

– 4 –

Dielectric Properties of Substances

Electric and magnetic interactions play an enormous role in chemistry and chemical technology; they govern the processes taking place in atoms and molecules, crystals, electrolysis, surfaces of solids electrolyzing of dielectric polymer materials and others. Because the electric field in molecular systems has a very complex structure, for the convenience of the reader, we will give the nomenclature of electric fields at the beginning of the chapter.

Let us start by briefly presenting the main information on electric charges and the characteristics of the fields they create.

4.1 ELECTROSTATIC FIELD

4.1.1 General laws of electrostatics

The main electric charge carriers are charged particles—electrons and protons. They carry a charge $|e| = 1.6 \cdot 10^{-19}$ C, electrons being negative and protons positive. In neutral atoms and molecules, negative electron charge is compensated for by a positive nuclear charge. By removing one or more electrons from an atom, one can make a positive (mono- or multicharged) ion and, conversely, by adding electrons, it is possible to create a negative ion from an originally neutral particle. In such a way, positive and negative carriers of charge are created (in an electrolyte, for instance).

When an excess or lack of electrons is created in a body, the body becomes charged, carrying a charge Q . The value Q is always proportional to $\pm|e|$. However, at large Q (in comparison with $|e|$), this discontinuity is not exhibited, so it is possible to consider the charge changing continuously.

The distribution of charge in a body can be described by the function $\rho(\mathbf{r})$ such that $\rho(\mathbf{r})dV = dq$, where dq is the charge, comprised in the volume dV . Function $\rho(\mathbf{r})$ is called the volume charge density. Charge distribution on a surface is described by surface charge density $\sigma(\mathbf{r})dS = dq$. Charge distribution along a line gives a linear charge density $\tau(l)$ so that $dq = \tau(l)dl$. (In the first two cases, \mathbf{r} is a radius vector of the elements dV and dS , and l is a coordinate of a point measured along the charged line.)

Electric charge is invariant with respect to Galileo transformations.

If an electric system is closed, its total algebraic charged is preserved.

The force of interaction of two point charges q and Q in a vacuum is defined by the Coulomb's law:

$$\mathbf{F} = \frac{1}{4\pi\epsilon_0} \frac{Qq}{r^2} \frac{\mathbf{r}}{r}, \quad (4.1.1)$$

where \mathbf{r} is the radius vector, drawn from one charge to another ($|\mathbf{r}|$ is the distance between charges) and ϵ_0 is the electric constant. Factor $1/4\pi\epsilon_0$ is included in the Coulomb's law in order to correspond to the International System: then q is measured in coulomb, r in meter and F in newton; Maxwell equations (Chapter 5.4) also appear very rational in this case.

Coulomb's law has much in common with Newton's law of gravity: in both laws, the same functional dependence on the distance ($1/r^2$) is present. There is a profound physical meaning in this fact which we will consider below. There exists however an essential difference: attraction between dissimilar charges and repulsion between similar charges are automatically taken into account in the Coulomb's law (i.e., Q and q are taken with their signs); however, in Newton's law, the negative sign of force always corresponds to the masses' attraction.

Comparing these two laws, we notice that Coulomb interaction is billions of times greater than Newton's law. If we calculate, for instance, the gravitational attraction of electrons and protons with their electric interaction, we would arrive at the enormous value of an order 10^{40} times. Therefore, in atomic systems gravitational interaction is not taken into consideration.

Note that eq. (4.1.1) is applicable only to the interaction of point charges; an exception is the interaction of two spherically symmetric balls uniformly charged over their volumes and/or surfaces (see below).

Eq. (4.1.1) cannot be applied directly to the calculation of interaction of nonregularly charged bodies. In this case the extensive charges have to be subdivided into elementary volumes dV ; knowing $\rho(r)$, find dq , then find the Coulomb interaction dF between elementary charges and then integrate these elementary forces over the volumes of both charges. The exception is the case when charges are spread over symmetrical bodies; then it is useful to apply mathematical methods to this problem, e.g., the Gauss theorem (refer to Section 4.1.3).

4.1.2 Strength of an electrostatic field

An electrostatic field is created by motionless (in the given system of coordinates) *charges*. If a charge q is located at any point near another charge Q , the Coulomb force (eq. (4.1.1)) is acting, and it can be accepted that charge Q creates an electrostatic field (see eq. (1.4.4)), in which a charge q is situated. If Q is a spherically symmetric body, the field also possesses spherical symmetry, i.e., is central (Figure 1.23).

It is convenient to describe a field by the force characteristic —strength of an electrostatic field \mathbf{E} . At a point A, the vector magnitude \mathbf{E} is numerically equal to force, acting on the positive dimensionless (point) unit charge.

$$\mathbf{E} = \frac{\mathbf{F}}{q} = \frac{1}{4\pi\epsilon_0} \frac{Q}{r^2} \frac{\mathbf{r}}{r}, \quad (4.1.2)$$

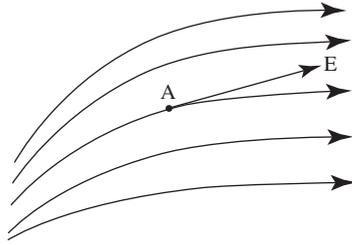


Figure 4.1 Force lines of a nonuniform electrostatic field and orientation of an electric field strength vector at a point A.

The force $\mathbf{F}(\mathbf{r})$ can be substituted by the strength $\mathbf{E}(\mathbf{r})$:

$$\mathbf{F}(\mathbf{r}) = q\mathbf{E}(\mathbf{r}), \quad (4.1.3)$$

with which the field acts on the point charge q .

The electrostatic field can be described by the so-called force lines (Figure 4.1): at a given point A the force is directed along the tangent to a line and the vector magnitude $|\mathbf{F}|$ being numerically equal to force, acting on the unit positive point charge placed in this point of space.

If q is equal to unity, \mathbf{E} is equal to \mathbf{F} . This permits us to investigate a field configuration by placing a probe point unit charge q at different points of the field and, measuring vector force \mathbf{F} , to find the distribution of \mathbf{E} . Consequently, the electrostatic field can be depicted by the force lines. Taking into account the general law, these lines are drawn in such a way that the tangent to them at any point gives the direction of vector \mathbf{E} at that point, and the density of lines per cross-sectional area gives the magnitude of \mathbf{E} . Looking at a picture of force lines, it is easy to judge the configuration of a particular field, the direction and the magnitude of vector \mathbf{E} at every point of space, gradient \mathbf{E} , etc. In Figures 4.2a and b, the central fields of positive and negative charges are depicted, and in Figure 4.2c, a uniform field (the plain capacitor with plates of infinite extent) is represented.

Electrostatic fields obey the general physical principle of superposition (first given in Section 2.9.1): if the electrostatic field is created by several charges, the field of every charge is created irrespective of the presence of other charges. The mathematical expression for this case is reduced to the total field \mathbf{E} as the geometric sum of strength of fields created by every point charge

$$\mathbf{E} = \sum_{i=1}^N \mathbf{E}_i, \quad (4.1.4)$$

where N is the total number of charges.

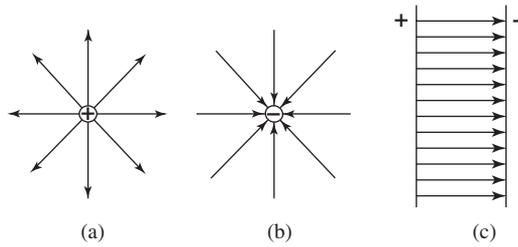


Figure 4.2 A central field of the point charges (a and b) and a uniform field of a plane condenser (c).

The field created by an extended body can be obtained by integration over the whole volume of a body V :

$$\mathbf{E} = \int_V d\mathbf{E}.$$

The integral from vector quantity can be calculated, having expanded the vector onto components along the unit orts vectors

$$\mathbf{E} = \mathbf{i} \int dE_x + \mathbf{j} \int dE_y + \mathbf{k} \int dE_z. \quad (4.1.5)$$

It is very important that the vector \mathbf{E} (as a polar vector) has its own axis of symmetry directed along it (vector \mathbf{E} can be rotated around itself at any angle, i.e., it possesses an axis of symmetry of an “infinite” order). This means that, if the charged body creating an electrostatic field has an axis of symmetry, the vector of the field strength \mathbf{E} is directed necessarily along this axis. Hence, when dealing with the problem of calculating the strength of electrostatic field \mathbf{E} it is strongly recommended first to discover the charged body symmetry: if the charged body has a symmetry axis, the overall strength \mathbf{E} must by all means be directed along this axis! There is then no need to derive E_y and E_z : they automatically become equal to zero. From the formula (4.1.5), only one item of sum remains

$$\mathbf{E} = \mathbf{i} \int dE_x. \quad (4.1.6)$$

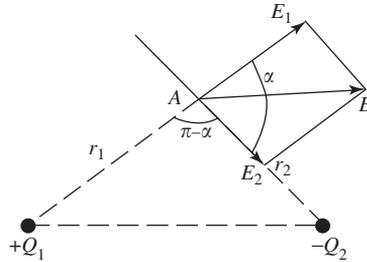
There is no problem calculating the integral from the scalar function.

EXAMPLE E4.1

The electric field is created by two point charges Q_1 and Q_2 . The distance between the charges is d . Determine the strength of electrostatic field E at a point which is removed at a distance r_1 from the first charge and r_2 from the second. The numerical values are $Q_1 = 30 \text{ nC}$, $Q_2 = -10 \text{ nC}$, $r_1 = 15 \text{ cm}$ and $r_2 = 10 \text{ cm}$.

Solution: According to the superposition principle of electric fields, each charge creates a field, irrespective of the presence of other charges. Therefore, the intensity

of a field at a specified point can be found as the vector sum of the fields, created by two charges separately, $\mathbf{E} = \mathbf{E}_1 + \mathbf{E}_2$. The strength of the electrostatic field can be determined by eq. (4.1.2). The vector relations can be seen in Figure E4.1. The



partial field strength created by each charge can be determined according to the Coulomb's law; they are

$$E_1 = \frac{|Q_1|}{4\pi\epsilon_0 r_1^2} \quad \text{and} \quad E_2 = \frac{|Q_2|}{4\pi\epsilon_0 r_2^2}.$$

The sum can be found according to the cosine theorem

$$E = \sqrt{E_1^2 + E_2^2 + 2E_1E_2 \cos \alpha},$$

whereas $\cos \alpha$ can be found from triangle (see figure)

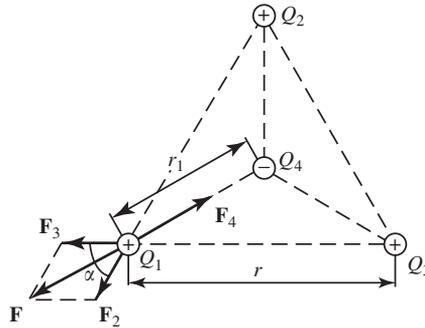
$$\cos \alpha = \frac{d^2 - r_1^2 - r_2^2}{2r_1 r_2} = 0.25.$$

$$E = \frac{1}{4\pi\epsilon_0} \sqrt{\frac{Q_1^2}{r_1^4} + \frac{Q_2^2}{r_2^4} + 2 \frac{|Q_1||Q_2|}{r_1^2 r_2^2} \cos \alpha}.$$

Substituting all data and executing calculations, we arrive at $E = 1.67 \times 10^4 = 16.7$ kV/m.

EXAMPLE E4.2

Three identical positive charges $Q_1 = Q_2 = Q_3 = 1$ nCb are located at the vertex of a flat equilateral triangle. What negative charge should be placed in the center of the triangle that would counterbalance the forces of mutual repulsion of the positive charges in the vertexes (Figure E4.2)?



Solution: All three charges located in the vertices of a triangle are in identical states. Therefore, for the solution of the problem, it is enough to find out what charge is necessary to place in the center of the triangle so that one of the charges, for example, Q_1 , would be in equilibrium. According to the principle of superposition each charge is exhibited irrespective of the presence of the others. Therefore, the charges will be in equilibrium if the vector sum of forces acting on them is equal to zero, $\mathbf{F}_2 + \mathbf{F}_3 + \mathbf{F}_4 = 0 = \mathbf{F} + \mathbf{F}_4$ where \mathbf{F}_2 , \mathbf{F}_3 and \mathbf{F}_4 being the forces with which charges Q_2 , Q_3 and Q_4 act on charge Q_1 ; \mathbf{F} is the resultant of forces \mathbf{F}_2 and \mathbf{F}_3 . Since forces \mathbf{F} and \mathbf{F}_4 are codirectional they can be substituted by scalar sum $F - F_4 = 0$ or $F_4 = F$. The force F can be presented as a sum $\mathbf{F}_2 + \mathbf{F}_3$, and as $F_2 = F_3$ we can write $F_4 = F_2\sqrt{2(1+\cos\alpha)}$ *. Applying Coulomb's law and taking into account that $Q_2 = Q_3 = Q_4$, one can find $Q_1Q_4/4\pi\epsilon_0r_1^2 = Q_1^2/4\pi\epsilon_0r^2\sqrt{2(1+\cos\alpha)}$, wherefrom

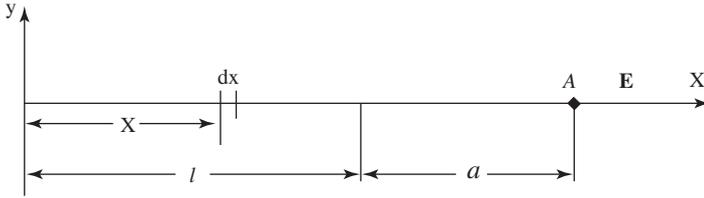
$$Q_4 = \frac{Q_1r_1^2}{r^2}\sqrt{2(1+\cos\alpha)}^*.$$

From geometrical considerations, we can obtain $r_1 = r/(2\cos 30^\circ) = r/\sqrt{3}$. Since $\cos\alpha = \cos 60^\circ = 0.5$, the formula * takes the form $Q_4 = Q_1/\sqrt{3}$. Taking into account that Q_1 is 1.0 nCb, the charge Q_4 is -0.58 nCb. Note that such electrostatic equilibrium is unstable.

EXAMPLE E4.3

The field is created by a uniformly charged thin rod of length l with a linear charge density τ . Define the strength of an electrostatic field at a point A lying on the line of the charged rod at a distance d from its end. Numerical values are: $\tau = 1.2 \mu\text{C}/\text{m}$, $l = 10$ cm and $d = 5$ cm.

Solution: Let us draw an x -axis along the rod, and let the origin be placed at the beginning of the rod (Figure E4.3). Because the problem has an element of symmetry (an axis of infinite order collinear to the direction of the rod), the vector of the field strength must certainly lie on this axis.



Since the electrostatic field is created by a continuous body (rod), it is not possible to apply Coulomb’s law directly to the solution. Therefore, we have to allocate an elementary charged segment on the rod, to calculate intensity created by it and to integrate this with the length of the whole rod. The element of the rod dx carries charge τdx . The elementary field strength is calculated using eq. (4.1.2)

$$dE = \frac{1}{4\pi\epsilon_0} \frac{\tau dx}{(\ell + a - x)^2}$$

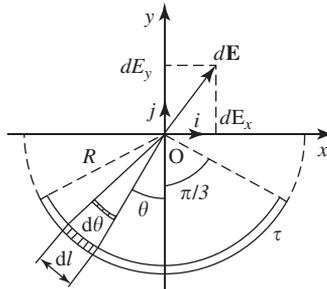
Integration gives

$$E = \frac{\tau}{4\pi\epsilon_0} \int_0^\ell \frac{dx}{(\ell + a - x)^2} = \frac{\tau}{4\pi\epsilon_0} \frac{1}{(\ell + a - x)} \Big|_0^\ell = \frac{\tau}{4\pi\epsilon_0} \left(\frac{\ell}{a(a + \ell)} \right)$$

It is easy to prove that the dimension corresponds to the field strength dimension. There are other ways to choose the origin, though all choices will give the same result.

EXAMPLE E4.4

One-third of the circle’s circumference of radius $R = 20$ cm made of a dielectric material is charged uniformly with linear charge density $\tau = 1 \times 10^{-6}$ C/m. Determine the strength of electrostatic field \mathbf{E} created by this piece of charged arc in its center—point O (Figure E4.4).



