1

Maxwell equations (for instance, Equations (I.2.82)–(I.2.85)¹⁾) also hold in the presence of matter, viz., dielectrics, conductors, magnetized media, and so on. However, the matter while as a whole electrically neutral in most cases, consists of the majority of charged particles, electrons, and atomic nuclei. The resulting electromagnetic field in matter is due to both **external charges and currents**, which do not belong to the matter, and particles of the matter itself. The field produced by external charges causes redistribution of charges and currents and leads to the occurrence of an additional field. For this reason, in matter we are generally dealing with a self-consistent electromagnetic field due to both external and intrinsic charges.

It is a priori clear that the presence of a great variety of natural and artificial materials differing in magnetic and electric properties implies many specific approaches to their description. Currently, there is no unified general method for studying electromagnetic phenomena in the macroscopic electrodynamics as in the microscopic vacuum theory. Therefore, along with consistent microscopic approaches considering the specific atomic structure of matter, one has to use phenomenological laws that generalize the data obtained in macroscopic experiments.

In this book, we will first consider the most general laws that hold for any matter, and thereafter turn our attention to more specific (though relatively simple) models of media exposed to polarization and magnetization, such as plasma, ferromagnetics, conductors, superconductors, dielectrics and modern artificial media, that is, metamaterials. Whenever necessary, we will use quantum mechanics, thermodynamics, statistical physics, and physical kinetics, which are the most significant for the consistent analysis of electromagnetic phenomena in media.

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¹⁾ Recall that labels (of equations, figures, chapters, examples, problems, appendices, and sections) which start with "I" refer to the monograph by Toptygin (2014). For instance, Equation (I.2.82) means Equation (2.82) from Toptygin (2014).

1.1

Averaging Microscopic Maxwell Equations. Vectors of Electromagnetic Fields in Media

In this section, the microscopic (exact) values of the electric and magnetic field strengths are denoted by calligraphic capital letters \mathcal{E} and \mathcal{H} , respectively. The Maxwell equations (I.2.82)–(I.2.85) for the microscopic fields can be written as

$$\operatorname{rot} \mathcal{E}(\mathbf{r}, t) = -\frac{1}{c} \frac{\partial \mathcal{H}(\mathbf{r}, t)}{\partial t}, \qquad (1.1)$$

$$\operatorname{rot} \mathcal{H}(\mathbf{r},t) = \frac{1}{c} \frac{\partial \mathcal{E}(\mathbf{r},t)}{\partial t} + \frac{4\pi}{c} (\mathbf{j}_{int}(\mathbf{r},t) + \mathbf{j}_{ext}(\mathbf{r},t)),$$
(1.2)

$$div \,\mathcal{E}(\mathbf{r},t) = 4\pi(\rho_{int}(\mathbf{r},t) + \rho_{ext}(\mathbf{r},t)),\tag{1.3}$$

$$div \mathcal{H}(\mathbf{r},t) = 0. \tag{1.4}$$

The charge and current densities in the right-hand sides of these equations consist of two parts associated with the particles of matter and external sources; they are labeled by subscripts "int" and "ext" respectively. We will assume that the external sources are given. Particles of the matter are affected by the fields \mathcal{E} and \mathcal{H} , and the quantities ρ_{int} and j_{int} are generally complicated functionals of these fields. In order to determine the motion of particles in the medium and calculate the charge and current densities, one has to use the equations of classical or (in most cases) quantum mechanics. Simultaneous solutions of the Maxwell equations and the equations of the particle motion in medium ensure, in principle, the determination of microscopic values of the fields \mathcal{E} and \mathcal{H} .

However, such a detailed description of the field is impossible due to the presence of a large amount of particles in the medium, and it is actually not needed in most cases. The quantities that are measured in macroscopic experiments are fields averaged over a statistical ensemble of medium states (i.e., over regular and random motions of the particles). In accordance with the general principles of statistical physics (Landau and Lifshitz (1980)), such averaging is equivalent to the averaging over a certain time interval Δt . Moreover, when measuring the fields by means of macroscopic devices, an additional averaging is performed over macroscopically small volumes ΔV containing a large number of elementary charges (this issue has already been outlined in the beginning of Section I.2.1). The necessity of such an averaging stems from the fact that a microscopic field in medium undergoes very large and irregular changes in space and time, for example, on length-scales of the order of 3×10^{-8} cm in a condensed medium (Problems I.2.15 and I.2.16).

A quantity averaged over space and time will be denoted by a bar and defined by

$$\overline{f}(\mathbf{r},t) = \frac{1}{\Delta V \Delta t} \int_{\Delta V} dV \int_{-\Delta t/2}^{\Delta t/2} d\tau f(\mathbf{r}+\boldsymbol{\rho},t+\tau),$$
(1.5)

where the integration over coordinates is performed within the volume ΔV . The macroscopic field defined in this way remains a function of coordinates and time. Differentiation of both sides of Equation (1.5) with respect to any coordinate or

1.1 Averaging Microscopic Maxwell Equations. Vectors of Electromagnetic Fields in Media 3

time yields the following relation:

$$\frac{\partial \overline{f}}{\partial t} = \overline{\frac{\partial f}{\partial t}},\tag{1.6}$$

that is, a derivative of an average value is equal to an average value of a derivative.

Since the Maxwell equations (1.1)-(1.4) contain derivatives with respect to coordinates and time, from Equation (1.6) we have

$$\overline{\operatorname{rot} \mathcal{E}} = \operatorname{rot} \overline{\mathcal{E}}, \qquad \overline{\frac{\partial \mathcal{H}}{\partial t}} = \frac{\partial \overline{\mathcal{H}}}{\partial t},$$

and so on. Let us introduce the following notations for the strengths of macroscopic fields:

$$\mathcal{E}(\mathbf{r},t) = \mathbf{E}(\mathbf{r},t), \qquad \overline{\mathcal{H}}(\mathbf{r},t) = \mathbf{B}(\mathbf{r},t). \tag{1.7}$$

The first quantity is referred to as an **electric field vector** and the second as a **magnetic induction vector**. In these notations, the Maxwell equations take the form

$$rot E(\mathbf{r}, t) = -\frac{1}{c} \frac{\partial B(\mathbf{r}, t)}{\partial t}, \qquad (1.8)$$

$$rot \mathbf{B}(\mathbf{r},t) = \frac{1}{c} \frac{\partial \mathbf{E}(\mathbf{r},t)}{\partial t} + \frac{4\pi}{c} (\bar{\mathbf{j}}_{int}(\mathbf{r},t) + \mathbf{j}_{ext}(\mathbf{r},t)),$$
(1.9)

$$div E(\mathbf{r}, t) = 4\pi (\overline{\rho}_{int}(\mathbf{r}, t) + \rho_{ext}(\mathbf{r}, t)), \qquad (1.10)$$

$$div \mathbf{B}(\mathbf{r},t) = 0. \tag{1.11}$$

Here, the external charges and currents must be macroscopic quantities. The macroscopic vectors E and B are the analogs of microscopic field strengths \mathcal{E} and \mathcal{H} (even though the name of the vector B was changed for historical reasons). They are just these quantities that are used to express the force acting on a small macroscopic body with a charge q moving in a medium with velocity u:

$$F = q\left(E + \frac{1}{c}\boldsymbol{u} \times \boldsymbol{B}\right). \tag{1.12}$$

The system of Equations (1.8)–(1.11) is incomplete since the quantities \bar{j}_{int} and $\bar{\rho}_{int}$ are not known in advance. They should be expressed in terms of macroscopic vectors E and B. The most consistent approach to this problem is based on the use of the distribution functions (in the classical case) or the density matrices (in the quantum case) for describing the particle motion in matter. This requires invoking corresponding kinetic equations and rather detailed information concerning microscopic parameters, which characterize the state of particles in matter. Such an approach can be consistently implemented only for the simplest models of medium. In most cases, one has to use various phenomenological models and experimental data.

