in the electrostatic field equals zero,  $\int_S rot \vec{E} dS = 0$ . That means that in the electrostatic field

$$rot \vec{E} = 0. \quad (3.41)$$

It gives the condition for the vector field to be potential: in the potential field circulation of the field vector over a closed path equals zero.

Equations

$$div \vec{E} = \frac{\rho}{\epsilon_0}; \quad rot \vec{E} = 0 \quad (3.42)$$

are the **basic equations of electrostatics**.

### ***Questions for self-control***

1. What is the electric flux?
2. Gauss's law



3. Gauss' law for the electric flux due to many point charges
4. Gauss' law for the electric flux due to the continuous distribution of charge
5. Divergence of the electric field vector
6. Ostrogradsky - Gauss theorem (divergence theorem)
7. Differential form of the Gauss' law
8. Curl of the electric field vector
9. Stokes' theorem
10. Basic equations of electrostatics

## *Lecture 19*

### *3.1.11 Application of gauss's law to various charge distributions*

Gauss's law is useful for determining electric fields when the charge distribution is highly symmetric. In such a case we can choose the gaussian surface over which the surface integral  $\oint_S \vec{E} d\vec{S}$  can be simplified and the electric field determined. The goal in this type of calculation is to determine a surface for which each portion of the surface satisfies one or more of the following conditions:

1. The value of the electric field can be argued by symmetry to be constant over the portion of the surface, so that  $E$  can be removed from the integral.
2. The dot product  $\vec{E} d\vec{S}$  can be expressed as a simple algebraic product  $EdS$  because vectors  $\vec{E}$  and  $d\vec{S}$  are parallel.
3. The dot product  $\vec{E} d\vec{S} = 0$  because vectors  $\vec{E}$  and  $d\vec{S}$  are perpendicular.
4. The electric field is zero over the portion of the surface.

Different portions of the gaussian surface can satisfy different conditions as long as every portion satisfies at least one condition. If the charge distribution does not have sufficient symmetry such that a gaussian surface that satisfies these conditions can be found, Gauss's law is not useful for determining the electric field for that charge distribution.

#### *3.1.11.1 Electric field due to a spherical charge distribution*

Let's consider an **electric field due to a spherical surface** of radius  $R$  and of total positive charge  $q$ , which is uniformly distributed over the surface, depending on a distance  $r$  from the center of the sphere.

Because the charge is distributed uniformly throughout the spherical surface, the charge distribution has spherical symmetry and we can apply Gauss's law to find the electric field. To reflect the spherical symmetry, let's choose a spherical gaussian

surface of radius  $r$ , concentric with the spherical surface, as shown in Figure 3.17. For

$$\text{this choice, } \oint_S \vec{E} d\vec{S} = \oint_S E dS = E \oint_S dS = E \cdot 4\pi r^2 .$$

- for the region inside the spherical surface ( $r < R$ )  
no charges are inside the gaussian surface, and

$$E = 0 ; \quad (3.43a)$$

- for the region outside the sphere and on its surface ( $r \geq R$ ), the total charge of the surface  $q$  is inside the gaussian surface, and according to the Gauss's law,

$$\oint_S \vec{E} d\vec{S} = E \cdot 4\pi r^2 = \frac{q}{\epsilon_0} . \text{ Then,}$$

$$E = \frac{q}{4\pi\epsilon_0 r^2} = k \frac{q}{r^2} . \quad (3.43b)$$

The plot of the  $E(r)$  dependence for the charged spherical surface is shown in Figure 3.18.

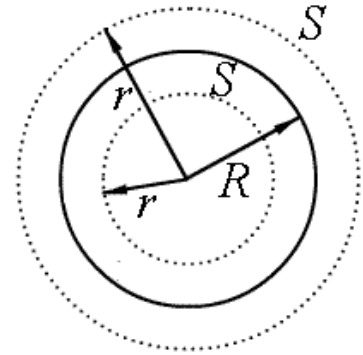


Figure 3.17.

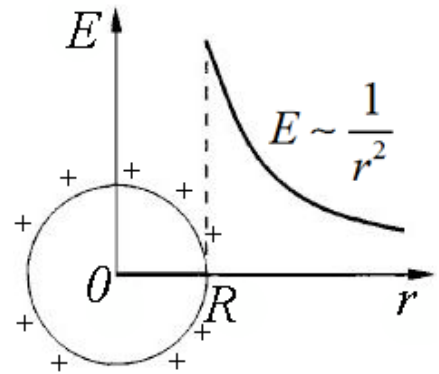


Figure 3.18.

Now let's consider an **electric field due to a sphere** of radius  $R$  and of total positive charge  $q$ , which is uniformly distributed over the volume with volumetric charge density  $\rho$ .

Because the charge is distributed uniformly throughout the sphere, the charge distribution has spherical symmetry and we can apply Gauss's law to find the electric field. As in the previous case, let's choose a spherical gaussian surface of radius  $r$ , concentric with the sphere, as shown in Figure 3.19. For this choice,

$$\oint_S \vec{E} d\vec{S} = \oint_S E dS = E \oint_S dS = E \cdot 4\pi r^2 .$$

– for the region inside the sphere ( $r < R$ ), according to the Gauss's law

$$\oint_S \vec{E} d\vec{S} = E \cdot 4\pi r^2 = \frac{1}{\epsilon_0} \int_V \rho dV = \frac{\rho}{\epsilon_0} \int_V dV, \text{ where } V \text{ is the volume of the smaller sphere}$$

bounded by the gaussian surface,  $V = \frac{4}{3}\pi r^3$ . Then,  $E \cdot 4\pi r^2 = \frac{\rho}{\epsilon_0} \cdot \frac{4}{3}\pi r^3$  and,

considering that the total charge  $q = \rho \frac{4}{3}\pi R^3$ ,

$$E = \frac{\rho}{3\epsilon_0} r = k \frac{q}{3R^3} r; \quad (3.44a)$$

– for the region outside the sphere and on its surface ( $r \geq R$ ), according to the Gauss's

law  $E \cdot 4\pi r^2 = \frac{\rho}{\epsilon_0} \int_V dV$ , where  $V$  is the volume of the charged sphere because now

the total charge of the sphere  $q$  is inside the gaussian surface,  $V = \frac{4}{3}\pi R^3$ . Then,

$$E \cdot 4\pi r^2 = \frac{\rho}{\epsilon_0} \cdot \frac{4}{3}\pi R^3 = \frac{q}{\epsilon_0}; \quad E = \frac{q}{4\pi\epsilon_0 r^2} = k \frac{q}{r^2}. \quad (3.44b)$$

The plot of the  $E(r)$  dependence for the charged sphere is shown in Figure 3.20.

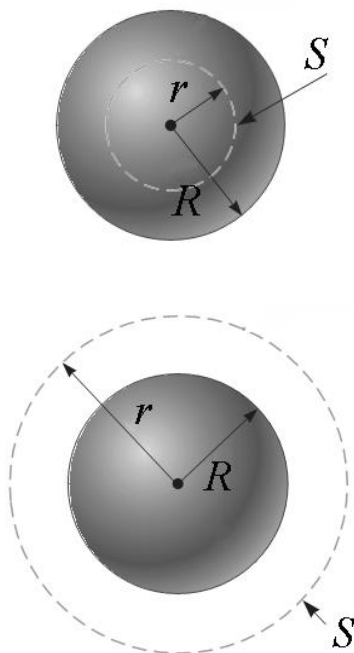


Figure 3.19.