Solution: It is impossible to apply Coulomb's law directly to the whole part of the ring because it is extensive (not a point). We must divide an arc body into pieces and apply the law mentioned to each elementary piece. Notice that the whole problem has an axis of symmetry of the second order passing through the middle of the arc and the arc center O. This means that the resulting electric strength vector is directed along this axis (why?). Therefore, we direct an axis y along an axis of symmetry. Axis x is of no significance; let it be perpendicular to the y -axis. We allocate an elementary piece dl , bearing charge dq , $dq = \tau dl$. This charge creates an elementary field strength $d\mathbf{E}$ at the point O. This vector should be projected onto the y -axis in order to be able to make further integration over the whole charged arc. The projection dE_y on y -axis is .

$$dE_y = \tau dl \cos\theta / 4\pi\epsilon_0 R^2 = \tau d\theta \cos\theta / 4\pi\epsilon_0 R$$

The component dE_x can be ignored, because we definitely know that after integration the x -component should give zero ("why?" check up by integration). We have to express two variables l and θ through one, let it be θ : $d\theta = dl/R$. Hence

$$E = \int_{-\pi/3}^{\pi/3} dE_y = 2 \int_0^{\pi/3} dE_y = \frac{2\tau}{4\pi\epsilon_0 R} \int_0^{\pi/3} \cos\theta d\theta = \frac{\tau}{2\pi\epsilon_0 R}$$

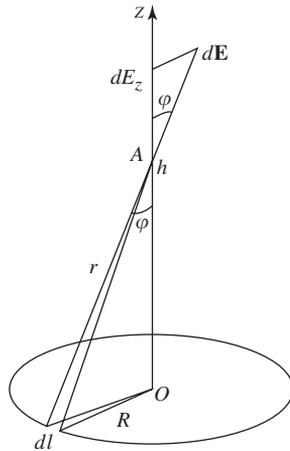
(pay attention to the integration limits, to coefficient 2 and to the way of measuring the θ value). To substitute the given and the physical constants, we arrive at the value $E = \sqrt{3}\tau/2\pi\epsilon_0 R$; executing the calculations we obtain $E = 2.18$ kV/m.

EXAMPLE E4.5

Along a ring of radius $R = 1$ m, a charge $Q = 1 \mu\text{C}$ is uniformly distributed. Find an electric field strength $E(h)$ in points lying on the axis that pass through the center of the circle perpendicular to the plane of the ring.

Solution: As the field strength E is a polar vector, therefore in this problem it must certainly coincide with the coordinate axis z . The linear charge density is $\tau = Q/2\pi R$. Allocate an elementary vector dl at the ring. This segment carries the charge $dq = \tau dl = Qdl/2\pi R$; at point A it creates a field $|d\mathbf{E}| = dq/4\pi\epsilon_0 r^2$, where r is the distance from dl to the point A. Vector $d\mathbf{E}$ is directed along the line joining the element dl with the point A. Since we *a priori* know the general direction of the electric field strength \mathbf{E} (along the axis z), we have to project the $d\mathbf{E}$ vector on the z -axis and integrate projections (since an integral over perpendicular components must be equal to zero). It can be seen from Figure E4.5 that $dE_{\parallel} = |d\mathbf{E}| \cos \varphi$, $\cos \varphi$ being equal to $h/\sqrt{h^2 + R^2}$. Therefore

$$dE = \frac{\tau h}{4\pi\epsilon_0 (h^2 + R^2)^{3/2}} dl.$$



The integration dE over the whole ring gives:

$$E = \frac{Q}{4\pi\epsilon_0} \frac{h}{(h^2 + R^2)^{3/2}}.$$

This general expression permits us to calculate the electric strength in any point of z -axis. In particular, it is very useful to use this example to investigate the extreme conditions. In fact, we know that the field in the center of the ring is zero. This corresponds to the limit $h \rightarrow 0$: indeed at $h = 0$ the relation obtained gives $E = 0$. From the other side, at $h \gg R$, or at $R \rightarrow 0$, $E \sim Q/h^2$ which corresponds to Coulomb's law.

EXAMPLE E4.6

A thin half-ring carries a charge uniformly distributed along the ring with a linear charge density $\tau = 10$ nC/m. Determine the electric potential φ in the center of ring O.

Solution: A ring element dl carries a charge τdl . This charge produces an electric potential equal to $d\varphi = dq/4\pi\epsilon_0 R = \tau dl/4\pi\epsilon_0 R$ in the point O. After integration of the scalar values over the whole half-ring ($-\pi/2 < \varphi < +\pi/2$), we arrive at $\varphi = \tau/4\epsilon_0 = 282$ V. Note that potential calculation is less troublesome than the field strength!

4.1.3 The Gauss law

A vector flux through an area and vector circulation along a closed contour is the basic characteristic of a vector field in vector algebra. The application of these concepts to an electrostatic field appears extremely fruitful.

We apply this concept, which we first met in Section 2.8.3, to a flux and density of flux. Accordingly, the elementary flux $d\Phi$ of the electrostatic field strength \mathbf{E} through an elementary area $d\mathbf{S}$ is

$$d\Phi = \mathbf{E} \cdot d\mathbf{S} \quad (4.1.7)$$

(see eq. (2.8.18)).

Having written down an expression of scalar product and then attributing $\cos \alpha$ first to \mathbf{E} and then to $d\mathbf{S}$, we obtain:

$$d\Phi = |\mathbf{E}| |d\mathbf{S}| \cos \alpha = E_n dS = E dS_n, \quad (4.1.8)$$

where E_n is the projection of the vector \mathbf{E} onto a normal \mathbf{n} to the elementary area dS , and dS_n is the projection of $d\mathbf{S}$ on a plane, perpendicular to \mathbf{E} (refer to Figure 2.24). It can be seen that the flux $d\Phi$ is subject to change not only due to \mathbf{E} magnitude, but also due to the mutual position of vectors \mathbf{E} and $d\mathbf{S}$ (due to the change of $\cos \alpha$) from $E dS$ up to $-E dS$, i.e., positive and negative.

If the field is produced by a point charge, the flux $d\Phi$ of the field strength is proportional to a solid angle $d\Omega$. The part of space confined by a conical surface (Figure 4.3) is referred to as a *solid angle*. A measure of a flat angle $d\varphi$ is the ratio of the length of an arc dl of a circle, drawn by an arbitrary radius r about a point O, to the value of the radius mentioned, i.e.,

$$d\varphi = \frac{dl}{r}; \quad (4.1.9)$$

accordingly a measure of a solid angle $d\Omega$ is the ratio of an elementary area of a spherical surface dS , drawn by any radius r around a point O, to the square of the radius r^2 mentioned (Figure 4.3):

$$d\Omega = \frac{dS}{r^2} = \frac{dS_n}{r^2}. \quad (4.1.10)$$

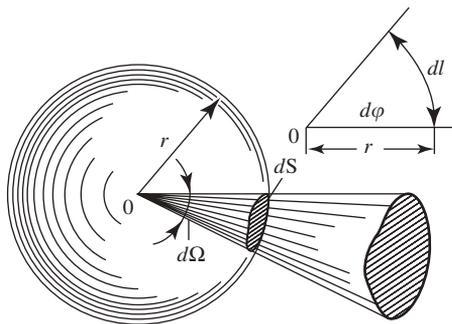


Figure 4.3 A measure of a solid angle.

(Replacement of dS by dS_n is permissible because the area dS is always perpendicular to the radius.) When dS_n is numerically equal to r^2 , the solid angle is equal to 1 sr (steradian).

Similar to the way in which the total flat angle is equal to $\int_0^{2\pi} dl/r = 2\pi r/r = 2\pi$ rad, the total solid angle is equal to

$$\oint \frac{dS_n}{r^2} = \frac{4\pi r^2}{r^2} = 4\pi \text{ sr.} \quad (4.1.11)$$

Gauss law asserts that: *the flux of an electrostatic field strength vector through any closed surface S is equal to the algebraic sum of the charges confined by surface S divided by ϵ_0 .* We shall call this virtual (imaginary) surface the Gauss surface. Note that we ourselves choose the form and size of a Gauss surface!

Let us prove the theorem taking a single point charge Q as an example. We place it in a point O and cover this charge by a closed spherical Gauss surface S with the center in the charge Q position (Figure 4.3). Let us find the value of the elementary flux $d\Phi$ of the vector \mathbf{E} through the elementary surface dS : $d\Phi = E dS_n$. The magnitude E is defined by expression (4.1.2) and therefore

$$d\Phi = \frac{1}{4\pi\epsilon_0} \frac{Q}{r^2} dS_n = \frac{1}{4\pi\epsilon_0} \frac{Q}{r^2} r^2 d\Omega \quad (4.1.12)$$

(we used here the expression (4.1.10)). After integrating over the total solid angle, we arrive at

$$\Phi = \oint_S E_n dS = \oint_S \frac{1}{4\pi\epsilon_0} Q d\Omega = \frac{Q}{4\pi\epsilon_0} \oint_S d\Omega = \frac{1}{\epsilon_0} Q,$$

or, keeping in mind expressions (4.1.7) and (4.1.8),

$$\oint_S \mathbf{E} d\mathbf{S} = \frac{1}{\epsilon_0} Q. \quad (4.1.13)$$

Let us comment on the expression derived. In this expression the point charge Q is comprised of a Gauss surface S . It was taken in spherical form, but it can also be a irregular shaped surface. On the right-hand side the charge Q can be seen which we encompassed by the Gauss surface (Figure 4.4).

If the charge is outside, the flux through the Gauss surface is equal to zero (Figure 4.5) since part of the flux is negative and the other part is positive (because of various orientations of a normal \mathbf{n} to the surface relative to vector \mathbf{E}). This is the case for all those charges which lie outside the Gauss surface; they can be excluded from consideration.

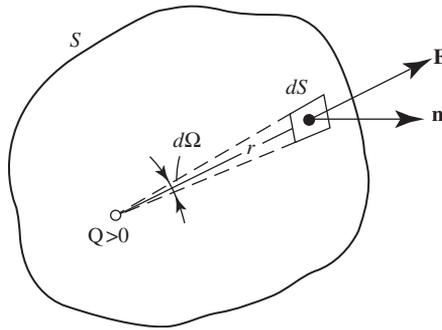


Figure 4.4 The Gauss theorem: Q is a charge, S is a closed Gauss surface, dS is an elementary area and \mathbf{n} is a unit vector to dS .

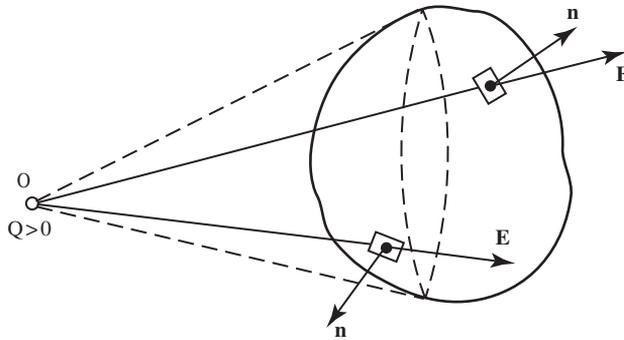


Figure 4.5 The zero total flux of the electric field strength for a particular case when an electric charge is outside the Gauss surface.

Values Q can be determined if distribution of the charge in a given problem is known. If the field is produced by a sum of N individual charges, then according to the superposition principle

$$\oint_s \mathbf{E} dS = \frac{1}{\epsilon_0} \sum_{i=1}^N Q_i. \quad (4.1.14)$$

If the field is set up by a volume charged body, the expression can be modified as follows:

$$\oint_s \mathbf{E} dS = \frac{1}{\epsilon_0} \int_V \rho(\mathbf{r}) dV, \quad (4.1.15)$$

where $\rho(\mathbf{r})$ is a charge density distribution function. If the field is set up by a charged surface with the surface charge density $\sigma(\mathbf{r})$, the Gauss law looks like:

$$\oint_s \mathbf{E} dS = \frac{1}{\epsilon_0} \int_{S'} \sigma(\mathbf{r}) dS. \quad (4.1.16)$$

If the source of field is a charged line, the Gauss law can be given as

$$\oint_s \mathbf{E} d\mathbf{S} = \frac{1}{\epsilon_0} \int_L \tau(l) dl, \quad (4.1.17)$$

where $\tau(l)$ is the linear charge density distribution function and l is the point coordinate along the charged line. The body volume V , charged surface S' and the length L of the charged line correspond to those parts of the charged physical bodies that are encompassed by the Gauss surface. Repeat once more that in Gauss law the total charge laying inside of the Gauss surface is present on the right side which is equal being divided by ϵ_0 to the electrostatic field strength flux on the left side.

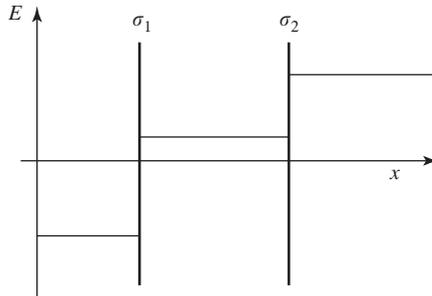
The Gauss law is valid for all forms of charged bodies and any Gauss surface. However, its most fruitful application is in calculating the field when the problem possesses some symmetry. In this case the skilful choice of the Gauss surface form permits one to achieve essential simplification: to provide that $E = E_n = \text{const.}$, to take E out of an integral and to integrate only upon a surface, or, in general, to arrange the field strength being $E_n = 0$ onto a part of a surface. Examples of application of the Gauss law given below will show calculations of fields of the charged physical body possessing some symmetry. These problems could be solved using only the principle of electric fields' superposition. However, this way is troublesome; it demands integration upon a volume. Application of the Gauss law allows many problems to be solved "in a single line".

EXAMPLE E4.7

An electrostatic field is created by two parallel, infinitely large, charged plates with surface charge density σ_1 and σ_2 . Define the electrostatic field strength created by these two plates between and behind them. Numerical values are $\sigma_1 = 0.4 \mu\text{C}/\text{m}^2$ and $\sigma_2 = 0.1 \mu\text{C}/\text{m}^2$.

Solution: According to the principle of superposition of electric fields, each charge creates a field irrespective of the presence of other charges. In this case it concerns the charged planes. Therefore, the intensity of a field in specified areas E can be found as the vector sum of the fields, created by two planes separately: $\mathbf{E} = \mathbf{E}_1 + \mathbf{E}_2$. The absolute values are in this case: $E_1 = \sigma_1/2\epsilon_0$ and $E_2 = \sigma_2/2\epsilon_0$, E_1 being higher than E_2 . The sign of each term depends on two peculiarities: the sign of the plate charge (objective characteristic) and the choice of the axis direction (subjective characteristic). Let us divide the problem into three parts (I, II and III) and choose an x -axis direction, we recommend that it is usually accepted from left to right (Figure E4.7). The superposition principle offers us the choice of the direction and absolute values of particular fields. Therefore, we recommend beginning the solution of the problem with the determination of $E(\text{I})$ and $E(\text{III})$

$$E(\text{I}) = E(\text{III}) = \frac{1}{2} \frac{\sigma(\text{I}) + \sigma(\text{III})}{\epsilon_0}.$$



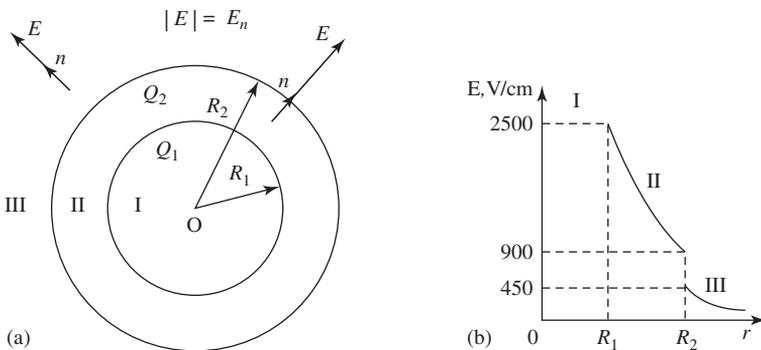
Between the plates the field is directed oppositely from both plates and therefore

$$E(\text{II}) = \frac{1}{2} \frac{|\sigma_1 - \sigma_2|}{\epsilon_0}.$$

The situation presented in this example can rarely be met in practice. Much more popular is the plane condenser, which differs from that given here by the fact that $\sigma_1 = -\sigma_2$; the electric field inside the condenser is $E = \sigma/\epsilon_0$, there is no field outside the condenser to say nothing on the edge effects (see Figure 4.11).

EXAMPLE E4.8

Two concentric spheres of radius $R_1 = 6 \text{ cm}$ and $R_2 = 10 \text{ cm}$, respectively, carry charges $Q_1 = 1 \text{ nC}$ and $Q_2 = -0.5 \text{ nC}$. Find the electric field strength at points $r_1 = 5 \text{ cm}$, $r_2 = 9 \text{ cm}$ and $r_3 = 15 \text{ cm}$ (Figure E4.8). Draw a graph of $E(r)$.



