Appendix 1

System of Units Used in the Book

Units of physical properties measurements, based on the International System of units (SI) are described below. According to this system the basic units in mechanics are: meter (m), second (sec), kilogram (kg); an additional unit is the radian—a unit of measurement of a flat angle (rad) and that of a solid angle steradian (sr). All other units of the SI system are derived and can be obtained with the help of corresponding transformations:

Area unit—square meter (area of a square with a 1 m side)

$$[S] = 1\,\mathrm{m}^2.$$

–Volume unit—cubic meter (volume of a cube with a 1 m side)

$$[V] = 1\,\mathrm{m}^3.$$

–Velocity unit—meter per second (velocity of uniform straight line motion; 1 m per 1 sec)

$$[\upsilon] = 1\,\mathrm{m/sec}.$$

–Acceleration unit—meter per square second (acceleration when the uniform straight line motion velocity change is 1 m/sec)

$$[a] = 1\,\mathrm{m/sec}^2.$$

–Frequency unit—second to the power of minus one (at revolution) and hertz (Hz) (unit of oscillation frequency; the frequency when a single periodic process is accomplished in 1 sec)

$$[v] = 1\,\mathrm{sec}^{-1}.$$

–Angular velocity unit—1 radian per second (angular velocity when a uniform rotating body turns by 1 rad in 1 sec)

$$[\omega] = 1\ \text{rad/sec}.$$

–Angular acceleration unit—1 radian per 1 sec in the second power (angular acceleration when angular velocity changes by 1 rad/sec in 1 sec)

$$[\varepsilon] = 1\ \text{rad/sec}^2.$$

–Force unit—newton (N) (the amount of force required to give a 1 kg mass body an acceleration of 1 m/sec^2)

$$[F] = 1\ \text{N} = 1\ \text{kg m/sec}^2.$$

–Density unit—kilogram per cubic meter (the density of a uniform substance whose mass per 1 m^3 is equal to 1 kg)

$$[\rho] = 1\ \text{kg/m}^3.$$

–Pressure unit—pascal (Pa) (pressure produced by a force of 1 N acting on an area of 1 m^2)

$$[P] = 1\ \text{Pa} = 1\ \text{N/m}^2.$$

–Momentum unit—kg m/sec (a body of mass 1 kg moving translational with a velocity of 1 m/sec)

$$[p] = 1\ \text{kg m/sec}.$$

–Force impulse—newton × second (a force impulse produced by a force of 1 N for 1 sec)

$$[F \cdot t] = 1\ \text{N sec}.$$

–Work (energy) unit—joule (J) (the amount of work done when an applied force of 1 N moves in the direction of the force through a distance of 1 m)

$$[A] = 1\ \text{J} = 1\ \text{N m}.$$

–Power unit—watt (W) (a watt is used to measure power or the rate of doing work; 1 W is a power of 1 J per second).

$$[W] = 1\ \text{W(J/sec)}.$$

–Torque unit—newton × meter (moment of force produced by a force of 1 N relative to a point which is at distance of 1 m away from the force action line)

$$[M] = 1\,\mathrm{N\,m}.$$

–Moment of inertia unit—kilogram × square meter (moment of inertia of a material point 1 kg in mass relative to a rotation axis 1 m away)

$$[I] = 1\,\mathrm{kg\,m}^2.$$

–Angular momentum unit—kilogram × square meter per second (angular momentum of a body with a moment of inertia in 1 kg m^2 rotated with angular velocity 1 rad/sec)

$$[L] = 1\,\mathrm{kg\,m}^2/\mathrm{sec}.$$

In addition to the units presented above in molecular physics following units are also used. Unit of heat energy or heat—calorie; 1 cal = 4.1868 J

$$[Q] = 1\,\mathrm{cal}.$$

Heat capacity unit—calorie per kelvin (amount of heat to warm a body by 1 K)

$$[C] = 1\,\mathrm{cal/K}.$$

–Specific heat capacity unit—calorie per kilogram × kelvin (amount of heat to warm 1 kg of a substance by 1 K)

$$[C_{\mathrm{sp}}] = 1\,\mathrm{cal/kg\,K}.$$

Mole heat capacity unit—calorie per mole × kelvin (amount of heat to warm one mole of substance by 1 K)

$$[C_{\mathrm{mole}}] = 1\,\mathrm{cal/mole\,K}.$$

In addition to the mechanical units of measurements, *in the sections describing electricity and magnetism*, one basic unit—the ampere (A) and a number of derivative units are used. In the SI system 1 A is defined as the force of that current which produces a specific force between two parallel infinitely long conductors which are 1 m apart, in 2×10^{-7} H/m.

Charge unit—coulomb (C) (the charge that runs through a cross-section of a conductor when a current of 1 ampere is flowing)

$$[q] = 1\ \mathrm{A} \times 1\ \mathrm{sec}\ (\mathrm{Asec})$$

(then an electric current I in 1 A corresponds to 1 coulomb transfer in 1 sec)

$$[I] = \frac{1\ \mathrm{C}}{1\ \mathrm{sec}} \quad (\mathrm{A}).$$

–Current density unit—ampere per square meter (electric current of 1 A per 1 m^2 of cross-section of a conductor)

$$[j] = \frac{1\ \mathrm{A}}{1\ \mathrm{m}^2} \quad (\mathrm{A/m}^2).$$

–Electric field strength unit—volt/meter (electric field strength, acting on a point charge 1 C with a force 1 N)

$$[E] = \frac{1\ \mathrm{N}}{1\ \mathrm{C}} = \frac{1\ \mathrm{V}}{1\ \mathrm{m}} \quad (\mathrm{kg\,m/A\,sec}^3).$$

–Electric displacement (induction) unit—coulomb/meter^2 (electric field strength multiplied by $\varepsilon\varepsilon_0$)

$$[D] = \varepsilon\varepsilon_0 E (\mathrm{A\,sec/m}^2).$$

–Electric field potential unit—volt (V) (electric field potential in which the charge of 1 C possesses potential energy 1 J)

$$[\varphi] = 1\ \mathrm{J}/1\ \mathrm{C}\ (\mathrm{kg\,m}^2/\mathrm{A\,sec}^3).$$