1.2

Equations of Electrostatics and Magnetostatics in Medium

Vectors of electric and magnetic polarization. In a static case, the electric and magnetic fields may exist separately: from the system of Equations (1.8)–(1.11) at $\partial B/\partial t = \partial E/\partial t = 0$ we obtain

$$rot E = 0, \qquad div E = 4\pi (\overline{\rho}_{int} + \rho_{ext}), \tag{1.13}$$

$$rot \mathbf{B} = \frac{4\pi}{c} (\mathbf{j}_{int} + \mathbf{j}_{ext}), \qquad div \mathbf{B} = 0.$$
(1.14)

The macroscopic densities $\overline{\rho}_{int}$ and \overline{j}_{int} can be conveniently expressed in terms of the vectors of the electric P(r) and magnetic M(r) polarization of matter, which are by definition the electric and magnetic dipole moments per unit volume:

$$P = \frac{\sum_{i} p_{i}}{\Delta V}, \qquad M = \frac{\sum_{i} m_{i}}{\Delta V}.$$
(1.15)

Here p_i and m_i are, respectively, the electric and magnetic moments of individual structural units of the medium (atoms or molecules); summation is over all particles in a macroscopically small volume ΔV .

Example 1.1

Show that the density of the induced volume charge inside medium is related to the electric polarization vector by the expression

$$\overline{\rho}_{int}(\mathbf{r}) = -div \, \mathbf{P}(\mathbf{r}). \tag{1.16}$$

What significance does this relation acquire on the boundary of a body?

Solution. Consider an electrically neutral body placed in vacuum in the presence of external electric charges ρ_{ext} . The total electric dipole moment of the body \mathcal{P} can be written as the integral of the electric polarization vector $\mathcal{P} = \int \mathbf{P}(\mathbf{r}) dV$ over the body's volume. On the other hand, the dipole moment can be written in terms of the charge macroscopic density $\mathcal{P} = \int \mathbf{r} \overline{\rho}_{int}(\mathbf{r}) dV$. The latter integral is independent of the choice of the coordinate origin provided the condition for electric neutrality $\int \overline{\rho}_{int}(\mathbf{r}) dV = 0$ is satisfied. We equate these two expressions for \mathcal{P} and multiply them by a constant vector \mathbf{a} :

(1)
$$\int (\boldsymbol{a} \cdot \boldsymbol{P}) \, dV = \int \overline{\rho}_{int}(\boldsymbol{a} \cdot \boldsymbol{r}) \, dV.$$

We use the identities $\mathbf{a} \cdot \mathbf{P} = (\mathbf{P} \cdot \nabla)(\mathbf{a} \cdot \mathbf{r}) = \nabla [\mathbf{P}(\mathbf{a} \cdot \mathbf{r})] - (\mathbf{a} \cdot \mathbf{r})(\nabla \cdot \mathbf{P})$ and apply the Gauss–Ostrogradskii theorem to the integral in Equation (1):

(2)
$$\int \overline{\rho}_{int}(\boldsymbol{a}\cdot\boldsymbol{r}) \, dV = \oint_{S} [\boldsymbol{P}(\boldsymbol{a}\cdot\boldsymbol{r})] \cdot \, d\boldsymbol{S} - \int (\boldsymbol{a}\cdot\boldsymbol{r}) (\nabla \cdot \boldsymbol{P}) \, dV.$$

The surface that encloses the integration volume in Equation (2) can be chosen outside the body, where P = 0. Omitting the vector a in the remaining equation,

we have

(3)
$$\int r\overline{\rho}_{int}(r) \, dV = -\int r \, div \, \boldsymbol{P} \, dV$$

It follows from this equation that the density of induced charges may be identified with the divergence of the electric polarization vector according to Equation (1.16). On the boundary of the body, the vector P jumps to zero. In this case, we have to perform the limiting transition in Equation (1.16), by analogy with that which led to Equation (I.2.18), and take into account that P = 0 outside the body. As a result, we find the density of the surface macroscopic charges induced on the surface of the polarized body:

The obtained charge densities (1.16) and (1.17) are restricted to dielectrics, that is, to media whose internal charges can be displaced only by microscopic distances. For this reason, these quantities are also referred to as densities of **bound charges**. Inside conductors, the charges move freely. Therefore, in these cases $\bar{\rho}_{int} = 0$ and P = 0. However, a surface charge, which is expressed in terms of the external field, may be present (Chapter 2).

Example 1.2

Show that in the absence of charges, which can freely propagate through the body (*free charges*), the volume current density induced inside medium (*magnetization current*) is related to the magnetic polarization vector by the expression

$$\mathbf{j}_{int}(\mathbf{r}) = c \operatorname{rot} \mathbf{M}(\mathbf{r}). \tag{1.18}$$

Write down the limiting form of this relation on the boundary of the body.

Solution. We use the same approach as in Example 7.1, that is, equate two integrals for the total magnetic moment of the body, \mathcal{M} , and multiply them by a constant vector \boldsymbol{a} . This gives

(1)
$$\boldsymbol{a} \cdot \boldsymbol{\mathcal{M}} = \frac{1}{2c} \int \boldsymbol{a} \cdot [\boldsymbol{r} \times \overline{\boldsymbol{j}}_{int}] \, dV = \int \boldsymbol{a} \cdot \boldsymbol{\mathcal{M}} \, dV.$$

Then we use the identity

(2)
$$2\mathbf{a} \cdot \mathbf{M} = \mathbf{M} \cdot rot[\mathbf{a} \times \mathbf{r}] = \mathbf{a} \cdot [\mathbf{r} \times rot \mathbf{M}] - \nabla \cdot [\mathbf{M} \times (\mathbf{a} \times \mathbf{r})]$$

and reduce Equation (1) to the form

(3)
$$\frac{1}{2c} \int \boldsymbol{a} \cdot [\boldsymbol{r} \times \bar{\boldsymbol{j}}_{int}] dV = \frac{1}{2} \int \boldsymbol{a} \cdot [\boldsymbol{r} \times \operatorname{rot} \boldsymbol{M}] dV,$$

from which Equation (7.18) follows. The limiting form of this formula on the body boundary, where M undergoes a discontinuity, can be obtained by analogy with Equation (I.2.58). A jump of the magnetization vector determines the surface current density according to the relation

$$\mathbf{i}_{int} = c \, \mathbf{n} \times \mathbf{M},\tag{1.19}$$

where *n* is the unit vector of the normal to the surface.

With the aid of Equations (1.16) and (1.18), Equations (1.13) and (1.14) for static fields take the form

$$rot E = 0, \qquad div D = 4\pi \rho_{ext}, \tag{1.20}$$

$$rot H = \frac{4\pi}{c} \boldsymbol{j}_{ext}, \qquad div \boldsymbol{B} = 0.$$
(1.21)

Here, two new field vectors are introduced: the electric induction vector

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi \boldsymbol{P},\tag{1.22}$$

and the magnetic field strength vector

$$H = B - 4\pi M. \tag{1.23}$$

Coupling equations. The sets of Equations (1.20) and (1.21) are not closed until the coupling between the vectors **D** and **E**, and also between **H** and **B**, is specified. It is possible to find the coupling equations for a broad class of media based on general physical considerations and experimental data of general character, without invoking accurate data on the internal structure of the medium. This holds true for media where in the absence of external fields the electric and magnetic polarizations are also absent. If external fields are weak compared with the interatomic fields, the electric polarization vector **P** and the magnetization vector **M** are linear functions of the components of the corresponding external fields. In this case, for isotropic bodies we have

$$P = \alpha E, \qquad M = \chi H, \tag{1.24}$$

where the coefficients α and χ are independent of external fields; they are referred to as **dielectric and magnetic susceptibilities**, respectively. Certainly, these quantities are not the same for different media, and depend on density and, in the general case, on temperature. In a constant electric field, we always have $\alpha > 0$, whereas the magnetic susceptibility may be either positive or negative. Substances with $\chi > 0$ are called **paramagnetics** and those with $\chi < 0$ **diamagnetics**.

If a conducting body, that is, a body containing free charges, presents a closed contour, then with the aid of a suitable source of energy (external electromotive force) a nonzero electric field and current can be maintained inside it. In the case of sufficiently weak fields, the relationship between the current density $j \equiv \overline{j}_{int}$ and the electric field *E* is given by the **Ohm law**

$$j = \kappa E, \tag{1.25}$$

where the **electric conductivity** κ is a macroscopic characteristic of medium and is independent of *E*.