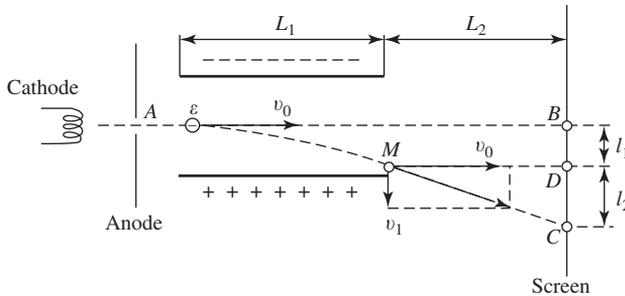
Solution: The three points mentioned are correspondingly disposed just inside the inner sphere (domain I, $r_1 < R_1$), between the two spheres (domain II, $R_1 < r_2 < R_2$) and outside the spheres (domain III). The two spheres really exist carrying a definite charge. Apply the Gauss theorem to solve the problem. First, we have to solve the

situation inside the smallest (internal) sphere. One should choose an imaginary sphere with $r_1 < R_1$ and write down the Gauss theorem for this domain: $\oint E_n dS = 0$. Because E_n on the sphere is constant, $E_n = |E| = E$, then $E \oint dS = E4\pi r^2 = 0$; since r^2 is not zero it means that $E_1 \equiv 0^*$.

In domain II, $R_1 < r_2 < R_2$, the Gauss surface should be chosen having $R_1 < R < R_2$. In this case the whole first real sphere occurred inside the Gauss surface. Therefore, $\oint E_n dS = Q_1/\epsilon_0$, $E4\pi r^2 = Q_1/\epsilon_0$ and $E = (Q_1/4\pi\epsilon_0)(1/r^2)^{**}$. (Sometimes the sphere charge is given through surface charge density σ and the whole charge of the sphere is $4\pi R^2\sigma$. Note that R is a number, but r is a variable.) In order to find the $E(r)$ function in the domain III, the Gauss surface radius should be larger than R_2 ; it incorporates both spheres. Therefore, $E \oint dS = (Q_1 + Q_2)/4\pi\epsilon_0 r^2$ ***. The values of E 's presented in the graph can be obtained from the marked functions E_2 and E_3 . Three marked equations permit us to draw the graph. Try to find yourself the values presented in Figures E4.8a and b.

EXAMPLE E4.9

An electron with zero initial speed has passed an electrical potential difference between a cathode and an anode $U_0 = 10$ kV and entered a space between horizontal plates of the flat condenser on line AB parallel to plates (Figure E4.9); the condenser is charged up to potential difference $U_1 = 100$ V. A distance d between plates is equal 2 cm. The length L_1 of the condenser plates in direction AB is equal 20 cm. Determine distance BC (BD + DC) between fluorescent screen spots at the distance from the condenser's end to a screen is $L_2 = 1$ m.



Solution: An electron movement inside the condenser consists of the two components: (1) by inertia, along the line AB with the constant speed v_0 acquired earlier by action of accelerating potential difference between anode and cathode U_0 which an electron has passed up to the condenser $\left(\frac{mv_0^2}{2} = eU_0\right)^*$ and (2) a uniform acceleration movement inside the condenser in a vertical direction due to an action of constant electric field. After leaving the condenser at point M, an electron moves uniformly and rectilinearly.

One can see from the figure that the sought distance consists of two values $BC = l_1 + l_2$, one of them l_1 being a distance on which the electron is displaced in a vertical direction during movement through the condenser, the other one l_2 between a point on the screen DC (see figure).

Let's estimate separately l_1 and l_2 . The value l_1 can be found using the formula of travel distance in the uniform acceleration movement $l_1 = at^2/2$ **, where a is the acceleration acquired by the electron under the action of the condenser's constant electric field and t is the time of its action.

According to the Newtonian second law, acceleration is $a = F/m$ (the force F which acts on the electron in condenser, m being its mass). In its turn, $F = eE = eU_1/d$.

The time of the electron flight inside the condenser l_1 we shall find by the formula of a uniform movement $t = L_1/v_0$.

Consequently, substituting values from other expressions into the formula * we can obtain $l_1 = U_1 L_1^2 / (4dU_0)$. We can find the length of a segment l_2 from corresponding triangles MDC and then build on vectors v_0 , v_1 and v assuming that the deviation from AB-direction is small, $l_2 = (v_1 L_2 / v_0)$ **, where v_1 is the electron speed in a vertical direction at point M; and L_2 is a distance from the condenser end up to the screen. We can find the speed v_1 using the formula $v_1 = at$ which in view of expressions for a , F , and t will become

$$v_1 = \frac{eU_1 L_1}{dmv_0}.$$

Having submitted the expression derived into the formula **, we obtain $l_2 = eU_1 L_1 L_2 / (d m v_0^2)$ or, having replaced v_0 from equation **, we found $l_2 = U_1 L_1 L_2 / 2 d U_0$. For the required distance $BC = l_1 + l_2$, we shall finally arrive at

$$BC = \frac{U_1 L_1^2}{4 d U_0} + \frac{U_1 L_1 L_2}{2 d U_0} = \frac{U_1 L_1}{2 d U_0} \left(\frac{L_1}{2} + L_2 \right).$$

Substituting all given values into the last expression and having made calculations, we arrive at $BC = 5.5$ cm.

Let us start with calculation of a field set up by a single charge Q . The field of the point charge depends only on the distance from a charge to a point of observation and does not depend on the direction, i.e., the field is spherically symmetric. Choose an arbitrary point A (arbitrary means that it is typical and not distinguished from any other). We shall carry out a spherical Gauss surface through this point at the radius r with the center in charge Q (Figure 4.6). We shall write down for this sphere S the Gauss law in the form $\int_S E_n dS = Q/\epsilon_0$. In this expression, E_n is the projection of vector \mathbf{E} on the normal vector \mathbf{n} to the sphere surface. Any line passing through point O is the axis of symmetry because any turn around it superposes a system with itself.

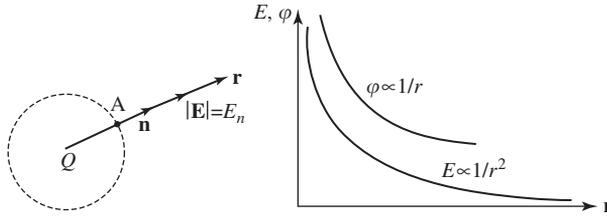


Figure 4.6 The electric field of a point charge. Point A is a point of observation, the dashed line represent a Gauss surface.

Therefore, the vector E coincides with the symmetry axis. It means that $|\mathbf{E}| = E_n$. Besides, as a consequence of the symmetry of the problem, $E = \text{const.}$ at any point of the Gauss sphere. Therefore, $\oint_s E dS = E \oint_s dS = E 4\pi r^2$. The right-hand side of the equation is equal to Q/ϵ_0 . So, $E 4\pi r^2 = Q/\epsilon_0$ or $E = Q/4\pi\epsilon_0 r^2$. This coincides with eq. (4.1.2). This coincidence is quite natural because while deriving the Gauss law, we use for simplicity the point electric charge.

It is worth mentioning here that the Gauss law is valid for all fields whose strength falls as $1/r^2$. Obviously, only in this case the r^2 terms in the nominators and denominators of the expression (4.1.12) are cancelled. We know two such fields: electrostatic and gravitation; in these two cases the Gauss theorem is valid.

Let us now apply the Gauss law to consideration of a field set up by both uniformly charged spherically symmetric bodies (sphere) and a ball uniformly charged upon the surface, the radius of spheres being R in both cases. This means that there is no charge inside the body. The charge surface density can be denoted as $\sigma = Q/S$, where S is the surface area. In both cases we have to signify two domains: domain I is the region inside the bodies ($r_A < R$, where r_A is the distance from the center of spheres to an arbitrary chosen point A) and domain II corresponds to outer space (Figure 4.7). As was valid above, any line passing through the center of the spheres is the symmetry axis and $|\mathbf{E}| = E_n = \text{const.}$ In the first domain $0 < r < R$, the Gauss integral is $\int_s E_n dS = 0$. As $E_n = |\mathbf{E}|$, then $E \oint_s dS = E 4\pi r^2 = 0$ and since $r^2 \neq 0$, then $E \equiv 0$.

In domain II, $r > R$, the arbitrary point A has to be chosen outside the spherical bodies. The total charge Q will here be fully encompassed by the Gauss surface. Therefore

$$E \int_s dS = E 4\pi r^2 = \frac{Q}{\epsilon_0}$$

and

$$E = \frac{Q}{4\pi\epsilon_0 r^2} = \left(\frac{1}{4\pi\epsilon_0} \right) \left(\frac{\sigma 4\pi R^2}{r^2} \right) = \frac{\sigma R^2}{\epsilon_0 r^2}.$$

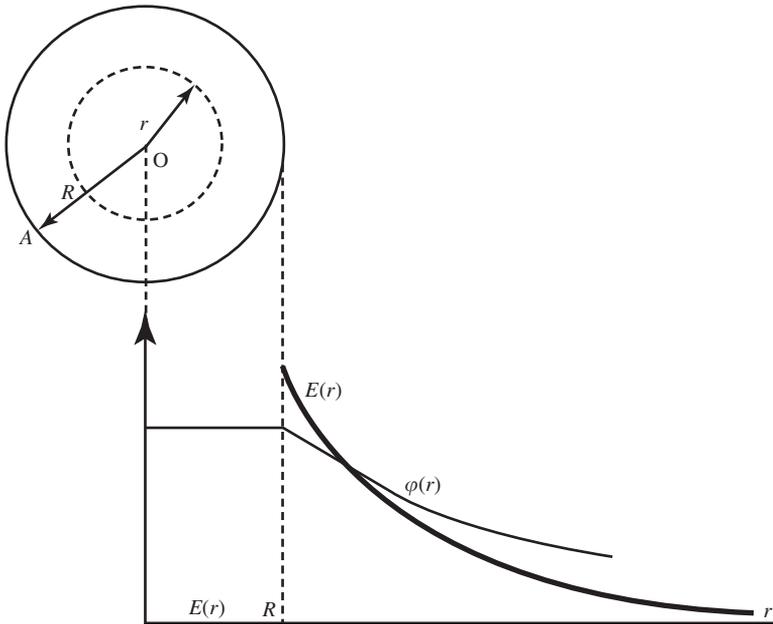


Figure 4.7 The electric field strength $E(r)$ and potential $\varphi(r)$ of the surface-charged sphere.

The result is depicted in Figure 4.7. It is apparent that the strength values on the internal and external sides of the surface are different, i.e., *the field strength on the charged surface experienced a break*.

In a similar way it is possible to obtain the values of the field strength of several spherical surfaces with the same center (e.g., for a spherical condenser).

If the sphere is charged homogeneously ($\rho = Q/V = \text{const.}$), the field inside is not equal to zero. As before, the problem has a spherical symmetry; therefore, the Gauss sphere should also be chosen in spherical form. With such a choice, $|\mathbf{E}| = E_n = \text{const.}$ at Gauss sphere. Accordingly, the arbitrary point A is chosen in two domains: inside the sphere ($r < R$) and outside it ($r > R$).

To find the electrostatic field strength dependence at the distance r from the charged sphere center inside it, we shall take advantage of eq. (4.1.15). We shall find the charge density by dividing overall charge by the volume $\rho = Q/(4/3)\pi R^3 = 3Q/4\pi R^3$. Then

$$\oint_s E_n dS = E \oint_s dS = E 4\pi r^2 = \frac{3Q}{4\pi\epsilon_0 R^3} \frac{4}{3} \pi r^3,$$

wherefrom

$$E(r) = \frac{Q}{4\pi\epsilon_0 R^3} r. \quad (4.1.18)$$

Pay attention that $E \sim r!$ This graph is given in Figure 4.8.

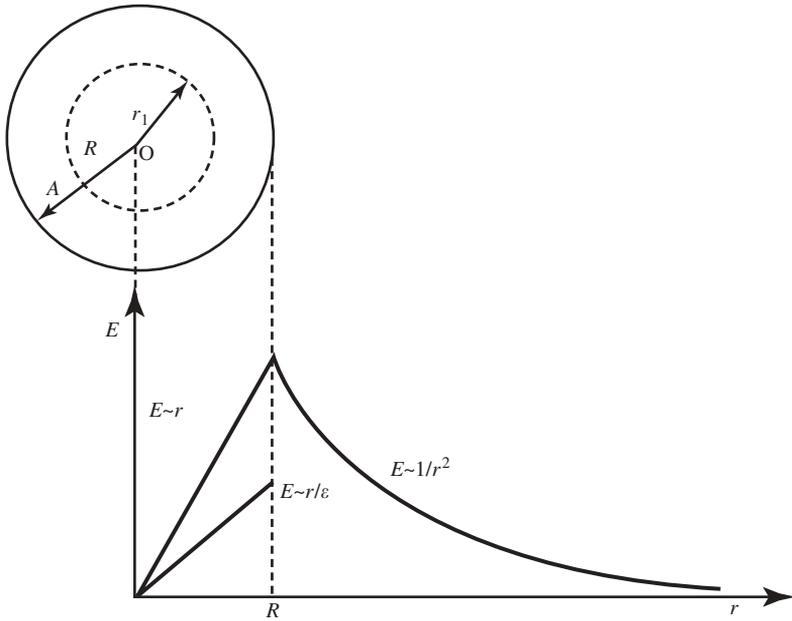


Figure 4.8 Field of a uniformly charged ball.

Calculation of the field outside the sphere is easier: the Gauss surface encompasses the whole sphere. Then

$$\oint_s E_n dS = E4\pi r^2 = \frac{Q}{\epsilon_0}$$

and

$$E = \frac{Q}{4\pi\epsilon_0 r^2}.$$

As previously seen E is proportional to $1/r^2$. If there is a material with definite ϵ (see below), the dependence $E(r)$ should contain term $1/\epsilon$ (Figure 4.8).

Let us generalize the result. In all three cases of spherical symmetry, a function $E(r)$ at $r > R$ is described by dependence $E \sim 1/r^2$. It means that an observer who is outside the sphere at any point r , knowing the fragment of the measured dependence $E(r)$ cannot judge whether the field is created by the point charge, a sphere

uniformly charged over its surface or the uniformly charged solid ball. In all three cases dependence $E(r)$ is identical! Moreover, in the case of spherical symmetry nothing prevents “swiping” the sphere or ball to a point and to consider a field as if it is created by point charge! Sometimes it essentially facilitates a problem. Remember that we have already done this in Chapter 1: in studying the force and potential energy of a gravitational field (a field of the earth), we dealt with formula $F(r) = GMm/r^2$ and $U(r) = -GMm/r$, where r is the distance from the center of the earth. We swiped the whole mass of earth to a point (see Section 1.4.5). The possibility of the generality of the results is in identical dependence on Coulomb and Newton forces from distance r !

Calculate now a field created by a body with *cylindrical symmetry*, for example, infinite and uniformly charged cylinder (for simplicity—over a surface) with linear charge density $\tau = dQ/dl = \text{const.}$ (Note that there are no such cylinders or infinite planes in nature. This physical problem is equivalent to the condition where the cylinder has finite length L , however, we consider a field near to the charged surface, i.e., at $r \ll L$. Then it is possible to neglect the edge effects and solve the problem for an infinite cylinder.)

Let us analyze a problem that has cylindrical symmetry, i.e., the axis of symmetry coincides with the axis of the cylinder; this means that in calculating the field strength, we deal with E (not with \mathbf{E}), it depends only on the distance from a cylinder axis to a point of observation r (but not from \mathbf{r} !). Furthermore, any straight line perpendicular to the cylinder axis and crossing it is an axis of symmetry of the second order (the turning of the infinite cylinder around the axis on π superposes it with itself). This means that vector \mathbf{E} should be directed along such a straight line.

Choose accordingly a closed Gauss surface in the form of a coaxial cylinder of length l (cyl) and end surfaces (end) perpendicular to the cylinder axes (Figure 4.9). Then the integral over the Gauss surface will be separated into three parts:

$$\oint_s E_n dS = \int_{\text{cyl}} E_n dS + 2 \int_{\text{end}} E_n dS.$$

The last item is equal to zero because $E_n = 0$ at end surfaces ($\mathbf{E} \perp \mathbf{n}$). Over all cylindrical surface, $\mathbf{E} \parallel \mathbf{n}$; therefore

$$\int_S E_n dS = \int_{\text{cyl}} E_n dS = 2\pi r \ell E.$$

At $r < R$ (not depicted in the scheme), $E = 0$ (according to the same consideration why the field inside an empty sphere is absent). At $r > R$, $E2\pi r l = Q/\epsilon_0 = \tau l/\epsilon_0$. Thus, $E(r) = \tau/2\pi\epsilon_0 r$. A graph of this dependence is presented in Figure 4.9.