–Electric dipole moment unit—coulomb × meter (dipole electric moment of a pair of opposite charges equal in value and being 1 m apart)

$$[p] = 1\ \mathrm{C} \times 1\ \mathrm{m}\,(\mathrm{A\ sec\ m}).$$

–Electric quadrupole moment—coulomb × meter^2 (quadrupole electric moment of a system of two pairs of opposite charge equal in value of 1 C displaced alternately in square corners at side length 1 m)

$$[Q] = 1\ \mathrm{C} \times 1\ \mathrm{m}^2\,(\mathrm{A\ sec\ m}^2).$$

Eelectric linear density unit—coulomb/meter (charge of 1 C uniformly distributed along a line of 1 m)

$$[\tau] = 1\,\mathrm{C}/1\,\mathrm{m}\,(\mathrm{A\,sec/m}).$$

Electric surface charge density unit—coulomb/meter^2 (charge of 1 C, uniformly distributed over an area of 1 m^2)

$$[\sigma] = \frac{1\,\mathrm{C}}{1\,\mathrm{m}^2} \quad (\mathrm{A\,sec/m^2}).$$

Electric volume charge density unit—coulomb/meter^3 (charge, uniformly distributed in a volume of 1 m^3)

$$[\rho] = \frac{1\,\mathrm{C}}{1\,\mathrm{m}^3} \quad (\mathrm{A\,sec/m^3}).$$

–Dielectric polarization unit—coulomb/meter^2 (a dielectric's volumetric dipole moment)

$$[\Re] = \frac{1\,\mathrm{C}}{1\,\mathrm{m}^2} \quad (\mathrm{A\,sec/m^2}).$$

Dielectric susceptibility unit—dimensionless (polarization of isotropic dielectric in a unit field strength divided by ε_0)

$$[\chi].$$

Dielectric permeability unit—dimensionless (a value indicating by how much an averaged macroscopic field in a dielectric is less than an external field)

$$[\varepsilon] = \frac{E_0}{E}.$$

Polarization of a molecule unit—meter^3 (a molecular dipole moment in a field of a unit strength divided by ε_0)

$$[\alpha] = \frac{p}{\varepsilon_0 \times E} \quad (\mathrm{m^3}).$$

Electronic capacitance unit—farad (F) (capacitance of conductor, which is charged to potential 1 V receiving a charge of 1 C)

$$[C] = \frac{1\,\mathrm{C}}{1\,\mathrm{V}} \quad (\mathrm{A^2\,sec^4/(kg\,m^2)});$$

–Magnetic moment unit—ampere × meter^2 (electric current of 1 A flowing around an area of 1 m^2)

$$[\mathcal{M}] = 1\ \mathrm{A} \times 1\ \mathrm{m}^2 (\mathrm{A\,m}^2).$$

–Off-system unit—Bohr magneton μ_6 (1 $\mu_6 = 0.927 \times 10^{-23}$ A m^2).

Magnetic field induction unit—tesla (T) (maximal magnetic force moment, acting on a unit magnetic moment)

$$[B] = \frac{1\ \mathrm{N}}{1\ \mathrm{A\,m}^2} \quad (\mathrm{kg/(A\,sec^2)}).$$

Strength of magnetic field unit—ampere/meter (magnetic field induction, divided by $\mu_0\mu$)

$$[H] = \frac{1\ \mathrm{A}}{\mathrm{m}} \quad (\mathrm{A/m}).$$

Magnetization unit—amper/meter (moment of an unit volume moment)

$$[\mathfrak{I}] = \frac{1\ \mathrm{A}}{1\ \mathrm{m}} = (\mathrm{A/m}).$$

Magnetic susceptibility unit—dimensionless (magnetization of an unit volume of a magnetic in an unit strength field)

$$[\chi].$$

–Specific magnetic susceptibility unit—meter^3/kilogram (magnetization of a unit mass of a magnetic in a field of unit strength)

$$[\chi_{sp}] = \frac{\chi}{\rho} \quad (\mathrm{m^3/kg}).$$

Mole magnetic susceptibility unit—meter^3/mole (magnetization of one mole of magnetics in a field of unit strength)

$$[\chi_{\mathrm{M}}] = \frac{M \times \chi}{\rho} \quad (\mathrm{m^3/mole}).$$

Magnetic permeability unit—dimensionless (shows how many times greater is the magnetic field than an external magnetic field)

$$[\mu] = \frac{B}{B_0}.$$

Magnetic flux unit—weber (Wb) (a magnetic field induction flux in 1 T through the surface of unit area)

$$[\Phi] = 1\,\mathrm{T} \times 1\,\mathrm{m}^2 = 1\,\mathrm{Wb}; \quad (\mathrm{kg\,m}^2/(\mathrm{A\,sec}^2)).$$

Inductance unit—henry (H) (inductance of a conductor in which at a current of 1 A appears a total magnetic leakage of 1 Wb)

$$[L] = 1\,\mathrm{Wb/1\,A}; \quad (\mathrm{kg\,m}^2/(\mathrm{A}^2\,\mathrm{sec}^2)).$$

Some important physical constants:

Acceleration of free falling	g = 9.81 m/sec^2
Gravitational constant	G = 6.67 × 10^{-11} m^3/(kg/sec^2)
Avogadro constant	N_A = 6.02 × 10^{23} mol^{-1}
Mole gas constant	R = 8.31 J/(K mol)
Molar volume at normal conditions	V_m = 22.4 × 10^{-3} m^3/mol
Boltzmann constant	κ = 1.38 × 10^{23} J/K
Elementar charge	$\lvert e\rvert$ = 1.60 × 10^{19} C
Electron mass	m_e = 9.11 × 10^{-31} kg
Specific electron charge	(e/m) = 1.76 × 10^{11} C/kg
Light velocity in vacuum	c = 3.00 × 10^8 m/sec
Stefan–Boltzmann constant	σ = 5.67 × 10^{-8} W/m^2 K^4
Win shift constant	C = 2.90 × 10^{-3} m K
Planck's constant	h = 6.63 × 10^{-34} J sec; $\hbar = h/2\pi$ = 1.05 × 10^{-34} J sec
Rydberg constant	R = 1.097 × 10^7 m^{-1}
First Bohr orbit radius	a = 5.29 × 10^{-11} m
Compton wavelength	λ_C = 2.43 × 10^{-12} m
Bohr magneton	μ_B = 9.27 × 10^{-24} J/T
Ionization energy of hydrogen atom	E_i = 2.16 × 10^{-18}; J = 13.56 eV
Atomic unit of mass	1 a.u.m = 1.66 × 10^{-27} kg
Nuclear magneton	μ_N = 5.05 × 10^{-27} J/T
Electric constant	ε_0 = 0.885 × 10^{-11} F/m
Magnetic constant	μ_0 = 1.26 × 10^{-6} H/m

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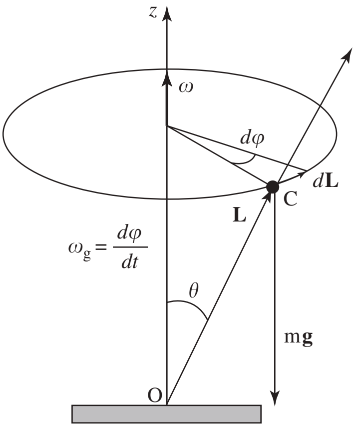
Appendix 2

Gyroscope Precession in a Gravity Field

A symmetric body with a single motionless point and able to rotate at high angular velocity ω around an axis z' passing through this motionless point is called a gyroscope. There are two types: balanced (the motionless point coincides with the center of inertia) and unbalanced (where this condition is not fulfilled). A child's spinning top is a primitive example of an unbalanced gyroscope.

Figure A2.1 shows an unbalanced gyroscope acquiring a rotation (precession) in a gravitational field. The pivot point O is a unique motionless point and the axis of rotation z′ passes through it. The gravity force is directed vertically downwards along axis z. The angle between axes z and z' is denoted by θ and is assumed to be small. In the figure, for simplicity, the angular momentum vector **L** terminates in the center of mass C, the distance OC being l_C. According to the basic equation of rotational motion dynamics, we can write $d\mathbf{L} = M dt$ (refer to (1.3.57)). The force momentum (torque) of the gravitational force relative to point C is $M = mgl_C \sin\theta$.



The rotation of the gyroscope's axis z' relative to the vertical axis z is referred to as gyroscope precession. Under the action of the gravity force momentum the vector of the angular momentum **L** of the unbalanced gyroscope obtains an increment $d\mathbf{L}$ directed along the vector **M** (see (1.3.57) and Figure 1.19). Since $d\mathbf{L}$ is perpendicular to **L** the modulus of **L** is constant and only precession takes place. The gyroscope precession angular velocity ω_g, as seen in Figure A 2.1, can be found as

$$\omega_\mathrm{g} = \frac{d\varphi}{dt} = \frac{mg\ell_C \sin\theta}{I\omega_{z'} \sin\theta} = \frac{mg\ell_\mathrm{C}}{I\omega_{z'}}. \tag{A2.1}$$

Note that the angle θ is small and I and ω regarding both axes, z and z', are approximately same. It can be seen that the precession angular velocity ω_g is higher, the lower the gyroscope's moment of inertia I and angular velocity $\omega_{z'}$; ω_g does not depend on the angle θ between axis z and z'.

Anyone can conduct an experiment using a child's spinning top.

Appendix 3

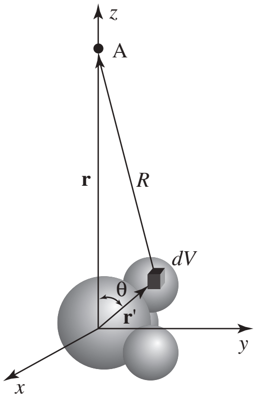
An Electrostatic Field of an Arbitrary Distributed Charge

Among the real problems the chemist can come across in practice, a simple situation with a discrete set of point charges is rarely seen. Any molecule consists of positively charged nuclei encircled by negative electrons, each particle being vibrated around positions of equilibrium. Therefore, the overall charge distribution is described in this case by the distribution function $\rho(r)$:

$$dq = \rho(\mathbf{r})dV. \tag{A3.1}$$

The charge density distribution $\rho(\mathbf{r})$ is of great importance because it permits the calculation of a wide number of molecular and crystal properties and enable us to follow the paths of chemical reactions.

Consider a field created by the electric charge system described by the function $\rho(\mathbf{r})$ (refer to Figure A3.1). Our task is to calculate the electrostatic field created by this system in a certain point A. Direct an axis z of the Cartesian coordinate system in such a way that



it crosses point A. The electrostatic potential in point A is the superposition of contributions from all elements *dq*.

$$\varphi(r) = \int_V \frac{\rho(r')dV'}{R} = \int_V \frac{\rho(r')dV'}{|r - r'|}, \tag{A3.2}$$

where r is the z component of the radius-vector of point A, r' is the argument of the function $\rho(r')$, $|\mathbf{R}| = |\mathbf{r}-\mathbf{r}'|$ is the distance from the element dV to point A. The integration is over the coordinate $\mathbf{r}'$ over the whole charge containing space. Denoting the angle between vectors $\mathbf{r}$ and $\mathbf{r}'$ as θ and using the cosine theorem; we obtain $R = (r^2 + r'^2 - 2rr' \cos\theta)^{1/2}$. Then the integral can be rewritten as $\varphi_\mathrm{A} = \int\rho(\mathrm{r}')dV'(r^2+r'^2 - 2rr' \cos\theta)^{-1/2}$. If we calculate the field far from the origin (i.e., $r' \ll r$) the expression