Using Equations (1.22)-(1.24) we find the coupling equations

$$\boldsymbol{D} = \boldsymbol{\varepsilon} \boldsymbol{E}, \qquad \boldsymbol{B} = \boldsymbol{\mu} \boldsymbol{H}, \tag{1.26}$$

where the coefficients of proportionality

$$\varepsilon = 1 + 4\pi\alpha$$
, and $\mu = 1 + 4\pi\chi$ (1.27)

are called dielectric **permittivity** and magnetic **permeability**, respectively. In anisotropic media the susceptibility, permittivity, permeability and electric conductivity are second-rank tensors representing the apparent generalization of Equation (1.27):

$$\varepsilon_{\sigma\nu} = \delta_{\sigma\nu} + 4\pi\alpha_{\sigma\nu}, \qquad \mu_{\sigma\nu} = \delta_{\sigma\nu} + 4\pi\chi_{\sigma\nu}. \tag{1.28}$$

In this case, the coupling Equation (1.26) takes the form

$$D_{\sigma} = \varepsilon_{\sigma \nu} E_{\nu}, \qquad B_{\sigma} = \mu_{\sigma \nu} H_{\nu}. \tag{1.29}$$

In very strong external fields, linear relations (1.24)-(1.26) do not hold, and the coupling equations become nonlinear. Moreover, there exist the media that exhibit spontaneous polarization at certain temperatures (ferroelectrics, ferromagnetics). In all these cases, the coupling equations are very complicated.

1.3 Polarization of Media in a Constant Field

Electric polarization. The electric permittivity or magnetic permeability of a certain medium, as a rule, can be calculated based on some simplified models. For rarefied molecular gases, the permeabilities are connected with polarizabilities of individual molecules by simple relations. In the general case, the polarization of a certain system of particles is described by a second-rank tensor, which relates the vector of the induced dipole moment p to the vector of the field E acting on the system:

$$p_{\kappa} = \beta_{\kappa\nu} E_{\nu}, \tag{1.30}$$

where $\beta_{\kappa\nu}$ is the polarizability tensor. Polarizabilities of atoms and molecules are calculated by quantum mechanical methods (Problems I.6.62, 1.5, 1.17, 1.19). If the molecules possess electric dipole moments in the absence of an external field, then in order to calculate the polarization vector in a given field, one should use the Boltzmann distribution

$$dN(q_i) = C \exp\left[-\frac{U(q_i)}{T}\right] d\Gamma.$$
(1.31)

Here dN is the number of particles in an elementary volume $d\Gamma$ in the space of generalized coordinates, $U(q_i)$ is the potential energy of one particle in an external field, q_i is a set of generalized coordinates characterizing position and orientation of the particle, T is the temperature in energy units, and C is the normalization constant. The distribution of particles over momenta in the equilibrium state is the Maxwell distribution:

$$dN = f_0(p)d^3p = \frac{n}{(2\pi mT)^{3/2}} \exp\left(-\frac{p^2}{2mT}\right) d^3p,$$
(1.32)

where *n* is the number density of the particles with all energies, which may depend on coordinates in a nonhomogeneous system, and *m* is a molecular mass. The Maxwell distribution assumes that particles move according to the classical laws.

Example 1.3

A rarefied, statistically equilibrated gas consists of identical dipole molecules of number density N, having an individual dipole moment p. Calculate the dependence of the polarization vector \mathbf{P} on an applied electric field \mathbf{E} , neglecting the inter-molecule interaction and deformation of molecular electron shells. Determine also the dielectric permittivity and find the applicability criterion of the linear dependence given by Equation (1.24).

Solution. We calculate the projection P of the polarization vector on the direction of an external field with the aid of the Boltzmann distribution (1.31):

(1)
$$P = Np \frac{\int_0^{\pi} \cos \vartheta \exp\left[(pE/T)\cos \vartheta\right] \sin \vartheta \, d\vartheta}{\int_0^{\pi} \exp\left[(pE/T)\cos \vartheta\right] \sin \vartheta \, d\vartheta} = \frac{\partial}{\partial a} \ln \int_{-1}^{1} e^{ax} \, dx,$$

where $U = -pE \cos \vartheta$ is the interaction energy between the dipole and the external field, and a = pE/T, $x = \cos \vartheta$. Calculations yield

(2)
$$P = Np \frac{d}{da} \ln\left(\frac{2}{a}\sinh a\right) = NpL(pE/T),$$

where L(a) is called the **Langevin**²⁾ function:

$$L(a) = \coth a - \frac{1}{a}.\tag{1.33}$$

The Langevin function is close to unity when $a \gg 1$, while for small *a* it can be expanded into a series

(3)
$$L(a) = \frac{a}{3} - \frac{a^3}{45} + \cdots, \qquad a \ll 1.$$

For this reason, at $pE \gg T$ the saturation takes place, and all dipoles are oriented along the field. When $pE \ll T$, the polarization depends linearly on the field with the proportionality coefficient $\alpha = Np^2/3T$. This leads to the dielectric permittivity

$$\varepsilon = 1 + \frac{4\pi N p^2}{3T}.\tag{1.34}$$

The dipole moments of simple molecules are of the order of the product of the elementary charge and a linear molecular size (the Bohr radius), that is, $p \approx 10^{-18}$ CGS units. The transition from the linear dependence of polarization on the field strength and the saturation range takes place at the field value $E_c \approx T/p$, or $E_c \approx 10^4$ CGSE $\approx 3 \times 10^6$ V/cm for $T \approx 300$ K ≈ 0.03 eV. For a gas under normal conditions ($N \approx 3 \times 10^{19}$ cm⁻³), one has $\varepsilon - 1 \approx 4 \times 10^{-3}$.

Example 1.4

The molecules of a dielectric are spherically symmetric and have no dipole moments in the absence of the field. The number density N and polarizability β of

Paul Langevin (1872–1946), outstanding French physicist, founder of numerous physical schools (L. de Broglie, M. de Broglie, F. Joliot-Curie, F. Perren, etc.)

the molecules are known. Find the dependence of the dielectric permittivity ε on N and polarizability. Take into account a possible difference between the electric field \mathcal{E} acting on a molecule and the average (macroscopic) field \mathcal{E} due to other molecules.

Solution. If the field acting on the molecule is equal to the average field, that is, $\mathcal{E} = E$, the induced dipole moment of a single molecule is $\mathbf{p} = \beta E$, and the polarization vector is $\mathbf{P} = N\mathbf{p} = N\beta E = \alpha E$,

$$\varepsilon = 1 + 4\pi\alpha = 1 + 4\pi N\beta. \tag{1.35}$$

In order to include the effect of surrounding molecules, we enclose a given molecule by a sphere of radius $a \gg N^{-1/3}$ (Figure 1.1) and present the acting field as a sum of two fields $\mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2$, where \mathcal{E}_1 is the field which is produced by the external charges and all molecules localized outside the sphere of radius *a*.

The field \mathcal{E}_1 is macroscopic and can be calculated as the field in the center of the sphere carved in a uniformly polarized dielectric. In accordance with the superposition principle, $\mathcal{E}_1 = \mathbf{E} - \mathbf{E}_i$, where $\mathbf{E}_i = -4\pi \mathbf{P}/3$ is the field inside the uniformly polarized sphere (Problem 1.3). As a result, $\mathcal{E}_1 = \mathbf{E} + 4\pi \mathbf{P}/3$.