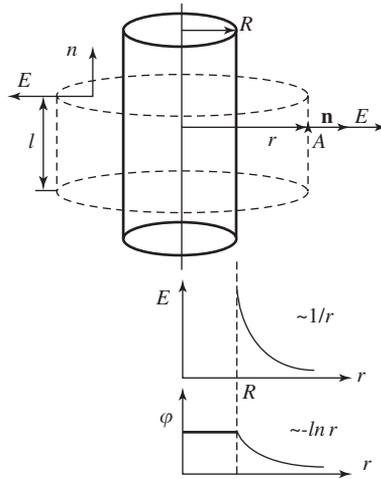


Figure 4.9 Field and potential of a system with cylindrical symmetry.

Let us now calculate a field created by an infinite plane (i.e., with linear sizes much larger than the distance from the plane to an observation point), the plane being uniformly charged ($\sigma = dQ/dS = \text{const.}$). Any straight line perpendicular to the infinite plane is the axis of symmetry (because any turn around it will impose a plane on itself). Therefore, \mathbf{E} in any point should be directed along this axis, i.e., perpendicular to the plane. In this case, it is expedient to choose the Gauss surface to be a cylinder with the generatrix perpendicular to the plane, as is shown in Figure 4.10. Therefore, the electric strength flux through a side of the cylinder surface is zero, whereas the flux through two ends is

$$\oint_s E_n dS = 2 \int_{S_{\text{bot}}} E_n dS = 2ES_{\text{end}}.$$

According to the Gauss theorem, this expression is equal to the charge inside the Gauss surface, i.e., σS_{end} . So $2ES_{\text{end}} = \sigma S_{\text{end}}/\epsilon_0$, i.e., $E = \sigma/2\epsilon_0 = \text{const}$ (see Figure 4.10)

$$E = \frac{\sigma}{2\epsilon_0}. \tag{4.1.19}$$

It can be seen that the field strength near to plane does not depend on distance (!). Negative value of E to the left of the plane means that vector \mathbf{E} is directed opposite to the axis x .

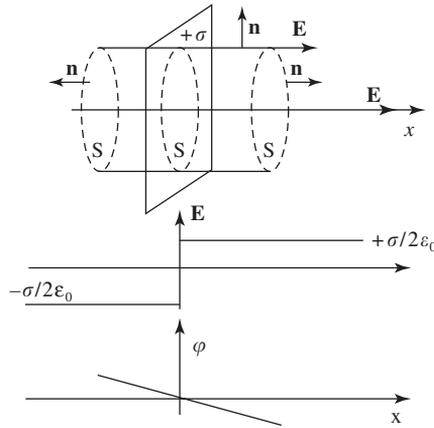


Figure 4.10 Field of a uniformly charged plate.

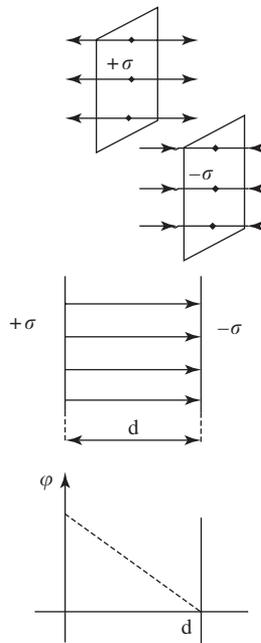


Figure 4.11 A Uniform condenser field.

The system of two similar planes carrying an equal charge with an equal charge density represents a plane condenser, provided they carry charges of opposite signs. According to the superposition principle, the field in the condenser is an algebraic

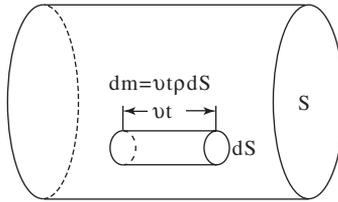


Figure 4.12 A Gauss theorem and a liquid's flow.

sum of the fields created by each plane separately (Figure 4.11). So, the field inside the plane condenser is

$$E_{\Sigma} = 2E = \frac{\sigma}{\epsilon_0}; \quad (4.1.20)$$

however, the field outside it is zero. The plane condenser is a source of a uniform electric field.

In summary, we make two more remarks on the Gauss theorem. The first concerns the physical nature of the equation. Because in eq. (4.1.13) an electric charge is presented on the right-hand side, the theorem asserts that *the source of an electrostatic field is electric charge*.

Another concerns the general meaning of the theorem, wider than only electrostatics. Imagine, for instance, a flow of a liquid in a pipe (Figure 4.12). Each particle of the liquid moves with speed u . The mass of the liquid will cross a surface dS in time t , making $dm = ut\rho dS$. The mass of the liquid $m = \int_S v t \rho dS = t\rho \int_S v dS$ will pass through surface S in time t , and if S and dS are directed parallel to each other, $m = t\rho \int v dS$. On one hand, these equations allow us to calculate the mass of the liquid at its flow in pipes (at known distribution of speed, at turbulent or laminar current), and, on the other hand, to formulate a criterion for liquid incompressibility, $\oint_S v dS = \text{constant}$. If there is a source of liquid inside the Gauss surface, $\rho \oint_S v dS = j$, where $j = m/t$ is a source power.

4.1.4 Work of an electrostatic field force and potential of an electrostatic field

Coulomb forces are central and, consequently, conservative; the field of these forces is potential (refer to Section 1.4.4, Figure 1.29 and eq. (1.4.24)). Indeed, by definition, an elementary work dA of a force F on a displacement dl is determined as: $dA = F dl = qE dl = qE dl \cos \alpha$, where $E = Q/4\pi\epsilon_0 r^2$ and $dl \cos \alpha = dr$. Then $dA = qQ dr/4\pi\epsilon_0 r^2$ and $A_{12} = (qQ/4\pi\epsilon_0) \int_{r_1}^{r_2} dr/r^2$. Therefore,

$$A_{12} = \frac{qQ}{4\pi\epsilon_0} \left(\frac{1}{r_1} - \frac{1}{r_2} \right),$$

i.e., the work in fact does not depend on the distance traveled but on r_1 and r_2 , the radius vectors of the initial and final points. If a charge starting from the initial point returns to it, the work of electrostatic forces is equal to zero: $A = q \int_L E_l dl = 0$, where $E_l = E \cos \alpha$ is a projection of vector \mathbf{E} on the displacement vector $d\mathbf{l}$. Then $\oint_L E_l dl = 0$: circulation of the electrostatic field strength along the closed trajectory is equal to zero. This is the definition of the potential character of a force field.

From equation $\oint_L E_l dl = 0$ it follows that the force lines of an electrostatic field cannot be closed (otherwise with a positive detour the integral would be essentially positive). They start from the positive charges and end at negative charges (or pass into infinity).

The work of electrostatic field forces can be presented as a potential energy decrease, $A = U_1 - U_2 = -\Delta U$. From a comparison of this equation with that given above, the potential energy of a charge q in a field of another charge Q can be written as $U = (qQ/4\pi\epsilon_0 r) + C$. If one accepts that at $r = \infty$ the potential energy $U(\infty)$ is equal to zero, then $C = 0$ and the potential energy is finally

$$U = \frac{qQ}{4\pi\epsilon_0 r}. \quad (4.1.21)$$

The electrostatic potential φ is a value numerically equal to the potential energy of a unit positive point charge placed into the given field point. Then

$$\varphi = \frac{U}{q}. \quad (4.1.22)$$

The point charge potential is therefore

$$\varphi = \frac{Q}{4\pi\epsilon_0 r}. \quad (4.1.23)$$

Inasmuch $U = q\varphi$, then

$$A_{12} = U_1 - U_2 = q(\varphi_1 - \varphi_2) = -q \Delta \varphi. \quad (4.1.24)$$

If one assumes $\varphi(\infty) = 0$, then $A_{1\infty} = q\varphi_1$; therefore, $\varphi_1 = A_{1\infty}/q$. This means that the potential is numerically equal to the force work done on the displacement of the unit positive point charge from the given point to infinity.

The field potential is the scalar power characteristic of an electrostatic field. The potential of a field having been created by a system of motionless charges obeys the superposition principle, i.e., *each charge creates a field irrespective of the presence of other charges in the space*. As the potential is a scalar value, the potential in any point of the field, created by the system of charges, is equal to the algebraic sum of potentials of fields created by each charge individually:

$$\varphi(\mathbf{r}) = \sum_{i=1}^N \varphi_i(\mathbf{r}), \quad (4.1.25)$$

where N is the total number of charges.

From the point of view of the potential distribution, the electrostatic field can be graphically characterized by surfaces of equal potential, i.e., by equipotential surfaces with $\varphi = \text{constant}$ (Figure 4.13). The force lines are always normal to them.

Because electric field strength $\mathbf{E}(\mathbf{r})$ and potential $\varphi(\mathbf{r})$ are functions of a point radius vector \mathbf{r} , there should be an interrelation between them. Let us find it. The elementary work of a field force can be determined as either $dA = F dl = qE dl$ or $dA = -dU = -q d\varphi$. Comparing them, we can arrive at $E_l = -d\varphi/dl$.

If the field is created by a spherically symmetric charge, E and φ are both r -dependent; therefore

$$E_r(r) = -\frac{d\varphi(r)}{dr}. \quad (4.1.26)$$

In the case of linear dependence

$$E_x(x) = -\frac{d\varphi(x)}{dx}. \quad (4.1.27)$$

In the general case, $\mathbf{r}(x, y, z)$, $\mathbf{E}(\mathbf{r})$ and $\varphi(\mathbf{r})$ are interconnected by

$$\mathbf{E}(\mathbf{r}) = -\left(\frac{d\varphi}{dx}\mathbf{i} + \frac{d\varphi}{dy}\mathbf{j} + \frac{d\varphi}{dz}\mathbf{k}\right) = -\text{grad}\varphi(\mathbf{r}), \quad (4.1.28)$$

i.e., the electrostatic field strength is equal to the electric field potential gradient taken with opposite sign. One can see that the field strengths' vector is always normal to equipotential surfaces (Figure 4.13).

It follows from eqs. (4.1.26)–(4.1.28) that the function $\varphi(r)$ cannot be a discontinuous function. In fact, if a function undergoes a break (for instance, in the point x_0), then, according to eq. (4.1.27),

$$E(x_0) = \lim_{\Delta x \rightarrow 0} \frac{\Delta\varphi}{\Delta x} \rightarrow \infty,$$

since in this point $\Delta x \rightarrow 0$, but $\Delta\varphi$ tends to a finite difference; this means that $E(x_0)$ is equal to infinity. This cannot be the case.

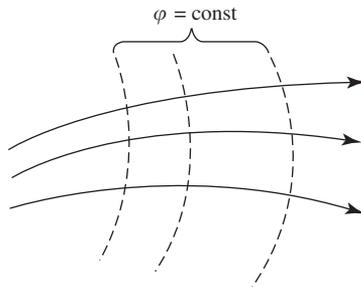


Figure 4.13 Force lines and equipotential surfaces.

The relation established between the electrostatic field strength and potential allows us to find dependence $\varphi(r)$ knowing the function $E(r)$ for all examples considered above. In fact, it follows from eqs. (4.1.26) and (4.1.27) that

$$\varphi(r) = -\int E(r)dr + C$$

and

$$\varphi(x) = -\int E(x)dx + C.$$

Substituting here the already known functions $E(r)$ and $E(x)$, we can calculate functions $\varphi(r)$ and $\varphi(x)$. The constant C reflects the fact that the function φ , as well as potential energy, is known to be within a constant; it can be found from boundary conditions. The choice of C can provide a continuity of function φ . Thus, the potential for the problems considered can be obtained. Corresponding graphs are depicted in Figures 4.6, 4.7, 4.9–4.11.

In order to calculate the potential difference $\Delta\varphi$, integration should be carried out in certain limits. So, for instance, the potential difference in a plane condenser is

$$\Delta\varphi = -\int_0^d E(\mathbf{x})d\mathbf{x} = -E\int_0^d d\mathbf{x} = -Ed,$$

where d is the distance between the plates.

The reverse problem (knowing φ , calculate E) can be obtained as well. This method will be used, for example, when we calculate an electric dipole field (because potential calculation is easier than calculating the field strength since the former is a scalar value, whereas the latter is of vector quality).

4.1.5 Electrical field of an electric dipole

A system consisting of two charges, equal in absolute value and opposite in sign, is referred to as an *electric dipole*. The vector drawn from a negative charge to a positive one l is called a dipole arm. The vector \mathbf{p} equal to a product of the charge and arm is referred to as *electric dipole moment* (Figure 4.14):

$$\mathbf{p} = ql. \quad (4.1.29)$$

It can be seen that the unit of dipole moment measurement is C m. This is a very large value and therefore a significantly smaller one is used in chemistry, namely 1 Debye (D): 1 D is equal to 3.33×10^{-30} C m.

When a dipole field is studied at a distance much larger than the dipole arm, it is called the point dipole. In spite of the fact that a dipole seemed to be an electrically neutral particle, it produces an electric field; this field has different properties compared to a field of

point charges. In order to describe a dipole field, we use the superposition principle:
 $\varphi = \varphi_+ + \varphi_-$, i.e.,

$$\varphi = (|q|/4\pi\epsilon_0 r_+) - (|q|/4\pi\epsilon_0 r_-) = |q|(r_- - r_+)/4\pi\epsilon_0 r_+ r_- ,$$

We consider the point dipole ($l \ll r$) (Figure 4.14); therefore, $r_- r_+ \approx r^2$, $r_- - r_+ \approx l \cos \theta$ which means that

$$\varphi(r, q) = \frac{|q|\ell}{4\pi\epsilon_0 r^2} \cos \theta = \frac{p}{4\pi\epsilon_0 r^2} \cos \theta. \tag{4.1.30}$$

In order to determine the strength of the dipole field at point A, the relationship between strength and potential can be used. We use a polar coordinate r and θ with a polar axis coinciding with the dipole arm direction (Figure 4.15). Component E_r (projection \mathbf{E} on the radius vector \mathbf{r}) is

$$E_r = \frac{d\varphi}{dr} = \frac{2p}{4\pi\epsilon_0 r^3} \cos \theta.$$

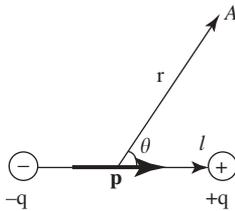


Figure 4.14 An electric dipole model.

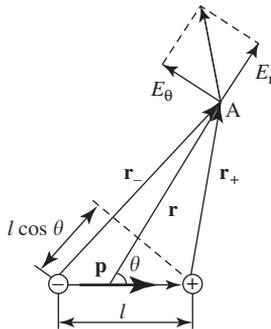


Figure 4.15 Dipole electric field calculation.

The E_θ component perpendicular to \mathbf{r} is equal to

$$E_\theta = \frac{d\varphi}{r d\theta} = \frac{p}{4\pi\epsilon_0 r^3} \sin\theta,$$

where $r d\theta$ is the length of an arc with radius r . Then, the total electric field strength at point A is

$$E = \sqrt{E_r^2 + E_\theta^2} = \frac{p}{4\pi\epsilon_0 r^3} \sqrt{1 + 3\cos^2\theta}. \quad (4.1.31)$$

The potential and strength of the dipole field are defined not by a value of charge q but by the dipole electric moment $p = |q|l$. With distance, the dipole potential and strength decrease faster ($\varphi \sim 1/r^2$, $E \sim 1/r^3$) than those of a field of a point charge ($1/r$ and $1/r^2$, respectively). A configuration of the dipole electric field is shown schematically in Figure 4.16.

In a uniform electric field a torque \mathbf{M}_F aspires to turn the dipole moment \mathbf{p} to be oriented along the field \mathbf{E} . A force couple \mathbf{M}_F is equal to the product of force $\mathbf{F} = |q|\mathbf{E}$ and the force arm $l \sin \alpha$ (Figure 4.17), i.e., $M = |q|El \sin \alpha = pE \sin \alpha$ or, in vector form,

$$\mathbf{M}_F = [\mathbf{p}\mathbf{E}]. \quad (4.1.32)$$

The vector \mathbf{M} is directed perpendicular to the plane of drawing from a spectator. The resulting force in the uniform electric field is zero.