$$\frac{1}{R} = \frac{1}{(r^2 + r'^2 - 2rr'\cos\theta)^{1/2}} = \frac{1}{r}\left[1 + \left(\frac{r'^2}{r^2} - 2\frac{r'}{r}\cos\theta\right)\right]^{-\frac{1}{2}}$$

can be decomposed into a series and can be expanded over the r' orders

$$(1+\beta)^{-1/2} = 1 - \frac{1}{2}\beta + \frac{3}{8}\beta^2 + \cdots,$$

where

$$\beta = \left[\left(\frac{r'}{r}\right)^2 - 2\frac{r'}{r}\cos\theta\right].$$

Summing up all the terms with the same order of r'/r and neglecting the terms of higher orders than quadratic, we obtain the expression

$$\frac{1}{R} = \frac{1}{r}\left[1 + \frac{r'}{r}\cos\theta + \left(\frac{r'}{r}\right)^2 \times \frac{1}{2}(3\cos^2\theta - 1)\right].$$

Introducing this expression into eq. (A3.2) and taking into account that integration is accomplished over r', we can obtain for φ_A the sum

$$\begin{aligned}\varphi_A = {} & \frac{1}{r}\int \rho(r')dV' + \frac{1}{r^2}\int r'\cos\theta\rho(r')dV' \\ & + \frac{1}{r^3}\int r'^2 \times \frac{1}{2}(3\cos^2\theta - 1)dV'.\end{aligned} \tag{A3.3}$$

The magnitude of each of these integrals depends only on the properties of the electron density function $\rho(\mathbf{r}')$. Being calculated for the given system they can be expressed as numbers k_0, k_1 and k_2 correspondingly. The dependence of φ_A on $|\mathbf{r}|$ will be expressed by the sum

$$\varphi_A = \frac{k_0}{r} + \frac{k_1}{r^2} + \frac{k_2}{r^3}. \tag{A3.4}$$

The k_n are referred to as the electric moments of the system.

Let us analyze each term of this sum. The k_0 value is expressed by an integral

$$k_0 = \int \rho(r')dV'. \tag{A3.5}$$

and is the total charge of the system concentrated in origin. It is referred to as a monopole moment or simply a monopole. For a neutral system $k_0 = 0$.

The coefficients k_1 and k_2, unlike k_0, depend on charge distribution. The coefficient k_1 characterizes an electric dipole moment

$$k_1 = \int r' \cos\theta \, \rho(r')dV'. \tag{A3.6}$$

Since the value $r'\cos\theta$ is z-coordinate of element dV', this term characterizes the relative displacements of the positive and negative charges $\rho(r')dV'$ along this axis. Indeed, if one imagines a system consisting of two dissimilar charges q in points $(0,0,z)$ and $(0,0,-z)$ with $z = 1/(2l)$, then a value $r'\cos\theta = \pm(1\backslash 2)\ell$ can be factorized from the integral. The resultant expression $\int\rho(\mathrm{r}')dV'$ will be equal to q and the whole coefficient k_1, which is now equal to $lq = p$, composes the electric dipole moment oriented along the z-axis (see Section 4.1.5 and eq. (4.1.29)).

The coefficient k_2

$$k_2 = \int r'^2 \rho(r') \frac{1}{2}(3\cos^2\theta - 1)dV'. \tag{A3.7}$$

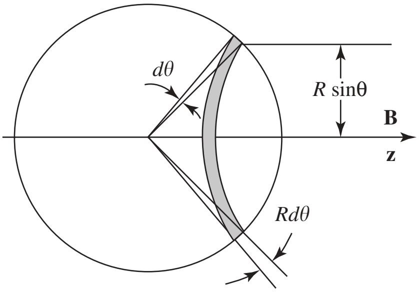
is a so-called *quadrupole moment.* Try to understand what electron density distribution is described by such a factor. For spherically symmetric electron distribution $k_2 = 0$. It follows from a specific type of k_2 factor: keeping in mind that $r'^2 = x^2 + y^2 + z^2$ for the specified symmetry all three coordinates are equivalent, therefore $x^2 + y^2 + z^2 = 3z^2$ and, consequently, $3z^2 - r'^2 = 0$. A flattened out electron density model is the charge q rotating around an z-axis at a level $z = 0$ at a distance r_0 from the axis. Then $\theta = \pi/2$ and the expression in brackets becomes negative. Since $r = \text{const.}$, then k_2 is equal to $-r_0^2 q$ for a positive charge and $+r_0^2 q$ for a negative charge. It is reasonable to assume that as for every “flattened out” distribution the quadrupole moment has such signs. It is easy to show that for the “extended” model distribution the signs will be the opposite.

Expression (A3.4) shows that in the electrostatic field created by a particular system, the electric potential falls differently with distance (refer to Table 8.1) the higher the order of the moment, the sharper the potential falling down. Even neutral systems (atoms, molecules) create an electric field by means of which these systems interact with each other. Accordingly, the higher the order of the moment, the lower the energy of interaction; for example, dipole–dipole interaction is appreciably weaker than the interaction of monopoles (Coulomb interaction). All this information is useful in Chapter 8.

Appendix 4

Langevin Theorem

Consider a system consisting of identical molecules weakly interacting with each other, characterized by a magnetic dipole moment $\mathcal{M}$. An external magnetic field **B** acts on the system trying to orient all magnetic moments along z axis contrary to chaotic thermal motion. Allocate in this system a spherical volume V of a radius R. Suppose that there are a large enough number of molecules in this volume with all possible orientations of magnetic moments. Among all N molecules in the volume V we shall denote as $dN(\theta)$ such molecules whose magnetic moments form an angle from θ up to $\theta + d\,\theta$ with a direction of vector **B** (Figure A4.1).