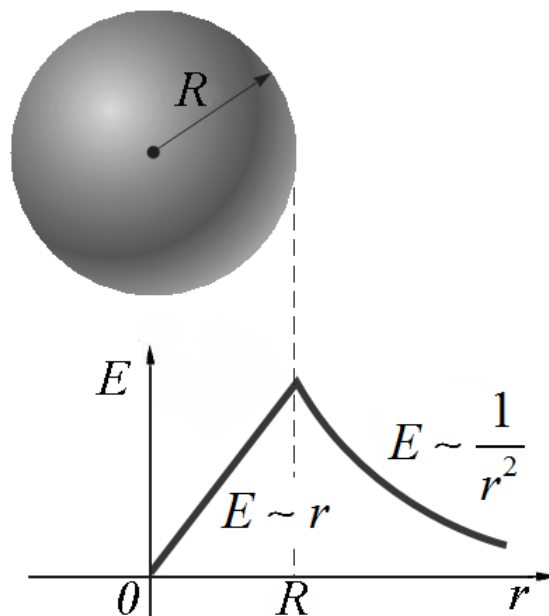


Figure 3.20.

The electric field due to a uniformly charged sphere of total charge  $q$  in the region external to the sphere is equivalent to that of a point charge  $q$  located at the center of the sphere. The field external to a spherically symmetric charge distribution varies as  $1/r^2$ .

### 3.1.11.2 Electric field due to a cylindrical symmetry charge distribution

Let's consider an electric field at a distance  $r$  from a line of infinite length having total positive charge  $q$  and constant linear charge density  $\lambda$ .

Because the charge is distributed uniformly along the line, the charge distribution has cylindrical symmetry and we can apply Gauss's law to find the electric field. To reflect the symmetry of the charge distribution, let's choose a cylindrical gaussian surface of radius  $r$  and length  $l$ , that is coaxial with the line charge (Figure 3.21). For the lateral surface of the cylinder,  $\vec{E}$  is constant in magnitude and perpendicular to the surface at each point.

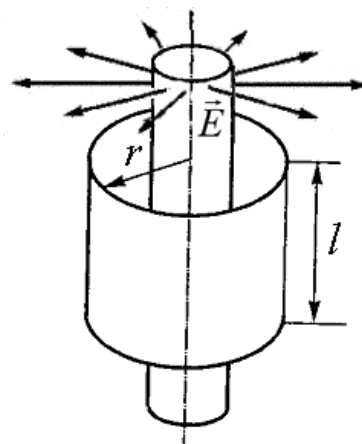


Figure 3.21.

Furthermore, the flux through the ends of the gaussian cylinder is zero because  $\vec{E}$  is parallel to these surfaces. That is, we must take the surface integral in Gauss's law over the lateral surface of the cylinder because  $\vec{E}d\vec{S} = 0$  for the flat ends. Then,

$$\oint_S \vec{E}d\vec{S} = E \oint_S dS = E \cdot 2\pi r l . \text{ Considering that } q = \lambda l, \text{ we obtain } E \cdot 2\pi r l = \frac{q}{\epsilon_0} = \frac{\lambda l}{\epsilon_0} \text{ and}$$

$$E = \frac{\lambda}{2\pi\epsilon_0} \cdot \frac{1}{r} = 2k \frac{\lambda}{r} . \quad (3.45)$$

The electric field due to a cylindrically symmetric charge distribution varies as  $1/r$ .

### 3.1.11.3 Electric field due to a planar charge distribution

Let's find the electric field due to an infinite plane of positive charge with uniform surface charge density  $\sigma$ .

Because the charge is distributed uniformly on the plane, the charge distribution is symmetric; hence, we can use Gauss's law to find the electric field. By symmetry,

$\vec{E}$  must be perpendicular to the plane at all points. The direction of  $\vec{E}$  is away from positive charges, indicating that its direction on one side of the plane must be opposite its direction on the other side as shown in Figure 3.22.

A gaussian surface that reflects the symmetry is a small cylinder whose axis is perpendicular to the plane and whose ends each have an area  $S$  and are equidistant from the plane. Because  $\vec{E}$  is parallel to the lateral surface,  $\vec{E}d\vec{S} = 0$  and there is no contribution to the surface integral from the lateral surface.

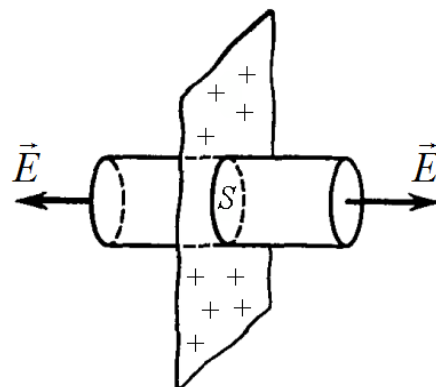


Figure 3.22.

For the flat ends of the cylinder,  $\vec{E}$  is perpendicular to the surface and the flux through each end of the cylinder is  $ES$ ; hence, the total flux through the entire gaussian surface is just that through the ends  $\oint_S \vec{E}d\vec{S} = 2ES$ . Considering that  $q = \sigma S$ , we obtain

from the Gauss's law  $2ES = \frac{q}{\epsilon_0} = \frac{\sigma S}{\epsilon_0}$ , and

$$E = \frac{\sigma}{2\epsilon_0}. \tag{3.46}$$

Electric field due to a plane of charge is uniform.

**Electric field due to two parallel infinite planes** of opposite charge with equal in magnitude surface density  $\pm\sigma$  (Figure 3.23):

- in the region between the planes electric fields add, resulting in a uniform electric field of magnitude

$$E = \frac{|\sigma|}{\epsilon\epsilon_0}; \tag{3.47a}$$

- in the region outside the planes electric fields cancel each other, and

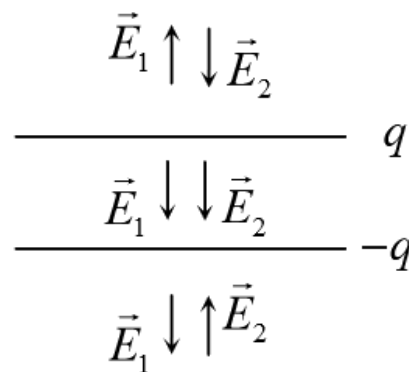


Figure 3.23.

$$E = 0.$$

$$(3.47b)$$

### *Questions for self-control*

1. Conditions for application of the Gauss's law for determining the electric field
2. Electric field due to a charged spherical surface (electric charge distributed over the surface) inside the sphere
3. Electric field due to a charged spherical surface (electric charge distributed over the surface) outside the sphere
4. Electric field due to a charged sphere (electric charge distributed over the volume) inside the sphere
5. Electric field due to a charged sphere (electric charge distributed over the volume) outside the sphere
6. Electric field due to a cylindrical charge distribution
7. Electric field due to an infinite plane
8. Electric field due to a system of two parallel planes

## Topic 3.2. Dielectrics and conductors in the external electric field

### Lecture 20

#### 3.2.1 Conductors in the electric field

**Electrical conductor** is the type of material that contains charges (electrons) that are not bound to any atom and therefore are free to move about within the material. Materials made of metal are common electrical conductors.

When there is no net motion of charge within a conductor, the conductor is in **electrostatic equilibrium**. A conductor in electrostatic equilibrium has the following properties:

1. The electric field is zero everywhere inside the conductor, whether the conductor is solid or hollow.
2. If the conductor is isolated and carries a charge, the charge resides on its surface.
3. The electric field at a point just outside a charged conductor is perpendicular to the surface of the conductor and has a magnitude  $\frac{\sigma}{\epsilon_0}$ , where  $\sigma$  is the surface charge density at that point.
4. On an irregularly shaped conductor, the surface charge density is greatest at locations where the radius of curvature of the surface is smallest.