In order to calculate the potential energy of a dipole in the uniform electric field we use the recipe given in Section 1.4.5. To calculate the potential energy we should first

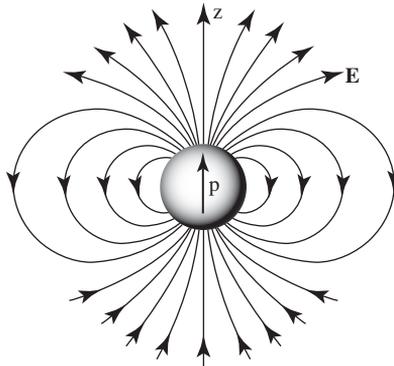


Figure 4.16 A dipole electric field configuration.

find the elementary work of the force couple ($dA = dU$, where $dA = M_F d\alpha$ is the force couple work and dU is the increment of the potential energy). Then

$$U = \int M_F d\alpha = \int pE \sin \alpha d\alpha,$$

after integration we can obtain $U(\alpha) = -pE \cos \alpha + C$. If we accept $U(\pi/2) = 0$, then $C = 0$ and $U = -pE \cos \alpha$ or in vector form

$$U = -(\mathbf{pE}). \tag{4.1.33}$$

A graph of dependence $U(\alpha)$ is given in Figure 4.18. When the vector \mathbf{p} coincides with vector \mathbf{E} , the dipole potential energy acquires the lowest value ($\alpha = 0, U_{\min} = -pE$): the dipole is in a stable equilibrium; the force couple is also equal to zero. When the vector \mathbf{p} is oriented perpendicular to the vector \mathbf{E} , the dipole energy is equal to zero ($\alpha = \pi/2, U = 0$). When the vector \mathbf{p} is directed opposite to the vector \mathbf{E} , the dipole energy is maximum ($\alpha = \pi, U_{\max} = pE$), the dipole is in an unstable equilibrium: any deviation from this state leads to turn-off of the dipole.

In a nonuniform electric field, forces acting on dipole charges are not equal in absolute value and direction. In Figure 4.19, a graph of a nonuniform field ($dE/dx < 0$) with a dipole \mathbf{p} in this field is depicted. Both the force couple \mathbf{M}_F and resulting force \mathbf{F} will act on the dipole.

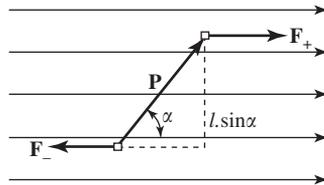


Figure 4.17 Electric dipole in a uniform electric field.

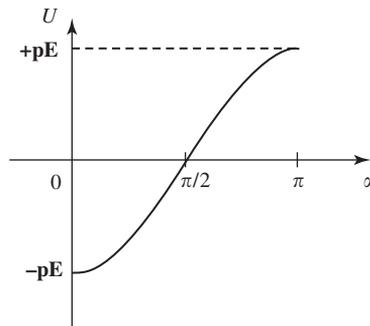


Figure 4.18 A dipole potential energy in a uniform electric field.

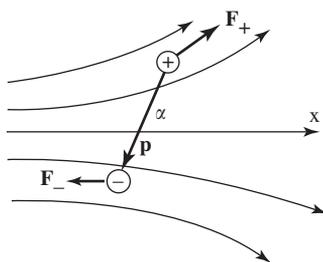


Figure 4.19 An electric dipole in a nonuniform electric field.

To calculate a force projection on x -axis, we can use eq. (1.4.33) where the relation of the force projection with the field nonuniformity is given ($F_x = -\partial U/\partial x$); in our instance, $U = -pE \cos \alpha$ and then

$$F_x = p \frac{\partial E}{\partial x} \cos \alpha. \quad (4.1.34)$$

If a dipole in the electric field is in a stable state ($\cos \alpha = 1$), then the force will draw the dipole into an area of stronger field (for Figure 4.19, $F_x < 0$).

The ratio (eq. (4.1.34)) shows that an interaction force can exist even between neutral molecules, though having the dipole moments. In fact, if an electrically neutral polar molecule creates the nonuniform field described by expression (4.1.31) and another molecule with a dipole moment \mathbf{p} is in this field, a *dipole–dipole interaction* appears between them.

4.2 DIELECTRIC PROPERTIES OF SUBSTANCES

4.2.1 Conductors and dielectrics: a general view

From the point of view of electric properties, all substances can be divided into two main classes—conducting and nonconducting an electric current. Metals, their alloys and a small number of chemical compounds with metal character of interatomic interactions relate to the class of conductors. The second class includes other substances and represents the overwhelming majority. Conductivity is defined by the presence of free charge carriers in a substance; their absence determines dielectric properties. So, dielectrics are substances in which there are no free charges capable of covering long distances in the substance (in comparison with molecular sizes).

Depending on their molecular structure, all dielectrics can, in turn, be divided into two large groups—polar and nonpolar. In polar dielectrics, molecules themselves represent the electric dipoles with the electric moment \mathbf{p} ; it appears due to displacements of electric charges from positions of their equilibrium in free atoms as a result of chemical bonding (e.g., H_2O , HCl and NH_3). The molecular dipoles of polar dielectrics participate in thermal motion; this can be translational motion (in gases and liquids), oscillation

about equilibrium positions (solids and liquids) and rotation around the center of mass. As a result, the dipole electric moments \mathbf{p} are chaotically distributed along directions (Figure 4.20a). For the whole dielectric, the vector sum $\sum_{i=1}^N \mathbf{p}_i$ is equal to zero. Therefore, in spite of the fact that each molecule possesses a dipole moment, the whole sample does not.

Molecules of nonpolar dielectrics do not possess a dielectric moment. This means that the positions of the positive and negative charge centers in the molecules coincide. Examples of nonpolar molecules are H_2 , CCl_4 , C_6H_6 , CH_4 , etc. In this case, the macroscopic dielectric sample does not possess a dipole macroscopic moment either.

However, when placed in an external electric field E_0 , all dielectrics regardless of their molecular properties are polarized, i.e., $\sum \mathbf{p}_i$ becomes nonzero, the dielectric acquires a macroscopic dipole moment (Figure 4.20b).

For the quantitative description of dielectrics, the notion of the polarization (degree) or the polarization vector \mathfrak{P} is introduced; numerically, it is equal to the electric dipole moment of a unit volume. Accordingly

$$\mathfrak{P} = \frac{1}{\Delta V} \sum_{i=1}^N \mathbf{p}_i. \quad (4.2.1)$$

In this expression ΔV is a so-called physically infinitesimal volume, i.e., a volume containing enough dipoles that the vector sum in eq. (4.2.1) adequately reflects the macroscopic dielectric state of this volume, but, simultaneously, small enough that within the limits of this volume the polarization degree can be considered as uniform. It is important to notice once more that the sum in eq. (4.2.1) is of a vector character.

However, in the case when all N (identical) moments are directed along one and the same axis (we shall choose an x -axis), expression (4.2.1) can be written as

$$\mathfrak{P}_x = \frac{\sum p_x}{\Delta V} = \frac{N p_x}{\Delta V} = n p_x = n p, \quad (4.2.2)$$

where $p = p_x$ (because all vectors \mathbf{p} are focused along axis x).

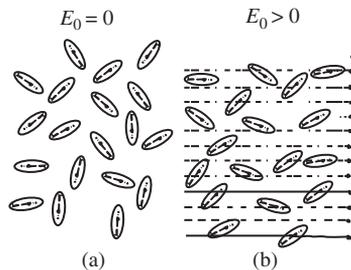


Figure 4.20 Mutual orientation of a dielectric's molecules in the absence (a) (random orientation) and in a presence of an external electric field (b).

There are two approaches to the description of dielectric properties: phenomenological which includes the description of macroscopic dielectric characteristics (subject to direct measurement) and microscopic which includes the analysis of dielectric behavior taking place at an atomic and molecular level.

We shall begin by considering dielectric behavior in an external electric field from the macroscopic point of view.

4.2.2 Macroscopic (phenomenological) properties of dielectrics

Consider now what occurs with a dielectric if it is placed in an external field \mathbf{E}_0 (Figure 4.21), created, for example, by a plane condenser. As was mentioned above, the dielectric polarizes. All charges inside a volume remain mutually compensated; however, there is no compensation near surfaces. Bound charges with density σ' are created at the edges of a body. These charges cannot be taken from the dielectric surfaces; therefore, they are referred to as bounded charges (opposite to those free charges which are on capacitor plates and form a field \mathbf{E}_0 ($E_0 = \sigma_{\text{free}}/\epsilon_0$) (4.1.19)). The surface-bounded charges produce another charged condenser-like “plate” which creates the electric field \mathbf{E}_1 directed opposite to the external field \mathbf{E}_0 (Figure 4.21). This field is referred to as a depolarized field or an electric field of bounded charges.

The electric field \mathbf{E} inside dielectrics can be treated as a superposition of two fields: the external field \mathbf{E}_0 and the depolarized field \mathbf{E}_1 , i.e., $\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1$, or in scalar form

$$\mathbf{E} = \mathbf{E}_0 - \mathbf{E}_1. \quad (4.2.3)$$

Thus, the resulting average field \mathbf{E} in the dielectric body is always less than external field \mathbf{E}_0 . This field is referred to as an average macroscopic field E in the dielectric; the average field represents the result of superposition of an external field and electric fields of bounded charges. The value equal to a ratio of the strength E_0 of an external electric field to the strength E of an average field in the dielectric is referred to as dielectric permeability of the dielectric medium.

$$\epsilon = \frac{E_0}{E}. \quad (4.2.4)$$

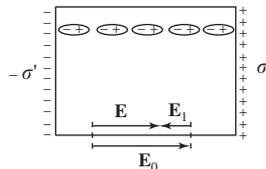


Figure 4.21 Dielectric in an external electric field \mathbf{E}_0 ; formation of surface-bounded charges with surface density σ' is shown.

Namely this value has to be introduced into the Coulomb's law (4.1.1) in order to determine a force acting between two point charges in a medium with dielectric permeability ϵ .

$$\mathbf{F} = \frac{1}{4\pi\epsilon_0\epsilon} \frac{Qq}{r^2} \frac{\mathbf{r}}{r}. \tag{4.2.5}$$

There is a certain correlation between the polarization and the surface-bounded charges' density. To establish this, we must imagine that we have cut in a flat dielectric plate an elementary volume (e.g., in the form of a cylindrical rod) along the field force lines perpendicular to the dielectric's surfaces (Figure 4.22). Assume the face area to be ΔS , the cylinder length l and the bounded charges density σ' . Therefore $\Delta q = \Delta S \sigma'$ and the induced electric dipole moment $p = \Delta ql = \sigma' \Delta Sl$. Then the polarization \mathfrak{P} of the allocated dielectric rod shall be found relating the electric moment p of the rod to its volume ΔV , i.e., $\mathfrak{P} = p/\Delta V$. As an elementary volume is $\Delta V = \Delta Sl$ (see Figure 4.22) and $p = \sigma' \Delta Sl$, then by definition (see (4.2.1))

$$\mathfrak{P} = \frac{\sigma' \Delta S l}{\Delta S l} = \sigma'.$$

So, the surface density of the bounded charges is numerically equal to the dielectric polarization.

$$\sigma' = \mathfrak{P}. \tag{4.2.6}$$

As experiments show, the isotropic dielectric polarization is proportional to the electric field strength E and coincides with it directionally ($\mathfrak{P} \sim \mathbf{E}$). In the SI, the relation between \mathfrak{P} and \mathbf{E} is written as

$$\mathfrak{P} = \kappa\epsilon_0 \mathbf{E}, \tag{4.2.7}$$

where κ is dielectric susceptibility. Note that \mathbf{E} in this expression is the strength of the average electric field (4.2.3).

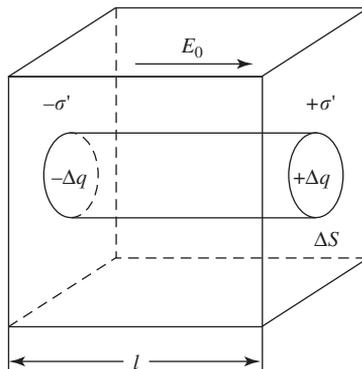


Figure 4.22 Relationship of the bounded charges' field and a body polarization.

Dielectric susceptibility κ characterizes the dielectric from the point of view of its ability to be polarized in the electric field. The dielectric susceptibility in the SI is numerically equal to dielectric polarization divided by ϵ_0 of the dielectric polarization in the field of the unit electrostatic field strength.

Thus, the ability of a dielectric to be polarized is characterized by two values: dielectric permeability ϵ and dielectric susceptibility κ . There must be an interconnection between them. Indeed, the average field in a dielectric, according to (4.2.3), is $E = E_0 - E_1$. From the other side, $E_0 = \epsilon E$ and $E_1 = \sigma'/\epsilon_0$. Then $E = \epsilon E - \sigma'/\epsilon_0$. Taking into account (4.2.6), we can write $E = \epsilon E - \mathfrak{P}/\epsilon_0 = \epsilon E - \kappa\epsilon_0 E/\epsilon_0$, and therefore

$$\epsilon = 1 + \kappa. \quad (4.2.8)$$

The numerical values of dielectric permeability of various substances change over a wide range and depend on the frequency of the external electric field. We shall discuss this question in more detail below. For the majority of nonpolar liquids, dielectric permeability is 2–2.5; for polar liquids, it is significantly higher at 10–80. For the majority of solids, $\epsilon = 1.5$ –2.5; however, for ferroelectrics (see Section 9.6), ϵ achieves a value of 10^4 . For gases, ϵ differs a bit from unity.

In order to characterize an electric field inward the dielectric, it is convenient to use one more value similar to electric field strength, namely a vector of an electric induction (or a vector of electric displacement) \mathbf{D} . In isotropic dielectrics, $\mathbf{D} = \epsilon_0\epsilon\mathbf{E}$. If ϵ does not depend on E , values \mathbf{D} and \mathbf{E} are proportional to each other. From the above-mentioned relationships, it follows:

$$\mathbf{D} = \epsilon_0\mathbf{E} + \mathfrak{P}.$$

If \mathbf{E} depends on whether dielectrics are present in the field and what their dielectric permeability is, \mathbf{D} does not depend on these circumstances and does not change its value at the transition from vacuum to dielectrics (remember that this concerns isotropic dielectrics). If ϵ depends on E , as it sometimes takes place (e.g., in ferroelectrics, see Section 9.6), then \mathbf{D} nonlinearly depends on \mathbf{E} , remaining independent of the presence in space of other dielectrics.

4.2.3 Microscopic properties of dielectrics

Among the microscopic properties of a dielectric, the basic place is occupied by the molecular dipole moment \mathbf{p} ; this depends, in turn, on atomic structure and chemical bonding. In Figure 4.23 examples of molecules are given and both directions and values of the dipole moments (in D) are specified. Note that the concept of molecular dipole moments is one of the most important in chemistry.

Some main principles connecting a molecule structure with its dipole moment can be noted. Firstly, the polarity of multiatomic molecules depends on the polarity of a given chemical bond and their mutual arrangement. On a simplified level, the electric dipole moment of a multiatomic molecule can be considered as a result of geometrical summation of the individual moments of each bond. Such an approach is based on the additive property of the total dipole moment: each chemical bond being considered as a dipole

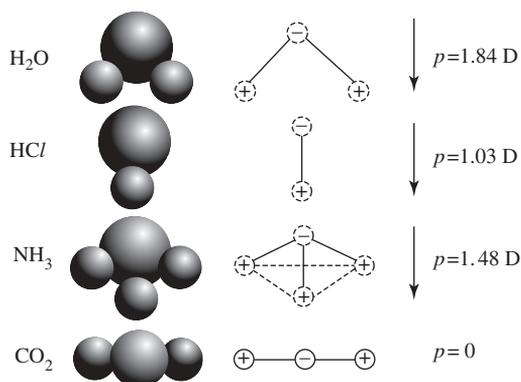


Figure 4.23 Molecular models and dielectric properties of some molecules.

moment, the total moment is obtained as a vector sum of the moments of a particular bond. The transferability of chemical bonds polarity is used here as well: it is accepted that the dipole moment is the specific property irrespective of in which particular molecule these bonds participate. At the same time, if a molecule possesses the center of symmetry (e.g., C₆H₆, CO₂, etc.), its dipole moment *a priori* is equal to zero. This statement follows from the fact that the polar dipole moment vector is incompatible with the center of symmetry because any vector itself does not possess that center.

Secondly, the molecular dipole moment strongly depends on the charge transfer from one atom to another. So, the diatomic molecules consisting of identical atoms, due to the symmetry of the electron pair arrangement, do not possess polarity at all; their electric dipole moment is equal to zero. The diatomic molecules consisting of different atoms are, in most cases, polar. The polarity of the bond is determined by the electron affinity of the constituent atoms. The greater the difference in the electron density, the more polar is the bond. The polarity reaches the highest value at a purely ionic bond. Thus, the electric dipole moment characterizes the degree of ionicity of a chemical bond. For example, the dipole moment of halogen–hydrogen bonds increases from HI to HF according to increase of electronegativity of the halogen atoms (see Table 4.1).

Molecular dipole moments can be calculated by modern methods of quantum chemistry from the first principles (for small molecules). Experimentally dipole moments can be derived from X-ray diffraction experiments using a function of electron density distribution $\rho(r)$.