These $dN(\theta)$ molecules account for a physically infinitesimal elementary volume $dV(\theta)$. Then the concentration of such molecules is

$$n_\theta = \frac{dN}{dV}. \tag{A4.1}$$

An equilibrium distribution of noninteracting particles in an internal force field is described by the Boltzmann formula $n = C\exp(-U/\kappa T)$, where C is a normalizing coefficient. Since the potential energy of the dipoles in the external field is determined by a ratio (eq. (5.1.31)) ($U = -\mathcal{M}B\cos\theta$), the equilibrium distribution of dipoles upon potential energies (i.e., on various orientations of the magnetic moments) in field B can be written as:

$$n_\theta = C\exp\left(\frac{\mathcal{M}B}{\kappa T}\cos\theta\right). \tag{A4.2}$$

From the last two equations we can derive

$$dN(\theta) = C\exp\left(\frac{\mathcal{M}B}{\kappa T}\cos\theta\right)dV(\theta). \tag{A4.3}$$

Express an elementary volume $dV(\theta)$, occupied by a molecule the magnetic moment of which is directed at an angle θ, through the angles θ and $d\theta$. Since $\mathrm{d}V(\theta) = (V/4\pi)d\Omega$, where $d\Omega$ is an elementary solid angle obtained by two coaxial cones with a common vertex at point 0 and openings of 2θ and $2\theta + d\theta$, then from the solid angle definition (4.1.10) and Figure A4.1, it follows that

$$d\Omega = \frac{dS}{R^2} = \frac{2\pi(R\sin\theta)(R\,\mathrm{d}\theta)}{R^2} = 2\pi\sin\theta\,\mathrm{d}\theta.$$

Then $dV(\theta) = (1/2)\ V\sin\theta\, d\theta$ and (A4.3) could be rewritten as

$$dN = \frac{1}{2}CV\ \exp\left(\frac{\mathcal{M}B}{\kappa T}\cos\theta\right)\sin\theta\, d\theta. \tag{A4.4}$$

The constant C can be determined from the normalizing procedure: the integral from $dN(\theta)$ over all possible orientation of θ angles (from 0 to π) must equal the total number of molecules N in volume V, that is:

$$\int_0^\pi dN(\theta) = N. \tag{A4.5}$$

To simplify further calculations mark $(\mathcal{M}B/\kappa T)$ as a and $\cos\theta$ as x; then $\sin\theta\ \ d\theta = -dx$. This change brings about the change in limits in (A4.5): instead of the inferior limit there will be 1 ($\cos\theta = 1$), and the superior limit will be -1 ($\cos\pi = -1$). After such transformation and change of a sign before an integral one arrives at

$$\frac{1}{2}CV\int_{-1}^{1} \mathrm{e}^{ax}\, dx = N.$$

After these transformations we obtain

$$\frac{1}{2}CV\frac{\mathrm{e}^{a} - \mathrm{e}^{-a}}{a} = N,$$

hence

$$C = \frac{2aN}{(\mathrm{e}^{a} - \mathrm{e}^{-a})V} \quad \text{or} \quad C = \frac{2a}{(\mathrm{e}^{a} - \mathrm{e}^{-a})}n,$$

where $n = N/V$ is the total molecules concentration. Then $dN(\theta)$ can be rewritten as

$$d\mathrm{N}(\theta) = \frac{a}{\mathrm{e}^{a} - \mathrm{e}^{-a}} nV\mathrm{e}^{a\cos\theta} \sin\theta \, d\theta. \tag{A4.6}$$

These $dN(\theta)$ dipoles make a contribution of $d\mathfrak{J}(\theta)$ to the general magnetization $\mathfrak{J}$.

Taking into account the magnetization definition (5.2.3) $d\mathfrak{J}(\theta)$ we can obtain

$$d\mathfrak{J}(\theta) = \frac{\mathcal{M}\cos\theta \, dN(\theta)}{V}.$$

Changing in this expression $dN(\theta)$ according to (A4.4), we can obtain

$$d\mathfrak{J}(\theta) = \frac{an\mathcal{M}}{\mathrm{e}^{a} - \mathrm{e}^{-\mathrm{a}}} \mathrm{e}^{a\cos\theta} \cos\theta \sin\theta \, d\theta.$$

The total magnetization can be found by integration

$$\mathfrak{J} = \frac{an\mathcal{M}}{\mathrm{e}^{a} - \mathrm{e}^{-\mathrm{a}}} \int_{-1}^{1} x\mathrm{e}^{ax} \, dx. \tag{A4.7}$$

Integration by parts ($u = x$, $\mathrm{d}v = \mathrm{e}^{ax}\, dx$) can give

$$\int_{-1}^{+1} x\mathrm{e}^{ax} \, dx = x\frac{\mathrm{e}^{ax}}{a}\Bigg|_{-1}^{+1} - \frac{1}{a}\int_{-1}^{+1} \mathrm{e}^{ax} \, dx.$$

After this integration and substituting the limits:

$$\int_{-1}^{+1} x\mathrm{e}^{\mathrm{ax}} \, dx = \frac{\mathrm{e}^{a} + \mathrm{e}^{-a}}{a} - \frac{\mathrm{e}^{a} - \mathrm{e}^{-a}}{a^{2}}.$$

Magnetization $\mathfrak{J}$ can now be presented as

$$\mathfrak{J} = \frac{an\mathcal{M}}{e^{a} - e^{-a}}\left(\frac{e^{a} + e^{-a}}{a} - \frac{e^{a} - e^{-a}}{a^{2}}\right) \quad \text{or} \quad \mathfrak{J} = n\mathcal{M}\left(\frac{e^{a} + e^{-a}}{e^{a} - e^{-a}} - \frac{1}{a}\right).$$

The expression in brackets is referred to as the Langevin function $L(a)$. Thus

$$L = \frac{e^{a} + e^{-a}}{e^{a} - e^{-a}} - \frac{1}{a}. \tag{A4.8}$$

Using the function $L(a)$ we can finally write the magnetization $\mathfrak{J}$ as

$$\mathfrak{J} = n\mathcal{M}L(a) \tag{A4.9}$$

At limiting values of a ($\mathcal{M}B/\kappa T$), the L(a) function can be decomposed into the MacLoren series. At small a values we can have

$$L(a) = \frac{1}{3}a - \frac{1}{45}a^{3} + \frac{2}{945}a^{5} - .$$

This series is alternating-signed and therefore it diminishes rather quickly. If we limit ourselves to the first term, then $L(a) \approx (1/3)a$. The expression already given can be obtained

$$\mathfrak{J} = \frac{n\mathcal{M}^{2}}{3\kappa T}B.$$

The paramagnetic molar magnetic susceptibility at $(\mathcal{M}B/\kappa T) \ll 1$ is obtained

$$\chi_{\mathrm{M}} = \frac{\mu_0 N_{\mathrm{A}} \mathcal{M}^{2}}{3\kappa T}. \tag{A4.10}$$

This expression coincides with eq. (5.2.23) derived from the very simple suppositions. The volumetric and specific susceptibilities can be calculated according to the formulas given above (refer to Section 5.2.2).