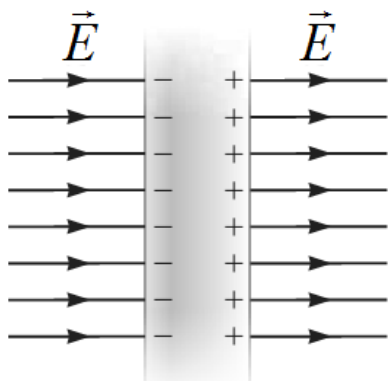


Figure 3.24.

We can understand the first property by considering a conducting slab placed in an external field  $\vec{E}$  (Figure 3.24). The existence of electrostatic equilibrium is consistent only with a zero field inside the conductor because nonzero field would cause motion of electrons due to the electric force.



Let's investigate how this zero field is accomplished. Before the external field is applied, free electrons are uniformly distributed throughout the conductor. When the external field is applied, the free electrons accelerate against the field (to the left in Figure 3.24), causing a plane of negative charge to accumulate on the left surface and a plane of positive charge on the right surface. These planes of charge create an additional electric field inside the conductor that opposes the external field. As the electrons move, the surface charge densities on the left and right surfaces increase until the magnitude of the internal field equals that of the external field, resulting in a net field of zero inside the conductor. The time it takes a good conductor to reach equilibrium is on the order of  $10^{-16}$  s, which for most purposes can be considered instantaneous.

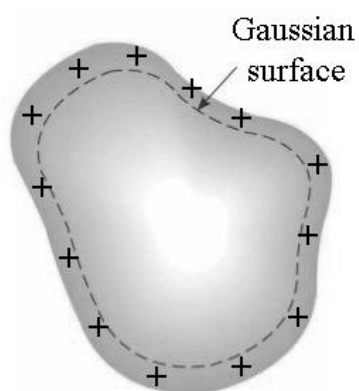


Figure 3.25.

Gauss's law can be used to verify the second property of a conductor in electrostatic equilibrium. Figure 3.25 shows an arbitrarily shaped conductor. A gaussian surface is drawn inside the conductor and can be very close to the conductor's surface. As we have just shown, the electric field everywhere inside the conductor is zero when it is in electrostatic equilibrium. Therefore, the electric field must be zero at every point on the

gaussian surface, and the net flux through this gaussian surface is zero. From this result and Gauss's law, we conclude that the net charge inside the gaussian surface is zero.

Because there can be no net charge inside the gaussian surface (which is arbitrarily close to the conductor's surface), any net charge on the conductor must reside on its surface.

To verify the third property, let's begin with the perpendicularity of the field to the surface. If the field vector  $\vec{E}$  had a component parallel to the conductor's surface, free electrons would experience an electric force and move along the surface; in such a case, the conductor would not be in equilibrium. Therefore, the field vector must be perpendicular to the surface.

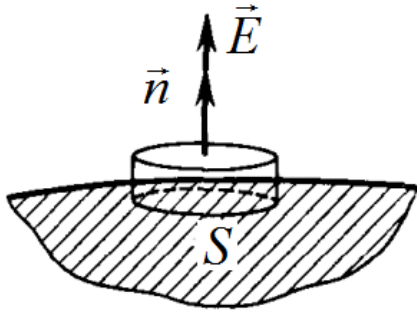


Figure 3.26.

To determine the magnitude of the electric field, we use Gauss's law and draw a gaussian surface in the shape of a small cylinder whose end faces are parallel to the conductor's surface (Figure 3.26). Part of the cylinder is just outside the conductor, and part is inside. The field is perpendicular to the conductor's surface from the condition of electrostatic equilibrium. Therefore, there is no flux through the

lateral surface of the gaussian cylinder because  $\vec{E}$  is parallel to that surface. There is no flux through the flat face of the cylinder inside the conductor because here  $\vec{E} = 0$ . Hence, the net flux through the gaussian surface is equal to that through only the flat face outside the conductor, where the field is perpendicular to the gaussian surface.

According to the Gauss's law,  $\oint_S \vec{E} d\vec{S} = ES = \frac{\sigma S}{\epsilon_0}$ , where  $E$  is the electric field just outside the conductor and  $S$  is the area of the cylinder's face. Then,

$$E_n = \frac{\sigma}{\epsilon_0} \quad (3.48)$$

is the electric field immediately outside a charged conductor.

Now let's consider two arbitrary points on the surface of a charged conductor. Along a surface path connecting these points,  $\vec{E}$  is always perpendicular to the displacement  $d\vec{l}$ . Therefore, the dot product  $\vec{E}d\vec{l} = 0$  and the potential difference between these points  $\Delta\phi = -\int_1^2 \vec{E}d\vec{l} = 0$ . We can make the following conclusions:

- The electric potential  $\phi$  is constant everywhere on the surface of a charged conductor in equilibrium.
- The surface of any charged conductor in electrostatic equilibrium is an equipotential surface: every point on the surface of a charged conductor in equilibrium is at the same electric potential.

- Because the electric field is zero inside the conductor, the electric potential is constant everywhere inside the conductor and equal to its value at the surface. If the conductor is hollow, the electric field inside the conductor is also zero, whether we consider points in the conductor or in the cavity within the conductor.
- Because of the constant value of the potential, no work is required to move a test charge from the interior of a charged conductor to its surface.

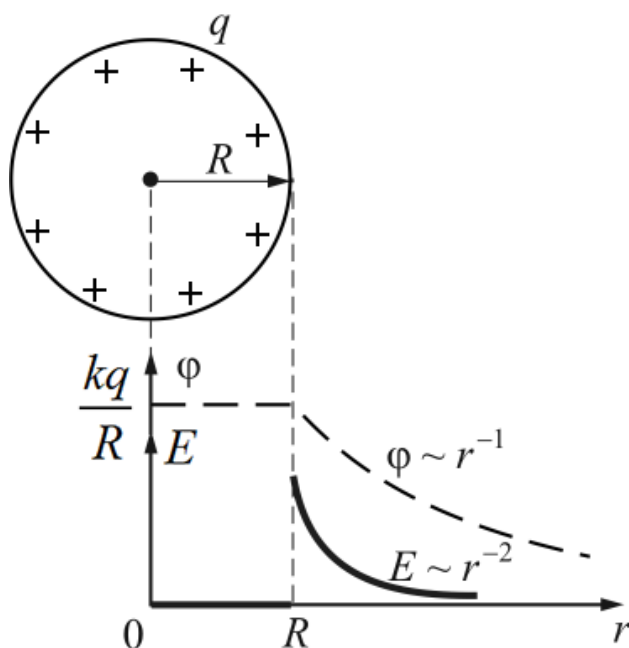


Figure 3.27 Electric field  $E$  and potential  $\phi$  due to a conducting sphere

Now let's consider a solid metal conducting sphere of radius  $R$  and total positive charge  $q$  as shown in Figure 3.27. As determined before, the electric field outside the sphere is  $k\frac{q}{r^2}$  and points radially outward. Because the field outside a spherically symmetric charge distribution is identical to that of a point charge, we expect the potential to also be that of a point charge.