Every dielectric at microlevel represents a discrete structure in which molecules or atoms are distributed in ordered (in crystals) or chaotic (in gases and liquids) manner. Therefore, the electric field strength at any point of the dielectric is the superposition of an external field and the fields of all neighboring molecules. The structure of an electric field in a dielectric is highly nonuniform; the value of an average field obtained above represents a highly averaged picture. It means that the electric field strength really acting on a given molecule is not equal to the averaged field: we should consider some effective field, referred to as a *local field*. The strength of the local field \mathbf{E}_{loc} is defined as the geometrical sum of the strengths of an external field \mathbf{E}_0 and the total field of all the dielectrics' dipoles except for the dipole being considered.

Table 4.1

Electric dipole moments of some of halogen–hydrogen molecules

Molecule	Dipole moments	
	10^{-30} C m	D
HF	6.37	1.91
HCl	4.33	1.03
HBr	2.63	0.79
HI	1.30	0.39

If an isotropic nonpolar dielectric is placed in an external electric field, the local field will act on each molecule. Displacement of charges of different signs will take place and a dipole will be created. Such a dipole is called an *induced* dipole. Its value is proportional to the strength of the local field. In SI units, this dependence is

$$p = \alpha \varepsilon_0 E_{\text{loc}}. \quad (4.2.9)$$

The α value characterizes the ability of a molecule to be polarized in an electric field, and is referred to as polarizability.

Formula (4.2.9) permits us to rewrite the expression for dielectric polarization. Starting from (4.2.2), we arrive at

$$\mathfrak{P} = n\mathbf{p} = n\alpha \varepsilon_0 \mathbf{E}_{\text{loc}}. \quad (4.2.10)$$

We can compare the expression for polarization \mathfrak{P} with that derived earlier (see eq. (4.2.7)) on the basis of macrorepresentations. Analysis shows that they are identical when $E \approx E_{\text{loc}}$, i.e., when the depolarizing field \mathbf{E}_1 is rather small. This corresponds in particular to a low molecule concentration. Then

$$\kappa = n\alpha. \quad (4.2.11)$$

Of course, this is valid for low dielectric polarization. The connection between κ and $n\alpha$ at significant polarization is given in Section 4.2.7.

4.2.4 Three types of polarization mechanisms

There are several mechanisms of dielectric polarization, each being directly dependent on the molecules' structure.

Let us distinguish a deformation and an orientation polarization. In the first case the molecule deformation takes place when imposing it in the external field. Deformation can touch both the single atom and the whole molecule. We shall consider each of these mechanisms separately.

Electronic polarization

Relates to the deformation type of polarization and appears as a result of the displacement of an atomic electron shell relative to the nucleus which, accordingly, leads to an induced dipole moment. Certainly, such a polarization mechanism takes place in all systems containing atoms, i.e., in all dielectrics; however, in a pure state it can be seen in the case of nonpolar homo-atomic molecules and atoms.

Let us estimate the value of electronic polarization. As an example, take a simplified model of an atom. Assume that the electron charge Ze is uniformly distributed around the nucleus in a sphere of radius R , i.e., with constant electron density $\rho = Q/((4/3)\pi R^3) = Z|e|/((4/3)\pi R^3)$. In the absence of an external electric field, the nucleus is in the center of a spherically symmetric electronic cloud, the centers of positive and negative charges coincide; the atom does not possess a dipole moment. We can impose an origin with negative charge center.

Let us place an atom in an external electric field. Under the action of this field, the centers of charges of both signs will shift away from each other and an induced dipole moment will appear (Figure 4.24)

$$p = Z|e|l, \quad (4.2.12)$$

where $Z|e|$ is a nuclear charge and that of the electron cloud as well and l is the displacement value of charges; the direction of dipole moment \mathbf{p} coincides with the direction of external field \mathbf{E}_{loc} . A nucleus displaced from its center will be under the action of two competitive forces: the action of a local electric field,

$$F' = Z|e|E_{\text{loc}}, \quad (4.2.13)$$

and an internal atomic electric field,

$$F'' = Z|e|\frac{\rho}{3\epsilon_0}r = Z|e|\frac{Z|e|}{4\pi\epsilon_0 R^3}l, \quad (4.2.14)$$

where l is the dipole arm; the latter force F'' tries to remove the nucleus in the initial central position. Because the forces are balanced, $F' = F''$ and $E_{\text{loc}}Z|e| = Z|e|(Z|e|/4\pi\epsilon_0 R^3)l$, wherefrom, after cancellation on $Z|e|$, it follows that $Z|e|l = 4\pi\epsilon_0 R^3 E_{\text{loc}}$. The expression for

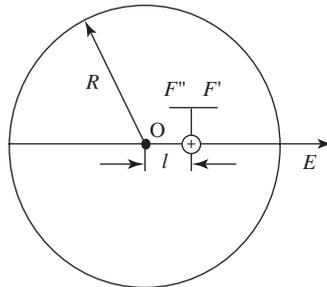


Figure 4.24 A model of the electron polarization.

the dipole moment is written on the left-hand side. Therefore, $p = 4\pi\epsilon_0 R^3 E_{\text{loc}}$. Comparing this expression with eq. (4.2.9), we can conclude that the electron polarization coefficient is

$$\alpha_{el} = 4\pi R^3. \quad (4.2.15)$$

It can be seen that the atomic electron's ability to be polarized is proportional to its volume. Although the result has been obtained at a certain level of simplification, it is qualitatively correct in describing a real picture of electron polarization. It can be seen from Table 4.2 that a cube of atomic radius increase and an electronic polarizability change in parallel.

Let us estimate to an order of magnitude the value of electronic polarizability. We estimate 3×10^{-10} m for atomic radius, then $\alpha \sim 4\pi R^3 \sim 10 \times 10^{-30} \text{ m}^3 \sim 10^{-29} \text{ m}^3$ which coincides with the values of electronic polarizability of middle-sized atoms.

The electron polarization is determined by the atomic electron shell. Therefore, it does not depend on temperature. Note that it consists of a shift of a light part of the atom regarding heavy nuclei and therefore possesses low persistence.

Atomic (ionic) polarization

Is observed in heteroatomic molecules in which atoms, due to different electronegativity, endure a redistribution of electron density. Therefore, each atom appears carrying an excessive (positive and/or negative) charge (Table 4.3). This charge δ is referred to as effective atomic charge and is defined in terms of an electron charge, i.e., $\delta = q/|e|$. Certainly, the sum of all δ over the whole molecule is equal to zero.

Depending on the effective charges and interatomic distance, the hetero-atomic molecules exhibit a permanent dipole moment even in the absence of an external electric field

Table 4.2

Electron polarizability of some atoms

Atom	Polarizability coefficient, α_{el} (10^{-30} m^3)	Cube of atomic radius, R^3 (10^{-30} m^3)
He	2.3	0.78
Ne	4.7	1.4
Ar	16	3.6
Kr	25	4.8
Xe	41	6.9

Table 4.3

The effective charges of atoms in selected molecules

Substance	Atom	δ	Substance	Atom	δ
Na ₂ O	O	-0.81	NaF	Na	+0.58
MgO	O	-0.35	NaBr	Na	+0.83
Al ₂ O ₃	O	-0.31	NaCl	Na	+0.92
P ₂ O ₅	O	-0.13	MgO	Mg	+1.01
SO ₃	O	-0.06	MgBr ₂	Mg	+1.38
Cl ₂ O ₇	O	-0.01	MgCl ₂	Mg	+1.5

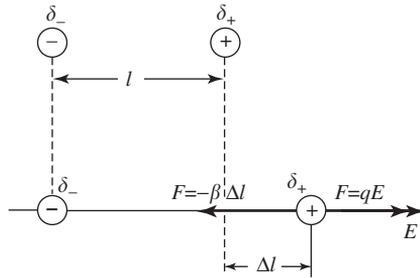


Figure 4.25 Upper (without the external field) and lower (a molecule in the external field).

$p = |q|l$. However, under the action of an electric field, there is additional displacement of the atoms relative to each other. Therefore, the interatomic distance is enlarged and the dipole moment increased. An additional (induced) electric dipole moment appears which causes the additional polarization.

In order to estimate the atomic polarization, we can use a model: consider a molecule consisting of two atoms with effective charges δ_+ and δ_- (Figure 4.25) bounded by a quasi-elastic force with rigidity coefficient β . In the absence of the external electric field, its dipole moment is $p = \delta l$ (Figure 4.25, upper). Under the external field action, the interatomic distance l undergoes an enlargement Δl (Figure 4.25, lower). Two acting forces ($|q|E$ and $\beta \Delta l$) are balanced in absolute value: $\beta \Delta l = |q_{\text{ef}}|E_{\text{loc}}$. We can find the interatomic distance enlargement $\Delta l = (|q_{\text{ef}}|/\beta)E$. Due to the action of the local electric field, the molecules acquire an additional dipole moment

$$\Delta p = |q|\Delta l = \frac{q_{\text{ef}}^2}{\beta} E_{\text{loc}}. \quad (4.2.16)$$

Denote the polarization coefficient by α_{at} . Then the additional dipole moment can be rewritten as $\Delta p = \alpha_{\text{at}} \varepsilon_0 E$, wherefrom $\alpha_{\text{at}} = \Delta p / \varepsilon_0 E_{\text{loc}}$. Substituting Δp according to (4.2.16), we arrive at

$$\alpha_{\text{at}} = \frac{q_{\text{ef}}^2}{\varepsilon_0 \beta} = \frac{\delta^2 e^2}{\varepsilon_0 \beta}. \quad (4.2.17)$$

Evaluation of α_{at} , for a HCl molecule, for instance, gives: at $\delta = 0.2|e|$, $\beta = 10$ N/m, the coefficient of atomic polarization is $\alpha_{\text{at}} = ((0.2 \times 1.6)^2 \times 10^{-38}) / (10^{-11} \times 10^2) \approx 10^{-29} \text{ m}^3$. This is a bit lower than α_{el} for the same molecule.

At moderately high temperatures when electronic density and, accordingly, interatomic forces can be considered as constants, the atomic polarization does not depend on temperature. The nuclear subsystem participates in atomic polarization and, therefore, atomic polarization possesses greater persistence than the electronic one.

Orientation polarization

Consider a polar dielectric, each molecule of which possesses an inherent, permanent dipole moment p . In the absence of an external field, dipoles are oriented chaotically due to the

molecules' thermal motion; this means that the dielectric's polarization \mathfrak{P} (4.2.1) is zero (Figure 4.21). In an external field, due to the action of force pairs (refer to Section 4.1.5 and formulas (4.1.32) and (4.1.33)), each dipole will acquire a tendency to be oriented by the field, but the thermal motion will prevent it. The general problem of the behavior of an ensemble of permanent dipoles (magnetic and electric) in an external permanent field was solved by the French scientist P. Langevin. Here, we shall take advantage of his unsophisticated dielectric model which arrived, nevertheless, at the correct result.

Consider a molecular system consisting of the permanent moments \mathbf{p} with concentration n . Accept a model in which dipoles are focused with equal probability along three coordinate axes, so $\mathfrak{P} = 0$. In the absence of an external field in any direction (positive or negative) of each coordinate axis, $n/6$ of all molecules will be directed. Assume now that operating on each molecule is a field whose direction coincides with the positive direction of the axis y (Figure 4.26). This means that each molecule will obtain a potential energy $U = -\mathbf{p}\mathbf{E} = -pE \cos \alpha$, where α is the angle between vectors \mathbf{p} and \mathbf{E} . For molecules whose dipole moments are directed along the field ($\alpha = 0$, $\cos \alpha = 1$), $U = -pE$. For molecules whose dipole moments are directed oppositely ($\alpha = \pi$, $\cos \alpha = -1$), $U = +pE$. Assume also that dipoles directed along axes x and z do not participate in polarization.

The competition between ordering tendency of an external field (in our case, this action is described by the value of potential energy U) and disordering tendency caused by thermal chaotic molecule movements (with energy κT) is described by the Boltzmann factor (see Section 3.2.4). This competition results in the fact that the concentration of molecules with dipoles oriented along the field (n_+) and oppositely (n_-) will be different and equal

$$n_+ = \frac{n}{6} \exp\left(\frac{pE_{\text{loc}}}{\kappa T}\right) \quad \text{and} \quad n_- = \frac{n}{6} \exp\left(-\frac{pE_{\text{loc}}}{\kappa T}\right).$$

Since the concentration of molecules whose dipoles are oriented in a positive and negative y -axis direction will be different, the resulting dipole moment appears in a positive direction. According to (4.2.2), it is equal, $\mathfrak{P}_y = (n_+ - n_-)p$.

We will restrict our consideration to weak fields for which $pE_{\text{loc}} \ll \kappa T$ (the potential energy of dipole interaction with an external field U is significantly less than the energy

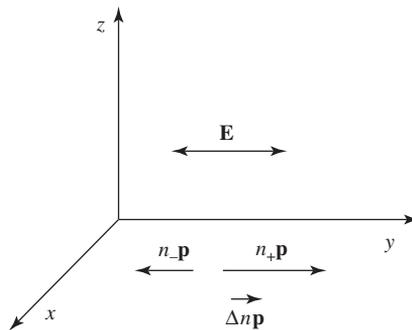


Figure 4.26 To the model of a orientational polarization.

of the molecules' thermal motion κT). In this case, an exponent function can be decomposed in a series: we will limit ourselves to only the first two terms: $n_+ \approx (n/6)(1 + (pE_{\text{loc}}/\kappa T))$ and $n_- \approx (n/6)(1 - (pE_{\text{loc}}/\kappa T))$. Then an excess of dipole concentration directed along the electric field will be $\Delta n = n_+ - n_- = (n/3)(pE_{\text{loc}}/\kappa T)$ and the polarization will be

$$\mathfrak{R} = \frac{n}{3} \frac{pE_{\text{loc}}}{\kappa T} p = \frac{np^2}{3\kappa T} E_{\text{loc}} = \frac{np^2}{3\varepsilon_0\kappa T} \varepsilon_0 E_{\text{loc}}. \quad (4.2.18)$$

The averaged effective dipole moment counting on a single molecule can be obtained by dividing \mathfrak{R} by n :

$$\mathfrak{R}_{\text{ef}} = \frac{\mathfrak{R}}{n} = \frac{p^2}{3\kappa T} E_{\text{loc}}.$$

The orientation polarization can be characterized by the coefficient of orientation polarization α_{op} . Then $p = \alpha_{\text{op}} \varepsilon_0 E_{\text{loc}}$, wherefrom

$$\alpha_{\text{op}} = \frac{p^2}{3\varepsilon_0\kappa T}. \quad (4.2.19)$$

Evaluation of α_{or} for an HCl molecule gives $p = 1 \text{ D} = 3.33 \times 10^{-30} \text{ C m}$ and $T = 300 \text{ K}$

$$\alpha_{\text{or}} = \frac{((1/3) \times 10^{-29})^2}{(3 \times 10^{-11}) \times 10^{-23} \times 300} \approx 10^{-28} \text{ m}^3,$$

which is higher than α_{el} . The value of α_{or} is inversely proportional to absolute temperature and is proportional to the square of the molecular dipole moments.

In extreme conditions (in very high fields or at very low temperatures when $pE > \kappa T$ —something that is technically very difficult to achieve), all dipoles are built along an external field; further increase does not essentially change polarization, the polarization reaches *saturation*. The polarization value in this condition depends only on dipole moment value p and concentration n .

In Figure 4.27 a graph of polarization versus external electric field strength is given. At $pE \ll \kappa T$ this function is linear (eq. (4.2.18)), the higher the molecular dipole moment and the lower the temperature, the steeper is the linear function, i.e., $\tan \beta = d\mathfrak{R}/dE$. In the other limiting case ($pE \gg \kappa T$), polarization is constant ($\mathfrak{R} = \text{constant}$, saturation state). A smooth curve connects these two extremes.

It is obvious that in polar dielectrics all three mechanisms of polarization (two of deformation and one of orientation) are exhibiting simultaneously. The total polarization of isotropic polar dielectrics \mathfrak{R}_{el} , atomic \mathfrak{R}_{at} and orientation \mathfrak{R}_{or} is a sum: $\mathfrak{R} = \mathfrak{R}_{\text{el}} + \mathfrak{R}_{\text{at}} + \mathfrak{R}_{\text{or}}$. The total polarization can also be given as the sum

$$\mathfrak{R} = (\alpha_{\text{el}} + \alpha_{\text{at}} + \alpha_{\text{or}}) n \varepsilon_0 E_{\text{loc}}, \quad (4.2.20)$$

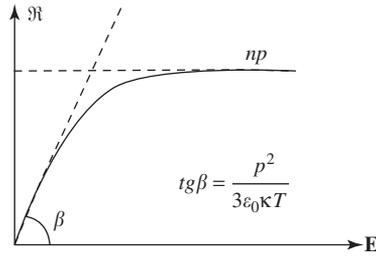


Figure 4.27 A relationship of a dielectric polarization \mathfrak{P} and the external electric field strength \mathbf{E} at orientational polarization.

a molecule can be characterized by a total averaged polarization coefficient

$$\alpha = \alpha_{\text{el}} + \alpha_{\text{at}} + \alpha_{\text{or}}. \quad (4.2.21)$$

In different molecules each term can exhibit differently depending on structure and electron density distribution as well as syntheses, temperature, experimental methods, etc.