Appendix 5

Maxwell Equations in Differential Form: Electromagnetic Wave Propagation in Vacuum

Vector algebra provides us with a good opportunity to write Maxwell equations in differential form, i.e., to characterize an electromagnetic field in a point. It allows us to see most clearly the physical sense of the equations and their importance for understanding the laws of electrodynamics.

Let us start with the equation of a Gauss law, which in the integral form looks like:

$$\oint_S \mathbf{D}d\mathbf{S} = \int_V \rho(r)dV. \tag{A5.1}$$

Remember that in differential form, the divergence of a vector **D** in a point **r** is the limit to which the left-hand side of this equation tends under a contraction *S* (and *V*) to a point:

$$\lim_{\Delta V \to 0} \frac{1}{\Delta V} \oint DdS = \operatorname{div} D(r). \tag{A5.2}$$

The symbol div means the sum of first particular derivatives. Therefore,

$$\operatorname{div} D(r) = \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right) D(xyz) = \nabla D(r).$$

Here an operator **∇** is introduced, well known in mathematics

$$\nabla = \mathbf{i}\left(\frac{\partial}{\partial x}\right) + \mathbf{j}\left(\frac{\partial}{\partial y}\right) + \mathbf{k}\left(\frac{\partial}{\partial z}\right).$$

Correspondingly, div$D(r)$ is the scalar product of an operator **∇** and a vector **D**(**r**). In fact, the divergence is the flow of **D** vector “outflows” from a point **r**. Integrating the divergence over the whole volume V, we arrive at the total power of the source, i.e., the flow through the closed surface S comprising the volume V.

$$\int_V \operatorname{div} D(r)dV = \oint_S DdS.$$

This equation is referred in mathematics as the Ostrogradski theorem, from which an important expression originates:

$$\operatorname{div} \mathbf{D}(r) = \rho(\mathbf{r}). \tag{A5.3}$$

The divergence of a vector of an electric displacement in a point **r** *(x, y, z) is equal to the density of an electric charge (that is the source power of the electrostatic field) in this point.* This is the Causs theorem in differential form. It follows that the force lines of an electrostatic field proceed from a positive electric charge (a source), come to an end in a negative electric point charge (a drain) or go to infinity; at the drain divergency has a negative sign.

Previous consideration (see Chapter 5) shows that there are no magnetic charges in nature, therefore one can write

$$\operatorname{div} \mathbf{B}(\mathbf{r}) = 0, \tag{A.5.4}$$

This expression is also a Maxwell equation. Hence, the magnetic field force lines are closed.

The next Maxwellian equation is the law of electromagnetic induction. This equation describes the nature of producing the electric field **E** by variation of the magnetic field induction **B**

$$\int_L \mathbf{E}\, dl = -\int_S \left(\frac{\partial \mathbf{B}}{\partial t}\right)_n d\mathbf{S}. \tag{A5.5}$$

Note that a rotor of vector **E** in a point **r** is the limit of the ratio of the electric field circulation E over the closed contour L, comprises an area ΔS, to the area ΔS while aspiring tightening contour L (and area ΔS) to zero (see Figure 5.11), that is

$$\lim_{\Delta S \to 0} \frac{1}{\Delta S} \oint_L \mathbf{E}dl = \operatorname{div} \mathbf{E}(\mathbf{r}). \tag{A5.6}$$

Integrating rot **E** upon surface ΔS, we obtain circulation of vector **E** along a contour that comprises this area

$$\oint_L Ed\ell = \int_S \operatorname{rot} EdS.$$

In mathematics this equation is referred to as Stokes' theorem. Comparing this expression with (A5.5),

$$\operatorname{rot} E(r) = -\frac{\partial B(r)}{\partial t} = \dot{B}(r), \tag{A5.7}$$

that is, *the rotor of the electric field strength in point* $\mathbf{r}$ *is equal to the time derivative from the magnetic induction in the same point.* This implies that the induction electric field is a curling (vortical) field in contrast to the electrostatic potential field. Using the previous notions, we can write instead of rot $\mathbf{E}$ the vector product ∇ and $\mathbf{E}$, that is $[\nabla\mathbf{E}] = -\dot{\mathbf{B}}(\mathbf{r})$.

In the same way the next Maxwellian equation can be derived which connects the circulation of magnetic field strength and currents. It has the form rot $\mathbf{H}(\mathbf{r}) = -\dot{\mathrm{D}}(\mathbf{r}) + \mathbf{j}_{\text{cond}}(\mathbf{r})$. There are no electric currents in vacuum ($\mathbf{j}_{\text{cond}} = 0$), therefore, the equation simplifies to

$$\operatorname{rot} \mathbf{H}(\mathbf{r}) = -\dot{D}(\mathbf{r}) \tag{A5.8}$$

This means that the *source of the magnetic field in the point* $\mathbf{r}$ *is the time changeable electric field* (*in the same point* $\mathbf{r}$).