**Electric potential due to a conducting sphere** is

$$\phi = k\frac{q}{r}, \text{ (for the region outside the sphere } r > R\text{).} \quad (3.49a)$$

At the surface of the conducting sphere, the potential must be  $\phi = k\frac{q}{R}$ . Because the entire sphere must be at the same potential, the potential at any point within the sphere must also be

$$\phi = k\frac{q}{R}, \text{ (for the region inside the sphere } r \leq R\text{).} \quad (3.49b)$$

### 3.2.1.1 A cavity within a conductor

Suppose a conductor of arbitrary shape contains a cavity (Figure 3.28). Let's assume no charges are inside the cavity. As the electric field is zero everywhere inside the conductor, it must be zero inside the cavity too. All the charges are distributed on the surface of the conductor and do not create electric field inside the cavity. Furthermore, the field in the cavity is zero even if an electric field exists outside the conductor. To prove this point, remember that every point on the conductor is at the same electric potential. Therefore, for any two points on the cavity's surface the potential difference  $\Delta\varphi = -\int \vec{E}d\vec{l}$  must be zero. The only way that can be true for all paths between any two points if the electric field throughout the cavity is zero  $\vec{E} = 0$ .

Therefore, a cavity surrounded by conducting walls is a field-free region as long as no charges are inside the cavity. The application of this effect is known as the

Faraday shield used to block electromagnetic fields. A Faraday shield may be formed by a continuous shell of conductive material or by a mesh of such materials. An external electrical field causes the electric charges within the shield's conducting material to be distributed such that they cancel the field's effect in the cage's interior.

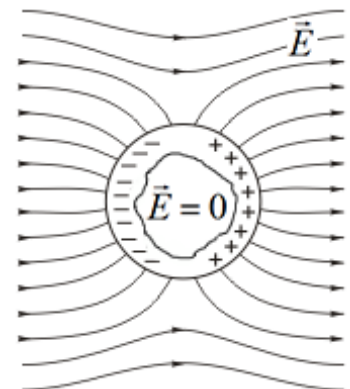


Figure 3.28.

### 3.2.2 Dielectrics

A **dielectric** (or dielectric material) is a nonconducting material with a high polarizability. When a dielectric is placed in an electric field, electric charges do not flow through the material as they do in a conductor, but only slightly shift from their average equilibrium positions causing dielectric **polarization**: positive charges are displaced toward the field and negative charges shift in the opposite direction.

Molecules are said to be polarized when a separation exists between the average position of the negative charges and the average position of the positive charges in the molecule, that is, when the molecule has electric dipole moment. In some molecules

such as water, this condition is always present; such molecules are called **polar molecules**. Molecules that do not possess a permanent polarization are called **nonpolar molecules**.

Consider a dielectric made up of polar molecules placed in the external electric field. The dipoles are randomly oriented in the absence of an electric field as shown in Figure 3.29a. When an external field  $\vec{E}_{ex}$  is applied, a torque is exerted on the dipoles, causing them to partially align with the field as shown in Figure 3.29b. The dielectric is now polarized. If the molecules of the dielectric are nonpolar, the external electric field produces an induced polarization in the molecule. These induced dipole moments tend to align with the external field, and the dielectric is polarized too. Therefore, a dielectric can be polarized by an external field

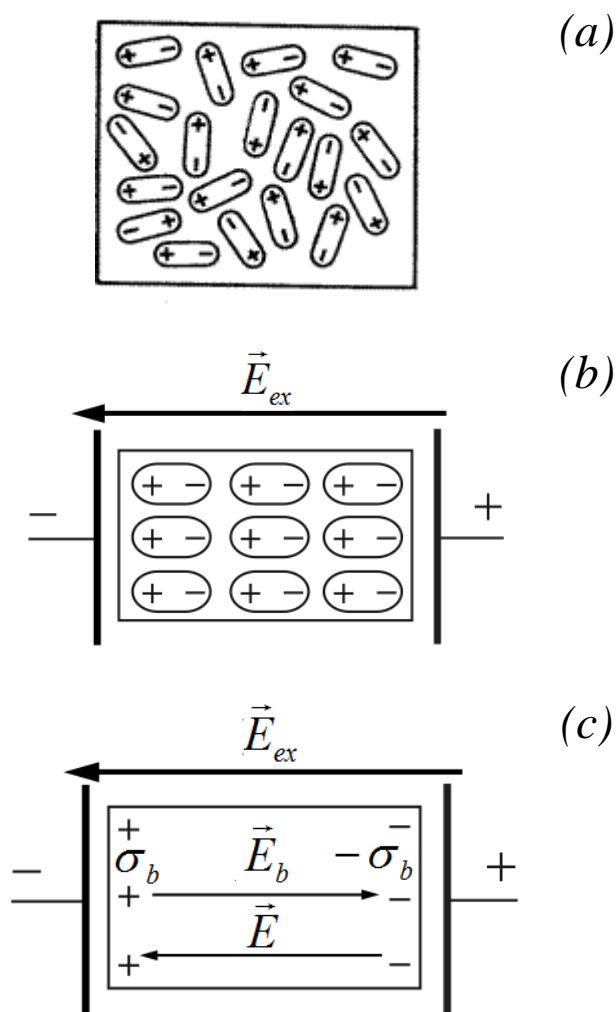


Figure 3.29.

regardless of whether the molecules in the dielectric are polar or nonpolar.

**Polarizability** is the property of material to form instantaneous dipoles as a response to external field. **Polarization density** is defined as the total electric dipole moment per unit volume:

$$\vec{P} = \frac{1}{\Delta V} \sum \vec{\rho}_i, \text{ or} \quad (3.50)$$

$$\vec{P} = n_0 \vec{\rho}, \quad (3.51)$$

where concentration  $n_0$  is the number of electric dipoles per unit volume.

The net charge appearing as a result of polarization of the medium is called a **bound charge** because it cannot move through the material, but only can slightly shift from the equilibrium position. The electric field in the dielectric material is the superposition of the external electric field  $\vec{E}_{ex}$  and the electric field due to the induced bound charges  $\vec{E}_b$  :

$$\vec{E} = \vec{E}_{ex} + \vec{E}_b .$$

In a homogeneous, linear and isotropic dielectric medium, the polarization is aligned with and proportional to the electric field:

$$\vec{P} = \chi_e \epsilon_0 \vec{E} , \tag{3.52}$$

where  $\epsilon_0$  is the electric constant, and  $\chi_e$  is the electric susceptibility of the medium.

The **electric susceptibility**  $\chi_e$  of a dielectric material is a measure of how easily it polarizes in response to an electric field. In the case of isotropy of the dielectric  $\chi_e$  is a scalar, although more generally it is a tensor relating the induced dielectric polarization density to the electric field.

The **relative permittivity**  $\epsilon_r$  (**dielectric constant**) of the medium is the measure of resistance that is encountered when forming an electric field in this medium. The susceptibility of a medium is related to its relative permittivity by

$$\chi_e = \epsilon_r - 1 . \tag{3.53}$$

Relative permittivity is the factor by which the electric field  $E$  in the material is decreased relative to the field in vacuum  $E_{ex}$  :

$$\epsilon_r = \frac{E_{ex}}{E} . \tag{3.54}$$

Let's consider a slab of dielectric material placed in a uniform electric field  $\vec{E}_{ex}$  created by the two parallel plates as shown in Figure 3.29b. The net effect on the dielectric is the formation of an induced positive surface charge density  $\sigma_b$  on the left face and an equal-magnitude negative surface charge density  $-\sigma_b$  on the right face as

shown in Figure 3.29c. The induced surface charges on the dielectric give rise to an induced electric field due to the bound charges  $\vec{E}_b$  in the direction opposite the external field  $\vec{E}_{ex}$ . Therefore, the net electric field in the dielectric has a magnitude  $E = E_{ex} - E_b$ . In the parallel-plate configuration the external field is related to the charge density on the plates as  $E_{ex} = \frac{\sigma}{\epsilon_0}$ . The induced electric field in the dielectric is related to the induced charge density as  $E_b = \frac{\sigma_b}{\epsilon_0}$ . Because  $E = \frac{E_{ex}}{\epsilon_r}$ , we obtain  $\frac{\sigma}{\epsilon_r \epsilon_0} = \frac{\sigma}{\epsilon_0} - \frac{\sigma_b}{\epsilon_0}$ , and the surface charge density due to the induced bound charges is

$$\sigma_b = \left( \frac{\epsilon_r - 1}{\epsilon_r} \right) \sigma. \quad (3.55)$$

This expression shows that the charge density of bound charges  $\sigma_b$  induced on the dielectric is less than the charge density  $\sigma$  on the plates.