The field \mathcal{E}_2 can be easily calculated in two limiting cases: (a) molecules inside the sphere are distributed quite randomly; the field of a single dipole, averaged over the sphere volume, is zero, that is, $\mathcal{E}_2 = 0$; (b) molecules are localized at the sites of a cubic lattice, and, hence, $\mathcal{E}_2 = 0$ from symmetry considerations (see the field of a single dipole in Example I.2.5). For these cases

$$\mathcal{E} = E + \frac{4\pi}{3}P,\tag{1.36}$$

and $\boldsymbol{P} = N\beta \boldsymbol{\mathcal{E}} = N\beta (\boldsymbol{E} + 4\pi \boldsymbol{P}/3)$. Hence

$$\mathbf{P} = \frac{N\beta E}{1 - 4\pi N\beta/3} = \alpha E, \qquad \varepsilon = 1 + 4\pi\alpha = 1 + \frac{N\beta}{1 - 4\pi N\beta/3}$$

or

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\beta.$$



Figure 1.1 To calculation of the field acting on an individual molecule.

9

(1.37)

Equations (1.36) and (1.37) are called the **Clausius–Mossotti formulas**.³⁾ For the optical range of spectrum they are expressed in terms of the refraction coefficient $n = \sqrt{\varepsilon}$ (Chapter 6) and referred to as the **Lorenz–Lorentz**.⁴⁾ The validity of these relations is confirmed by experimental data on polarization of liquids consisting of molecules with quasi-elastic dipoles; however, they do not describe a matter with solid dipoles.

Magnetic polarization of matter is a purely quantum phenomenon. When a system of charged particles is in a magnetic field and is in a state of statistic equilibrium, its magnetic moment is zero only if the motion of particles is governed by classical laws (Problems 1.15 and 1.21). The magnetic susceptibility is therefore calculated on the basis of quantum mechanics (Problems 1.17, 1.19, 1.22, and 1.23). Even the models that suggest the existence of classical electron orbits in atoms (Problems 1.16 and 1.18) are essentially of quantum character since in classical physics an atom is unstable and the stationary orbits cannot exist (see, for instance, Problem I.5.119).

Electric conductivity. In order to calculate the electric conductivity, it is necessary to find an electric current produced by a weak electric field. These problems are solved by using either the classical distribution function or the quantum mechanical density matrix, depending on the character of particle motion. The equation for the density matrix is presented in (I.C42). The distribution function f(r, p, t) of charged particles exposed to an electromagnetic field satisfies the **Boltzmann equation**

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + e\left(\boldsymbol{E} + \frac{1}{c}\boldsymbol{v} \times \boldsymbol{B}\right) \cdot \frac{\partial f}{\partial \boldsymbol{p}} = I[f].$$
(1.38)

The distribution function is normalized by the condition

$$\int f(\boldsymbol{r}, \boldsymbol{p}, t) d^3 \boldsymbol{p} = \boldsymbol{n}(\boldsymbol{r}, t), \qquad (1.39)$$

where $n(\mathbf{r}, t)$ is the particle number density. In a multi-component system, each component should be described by its own distribution function.

The right-hand side of Equation (1.38) is called the **collision Integral**. The collision integral describes processes of mutual scattering of particles and must contain detailed information their interaction. As a rule, it has a specific and rather complicated form for each system. In most (may be in all) cases, Equation (1.38) is an integro-differential equation with respect to the distribution function. The collision integral is frequently written in the **relaxation time approximation** to obtain semi-qualitative results:

$$I[f] = -\frac{f - f_0}{\tau(p)},\tag{1.40}$$

³⁾ Clausius Rudolf (1822–1888), German physicist theorist. His basic works are in thermodynamics and kinetic theory of gases. He formulated the second law of thermodynamics and introduced the concept of entropy. Mosotti Ottaviano Fabricio (1791–1863), Italian physicist.

Lorentz Ludvig Valentin (1829–1891), Danish physicist, constructed, independently of Maxwell, the electromagnetic theory of light.

where f_0 is the equilibrium distribution function and $\tau(p)$ is the relaxation time that may depend on the energy of particles. This quantity should be considered a phenomenological adjustable parameter, which must show the best correlation with experimental data or with a more rigorous theory. The physical meaning of this parameter becomes apparent from a consideration of a spatially homogeneous system in the absence of external fields:

$$\frac{\partial f(p,t)}{\partial t} = -\frac{1}{\tau} [f(p,t) - f_0(p)].$$

It gives the exponential relaxation of the nonequilibrium distribution:

$$f(p,t) = f_0(p) + \delta f(p,0) e^{-t/\tau(p)}.$$
(1.41)

Here $f_0(p) + \delta f(p, 0)$ is the initial nonequilibrium distribution function. One should bear in mind that this relaxation may become more complicated as the equilibrium is approached (e.g., several different relaxation times are possible); therefore, in each specific case it is necessary to verify that approximation (1.40) can be used.

Example 1.5

Calculate the electric conductivity of a semiconductor, in the relaxation time approximation $\tau = \text{const.}$ The number density n of free charge carriers is sufficiently low. Therefore, the equilibrium distribution function can be treated as classical (Maxwell distribution), see Equation (1.31).

Solution. The stationary kinetic equation for a homogeneous system of charged particles in a uniform electric field is

(1)
$$eE \cdot \frac{\partial f}{\partial p} = -\frac{\delta f}{\tau}.$$

Let *E* be small $(eE\tau \ll p)$ and linearize Equation (1) remembering that the nonequilibrium additive correction to the distribution function is also of the order of *E*:

(2)
$$eE \cdot \frac{\partial f_0}{\partial p} = -\frac{\delta f}{\tau}.$$

Substituting the Maxwell distribution (1.31) for f_0 in Equation (2), we find the nonequilibrium component of the distribution function:

(3)
$$\delta f = \frac{\tau e}{T} E \cdot v f_0(p).$$

The electric current is calculated using the formula

(4)
$$\mathbf{j} = e \int \mathbf{v} \delta f(\mathbf{p}) \, d^3 p.$$

Then for the electric conductivity tensor we have

(5)
$$\kappa_{\alpha\beta} = \frac{e^2\tau}{T} \int v_{\alpha}v_{\beta}f_0(p) d^3p.$$

If the distribution of particles over momenta is isotropic, the electric conductivity is also isotropic: $\kappa_{\alpha\beta} = \kappa \delta_{\alpha\beta}$, where

$$\kappa = \frac{ne^2\tau}{m} \tag{1.42}$$

is the **Drude formula**.⁵⁾

Suggested literature: Maxwell (1989); Frenkel (1926a,b); Landau *et al.* (1984); Landau and Lifshitz (1980); Landau and Lifshitz (1977); Tamm (1976); Bredov *et al.* (2003); Sivukhin (1977); Peierls (1979); Pitaevskii and Lifshitz (1980); Frohlich (1958); Toptygin (2014)

Problems

- **1.1** Derive Equation (1.16) by a physically transparent method: assume that the electric polarization P is produced in matter by identical elementary dipoles p = el, and calculate the charge inside an arbitrary closed surface.
- **1.2** Derive Equation (1.18) by a physically transparent method: assume that the magnetic polarization M is due to the closed circular microscopic currents circulating in matter, and calculate the current through an arbitrary surface inside the matter.
- **1.3** A dielectric sphere of radius *a* is uniformly polarized (polarization vector P = const) and is in vacuum. Calculate the electric field inside and outside the sphere using the model that considers a small relative displacement of positive and negative charges.
- **1.4** Calculate the polarizability β of a hydrogen atom in a weak electric field with the aid of the classical model that suggests that the electron cloud density is described by the function $\rho(r) = -(e_0/\pi a_B^3) \exp(-2r/a_B)$, where e_0 is the elementary charge and a_B is the constant (Bohr radius). Neglect the deformation of the electron cloud. Find the change in the polarizability assuming that the electron cloud has a constant density inside a sphere of radius a_B .
- **1.5**[★] Calculate the polarizability of a hydrogen atom in the ground state by the quantum mechanical method (see the general formula in Problem I.6.62).
- **1.6**^{*} A molecule consists of two atoms that are at a distance *a* from each other. The atoms are spherically symmetric and have the polarizabilities β' and β'' . Find the polarizability tensor of the molecule assuming the atomic radii are small in comparison with *a*. Consider, in particular, the case $\beta' = \beta''$.
- **1.7** On the basis of energy conservation, prove that the polarizability tensor of a molecule in a constant field is symmetric.
- 5) Drude Paul (1863–1906), German physicist, who laid the foundation for the electronic theory of metals.