EXAMPLE E4.10

An electric dipole with a moment $p = 2 \text{ nC m}$ is in a uniform electric field $E = 30 \text{ kV/m}$; vector \mathbf{p} is oriented at $\alpha = 60^\circ$ to \mathbf{E} . Determine the work A of external forces to rotate the dipole at an angle 30° .

Solution: From the initial position the dipole moment can be turned on $\beta = \pi/6 = 30^\circ$ in two directions: (1) clockwise at an angle $\alpha_1 = \alpha_0 - \beta = \pi/3 - \pi/6 = \pi/6$ or (2) anticlockwise at $\alpha_2 = \alpha_0 + \beta = \pi/3 + \pi/6 = \pi/2$. In the first case, the rotation occurs under the action of inner forces, therefore the work is negative; in the second case, only external forces can do the turn and correspondingly the work is positive.

The work can be determined by two methods: (1) direct integration and (2) using the relation between work and potential energy change.

The first method comes to the integration $dA = M d\alpha = pE \sin \alpha d\alpha$ in the limits from α_0 to α

$$A = \int_{\alpha_0}^{\alpha} pE \sin \alpha d\alpha = pE \int_{\alpha_0}^{\alpha} \sin \alpha d\alpha;$$

executing the calculation we obtain $A = pE(\cos \alpha_0 - \cos \alpha)$. Accordingly, the clockwise rotation gives $A = pE(\cos \alpha_0 - \cos \alpha_1) = -21.9 \mu\text{J}$ and in anticlockwise rotation, $A = pE(\cos \alpha_0 - \cos \alpha_2) = 30 \mu\text{J}$.

We think that the second method is preferable. In fact, $A = U_2 - U_1$ (see Section 1.4.5) and $A = pE(\cos \alpha_0 - \cos \alpha)$. This coincides with the previous expression.

EXAMPLE E4.11

In an iodine atom at a distance $r = 1$ nm from an α -particle, an induction dipole moment $p = 1.5 \times 10^{-32}$ C m appears. Find the polarization coefficient α of the iodine atom.

Solution: The polarization coefficient α can be found according to eq. (4.2.9), $\alpha = p/\varepsilon_0 E_{\text{loc}}$, where E_{loc} is the field in which a given atom occurs. In this case, the field created by an α -particle is a local field. Therefore, it is equal to $E_{\text{loc}} = E = 2|e|/4\pi\varepsilon_0 r^2$. Combining the last two expressions, we arrive at $\alpha = 2\pi r^2 p/|e|$. Executing the calculation, we obtain $\alpha = 5.9 \times 10^{-30}$ m³.

EXAMPLE E4.12

Krypton is under a pressure $p = 10$ MPa at a temperature $T = 200$ K. Find (1) the dielectric permittivity ρ of krypton and (2) its polarization \mathfrak{R} in an external field $E_0 = 1$ MV/m. Krypton polarizability α is 4.5×10^{-29} m³.

Solution: (1) Expression (4.2.26) is suitable for solving this problem $(\varepsilon - 1)/(\varepsilon + 2) = \alpha n/3$, where n is krypton concentration. Find the dielectric polarizability α from this equation: $\varepsilon = (1 + (2/3)\alpha n)/(1 - (1/3)\alpha n)$. The concentration is equal to $n = p/\kappa T$; therefore, $\varepsilon = (3\kappa T + 2\alpha p)/(3\kappa T - \alpha p)$. Substituting all data in the expression, we arrive at $\varepsilon = 1.17$. (2) In the uniform electric field krypton polarizability can be given by eqs. (4.2.2) and (4.2.10) $\mathfrak{R} = np$ and $p = \varepsilon_0 n E_{\text{loc}}$. To rewrite the local field via the external field for nonpolar substances ($E_{\text{loc}} = ((\varepsilon + 2)/3\varepsilon)E_0$) and $n = p/\kappa T = 3.6 \times 10^{27}$ m³, we obtain $p = \alpha \varepsilon_0 ((\varepsilon + 2)/3\varepsilon) n E_0$. Using all data obtained we arrive at $p = 1.30 \times 10^{-6}$ C/m².

4.2.5 Dependence of the polarization on an alternative electric field frequency

Polarization is a measure of a dielectric's "response" to the action of an external electric field. In a static electric field all the molecular dipoles align along the external field (we will not take the thermal motion into account at the moment). To measure total polarization in the static field is easy: having placed a dielectric sample in a condenser, its capacitance depends on the dielectric permeability of the material between the plates ($C = C_0 \varepsilon$, C_0 being the capacitance of an "empty" condenser, remember the ratio between susceptibility κ and permittivity ε). In an alternating electric field the molecular dipoles should have time to turn as a whole when the electric field changes its direction. While field frequency ν is not so high, the dipoles have time to reorient, following the change of field direction. In a field of high frequencies when $\nu \sim 10^6 - 10^7$ Hz due to the molecules' inertia, they begin to delay, being unable to follow the electric field reorientation. The higher the frequency, the greater is the delay. At very high frequencies the molecules will not be able to reorient and the polarization comes to naught.

We can conclude that in static electric field, all molecules regardless of their origin participate in overall polarization; therefore, such measurements give the sum of three polarization mechanisms (refer to (4.2.21) and Figure 4.28 in which a range of frequencies is given). When the electric field frequency reaches a value of 10^{11} Hz, the molecules are unable to turn over because of their great inertia; therefore, the orientation polarization is switched out.

Atomic polarization does not need the molecules' reorientation; in a high frequency field, the induced oscillations of atoms along the field direction take place. This will be preserved up to a frequency of approximately 10^{12} Hz. At this value, atomic oscillations also vanish and only electron oscillations (the lightest part of atoms) remain.

At $\nu \sim 10^{13}$ – 10^{15} Hz, only electrons can accomplish their oscillations. This frequency corresponds to oscillations of light vectors, magnetic and, mainly, electric. At such frequencies, only the electron part remains; at higher frequencies, even the electron part disappears.

The frequency dependence explains why the dielectric permeability of water measured in a static electric field is 81, but at optic frequencies is only 1.77: in the first case all polarization mechanisms are participating in the polarization but in the latter case only electron polarization takes place.

Otherwise the polarization is exhibited in solids. The ability of a molecule to change orientation or oscillate depends essentially on its geometrical form and interaction forces with its neighborhood. If the form of the molecule is close to spherical and its electric moment is not high, it can rather easily change its orientation (e.g., molecular group CH_4). Molecules HCl and H_2O are less symmetric; in solids they have some steady orientations and rather slowly pass from one to another. The average time τ of such a transition is referred to as relaxation time. The value reciprocal to the relaxation time is referred to as relaxation frequency. When the frequency of an external alternative electric field is higher than the relaxation frequency, the system will no longer react to the action of such a field.

The relaxation time depends on temperature and the aggregate substance state. So for water ($t = 200^\circ\text{C}$), $\tau = 3 \times 10^{-11}\text{c}$; however, for ice ($t = -20^\circ\text{C}$), $\tau = 10^{-3}\text{c}$.

4.2.6 A local electric field in dielectrics. Lorentz field

A local or microscopic electric field is a field acting on the given dipole in a dielectric. The strength of a local field is the geometrical sum of external field strength \mathbf{E}_0 and the

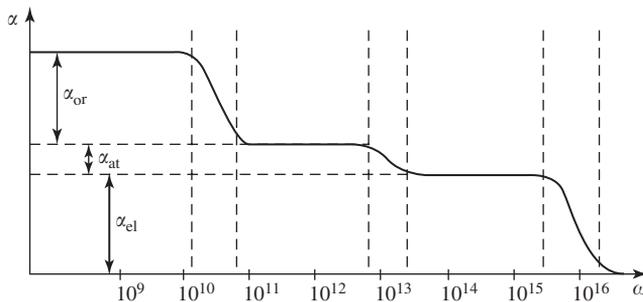


Figure 4.28 Dielectric polarization in the alternating field of different frequencies.

complex field $\sum \mathbf{E}_i$ created by all dipoles, except that on which this field operates ($\mathbf{E}_{\text{loc}} = \mathbf{E}_0 + \sum \mathbf{E}_i$). This field strongly changes within the limits of intermolecular distances and, owing to thermal molecular motion, changes as well in time. In fact, it is impossible to calculate \mathbf{E}_{loc} according to the formula presented because of the enormous number of dipoles. However, if the dielectric is polarized homogeneously, i.e., the polarization at any dielectric point is the same in magnitude and direction, it is possible, at a certain approximation, to calculate its value.

Without carrying out a detailed calculation (because of its complexity), we shall, nevertheless, note the general remarks that allowed H.A. Lorentz to solve this problem. His method is as follows. Remember that the further the dipole from the point of consideration, the less is its contribution to the local field (the dipole field falls down as $E \sim 1/r^3$, eq. (4.1.31)) but the larger their number. This allows him to replace summation upon individual dipoles onto integration, i.e., calculate a local field macroscopically.

Lorentz suggested allocating in a homogeneously polarized dielectric a sphere of rather small radius, inside which there exist a large but, nevertheless, limited number of dipoles. The center of the Lorentz sphere should coincide with the point of observation (Figure 4.29). In an external field, polarization will take place, including the allocated sphere. We shall mentally remove the originally allocated sphere from the dielectric body. There appears a spherical cavity with charges distributed on its internal surface. The strength of the local field can now be given by four terms $\mathbf{E}_{\text{loc}} = \mathbf{E}_0 + \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3$, where \mathbf{E}_0 is the external field, \mathbf{E}_1 is the depolarizing field created by bounded charges distributed on an external dielectric surfaces, \mathbf{E}_2 is the field created by the bounded charges on the internal surface of the spherical cavity (Lorentz field) and \mathbf{E}_3 represents the field of the nearest neighbors; in isotropic dielectrics (in gases, liquids and isotropic crystals), this field is equal to zero. The values \mathbf{E}_0 and \mathbf{E}_1 have already been considered above, and calculation of the strength of the field \mathbf{E}_2 is the subject of our consideration. Integration over the internal cavity surface gives a field E_2 which is referred to as a Lorentz field:

$$\mathbf{E}_2 = \frac{1}{3} \frac{\mathfrak{P}}{\epsilon_0}. \quad (4.2.22)$$

Correspondingly, the local field strength can be written as:

$$\mathbf{E}_{\text{loc}} = \mathbf{E} + \frac{\mathfrak{P}}{3\epsilon_0}. \quad (4.2.23)$$

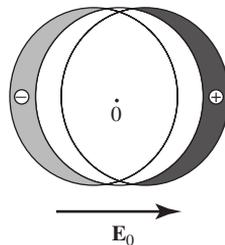


Figure 4.29 A dielectric's body polarization.

In scalar form, it can be given as

$$E_{\text{loc}} = E + \frac{1}{3} \frac{\mathfrak{R}}{\epsilon_0}. \quad (4.2.24)$$

This field should be presented in all expressions in which a local field appears.

4.2.7 Clausius–Mossoti formula

For rarefied dielectrics, eq. (4.2.11) connecting the macroscopic characteristic κ with the microscopic one α , which in turn provides access to the analysis of the molecule properties, was given. In more complex cases of the more condensed matter at $n\alpha$ noticeably larger than unity, the given simple ratio is not fair. In order to find the proper ratio in more dense substances we should substitute in the expression (4.2.10) the local field E_{loc} by eq. (4.2.24):

$$\mathfrak{R} = \alpha n \epsilon_0 E_{\text{loc}} = \alpha n \epsilon_0 \left(E + \frac{1}{3} \frac{\mathfrak{R}}{\epsilon_0} \right) = \alpha n \epsilon_0 E + \frac{\alpha n}{3} \mathfrak{R}.$$

Solving this equation relative to \mathfrak{R} , we obtain

$$\mathfrak{R} = \frac{n\alpha}{1 - (n\alpha/3)} \epsilon_0 E.$$

If we accept $n\alpha \ll 1$, it goes to (4.2.10), i.e., $\kappa = n\alpha$. However, if this is not the case, then we have to compare it with eq. (4.2.7). The comparison gives

$$\kappa = \frac{n\alpha}{1 - (n\alpha/3)} = \frac{3n\alpha}{3 - n\alpha},$$

or

$$\frac{n\alpha}{3} = \frac{\kappa}{\kappa + 3}. \quad (4.2.25)$$

Substituting here κ (4.2.8) accordingly, we arrive at

$$\frac{1}{3} n\alpha = \frac{\epsilon - 1}{\epsilon + 2}. \quad (4.2.26)$$

This is one of the forms of the Clausius–Mossoti law. It connects the macroscopic value of the susceptibility ϵ with polarizability α of molecules.

One can express a molecule concentration n in eq. (4.2.26) via the Avogadro constants N_A and a molar volume M/ρ : $n = N_A/(M/\rho) = (\rho/M)N_A$. Then the Clausius–Mossotti formula can be written as

$$\frac{M}{\rho} \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3} \alpha N_A. \quad (4.2.27)$$

Clausius and Mossotti independently obtained eq. (4.2.27) for nonpolar dielectrics in the middle of the 19th century. In 1912, using Langevin theory for magnetization of paramagnetic substances, Debye obtained for polar dielectrics a connection between polarization and electric dipole moments. He suggested a concept of orientation polarizability of polar molecules and has generalized the Clausius–Mossotti equation for the case of polar dielectrics. This Debye–Langevin formula is usually written as

$$\frac{M}{\rho} \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3} \left(\alpha_{\text{def}} + \frac{p^2}{3\varepsilon_0 kT} \right) N_A, \quad (4.2.28)$$

where α_{def} is the deformational polarization (see Section 4.2.4) or the polarization of elastic displacement, which is the sum of electronic α_{el} and atomic α_{at} polarizations. Taking into account all three types of polarization mechanisms, the Debye–Langevin formula can be written as:

$$\frac{M}{\rho} \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3} \left(\alpha_{\text{el}} + \alpha_{\text{at}} + \frac{p^2}{3\varepsilon_0 kT} \right) N_A. \quad (4.2.29)$$

The Debye–Langevin formula is applicable to polar dielectrics at definite restrictions. It achieves good fulfillment for gases and vapors at low pressure, and for highly dissolved solutions of polar liquids in nonpolar solvents. This formula is of great importance in the interpretation of molecular structures.

Being written as

$$\frac{M}{\rho} \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3} (\alpha_{\text{el}} + \alpha_{\text{at}}) N_A,$$

it successfully describes nonpolar gases at low and average pressures (500 kPa and lower), can be applied approximately for nonpolar gases at elevated pressures (above 500 kPa) and nonpolar liquids, and is good enough for crystals with face-centered lattice if atoms possess only electronic polarization and approximate for ionic crystals with a cubic lattice (see Section 9.6).

As was already mentioned in Section 4.2.5, the polarizability of molecules depends on the frequency of the alternative electric field, especially at high frequencies. In the Maxwell electromagnetic theory, the ratio between a refraction index n and the dielectric permeability ε of substances is given. For low-magnetic substances, $n = \sqrt{\varepsilon}$. If in eq. (4.2.27) we substitute ε by n^2 and take into account that at optical frequencies

($\nu \sim 10^{15} - 10^{16}$ Hz) all polarizability mechanisms, except the electronic one, are suppressed, it is possible to write

$$\frac{M}{\rho} \frac{n^2 - 1}{n^2 + 2} = \frac{1}{3} \alpha_{\text{el}} N_A. \quad (4.2.30)$$

This is the H.A. Lorentz–L. Lorentz formula. The right-hand side of this equation is a molar refraction R . It is fair for gases, nonpolar liquids and isotropic crystals (with cubic lattices). It is approximately applicable to nonpolar liquids at relatively high frequencies when the orientation polarization is not exhibiting.

EXAMPLE E4.13

The density of liquid benzene is $\rho = 899 \text{ kg/m}^3$ and its refraction index $n = 1.50$. Determine the benzene electron polarizability α_{el} .