On the other hand, the surface charge density  $\sigma_b = \frac{Nq_0}{S} = n_0 q_0 l$ , where  $N$  is the total number of dipoles,  $q_0$  is the charge of one dipole,  $n_0 = N/V$  is concentration of the dipoles. But  $q_0 l$  is the electric dipole moment  $\rho$ , and  $n_0 \rho = P_n$ , consequently, for the bound charges

$$\sigma_b = P_n, \quad (3.56)$$

where  $P_n$  is normal projection of the polarization density vector. Then, electric field in the dielectric  $E = E_{ex} - E_b = \frac{\sigma - \sigma_b}{\epsilon_0} = \frac{\sigma - P_n}{\epsilon_0} = \frac{\sigma - \chi_e \epsilon_0 E}{\epsilon_0}$ . So, we can find that

$E = \frac{\sigma}{\epsilon_0} \frac{1}{1 + \chi_e}$ , which means that electric field in the dielectric decreases  $1 + \chi_e$  times

comparing to that in vacuum, and that relative permittivity  $\epsilon_r = 1 + \chi_e$ .

### 3.2.2.1 Gauss's law for the polarization density field

For a given volume  $V$  enclosed by a surface  $S$ , the flux of  $\vec{P}$  through  $S$  is equal to the bound charge  $q_b$  inside the surface  $S$  taken with the negative sign, or

$$\oint \mathbf{P}_n dS = \oint \vec{\mathbf{P}} d\vec{\mathbf{S}} = -q_b. \quad (3.57)$$

By the divergence theorem, Gauss's law for the field  $\vec{\mathbf{P}}$  can be stated in differential form as:

$$\text{div} \vec{\mathbf{P}} = -\rho_b, \quad (3.58)$$

where  $\rho_b$  is the bound charge density contained inside the given surface  $S$ .

### 3.2.2.2 Boundary conditions for polarization density at dielectric interfaces

Consider an interface between two different homogeneous isotropic dielectrics. Polarization density is different in different material when they are placed in the same electric field. The bound charges will accumulate at the interface between them as the result of polarization.

Consider a gaussian surface as a very small cylinder whose axis is perpendicular to the interface between dielectrics and whose ends each have an area  $\Delta S$  and are equidistant from the interface (Figure 3.30). Because the cylinder is very small we can consider that the vector  $\vec{\mathbf{P}}$  is constant within each of the flat ends of the cylinder.

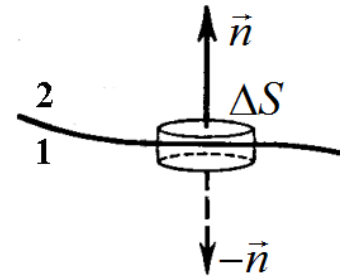


Figure 3.30.

Then, according to the Gauss's law for the vector  $\vec{\mathbf{P}}$ ,  $P_{2n}\Delta S - P_{1n}\Delta S = -\sigma_b\Delta S$ , where  $\sigma_b$  is the surface charge density of the bound charges at the interface,  $P_{1n}$  and  $P_{2n}$  are projections of the polarization vector on the normal  $\vec{n}$  in the first and second dielectric material. Then,

$$P_{2n} - P_{1n} = -\sigma_b. \quad (3.59)$$

If the second material is vacuum,  $P_{2n} = 0$ , and the normal component of the polarization density at the dielectric interface

$$P_n = \sigma_b. \quad (3.60)$$



### 3.2.3 Electric displacement field

As far as the presence of an electric field  $\vec{E}$  in a dielectric material causes the bound charges in the material to slightly separate, inducing a local electric dipole moment, the electric displacement field appears.

Consider the basic equation of electrostatics  $div\vec{E} = \frac{\rho}{\epsilon_0}$  for the dielectric. It will be rewritten as  $div\vec{E} = \frac{\rho + \rho_b}{\epsilon_0}$ , where the total volume charge density is the sum of free and bound charges. The density  $\rho_b$  can be rewritten as a function of the polarization  $\rho_b = -div\vec{P}$ , so  $div\vec{E} = \frac{\rho - div\vec{P}}{\epsilon_0}$ ;  $div\left(\vec{E} + \frac{\vec{P}}{\epsilon_0}\right) = \frac{\rho}{\epsilon_0}$ ;  $div(\epsilon_0\vec{E} + \vec{P}) = \rho$ . The quantity  $\epsilon_0\vec{E} + \vec{P}$  is defined as the **electric displacement**  $\vec{D}$ . Equivalently,

$$\vec{D} = \epsilon_0\vec{E} + \vec{P} = \epsilon_0(1 + \chi_e)\vec{E} = \epsilon_0\epsilon_r\vec{E}. \quad (3.61)$$

The displacement field satisfies Gauss's law in a dielectric:

$$div\vec{D} = \rho \text{ (differential form), or} \quad (3.62a)$$

$$\oint \vec{D}d\vec{S} = \oint D_n dS = q \text{ (integral form),} \quad (3.62b)$$

where  $q$  is the total free charge inside the surface  $S$ .

### 3.2.4 Boundary conditions at dielectric interfaces

Consider an interface between two different dielectrics. Let's take a gaussian surface as a very small cylinder whose axis is perpendicular to the interface between dielectrics and whose ends each have an area  $\Delta S$  and are equidistant from the interface (Figure 3.31). Because the cylinder is very small we can consider that the displacement field  $\vec{D}$  is constant within each of the flat ends of the cylinder.

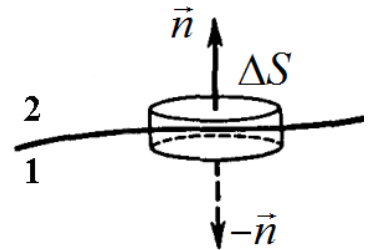


Figure 3.31.

Then, according to the Gauss's theorem for the displacement field,  $D_{2n}\Delta S - D_{1n}\Delta S = \sigma\Delta S$ , where  $\sigma$  is the surface charge density of the free charges at the interface,  $D_{1n}$  and  $D_{2n}$  are projections of the displacement field on the normal  $\vec{n}$  in the first and second dielectric material. Then,

$$D_{2n} - D_{1n} = \sigma. \quad (3.63)$$

When there are no free charges at the interface,  $\sigma = 0$ , the normal component  $D_n$  is continuous across dielectric interfaces:

$$D_{2n} = D_{1n}. \quad (3.64)$$

Now consider circulation of the vector  $\vec{E}$  at the interface between two dielectrics. Let's choose contour across the interface which is small enough to consider field constant along its line segments (Figure 3.32).