- **1.8** A dielectric consists of identical molecules whose dipole moment is zero in the absence of an external field. The polarizability tensor β_{ik} of an individual molecule is known. Find the dielectric polarization coefficient α for two cases: (i) all molecules are equally oriented and (ii) all molecules are randomly oriented.⁶⁾ Take account of the difference between the field acting on the molecule and the average field with the aid of Clausius–Mossotti formula.
- **1.9**^{*} If the polarizability of a molecule is different in different directions, then the energy of interaction between the molecule and an external field will depend on the orientation of the molecule. For this reason, along with the deformation mechanism of polarization, the orientation mechanism will operate even though the molecule does not possess any constant electric moment. This results in the temperature dependence of the dielectric constant of the matter consisting of randomly oriented nonpolar molecules. Investigate this effect by considering a diatomic gas in a weak constant electric field. Calculate the dielectric p olarizability coefficient α . The longitudinal polarizability of a molecule of the gas is β_1 , and the transverse polarizability is β_2 .
- **1.10** Two molecules in a gas have the dipole moments p_1 and p_2 and are at a distance R from each other. Their orientation changes due to collisions with other molecules. The probability of a specified mutual orientation is determined by the Boltzmann formula (1.31), where U is the energy of interaction between the two dipoles. Assume that the condition $U \ll kT$ is satisfied and show that the quantity U averaged over the Boltzmann distribution⁷ has the form

$$U(R) = -\frac{2p_1^2 p_2^2}{3kTR^6}.$$

1.11 A molecule with an electric dipole moment p interacts with a nonpolar molecule of polarizability β . Show that the interaction energy averaged over orientations of the dipole moment has the form

$$U(R) = -\frac{\beta p^2}{R^6},$$

where R is the distance between the molecules.

1.12^{*} In a dielectric placed in a constant electric field, apart from the dipole moment (the polarization vector P), there exist higher-order moments. Find the densities of the volume and surface charges that are equivalent to the quadrupole polarization Q_{ik} (Q_{ik} are the components of the quadrupole moment per unit volume of the dielectric).

⁶⁾ Case (i) may take place in solid bodies, either crystalline or amorphous, and case (ii) can happen in gases, liquids, and solids. Note, however, that solid body unlike a gas is a complicated system of strongly interacting particles. Therefore, the idea of isolated molecules in the solid body may be questionable.

⁷⁾ When averaging over the directions of dipole moments in Problems 1.10 and 1.11, use the formulas obtained in Problem I.1.33.

- 14 1 Equations of Steady Electric and Magnetic Fields in Media
 - **1.13** For polar substances, the Clausius–Mossotti relation is inapplicable and their dielectric permittivity may be calculated by the following approximate method proposed by L. Onsager.

Consider a sphere as small as to contain a single molecule. Assume that outside the sphere there is a dielectric with permittivity ε , and inside the sphere there is vacuum, while the field is equal to the effective field acting on the molecule. This field is determined by solving the macroscopic electrostatic equations. Find the relation between the dielectric permittivity ε of the substance and the polarizability of its molecules β .

1.14^{*} A homogeneous isotropic dielectric of permittivity ε does not exhibit any spontaneous polarization in the absence of an external field. Due to this, in any given macroscopic volume *V*, in the absence of the external field, the dipole moment averaged over the equilibrium configurations of the charge distribution, is $\langle \mathcal{P} \rangle_0 = 0$. However, an instantaneous value of the moment is fluctuating and $\mathcal{P} \neq 0$. Hence, generally, $\langle \mathcal{P}^2 \rangle_0 \neq 0$. Show that $\langle \mathcal{P}^2 \rangle_0$ is expressed through the dielectric permittivity as

$$\left\langle \mathcal{P}^2 \right\rangle_0 = rac{VT(1+2\varepsilon)(\varepsilon-1)}{4\pi\varepsilon},$$

where *T* is the temperature, *V* is the volume of the macroscopic sphere inside the dielectric, and $\langle \mathcal{P}^2 \rangle_0$ is the mean square of the fluctuating dipole moment of this sphere (in the absence of any external field).

- 1.15[★] Show that the magnetic moment of a system of charged particles, which are moving in a magnetic field according to the **laws of classical mechanics**, is zero in the stationary state (the **Bohr–Van Leeuween theorem**). For this purpose, write down the energy of the system, averaged over Gibbs ensemble, in the presence and in the absence of the magnetic field and show that the energy is independent of the external field.
- **1.16** Atoms (molecules) of a statistically equilibrated rarefied gas (of number density *N* and temperature *T*) have the intrinsic magnetic moment μ . Assuming that atomic electrons move in stationary classical orbits, show that in the presence of a magnetic field each atom will acquire an additional kinetic energy $\Delta K = -\mu \cdot H$. Calculate the magnetic polarization vector *M* and the paramagnetic susceptibility of the gas due to the orientation of atomic magnetic moments. Are the results obtained in agreement with the theorem proved in Problem 1.15?
- 1.17* Carry out a quantum mechanical calculation of the magnetization and the paramagnetic susceptibility of a statistically equilibrated rarefied atomic gas placed in a weak magnetic field. The quantum mechanical operator of the total magnetic moment of an individual atom has the form (cf. Equation (I.6.86))

$$\hat{\boldsymbol{\mu}} = \boldsymbol{\mu}_{\boldsymbol{B}}(\hat{\boldsymbol{J}} + \hat{\boldsymbol{S}}),\tag{1.43}$$

where μ_B is the Bohr magneton, while $\hat{J} = \hat{L} + \hat{S}$ and \hat{S} are, respectively, the dimensionless operators of the total and spin mechanical moment of

an electron shell of the atom. The atom is in the ground state with fixed quantum numbers J, L, and S. The magnetic field is weak and unable to break the LS-binding.

- Let atoms in the quasi-classical model (Problem 1.16) be spherically sym-1.18 metric and have no intrinsic magnetic moments. Calculate the diamagnetic susceptibility of the atoms due to the Larmor precession of the electron shells in an external magnetic field.
- 1.19^{*} Carry out a quantum mechanical calculation of the diamagnetic susceptibility of an atomic gas. The electron shells of the atoms have the quantum numbers L = S = 0.
- 1.20 An atom with spherically symmetric charge distribution is placed in an external uniform magnetic field H. Show that the additional field near the nucleus due to a diamagnetic current (Larmor precession of electrons) is equal to

$$\Delta H = -\frac{eH}{3mc^2}\varphi(0),$$

where $\varphi(0)$ is the electrostatic potential near the nucleus due to atomic electrons; *e* and *m* are the electron charge and mass respectively.

- 1.21^{\star} Consider a system consisting of particles with charge *e* and mass *m*, each moving at a fixed distance *a* from a certain center (classic rotators). The system is in a magnetic field in the state of statistical equilibrium. Show that the total magnetic susceptibility of this system is zero.
- In the simplest model, free electrons in metals can be considered an 1.22 ideal Fermi-gas at temperature T close to absolute zero. Calculate the paramagnetic susceptibility of the electron gas due to orientation of the spin magnetic moments of the electrons in a weak magnetic field. The number density of electrons is N and the temperature T = 0. Ignore the effect of the magnetic field on the motion of the electrons in space.

Hint. The Fermi energy ϵ_F (i.e., the energy of the highest occupied level) in the absence of the magnetic field is $\epsilon_F = \hbar^2 (3\pi^2 N)^{2/3} / 2m$, where *m* is the electron mass.

1.23 A rarefied electron gas at temperature T is in a weak uniform magnetic field and obeys the Maxwell-Boltzmann statistics. Calculate the magnetic susceptibility of the electron gas and separate its part, which is due to orientation of spin magnetic moments and the contribution associated with the effect of the magnetic field on the orbital motion of particles. Make use of the quantum mechanical expression for the electron energy in the magnetic field.