Solution: The Lorentz–Lorentz formula (4.2.30) can serve us in solving this problem. Using it, we can solve it relative to α_{el}

$$\alpha_{\text{el}} = \frac{3M(n^2 - 1)}{\rho N_A (n^2 + 2)}.$$

In this equation all the entries are known except for mole mass M . Since the atomic composition of benzene is C_6H_6 , the benzene relative mole mass is 78. Therefore, the molar mass is $M = 78 \times 10^{-3} \text{ kg/mol}$. Substituting all the values, we arrive at $\alpha_{\text{el}} = 1.27 \times 10^{-28} \text{ m}^3$.

4.2.8 An experimental determination of the polarization and molecular electric dipole moments

Experimental determination of microscopic characteristics is based on the Debye–Langevin (eq. (4.2.28)) and Lorentz–Lorentz (eq. (4.2.30)) equations. They connect macroscopic molecular characteristics, measured directly in physical experiment, with microscopic ones. Measuring dielectric permeability ε in an electrostatic field, the molar polarization Π can be found:

$$\Pi = \frac{1}{3} (\alpha_{\text{el}} + \alpha_{\text{at}} + \alpha_{\text{or}}) N_A,$$

from which the total polarizability of a molecule can be obtained

$$\alpha = 3 \frac{\Pi}{N_A}$$

or

$$\alpha = 3 \frac{M}{\rho N_A} \frac{\varepsilon - 1}{\varepsilon + 2}. \quad (4.2.31)$$

Measurements of a refraction index n in an optical range of frequencies allows us to find the molar refraction R , and consequently, the molecule electron polarizability using eq. (4.2.30) ($R = \alpha_{\text{el}} N_A / 3$) or

$$\alpha_{\text{el}} = 3 \frac{M}{\rho N_A} \frac{n^2 - 1}{n^2 + 2}. \quad (4.2.32)$$

The difference between α and α_{el} gives the sum:

$$\alpha_{\text{el}} + \alpha_{\text{or}} = \alpha - \alpha_{\text{el}} = 3 \frac{\Pi - R}{N_A}. \quad (4.2.33)$$

There are two ways of separating atomic and orientation polarizabilities: either taking advantage of the frequency dependence of the polarizability or using the temperature dependence of the molar polarization Π ($\Pi_{\text{or}} \sim 1/T$). In the latter case the temperature dependence of molar polarization is removed and a graph $\Pi(1/T)$ (Figure 4.30) is drawn. The segment under the horizontal dashed line gives that part of the molar polarization which does not depend on temperature

$$\Pi_{\text{el}} + \Pi_{\text{at}} = \frac{1}{3} (\alpha_{\text{el}} + \alpha_{\text{at}}) N_A. \quad (4.2.34)$$

The value α_{el} can be determined by refractometric experiments (4.2.33) and α_{at} can be found according to formula (4.2.34)

$$\alpha_{\text{at}} = 3 \frac{\Pi_{\text{el}} + \Pi_{\text{at}}}{N_A} - \alpha_{\text{el}}. \quad (4.2.35)$$

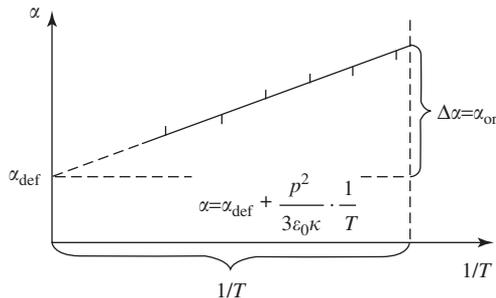


Figure 4.30 A relationship of a molar dielectric polarization versus reciprocal temperature.

The orientation polarization α_{op} , corresponding to a given temperature, can also be found from the graph: the angle coefficient $\tan \gamma$ is determined by α_{op} . Indeed,

$$\tan \gamma = \frac{\Delta \Pi}{\Delta(1/T)} = \frac{\Pi_{or}}{1/T} = \frac{1}{3} \alpha_{or} N_A T,$$

from which the orientation polarizability can be found

$$\alpha_{or} = \frac{3}{N_A T} \tan \gamma. \quad (4.2.36)$$

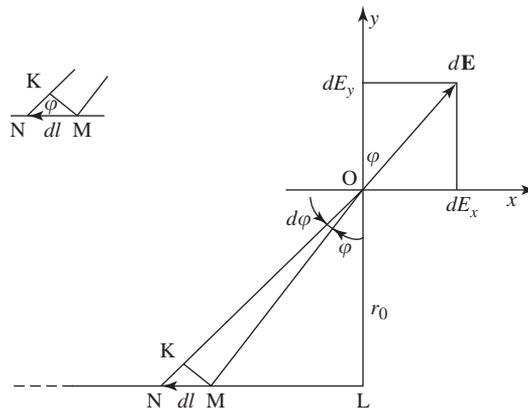
The $\tan \gamma$ value is determined by expression $\Delta \Pi / \Delta(1/T) \text{ m}^3 \text{ C/mol}$. Therefore, the slope has the same dimension. Note that α_{op} decreases with decrease in temperature. Knowing α_{or} , we can determine the molecular dipole moment. According to eq. (4.2.19), $p^2 = 3\epsilon_0 \kappa T \alpha_{or}$; substituting further α_{op} according to eq. (4.2.36), we can obtain $p^2 = (9/N_A) \epsilon_0 \kappa \tan \gamma$, from which

$$p = 3 \left(\frac{\epsilon_0}{N_A} \tan \gamma \right)^{1/2}. \quad (4.2.37)$$

We would like to underline once more that dielcometry is a relatively simple though rather powerful, method of chemical structure investigation.

EXAMPLE E4.14.

Thin semi-infinite rod is charged uniformly with linear density $\tau = 1 \mu\text{C/m}$. At a distance $r_0 = 20 \text{ cm}$ from the end of the rod perpendicular to it a point O is located (Figure E4.15). Calculate the electric field strength created by the charged rod in point O.



Solution: Allocate a piece of the rod with a charge $dQ = \tau dl$ in an arbitrary point of the rod. This charge create a field in the point O $dE = \frac{(1\tau dl / 4\pi\epsilon_0)}{r^2}$, r being the distance MO from the elementary charge to the point mentioned. Denoting angles MOL and, consequently MON , as φ we have $r = r_0/\cos \varphi$ and $dl = r d\varphi/\cos^2\varphi$.

Substitute these equations into formula for E , we can obtain $|d\mathbf{E}| = \frac{\tau}{4\pi\epsilon_0 r_0} d\varphi$.

Decompose the vector $|d\mathbf{E}|$ into two components: $dE_y = dE \cos\varphi$ and $dE_x = dE \sin\varphi$. Proceeding further, we can find $dE_y = (\tau \cos\varphi / 4\pi\epsilon_0 r_0) d\varphi$ and $dE_x = (\tau \sin\varphi / 4\pi\epsilon_0 r_0) d\varphi$. Integration over the limits $\varphi_1 = 0$ and $\varphi_2 = \pi/2$ (both ends of the semi-infinite rod) gives

$$E_y = \int_0^{\pi/2} \frac{\tau \cos\varphi}{4\pi\epsilon_0 r_0} d\varphi = \frac{\tau}{4\pi\epsilon_0 r_0} \quad \text{and} \quad E_x = \int_0^{\pi/2} \frac{\tau \sin\varphi}{4\pi\epsilon_0 r_0} d\varphi = \frac{\tau}{4\pi\epsilon_0 r_0}.$$

After summing these two vector components, we arrive at the final value $E = \frac{\sqrt{2}\tau}{4\pi\epsilon_0 r_0}$.

Substituting the numerical values we obtain $E = \frac{10^{-6} \times 9 \times 10^9 \times \sqrt{2}}{20 \times 10^{-2}} = 7.05 \text{ kV/m}$

(keeping in mind that numerically $\frac{1}{4\pi\epsilon_0} = 9 \times 10^9$).

PROBLEMS/TASKS

- 4.1. There are two similar small balls of mass 1 g each. Find the electric charge q which should be given to the balls in order to compensate for the force of their mutual Newtonian attraction.
- 4.2. In the semiclassical theory of the hydrogen atom, an electron is supposed to travel around a proton along a circular orbit. Determine its speed v if the orbit radius is $r = 53 \text{ pm}$ and the frequency of the electron's revolution.
- 4.3. In vertexes of an ideal hexagon with a side length $a = 10 \text{ cm}$, charges $Q, 2Q, 3Q, 4Q, 5Q$ and $6Q$ ($Q = 0.1 \mu\text{C}$) are situated. Find the force F , which acts on a point charge Q placed in the center of the hexagon.
- 4.4. A thin rod of $l = 10 \text{ cm}$ in length is uniformly charged with $\tau = 10^3 \text{ nC/m}$. On an extension of it at $a = 20 \text{ cm}$ from its end, a point charge $Q = 100 \text{ nC}$ is placed. Determine the interaction force between the rod and the charge.
- 4.5. A thin ring of $R = 10 \text{ cm}$ radius carries a uniformly distributed charge $Q = 10^2 \text{ nC}$. On a plane perpendicular to the ring, just over its center, is a point charge $Q_1 = 10 \text{ nC}$ at heights of (1) $l_1 = 20 \text{ m}$ and (2) $l_2 = 2 \text{ m}$. Determine the interaction force of the ring and the point charge.

- 4.6. There are two coaxial cylinders made of thin metal foil of radius R and $2R$. They carry uniformly distributed charges with density σ and $-\sigma$ ($\sigma = 60 \text{ nC/m}^2$). (1) Using the Gauss theorem find the electric field distribution inside both cylinders and between them (areas I and II) and outside them (area III). (2) Calculate the field strength at the point $E(3R)$. Draw a graph $E(r)$ in all areas and calculate the characteristic (border) values.
- 4.7. There are two concentric sphere made of thin metal foil of radius R and $2R$. They carry uniformly distributed charges -2σ and σ ($\sigma = 0.1 \text{ } \mu\text{C/m}^2$). Using the Gauss theorem find the electric field distribution inside both cylinders (areas I and II) and outside them (area III). Calculate the field strength at the point $E(3R)$. Draw a graph $E(r)$ in all areas and calculate the characteristic values.
- 4.8. In an area extending between two half-circled rings of radii R and $2R$ ($R = 10 \text{ cm}$), a charge $Q = 20 \text{ nC}$ is uniformly distributed. Find in the central point O (the center of the rings) the field $E(O)$.
- 4.9. An infinite thin wire is charged with a linear density $\tau = 0.2 \text{ } \mu\text{C/m}$. The wire is bent at right angle. Determine point A is denoted on a continuation of one of the wire side at a distance $r_o = 15 \text{ cm}$ from the corner. Determine at this point the field E.
- 4.10. An electric dipole $p = 0.4 \text{ } \mu\text{C m}$ is in a uniform electric field of strength $E = 25 \text{ kV/m}$ at an angle $\alpha_1 = \pi/6$. Find the work of external forces at dipole reorientation ($\alpha_2 = 7\pi/6$).
- 4.11. An electric dipole $p = 200 \text{ nC m}$ is in a uniform electric field of strength $E = 50 \text{ kV/m}$ at an angle $\alpha = \pi/3$. Find the change of its potential energy ΔU at its rotation anticlockwise at the angle $\beta = 2\pi/3$.
- 4.12. An electric dipole $p = 0.2 \text{ } \mu\text{C m}$ is in a nonuniform electric field with $dE/dx = -10 \text{ kV/m}^2$ oriented against the electric field E and electric field gradient. Find the force direction and calculate its F_x value.
- 4.13. Two HCl molecules with the same orientation of their electric dipole moments $p = 1.91 \text{ D}$ in value are at a distance $r = 5 \text{ nm}$ from each other. Considering the molecules as point ones, determine the potential U energy of their interaction.
- 4.14. Two polar molecules SO_2 ($p = 1.60 \text{ D}$) are at a distance $r = 8 \text{ nm}$ from each other. Considering them as a point dipole, determine the force of their interaction.
- 4.15. Argon is under normal conditions in an electric filed $E = 30 \text{ kV/m}$. Determine the shoulder l of the induced dipole moment of an Ar atom if the dielectric permeability at the same state is 1.000554.
- 4.16. The dielectric susceptibility κ of the gas Ar under normal conditions is 5.54×10^{-4} . Find the dielectric permeabilities ϵ_1 and ϵ_2 of liquid ($\rho_1 = 1.40 \text{ g/cm}^3$) and solid ($\rho_2 = 1.65 \text{ g/cm}^3$) argon.
- 4.17. What minimum velocity v_{\min} should a proton possess in order to reach the surface of a metallic sphere charged up to 400 V ?
- 4.18. From point 1 on the surface of an infinite negatively charged cylinder ($\tau = 20 \text{ nC/m}$) of radius R , an electron starts with zero velocity. Find the electron kinetic energy K at point 2 which is at a distance of $9R$ from the cylinder surface.
- 4.19. Knowing the electric dipole moment p_1 of a chlorobenzene (phenyl chloride) molecule ($\text{C}_6\text{H}_5\text{Cl}$) ($p_1 = 1.59 \text{ D}$), find the dipole moment of ortho-dichlorobenzene (ortho-di-phenyl chloride) p_2 .

- 4.20. A xenon atom (the polarizability of which is $\alpha = 5.2 \times 10^{-29} \text{ m}^3$) is at a distance $r = 1 \text{ nm}$ from a proton. Determine the xenon atom's induced electric moment p .

ANSWERS

4.1. $Q = 2m\sqrt{\pi\epsilon_0 G} = 86.7 \times 10^{-15} \text{ C}$ (G is a gravitational constant).

4.2. $v = \frac{|e|}{\sqrt{4\pi\epsilon_0 mr}} = 2.19 \times 10^6 \text{ m/sec}$; $n = v/(2\pi r) = 6.58 \times 10^{15} \text{ sec}^{-1}$.

4.3. $F = \frac{6Q^2}{4\pi\epsilon_0 a^2} = 54 \text{ mN}$.

4.4. $F = \frac{Q\tau\ell}{4\pi\epsilon_0(\ell+a)a} = 1.5 \text{ mN}$.

4.5. (1) $F_1 = \frac{QQ_1\ell_1}{4\pi\epsilon_0(R^2 + \ell_1^2)^{3/2}} = 15.7 \text{ kN}$; (2) $F_2 = \frac{QQ_1}{4\pi\epsilon_0\ell_2^2} = 2.25 \text{ }\mu\text{N}$.

4.6. (1) $E_I = 0$ ($r < R$); $E_{II}(r) = \frac{\sigma R}{\epsilon_0 r}$ ($R \leq r < 2R$); $E_{III}(r) = -\frac{\sigma R}{\epsilon_0 r}$ ($r \geq 2R$).

(2) $E_A = -\frac{\sigma}{3\epsilon_0} = -2.26 \text{ KV/m}$.

4.7. (1) $E_I = 0$ ($r < R$); $E_{II}(r) = \frac{2\sigma R^2}{\epsilon_0 r^2}$ ($R \leq r < 2R$); $E_{III}(r) = \frac{2\sigma R^2}{\epsilon_0 r^2}$ ($r \geq 2R$).

(2) $E_A = \frac{2\sigma}{9\epsilon_0} = 2.51 \text{ kV/m}$.

4.8. $E = \frac{Q \ln 2}{3\pi^2 \epsilon_0 R^2} = 5.29 \text{ kV/m}$.

4.9. $E = \frac{\sqrt{5}\tau}{4\pi\epsilon_0 r_0} = 26.8 \text{ kV/m}$.

$$4.10. A_{12} = 2pE \cos \alpha = 17.3 \text{ mJ.}$$

$$4.11. \Delta U = pE[\cos \alpha - \cos(\alpha + \beta)] = 15 \text{ mJ.}$$

$$4.12. F_x = p(dE/dx)\cos \alpha = 2 \text{ mN.}$$

$$4.13. U = -\frac{p^2}{2\pi\epsilon_0 r^3} = -5.82 \times 10^{-24} \text{ J } (-36.4 \mu\text{eV}).$$

$$4.14. F = -\frac{3p^2}{2\pi\epsilon_0 r^4} = -3.74 \times 10^{-16} \text{ N.}$$

$$4.15. \ell = \frac{(\epsilon - 1)\epsilon_0 E}{n_{\text{norm}} |e| Z} = 1.9 \times 10^{-18} \text{ m.}$$

$$4.16. \epsilon = \frac{3M - 2\kappa\rho Vom}{3M - \kappa\rho Vom}; \epsilon_1 = 1.51; \epsilon_2 = 1.61.$$

$$4.17. v_{\text{min}} = \sqrt{\frac{3|e|\varphi}{2m}} = 0.24 \times 10^6 \text{ m/sec.}$$

$$4.18. K = \frac{|e|\tau}{2\pi\epsilon_0} \ln 10 = 828 \text{ eV.}$$

$$4.19. p_2 = 2p_1 \cos \frac{\pi}{6}.$$

$$4.20. p = 6.6 \times 10^{-31} \text{ C/m.}$$