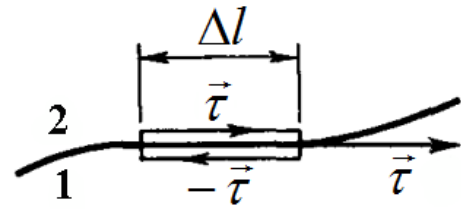


Figure 3.32.

Then, according to the conservative property of the electric field  $\oint \vec{E}d\vec{l} = 0$ ,  $E_{2\tau}\Delta l - E_{1\tau}\Delta l = 0$ , where  $E_{1\tau}$  and  $E_{2\tau}$  are tangential projections of the electric field in the first and second dielectric material. Then,

$$E_{2\tau} = E_{1\tau}, \quad (3.65)$$

and the tangential component of the electric field is continuous across dielectric interface.

### 3.2.5 Ferroelectrics

In most materials the induced polarization density is directly proportional to the applied electric field  $\vec{P} = \chi_e \varepsilon_0 \vec{E}$ , so the polarization is a linear function. However, some materials, known as **paraelectric** materials, have the electric permittivity not constant as in dielectrics but a function of the external electric field. Hence, they show a more enhanced and nonlinear polarization. **Ferroelectric** materials in addition to being nonlinear demonstrate a spontaneous nonzero polarization even when the applied field

is zero. **Ferroelectricity** is a property of certain materials to have spontaneous electric polarization. The distinguishing feature of ferroelectrics is that the spontaneous polarization can be reversed by a suitably strong applied electric field in the opposite direction; the polarization is therefore dependent not only on the current electric field but also on its history, yielding a **hysteresis loop**.

Typically, materials demonstrate ferroelectricity only below a certain phase transition temperature, called the Curie temperature, and are paraelectric above this temperature: the spontaneous polarization vanishes, and the ferroelectric crystal transforms into the paraelectric state.

The internal electric dipoles of a ferroelectric material are coupled to the material lattice so anything that changes the lattice will change the spontaneous polarization. The change in the spontaneous polarization results in a change in the surface charge. This can cause current flow even without the presence of an external electric field. Two stimuli that will change the lattice dimensions of a material are force and temperature. The generation of a surface charge in response to the application of an external stress to a material is called **piezoelectricity**. A change in the spontaneous polarization of a material in response to a change in temperature is called **pyroelectricity**.

### *Questions for self-control*

1. What is the electric conductor?
2. Properties of the conductor in electrostatic equilibrium
3. Electric field inside the conductor
4. Electric field at the surface of the charged conductor
5. Electric potential on the surface of the charged conductor
6. Electric potential inside the conductor
7. Electric potential due to a conducting sphere
8. Cavity within a conductor
9. What is a dielectric material?
10. The polar and non-polar molecules
11. Polarization of dielectrics
12. Polarization density

13. Electric susceptibility and relative permittivity of the medium
14. What is a bound charge?
15. Surface charge density of the bound charge
16. Gauss's law for the polarization density field
17. Boundary conditions for polarization density at dielectric interfaces
18. What is the electric displacement field?
19. Gauss's law for the electric displacement field
20. Boundary conditions at dielectric interfaces for the vector  $\vec{D}$
21. Boundary conditions at dielectric interfaces for the vector  $\vec{E}$
22. Ferroelectrics
23. Piezoelectric and pyroelectric effects

## Topic 3.3. Capacitance

### *Lecture 21*

**Capacitance** is the ability of a conducting body to store the electric charge. Any object that can be electrically charged exhibits self capacitance. The charge on the conductor is proportional to its electric potential with the constant coefficient of proportionality. So, the capacitance of a conductor is the ratio of the magnitude of the charge on the conductor to the magnitude of the potential produced by it:

$$C = \frac{q}{\phi}. \quad (3.66)$$

Mutual capacitance is the capacitance between two adjacent conductors. If two conductors carry charges of equal magnitude and opposite sign, then the capacitance is defined as the ratio of the magnitude of the charge on either conductor to the magnitude of the potential difference existing between them:

$$C = \frac{q}{U}. \quad (3.67)$$

The capacitance is a function only of the geometry of the design and the permittivity of the dielectric material between the conductors.

**Capacitor** is a combination of two parallel electrical conductors (plates) separated by a dielectric by a distance much smaller than the size of the plates.

#### *3.3.1 Parallel-plate capacitor*

A **parallel-plate capacitor** is a combination of two parallel, metallic plates of equal area  $S$  separated by a distance  $d$  (Figure 3.33). One plate carries a charge  $+q$ , and the other carries a charge  $-q$ . The surface charge density on each plate is  $\sigma = q/S$ . If the plates are very close together (in comparison with their length and width), we can assume the electric field is uniform between the plates and zero elsewhere. Then, the value of the electric field between the plates is  $E = \frac{\sigma}{\epsilon_0} = \frac{q}{\epsilon_0 S}$ . Because the field between

the plates is uniform, the magnitude of the potential difference between the plates equals  $Ed$ ; therefore,  $U = Ed = \frac{qd}{\epsilon_0 S}$ . Now we can find that the capacitance

$$C = \frac{q}{U} = \frac{q\epsilon_0 S}{qd} = \frac{\epsilon_0 S}{d}.$$

**Capacitance of parallel plates:**

$$C = \frac{\epsilon_0 S}{d}. \quad (3.68)$$

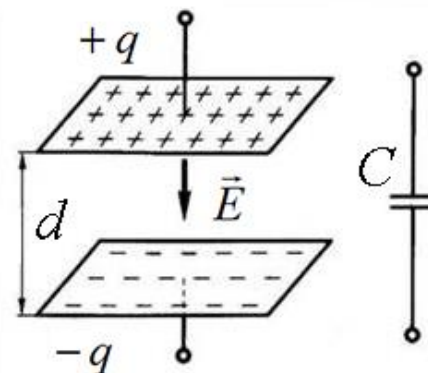


Figure 3.33.

**3.3.2 Cylindrical capacitor**

Cylindrical capacitor is a combination of two coaxial cylindrical conductors, a solid cylindrical conductor of radius  $a$  and charge  $q$  and a cylindrical shell of negligible thickness, radius  $b$ ,  $b > a$ , and charge  $-q$  (Figure 3.34). Assuming that length of the conductors is much greater than  $a$  and  $b$ , we can neglect end effects. In this case, the electric field is perpendicular to the long axis of the cylinders and is confined to the region between them and is given by the formula for the

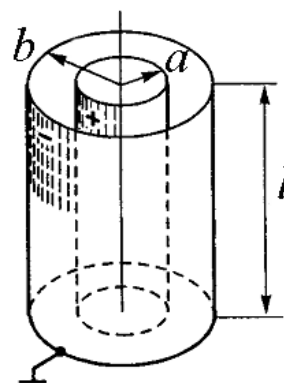


Figure 3.34.

cylindrically symmetric charge distribution  $E = 2k \frac{\lambda}{r}$ .

Then the potential difference between the cylinders

$$\Delta\varphi = -\int_a^b \vec{E}d\vec{l} = -\int_a^b E_r dr = -\int_a^b 2k \frac{\lambda}{r} dr = -2k\lambda \ln \frac{b}{a}, \quad \text{where } k = \frac{1}{4\pi\epsilon_0}.$$

Substitute the absolute value of  $\Delta\varphi$  into the expression for the capacitance and considering  $\lambda = q/l$ , we obtain

$$C = \frac{l}{2k \ln(b/a)}. \quad (3.69)$$

An example of this type of geometric arrangement is a coaxial cable, which consists of two concentric cylindrical conductors separated by an insulator.