Hint. An electron in a homogeneous magnetic field has the energy (Landau and Lifshitz (1977)) (cf. also Problem I.6.76)

$$\mathcal{E}_n = \left(n + \frac{1}{2}\right)\hbar\omega_B + \frac{p_z^2}{2m} - \mu_B m_s B.$$
(1.44)

Here $\omega_c = \omega_B = |e|B/mc$ is the cyclotron frequency, $n = 0, 1..., m_s =$ $\pm 1/2$. The values of energy degenerate due to the position uncertainty of

Larmor circle. Operators of coordinates

$$\hat{x}_0 = \hat{x} + \frac{c\hat{p}_y}{eB}, \quad \hat{y}_0 \frac{c\hat{p}_x}{eB}$$
 (1.45)

of Larmor circle centre mutually do not permutable. The number of quantum states in volume V per dp_z interval is

$$dQ = \frac{eBV}{(2\pi\hbar)^2 c} \, dp_z. \tag{1.46}$$

- **1.24**^{*} An ionized gas consists of ions (charge *Ze*, average number density N_0) and electrons (charge -e, average number density n_0). The gas as a whole is electrically neutral, that is, $ZN_0 = n_0$, and is in statistical equilibrium at temperature *T*. Find the charge density distribution near an individual ion on the assumption that the gas is described by classical statistics and that the energy of particle-particle interaction is low compared with the thermal energy *T*.
- **1.25** An infinite conducting plate, bounded by planes x = h and x = -h, is placed in a constant and uniform transverse electric field E_0 . The plate as a whole is electrically neutral, the average number density of "free charges" is N_0 , and the dielectric permittivity is ε . Assuming that the change in the number density under the action of the applied field is small $(|N N_0| \ll N_0)$, find the field distribution inside the plate and the thickness of the layer in which the "surface" charge is concentrated. The charge-carrying particles obey the Boltzmann distribution.
- **1.26**^{*} A layer of electrolyte is placed between two infinite plane electrodes, x = h and x = -h, at a potential difference $2\varphi_0$. The electrolyte consists of ions of two types with charges +e and -e. Their average number density is N_0 in the absence of an external field, and the dielectric permittivity of the electrolyte is ε . Find the potential distribution between the electrodes. The particles obey the Boltzmann distribution.

Hint. Use the same method as in Problem 1.24.

1.27[★] Find the charge and potential distribution around an impurity ion with the charge Ze in metal. Use the simplest model of the metal as degenerate electron gas $(T \rightarrow 0)$ with an average number density n_0 , whose charge is neutralized by motionless positive ions.

Hint. Make use of the Thomas–Fermi quasi-classical model (Landau and Lifshitz (1977)).

- **1.28** Calculate an electric conductivity of degenerate electron gas of number density *n* in the relaxation time approximation $\tau(\epsilon)$.
- **1.29** An equilibrium plasma with electron number density *n* and motionless ions is in a weak uniform magnetic field B = const. In the relaxation time approximation $\tau = const$, calculate the current in the plasma induced by a weak electric field, and also the electric conductivity tensor. In the expression for the current, take into account the terms not higher than the first-order terms with respect to *B*.

1.30* Solve Problem 1.29 without limitations on the magnetic field strength. Calculate the anisotropic electric conductivity tensor and analyze specific cases of weak and strong magnetic fields.

1.4

Answers and Solutions

1.1 Consider an arbitrary volume V inside a dielectric, which is enclosed by surface *S*, and calculate the electric charge $q_{int} = \int_V \rho_{int} dV$ inside this volume. This charge is produced only by the dipoles, which are intersected by the surface S (Figure 1.2).

All remaining dipoles are either wholly inside or outside the volume Vand make no contribution to the total charge. A surface element dS meets Nl·dS dipoles on average. Their charge enclosed by this surface element is $dq_{int} = -eNl \cdot dS = -P \cdot dS$. Hence, $q_{int} = -\oint_S P \cdot dS = -\int_V div P \, dV$, which leads to Equation (1.16).



To calculation of the density of bound charges in a dielectric. Figure 1.2



Figure 1.3 To calculation of magnetization current.



Figure 1.4 To calculation of an electric field of polarized sphere.

1.2 The magnetic moment of an individual elementary current can be written as m = isn/c, where *i* is the elementary molecular current, *s* is the circle area, and *n* is a unit normal to the plane of the circle (Equation (I.2.60)). Let us plot an arbitrary closed contour inside matter (Figure 1.3).

The magnetization current J_{int} through the surface *S* bounded by contour *l* is due to those closed elementary currents that are pierced by this contour. The remaining currents either cross the surface *S* twice or do not cross it at all, and, hence, do not contribute to J_{int} . The segment *dl* of the contour crosses $s(\mathbf{n} \cdot d\mathbf{l})N$ molecular currents on average and makes the contribution $dJ_{int} = is(\mathbf{n} \cdot d\mathbf{l})N = c\mathbf{M} \cdot d\mathbf{l}$ to the total current. Hence, we have $J_{int} = c \oint_l \mathbf{M} \cdot d\mathbf{l} = c \int_S rot \mathbf{M} \cdot d\mathbf{S}$. Since the contour has been chosen arbitraryly, from the latter relation follows we obtain Equation (1.18).

1.3 If the number density of elementary dipoles p = el in a polarized sphere is N, then the total dipole moment of the sphere is $\mathcal{P} = 4\pi a^3 P/3$, where P = Np is the polarization vector. At $l \ll a$, the polarized sphere can be treated as a system of two spheres with the charges $q = \pm 4\pi a^3 Ne/3$, whose centers are separated by the distance l (Figure 1.4). In the outer region, each sphere produces a field similar to that of a point charge localized at the corresponding center; in other words, the two spheres produce the field of the dipole with the moment $ql = \mathcal{P}$, whose potential is given by

(1)
$$\varphi_e(\mathbf{r}) = \frac{\mathbf{\mathcal{P}} \cdot \mathbf{r}}{r^3}$$

(Equation (I.2.21)). Inside the polarized sphere at a distance r < a from its center the field is only due to internal charges localized at distances smaller than r. The external charges produce no field in the inner region, and therefore formula (1) may be applied provided \mathcal{P} is replaced by the

dipole moment of the inner region, $\mathcal{P}r^3/a^3$:

(2)
$$\varphi_i(\mathbf{r}) = \frac{\mathbf{\mathcal{P}} \cdot \mathbf{r}}{a^3}$$

The field strength in the outer region was calculated in Problem I.2.21. For the inner region we have

(3)
$$E_i = \nabla \varphi_i(\mathbf{r}) = -\frac{\mathbf{p}}{a^3} = -\frac{4\pi}{3}\mathbf{P}.$$

- **1.4** $\beta = 3a_B^3/4$. In the case of uniform charge distribution in an electron cloud, $\beta = a_B^3$.
- **1.5** A hydrogen atom in the ground state is spherically symmetric and its polarizability tensor is diagonal. The general formula (see Equation (3) from the solution of Problem I.6.62) takes the form

(1)
$$\beta = 2\sum_{n} \frac{e^{2}|\langle n|z|0\rangle|^{2}}{\mathcal{E}_{n} - \mathcal{E}_{0}}.$$

The most difficult procedure in this expression is summation over intermediate states n. Following (Landau and Lifshitz (1977)), we replace the z-coordinate by the auxiliary operator

(2)
$$z = \frac{m}{\hbar} \frac{d\hat{\zeta}}{dt}$$

where *m* is the electron mass. The matrix element of the time derivative operator with the wave functions of stationary states is calculated according to the rule $\langle n | \hat{\zeta} | 0 \rangle = i(\mathcal{E}_0 - \mathcal{E}_n) \langle n | \hat{\zeta} | 0 \rangle / \hbar$, which allows one to eliminate the energy denominator in Equation (1) and carry out the summation:

(3)
$$\beta = \frac{2ime^2}{\hbar^2} \langle 0|z\hat{\zeta}|0\rangle.$$

We will now find the action of $\hat{\zeta}$ on the wave function of the ground state of an hydrogen atom by writing it in the form

(4)
$$\hat{\zeta}|0\rangle = q(\mathbf{r})|0\rangle$$

where $q(\mathbf{r})$ is a new unknown function. With the aid of equations (2), (4), and (I.C34), we have

(5)
$$z|0\rangle = \frac{m}{\hbar} \frac{d\hat{\zeta}}{dt}|0\rangle = \frac{im}{\hbar^2} (\hat{\mathcal{H}}\hat{\zeta} - \hat{\zeta}\hat{\mathcal{H}})|0\rangle = \frac{im}{\hbar^2} (\hat{\mathcal{H}} - \mathcal{E}_0)q(\mathbf{r})|0\rangle.$$

Substituting Equation (5) into the Hamiltonian of a hydrogen atom, given by

(6)
$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\Delta + U(r),$$

we obtain the equation for determining $q(\mathbf{r})$:

(7)
$$\frac{1}{2}|0\rangle\Delta q + \nabla q \cdot \nabla |0\rangle = iz|0\rangle.$$

We need only the specific solution of this equation which is expressed in terms of quantities entering its right-hand side.