It is expedient to put all equations analyzed above together.

$$\begin{array}{ll} \operatorname{div} \mathbf{D}(\mathbf{r}) = \rho(\mathbf{r}), & \operatorname{rot} \mathbf{E}(\mathbf{r}) = -\dot{B}(\mathbf{r}) \\ \operatorname{div} \mathbf{B}(\mathbf{r}) = 0 & \operatorname{rot} \mathbf{H}(\mathbf{r}) = -\dot{D}(\mathbf{r}) \end{array} \tag{A5.9}$$

To these equations it is expedient to add two, which connect the strength of both fields in vacuum and fields in an isotropic medium

$$\mathbf{B} = \mu_0 \mu \mathbf{H}, \qquad \mathbf{D} = \varepsilon_0 \varepsilon \mathbf{E}. \tag{A5.10}$$

The last equations are equitable only for isotropic media. In anisotropic media they have a tensor character.

The last equation in the Maxwellian system is the relation between the strength of an electric field in a point $\mathbf{r}$ with the current density in the same point (Ohm's law in differential form)

$$\mathbf{j} = \sigma \mathbf{E}. \tag{A5.11}$$

In these equations all electrodynamics is described!

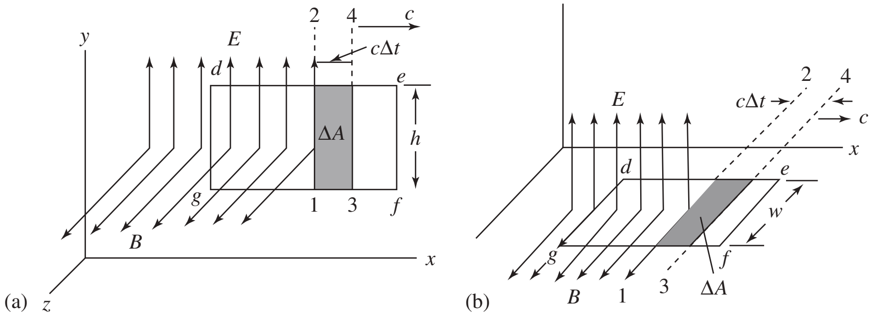
Try to estimate an electromagnetic wave's propagation speed based on the Maxwellian treatment of electrodynamics. As usual, let us make the task simpler, i.e., we shall analyze a certain physical model and look to see how far it corresponds with accepted representations. In this case our problem is the definition of the speed of propagation of an electromagnetic wave in vacuum. The Maxwell equation can be written in the form:

$$\oint_L E_\ell d\ell = -\left(\frac{\partial \Phi_B}{\partial t}\right), \tag{A5.12}$$

$$\oint_L B_\ell d\ell = -\left(\frac{\partial \Phi_E}{\partial t}\right) = \mu_0 \int_S \left(\frac{\partial D}{\partial t}\right) dS = \mu_0 \varepsilon_0 \int_s \left(\frac{\partial E}{\partial t}\right)_n dS. \tag{A5.13}$$

Let us imaging an electromagnetic wave as successive steps of "constant" electric and magnetic fields (with vectors **E** and **B** fixed in their magnitudes, perpendicular to each other), running along an x-axis with planes of vectors oscillation **E** in $x0y$ and **B** in $x0z$ (see Figure A5.1(a)) with a "wave" front motion speed, which we should define. Consider that in some instances, the front of the "wave" reaches line 1–2. Allocate to planes $x0y$ an imaginary rectangular contour defg and estimate the vector **B** flux through an area limited by the contour (Section 5.1.6, eq. (5.1.38)). In time dt the line 1–2 displaces to positions 4–3. The area ΔA limited by the specified contour is $\Delta A = c{\cdot}\Delta t \times h$, where h is the length of segment 1–2 and $c\Delta t$ is the distance run by the front of the "wave" in time Δt. As the vector **B** everywhere is perpendicular to the plane $x0y$,

$$\frac{d\Phi_B}{dt} = B\left(\frac{dA}{dt}\right) = \frac{Bhc\,dt}{dt} = Bhc \tag{A5.14}$$



In contrast, the circulation of the **E** vector along the contour 1–2–4–3, i.e., the left-hand side of eqs. (5.1.38, 5.4.6, 5.4.7 and A5.12), is equal to Eh. Therefore

$$\oint_L E_\ell d\ell = -Eh, \tag{A5.15}$$

since $E = 0$ on the segments 2–4, 4–3 and 3–1 (the wavefront has not yet reached them). From a comparison of eqs. (A5.14), (A5.15) and (A5.12), we can derive the ratio between E and B:

$$E = cB. \tag{A5.16}$$

Continuing to consider the same model, look what occurs in the plane $x0z$ (Figure A5.1(b)). Again we shall allocate a rectangular contour (into planes $x0z$) and we shall make the same calculations as in the previous case. Using eq. (5.1.2), circulation of the vector **B** (A5.13) gives Bw (w is the length of segment 2–4); the vector **E** flux through area ΔA (that is $\Delta\Phi_E$) gives $\mu_0\varepsilon_0 wc\Delta t$. Time derivation and successive cancellation on w gives

$$B = \mu_0\varepsilon_0 Ec. \tag{A5.17}$$

If we substitute in this equation the E value from (A5.17) and canceling by B we obtain $\mu_0\varepsilon_0 c^2 = 1$. Whence

$$c = \frac{1}{\sqrt{\mu_0\varepsilon_0}}. \tag{A5.18}$$

Three basic constants of electrodynamics appear connected with each other. Substituting values μ_0 and ε_0, we obtain for light speed in vacuum $c = 2.998 \times 10^8$ km/sec. The agreement of this value with that obtained experimentally was a triumph of Maxwell' theory.

A similar result can be obtained with a more exact model. It is also not so difficult to show that propagation of electromagnetic waves in a medium with dielectric susceptibility ε and magnetic susceptibility μ occurs with the speed

$$v = \frac{1}{\sqrt{\mu_0\varepsilon_0\mu\varepsilon}} = \frac{c}{\sqrt{\mu\varepsilon}} \tag{A5.19}$$

Since the refraction index is the ratio of the light propagation in a medium to that in a vacuum

$$n = \frac{1}{\sqrt{\mu\varepsilon}} \tag{A5.20}$$

Glossary of Symbols and Abbreviations

This glossary is intended to free the main text from multiple repetition of the explanation of the notation used. As a rule, an explanation is given on its first occurrence in the text and occasionally elsewhere. Since the vocabulary of physics is very broad, as well as the whole range of Greek letters, the same roman letters have been used several times, partly in different fonts. Vector values are given in bold.