### 3.3.3 Spherical capacitor

A spherical capacitor is a combination of two concentric spherical conductors, a spherical conducting shell of radius  $b$  and charge  $-q$  concentric with a smaller conducting sphere of radius  $a$  and charge  $q$  (Figure 3.35). As we know, the direction of the electric field outside a spherically symmetric charge distribution is radial and its

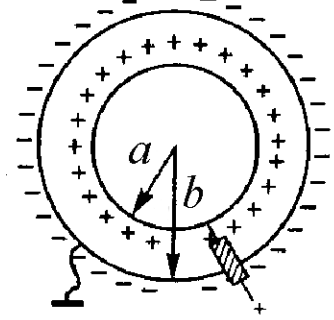


Figure 3.35.

magnitude is given by the expression  $E = k \frac{q}{r^2}$  for the

field between the spheres ( $a < r < b$ ). The potential difference between the two

conductors is  $\Delta\phi = -\int_a^b E_r dr = -\int_a^b k \frac{q}{r^2} dr = kq \left( \frac{1}{b} - \frac{1}{a} \right) = kq \frac{a-b}{ab}$ . Substitute the absolute

value of  $\Delta\phi$  into the expression for the capacitance, we obtain

$$C = \frac{ab}{k(b-a)}. \quad (3.70)$$

#### 3.3.3.1 Capacitance of an isolated charged sphere

Imagine a spherical, charged conductor. The electric field lines around this conductor are exactly the same as if there were a conducting, spherical shell of infinite radius, concentric with the sphere and carrying a charge of the same magnitude but opposite sign. Therefore, we can identify the imaginary shell as the second conductor of a two-conductor capacitor. The radius of the infinitely large imaginary shell  $b \rightarrow \infty$ .

Then,

$$C = \frac{1}{k \left( \frac{1}{a} - \frac{1}{b} \right)} = \frac{1}{k \left( \frac{1}{a} - 0 \right)} = \frac{a}{k} = 4\pi\epsilon_0 a. \quad (3.71)$$

### 3.3.4 Capacitors with dielectrics

If a dielectric is inserted between the plates of the capacitor (Figure 3.36), the electric field and, hence, voltage between the plates decreases by a factor  $\epsilon_r$ :  $\Delta\phi = \frac{\Delta\phi_0}{\epsilon_r}$ , where  $\epsilon_r$  is the dielectric constant of the material. Because the charge on the capacitor does not change, the capacitance must change to the value

$$C = \epsilon_r C_0. \quad (3.72)$$

The capacitance increases by the factor  $\epsilon_r$  when the dielectric completely fills the region between the plates. For example, the capacitance of a parallel-plate capacitor filled with a dielectric is

$$C = \frac{\epsilon_0 \epsilon_r S}{d}. \quad (3.73)$$

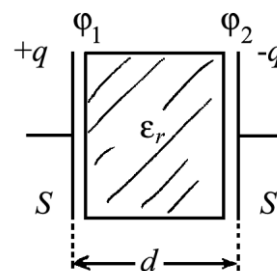


Figure 3.36.

### 3.3.5 Combinations of capacitors

Two or more capacitors often are combined in electric circuits and it is required to calculate the equivalent capacitance of certain combinations. In studying electric circuits, we use a simplified pictorial representation called a circuit diagram. The circuit symbols for capacitor is shown at the Figure 3.33.

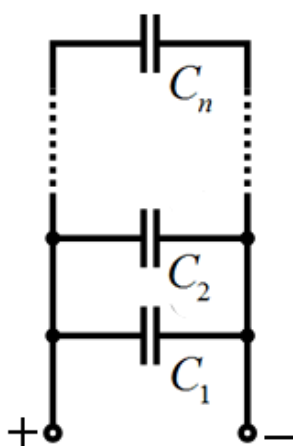


Figure 3.37.

A **parallel combination** of capacitors is shown in Figure 3.37. The left plates of the capacitors are connected to the positive terminal of the battery by a conducting wire and are therefore all at the same electric potential as the positive terminal. Likewise, the right plates are connected to the negative terminal and so are all at the same potential as the negative terminal. Therefore, the individual potential differences across capacitors connected in parallel are the same and are equal to the potential difference applied across the combination. That is,

$$U = U_1 = U_2 = \dots = U_n, \text{ where } U \text{ is the battery terminal voltage.}$$



After the battery is attached to the circuit, the capacitors quickly reach their maximum charge. The total charge stored by the combination of capacitors is the sum of the charges on the individual capacitors:  $q_{total} = q_1 + q_2 + \dots + q_n$ .

Suppose you wish to replace these capacitors by one equivalent capacitor having exactly the same effect on the circuit as the effect of the combination of the individual capacitors. That is, the equivalent capacitor of capacitance  $C$  must store charge  $q_{total} = CU$  when connected to the battery.

But,  $q_{total} = q_1 + q_2 + \dots + q_n = C_1U_1 + C_2U_2 + \dots + C_nU_n = U(C_1 + C_2 + \dots + C_n)$ , and the equivalent **capacitance for capacitors in parallel**:

$$C = C_1 + C_2 + \dots + C_n. \quad (3.74)$$

Therefore, the equivalent capacitance of a parallel combination of capacitors is (1) the algebraic sum of the individual capacitances and (2) greater than any of the individual capacitances. Statement (2) makes sense because we are essentially combining the areas of all the capacitor plates when they are connected with conducting wire, and capacitance of parallel plates is proportional to area.

A **series combination** of capacitors is shown in Figure 3.38.

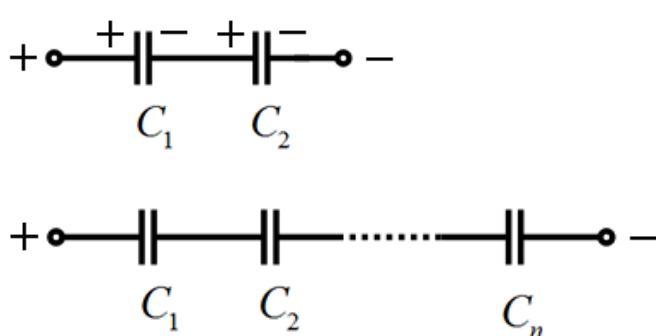


Figure 3.38.

Consider two capacitors connected in series. The left plate of capacitor 1 and the right plate of capacitor 2 are connected to the terminals of a battery. The other two plates are connected to each other and to nothing else; hence,

they form an isolated system that is initially uncharged and must continue to have zero net charge.

When the battery is connected, electrons are transferred out of the left plate of capacitor 1 and into the right plate of capacitor 2. As this negative charge accumulates on the right plate of  $C_2$ , an equivalent amount of negative charge is forced off the left

plate of  $C_2$ , and this left plate therefore has an excess positive charge (see Figure 3.38, upper panel). The negative charge leaving the left plate of  $C_2$  causes negative charges to accumulate on the right plate of  $C_1$ . As a result, both right plates end up with a charge  $+q$  and both left plates end up with a charge  $-q$ . Therefore, the charges on capacitors connected in series are the same. In general,  $q = q_1 = q_2 = \dots = q_n$ . The total voltage across the combination is split between the two capacitors. In general,  $U_{total} = U_1 + U_2 + \dots + U_n$ . Then for the equivalent capacitor of capacitance  $C$ ,

$$U_{total} = \frac{q}{C} = \frac{q}{C_1} + \frac{q}{C_2} + \dots + \frac{q}{C_n} = q \left( \frac{1}{C_1} + \frac{1}{C_2} + \dots + \frac{1}{C_n} \right).$$

So, equivalent **capacitance for capacitors in series**:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} + \dots + \frac{1}{C_n}. \quad (3.75)$$

This expression shows that (1) the inverse of the equivalent capacitance is the algebraic sum of the inverses of the individual capacitances and (2) the equivalent capacitance of a series combination is always less than any individual capacitance in the combination.