Substituting the wave function of the ground state $|0\rangle = \exp(-r/a_B)/\sqrt{\pi a_B^3}$, where $a_B = \hbar^2/me^2$ is the Bohr radius, and using the dependence on the polar angle ϑ defined by the right-hand side of $z = r \cos \vartheta$, we seek the solution in the form $q(\mathbf{r}) = f(r) \cos \vartheta$ and obtain the equation

(8)
$$\frac{1}{2}f'' + \left(\frac{1}{r} - \frac{1}{a_B}\right)f' - \frac{1}{r^2}f = ir,$$

whose particular solution is given by

(9)
$$f(r) = -ia_B r\left(a_B + \frac{r}{2}\right).$$

Finally, with the aid of Equations (2), (3), and (9) we find

(10)
$$\beta = \frac{2i}{a_B} \langle 0|rf(r)\cos^2 \vartheta |0\rangle = \frac{9}{2}a_B^3.$$

A comparison with the result of Problem 1.4 shows that the classical models give the correct order of magnitude (provided the value of atomic radius is borrowed from quantum mechanics) but do not allow us to obtain correct numerical factor.

1.6 It is clear from the symmetry of the molecule that one of the main polarization tensor axes lies along the axis of the molecule while two others can be chosen arbitrarily in the plane perpendicular to the molecular axis. Hence, only two of the three main values of the polarizability tensor are different, namely, $\beta^{(1)}$ and $\beta^{(2)} = \beta^{(3)}$. The following cases should be considered separately to find these values:

(a) The external field is directed along the axis of the molecule. It is clear that the induced dipole moment of each atom is directed along the external field. Denote these moments by p' and p'', respectively, and obtain two equations for them:

(1)
$$p' = \beta'(E + E'), \qquad p'' = \beta''(E + E''),$$

where *E* is the external field, and *E'* and *E''* are the additional fields in the center of each atom due to the presence of another atom. The fields *E'* and *E''* can be expressed in terms of dipole moments of the respective atoms with the aid of the formula for the strength of the field due to the dipole with moment *p*, taking into account that all vectors are directed along the axis of the molecule. Determining p' and p'' from Equation (1), and using the formula $p = p' + p'' = \beta^{(1)}E$, we find

(2)
$$\beta^{(1)} = \left[\frac{1}{\beta'} - \frac{2(a^3 + 2\beta')}{a^3(a^3 + 2\beta'')}\right]^{-1} + \left[\frac{1}{\beta'} - \frac{2(a^3 + 2\beta'')}{a^3(a^3 + 2\beta')}\right]^{-1}.$$

(b) The external field is perpendicular to the axis of the molecule. In a similar way, we arrive at

(3)
$$\beta^{(2)} = \beta^{(3)} = \left[\frac{1}{\beta'} + \frac{a^3 - \beta'}{a^3(a^3 - \beta'')}\right]^{-1} + \left[\frac{1}{\beta''} + \frac{a^3 - \beta''}{a^3(a^3\beta')}\right]^{-1}.$$

At $\beta' = \beta''$ the expressions $\beta^{(1)}$ and $\beta^{(2)}$ are simplified:

(4)
$$\beta^{(1)} = \frac{2\beta'}{(1-2\beta'/a^3)}, \qquad \beta^{(2)} = \frac{2\beta'}{(1+2\beta'/a^3)}$$

The average polarizability is given by

(5)
$$\overline{\beta} = \frac{1}{3}(\beta^{(1)} + \beta^{(2)}) = \frac{2}{3}\beta'\left(\frac{1}{1 - 2\beta'/a^3} + \frac{2}{1 + \beta'/a^3}\right).$$

1.8 (a) The dielectric is anisotropic as a whole. The principal values of the dielectric polarizability tensor (cf. Equation (1.37)) are given by

$$\alpha^{(i)} = \frac{N\beta^{(i)}}{1 - 4\pi N\beta^{(i)}/3}.$$

(b) In the case of a random orientation of molecules, there are no physically selected directions in macroscopic volumes of dielectric, except for the direction of external field. Hence, the average dipole moment of the molecule \overline{p} is proportional to the field \mathcal{E} acting on the molecule:

$$\overline{p} = \beta \mathcal{E}.$$

On the other hand, it is clear that

$$\overline{p}_i = \overline{\beta_{ik} \mathcal{E}_k} = \overline{\beta}_{ik} \mathcal{E}_k,$$

where the averaging is carried out over a macroscopically small volume. It follows from comparison of the two last formulas that

$$\beta = \overline{\beta}_{11} = \overline{\beta}_{22} = \overline{\beta}_{33}, \qquad \overline{\beta}_{ik} = 0 \quad (\text{at } i \neq k).$$

Thus,

$$\beta = \frac{1}{3}(\overline{\beta_{11} + \beta_{22} + \beta_{33}}).$$

However, the sum of the diagonal components of the tensor is Invariant, which is equal to the sum of the principal values $\beta^{(1)} + \beta^{(2)} + \beta^{(3)}$ (Equation (I.1.263)). Hence,

$$\beta = \frac{1}{3}(\beta^{(1)} + \beta^{(2)} + \beta^{(3)}).$$

The polarization coefficient of dielectric α relates to β by a usual formula (Example 1.4).

1.9 If the axis of the molecule is oriented at an angle θ to the direction of an external field E_0 , the energy of the molecule can be written down as

$$W = -\frac{1}{2}\boldsymbol{p} \cdot \boldsymbol{E}_0 = -\frac{1}{2}(\beta_1 \cos^2 \theta + \beta_2 \sin^2 \theta) \boldsymbol{E}_0^2.$$

The number of particles per unit volume with axes directed at an angle θ to the field E_0 is given by the Boltzmann formula (1.31). The polarization vector is defined by the formula $P = N\overline{p}$, where \overline{p} is the dipole moment of an individual molecule, averaged over the Boltzmann distribution, and N is the number density of particles. Since in the absence of the field, the

molecules are chaotically oriented, the vector \overline{p} has the same direction as the external field.

In line with this, we calculate the quantity \overline{p} by the formula

$$\overline{p} = \frac{1}{N} \int p_{\parallel} dN = \frac{E_0 \int_0^{\pi} \exp\left(-\frac{W(\theta)}{kT}\right) (\beta_1 \cos^2 \theta + \beta_2 \sin^2 \theta) \sin \theta \, d\theta}{\int_0^{\pi} \exp\left(-\frac{W(\theta)}{kT}\right) \sin \theta \, d\theta}$$

where p_{\parallel} denotes the component of the molecule dipole moment parallel to the field. According to the condition of the problem, the field is weak. Hence, it is sufficient to consider the terms linear in $a = (\beta_1 - \beta_2)E_0^2/2kT \ll 1$ only. Finally, with the use of formulas $P = N\overline{p} = \alpha E_0$ we obtain

$$\alpha = N\beta_2 + \frac{1}{3}N(\beta_1 - \beta_2) \left[1 + \frac{2}{15}\frac{(\beta_1 - \beta_2)E_0^2}{kT}\right]$$

It is clear from this formula that the dependence of P on E_0 appears to be nonlinear, and that α is not a proportionality coefficient, which is independent of E_0 . Let us estimate the value of the correction term at room temperatures (T = 300 K). If $\beta_1 - \beta_2$ is of the order of 10^{-24} cm³, then $T/(\beta_1 - \beta_2) \approx 10^6$. Thus, this term is small at $E_0 \ll 10^3$ V cm⁻¹. Neglecting the correction term, we obtain the previous expression for α :

$$\alpha = \frac{1}{3}N(\beta_1 + 2\beta_2)$$

(Problem 1.8).