Roman letters:

A	force work
$\boldsymbol{a}$, a	acceleration
$\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$	lattice periods
$\mathbf{B}$	vector of magnetic field induction
C	heat capacity of a body, system
C_{sp}	specific heat capacity
C_{M}	molar heat capacity
$\mathbf{D}$	vector of electric field displacement (induction)
D	diffusion coefficient
d, d_{hkl}	crystallographic interplanar spacing
$d_{\ni\Phi}$	molecule’s effective diameter
$\mathbf{E}$	vector of electric field strength
e, $\lvert e \rvert$	absolute value of the electron charge (elementary charge)
e	logarithmic natural base (exp)
e	thermal efficiency
E	energy, total mechanical energy
E_{F}	Fermi energy
$\mathbf{F}$	vector of force
$f(\upsilon)$	Maxwell molecular velocity distribution
$f(\varepsilon)$	molecule kinetic energy distribution
$\mathbf{g}$	free fall acceleration vector
g	gyromagnetic ratio, Lande factor
$\mathbf{H}$	vector of magnetic field strength
h	Planck’s constant
h,k,l	Miller indexes
I	electric current, moment of inertia (MI), intensity
I_{z}	moment of inertia relative to z-axis
i	number of degrees of freedom
i	imaginary unit
i, j, k	unit vectors (orts) of Cartesian coordinate

$\mathbf{j}$	vector of energy density
$\mathbf{k}$	wavevector ($\lvert\mathbf{k}\rvert = k = 2\pi/\lambda$)
K	kinetic energy, degrees of absolute thermodynamic temperature, performance factor
κ	Boltzmann constant
$\mathbf{L}$	angular momentum's vector
L_z	angular momentum relative to axis z
l, ℓ	length, distance
M	molar mass
$\mathbf{M}$	vector of force moment (torque)
M_z	force moment relative to axis z
$\boldsymbol{\mathcal{M}}$	vector of the magnetic dipole moment, electron atomic orbit or spin moment, nuclear magnetic moment
m	mass of a body, atom, molecule, total system's mass
n	concentration
$\mathbf{n}$	a unit vector of a normal
N_A	Avogadro's number
Π	a molar polarization
$\mathbf{p}$	vector of the electric dipole moment
$\mathbf{p}$	vector of momentum, pressure
P	power
Q	heat, activation energy
Q, q	electric charges
$R(\mathbf{r})$	a radial part of atomic wavefunction
R	molar refraction, heat emittance
$\mathbf{r}(x, y, z)$	Cartesian radius vector
$\mathbf{r}(r, \theta, \varphi)$	radius vector in a spherical coordinate system
S	area
S	entropy
s	wave polarization index
T	absolute thermodynamic temperature
t, τ	time
T	period
U	potential energy
U	internal energy of a molecular system
V	volume
V_M	molar volume
$\langle \upsilon \rangle$	average speed of a particle
$\upsilon_{\mathrm{rms}} = \sqrt{\langle \upsilon^2 \rangle}$	root mean square of a particle's speed
υ_{prob}	most probable value of a particle's speed
$\boldsymbol{\upsilon}$	velocity vector
W	thermodynamic probability
$Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$	angular part of the atomic wave function
Z	statistical sum

Greek letters:

α	angle, molecular polarizability
β	angle, a force constant
$\beta = \upsilon / c$	the relative speed coefficient in special relativistic theory
γ	coefficient of anharmonicity; adiabatic index
δ	attenuation coefficient
ε	dielectric susceptibility, a micro-object energy
$\langle \varepsilon \rangle$	average kinetic molecular energy
$\boldsymbol{\varepsilon}$	angular acceleration vector, thermal process efficiency
ε_0	electric constant
$\langle \varepsilon_{\mathrm{osc}} \rangle$	average energy of atomic oscillations in molecules
$\langle \varepsilon_{\mathrm{rot}} \rangle$	average energy of molecule rotation
η	coefficient of dynamical viscosity, coefficient of kinematic viscosity
κ	dielectric permeability, coefficient of molecular heat transfer
λ	wavelength, logarithmic attenuation decrement, mean free path length
μ	magnetic permeability, reduced molecular mass
μ_{o}	magnetic constant
μ_{B}	Bohr magneton
μ_{N}	nuclear magneton
v	coefficient of kinematic viscosity, frequency ($v = n$- speed of rotation)
ξ	displacement from equilibrium position
ρ	density of matter, electron density
σ	surface charge density
$\boldsymbol{\tau}$	unit vector of a tangent
τ	system's time of life, relaxation time, linear charge density
$\boldsymbol{\omega}$	angular velocity, $\omega = 2\pi v$
$\psi(x,y,z)$	time-independent wave function
Ψ	magnetic flux linkage/time-dependant wave fuction
Φ	flux
φ	angle, electric field potential
χ	magnetic susceptibility time-dependent wave function
Ω	solid angle

Others fonts:

$\mathfrak{I}$	magnetization
$\mathfrak{R}$	polarizability (polarization vector)
$\wp$	surface density of electrical current

Quantum numbers:

n, ℓ, m_ℓ, s, m_s	quantum numbers of one-electron atom
L, m_L, J, m_J , S, m_s	quantum numbers of multielectron atom
I, m_I	nuclear quantum numbers
s, p, d ...	one-electron states
S, P, D ...	many-electron atoms states

v	a molecule vibrational quantum number
j	a molecule rotational quantum number

Abbreviations:

MP	material point
CM	center of mass
MI	moment of inertia
IRB	ideal rigid body
IBB	ideal black body
SF	superfine

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