### ***Questions for self-control***

1. Capacitance of the conductor
2. What is the capacitor?
3. Capacitance of the parallel-plate capacitor
4. Capacitance of the cylindrical capacitor
5. Capacitance of the spherical capacitor
6. Capacitors with dielectrics
7. Parallel combination of capacitors
8. Series combination of capacitors

## Topic 3.4. Energy in the electrostatic field

### Lecture 22

#### 3.4.1 Energy of a system of point charges

Consider the potential energy of a system of two charged particles. If  $\varphi_2$  is the electric potential at a point  $P$  due to charge  $q_2$ , the work an external agent must do to bring a second charge  $q_1$  from infinity to  $P$  without acceleration is  $q_1\varphi_2$ . This work represents a transfer of energy into the system, and the energy appears in the system as potential energy  $W$  when the particles are separated by a distance  $r_{12}$ . As we know, the electric potential due to the point charge  $q$  at a distance  $r$  away from it is  $\varphi = k \frac{q}{r}$ .

Therefore, the **potential energy of the system of two point charges** can be expressed as

$$W = k \frac{q_1 q_2}{r_{12}}. \quad (3.76)$$

If the charges are of the same sign, then  $W$  is positive. Positive work must be done by an external agent on the system to bring the two charges near each other (because charges of the same sign repel). If the charges are of opposite sign, then  $W$  is negative. Negative work is done by an external agent against the attractive force between the charges of opposite sign as they are brought near each other; a force must be applied opposite the displacement to prevent  $q_1$  from accelerating toward  $q_2$ .

As far as charges  $q_1$  and  $q_2$  are symmetrical, the potential energy of the system can be written as

$$W = \frac{1}{2} \left( k \frac{q_2}{r_{12}} q_1 + k \frac{q_1}{r_{12}} q_2 \right) = \frac{1}{2} (q_1 \varphi_1 + q_2 \varphi_2) = \frac{1}{2} \sum_{i=1}^2 q_i \varphi_i, \quad (3.77)$$

where  $\varphi_1$  is the electric potential due to charge  $q_2$  at the point where the charge  $q_1$  is located, while  $\varphi_2$  is the electric potential due to charge  $q_1$  at the point where the charge  $q_2$  is located.

Now consider one point charge  $q$  in the presence of  $n$  point charges  $q_i$ . We must find the total electric potential due to a group of source charges at the point where the charge  $q$  is located:  $\varphi = \sum_{i=1}^n \varphi_i = \sum_{i=1}^n k \frac{q_i}{r_i}$ , where  $r_i$  is the distance between the point charges  $q$  and  $q_i$ . Then, the electrostatic potential energy of one point charge  $q$  in the presence of  $n$  point charges is:

$$W = q \sum_{i=1}^n k \frac{q_i}{r_i}. \quad (3.78)$$

The **total electrostatic potential energy stored in a system of  $n$  charges**  $q_1, q_2, \dots, q_n$  at positions  $r_1, r_2, \dots, r_n$  respectively, is equal to the algebraic sum of potential energies calculated for every individual pair of charges:

$$W = \frac{1}{2} \sum_{i=1}^n q_i \varphi_i = \frac{1}{2} \sum_{i,j=1}^n k \frac{q_i q_j}{r_{ij}}, \quad (i \neq j) \quad (3.79)$$

where, for each  $i$  value,  $\varphi_i$  is the electrostatic potential due to all  $(n - 1)$  point charges except the  $q_i$  at the point where the charge  $q_i$  is located.

For example, the total potential energy of the system of three charges:

$$W = W_1 + W_2 + W_3 = k \frac{q_1 q_2}{r_{12}} + k \frac{q_1 q_3}{r_{13}} + k \frac{q_2 q_3}{r_{23}},$$

where  $r_{12}$ ,  $r_{13}$ ,  $r_{23}$  are distances between the corresponding charges.

The **electrostatic potential energy stored in a system with continuous charge distribution** of volumetric charge density  $\rho$  and surface charge density  $\sigma$  is

$$W = \frac{1}{2} \left( \int_V \rho \varphi dV + \int_S \sigma \varphi dS \right). \quad (3.80)$$

**Work by the electric field** due to changing positions of charges

$$A = W_1 - W_2, \quad (3.81)$$

where  $W_1$ ,  $W_2$  are the potential energies for initial and final configurations of the charges.

### 3.4.2 Energy stored in a charged capacitor

Because positive and negative charges are separated in the system of two conductors in a capacitor, electric potential energy is stored in the system.

To calculate the energy stored in the capacitor, consider a charge-transfer process. Imagine the plates are disconnected from the battery and the charge is transferred through the space between the plates by the electric force. Therefore, the work on the charge is done by the electric force as the charge is transferred from one plate to the other.

At first, no work is required to transfer a small amount of charge  $dq$  from one plate to the other, but once this charge has been transferred, a small potential difference exists between the plates. Therefore, work must be done to move additional charge through this potential difference. As more and more charge is transferred from one plate to the other, the potential difference increases in proportion and more work is required.

Suppose  $q$  is the charge on the capacitor at some instant during the charging process, then the potential difference is  $\Delta\phi = \frac{q}{C}$ . The work necessary to transfer an increment of charge  $dq$  through the potential difference is  $dA = \Delta\phi dq = \frac{q dq}{C}$ . The total work required to charge the capacitor from  $q = 0$  to some final charge  $q = Q$  is  $A = \int_0^Q \frac{q dq}{C} = \frac{Q^2}{2C}$ . The work done in charging the capacitor equals to the electric potential energy  $W$  stored in the capacitor:

$$W = \frac{q^2}{2C} = \frac{CU^2}{2} = \frac{qU}{2}. \quad (3.82)$$

For a parallel-plate capacitor, the potential difference is related to the electric field through the relationship  $U = Ed$ . Furthermore, its capacitance is  $C = \frac{\epsilon_0 \epsilon_r S}{d}$ . So,

$W = \frac{1}{2} \frac{\epsilon_0 \epsilon_r S}{d} E^2 d^2 = \frac{1}{2} \epsilon_0 \epsilon_r S d E^2$ . Because the volume occupied by the electric field is

$V = Sd$ , the energy per unit volume  $w = W/Sd$ , known as the **energy density stored in electric field**, is:

$$w = \frac{W}{V} = \frac{\epsilon_r \epsilon_0 E^2}{2} = \frac{\vec{E}\vec{D}}{2}, \quad (3.83)$$

where the displacement field  $\vec{D} = \epsilon_r \epsilon_0 \vec{E}$ .

Although this equation was derived for a parallel-plate capacitor, the expression is generally valid regardless of the source of the electric field. That is, the energy density in any electric field is proportional to the square of the magnitude of the electric field at a given point.

### *Questions for self-control*

1. Potential energy of a system of two point charges
2. Potential energy of one point charge in the presence of  $n$  point charges
3. Total electrostatic potential energy stored in a system of  $n$  charges
4. Potential energy stored in a system with continuous charge distribution
5. Work by the electric field
6. Energy stored in a charged capacitor
7. Energy density
8. Energy density stored in electric field

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