1.12 The additional potential due to the quadrupole polarization of the dielectric can be written in the form

(1)
$$\varphi = \frac{1}{2} \int \frac{\partial^2 (1/R)}{\partial x_i \partial x_k} Q_{ik} \, dV,$$

where R is a distance between the volume element dV and point of observation; the integration is carried out over the volume of the dielectric. On the other hand, the potential of the volume and surface charges is generally given by

(2)
$$\varphi = \int \frac{\rho'}{R} dV + \int \frac{\sigma'}{R} dS + \int \tau' \cdot \nabla\left(\frac{1}{R}\right) dS,$$

where ρ' is the volume charge density, σ' is the surface charge density, and τ' is the thickness of the double layer. Reducing Equation (1) to the form of Equation (2), we get

(3)
$$\rho' = \frac{1}{2} \frac{\partial^2 Q_{ik}}{\partial x_i \partial x_k}, \quad \sigma' = -\frac{1}{2} \frac{\partial Q_{in}}{\partial x_i}, \quad \tau'_k = \frac{1}{2} Q_{ki} n_i.$$

Thus, the quadrupole polarization is determined by the volume charges ρ' inside the dielectric, the surface charges σ' , and the double electric layer with the power τ' on the surface of the dielectric. Since the densities of the

volume and surface charges are related to the polarization vector by formulas $\rho' = -div P'$, $\sigma' = P'_n$, it follows from Equation (3) that the quadrupole polarization is determined by the additional dipole polarization

$$P_k' = -\frac{1}{2} \frac{\partial Q_{ik}}{\partial x_i}$$

and the double layer with the power τ' . Equation (3) can also be obtained from the energy of dielectric in the presence of quadrupole polarization.

1.13 $\varepsilon = \frac{1}{4} \left[1 + 3x + 3 \left(1 + \frac{2}{3}x + x^2 \right)^{\frac{1}{2}} \right],$

where $x = 4\pi N\beta$. The polarizability β of polar materials in weak fields is given by the formula

$$\beta = \frac{p^2}{3T},$$

where p is the dipole moment of the molecule and T is the temperature in energy units.

For $x \ll 1$, when the difference between the field acting on the molecule and the average field becomes very small, we have

$$\varepsilon = 1 + x = 1 + 4\pi N\beta.$$

1.14 We will describe the charges inside the sphere using the microscopic approach, on the base of the classical Boltzmann distribution (1.31), while outside the sphere we consider the dielectric as a continuous medium of permittivity ε . Let an *a*th charge inside the sphere be displaced by a vector u_a with respect to the equilibrium position. A set of such displacements is denoted by $Q = Q(u_1, \dots u_a, \dots)$. In the absence of an external field, these displacements are of pure fluctuation character. The interaction between the charges is described by the potential energy $U_0(Q)$, which includes also the interaction between the charges outside the sphere occurs on the surface and is negligibly small by virtue of the macroscopic sizes of the sphere. The dipole moment of the sphere is given by

(1)
$$\mathcal{P} = \sum_{a} e_{a} u_{a}.$$

Since there is no spontaneous polarization, the statistical average of the dipole moment is equal to zero:

(2)
$$\langle \mathcal{P} \rangle_0 = \int \mathcal{P} \exp\left(-\frac{U_0(Q)}{T}\right) dQ = 0.$$

The presence of an external field gives rise to a uniform electric field inside the sphere whose strength is given by (Problem 2.11)

(3)
$$\mathcal{E} = \frac{3\varepsilon}{2\varepsilon + 1} E$$

This field is produced by the external sources and external (with respect to the sphere) charges of the dielectric. As a result, the potential energy of the charges inside the sphere acquires the additional term

(4)
$$U(Q, E) = U_0(Q) - \sum_a e_a u_a \cdot \mathcal{E} = U_0(Q) - \frac{3\varepsilon}{2\varepsilon + 1} \mathcal{P} \cdot E$$

This potential energy should be used now in the Boltzmann distribution to calculate the dipole moment induced by the external field:

(5)
$$\langle \mathcal{P}(E) \rangle = \int \mathcal{P} \exp\left(-\frac{U}{T}\right) dQ / \int \exp\left(-\frac{U}{T}\right) dQ$$

Assuming the field E to be weak, we expand the exponent into a series to obtain

(6)
$$\exp\left(-\frac{U}{T}\right) = \left[1 + \frac{3\varepsilon}{2\varepsilon + 1}\frac{\mathcal{P}\cdot E}{T}\right]\exp\left(-\frac{U_0}{T}\right).$$

Using Equation (2) we find

(7)
$$\langle \mathcal{P}_{\mu}(\boldsymbol{E}) \rangle = \frac{3\varepsilon E_{\nu}}{(2\varepsilon+1)T} \frac{\int \mathcal{P}_{\mu}\mathcal{P}_{\nu} \exp\left(-\frac{U_{0}}{T}\right) dQ}{\int \exp\left(-\frac{U_{0}}{T}\right) dQ} = \frac{3\varepsilon E_{\nu}}{(2\varepsilon+1)T} \langle \mathcal{P}_{\mu}\mathcal{P}_{\nu} \rangle_{0}.$$

We transform the average over components of the dipole moment using the symmetry considerations:

(8)
$$\langle \mathcal{P}_{\mu}\mathcal{P}_{\nu}\rangle_{0} = \frac{1}{3}\langle \mathcal{P}^{2}\rangle_{0}\delta_{\mu\nu}.$$

The left-hand side of Equation (7) can be written in terms of the projection P_{μ} of the electric polarizability vector:

(9)
$$\langle \mathcal{P}_{\mu}(E) \rangle = V \mathcal{P}_{\mu} = \frac{V(\varepsilon - 1)}{4\pi} E_{\mu}.$$

Substituting Equations (8) and (9) into Equation (7), we obtain the formula given in the statement of the problem.

We stress that this formula relates the response of the medium, characterized by permittivity ε , to an external perturbation with the fluctuation of the internal parameter of the medium $\langle \mathcal{P}^2 \rangle_0$ corresponding to the statistical equilibrium in the absence of any external perturbation. This relation is actually a specific case of the fluctuation-dissipative theorem (FDT). The general relation of such kind for the time-dependent disturbance can be found in Section 7.2.

1.15 Consider a system of particles whose Hamiltonian function in the absence of any external magnetic field is given by

(1)
$$\mathcal{H}_0 = \sum_a \frac{p_a^2}{2m_a} + U,$$

where the potential energy U is the function of coordinates. In the presence of a magnetic field, the Hamiltonian function takes the form [(I.4.65')]

(2)
$$\mathcal{H} = \sum_{a} \frac{1}{2m_a} \left(\boldsymbol{P}_a - \frac{\boldsymbol{e}_a}{c} \boldsymbol{A}_a \right)^2 + \boldsymbol{U},$$

where P_a is the generalized momentum of an *a*th particle, and A_a is the vector potential of the external field at the point where the particle is localized. The energy of the system averaged over the Gibbs ensemble (its internal energy in the thermodynamic approach) is expressed as an integral over the phase space

(3)
$$\overline{\mathcal{E}} = \frac{1}{Z} \int \mathcal{H} \exp\left(-\frac{\mathcal{H}}{T}\right) d\Gamma,$$

where $d\Gamma = \prod_i dP_i dx_i$ is an element of phase space. Let us change momentum variables in Equation (3)

(4)
$$\boldsymbol{P}_a - \frac{\boldsymbol{e}_a}{c} \boldsymbol{A}_a \to \boldsymbol{p}_a,$$

keeping the same coordinates. With such a replacement, \mathcal{H} becomes \mathcal{H}_0 , and $d\Gamma = \prod_i dp_i dx_i$ because the Jacobian of transition to the new variables equals 1. As a result, the internal energy of the system in a magnetic field is expressed just as it is expressed in the absence of the field, that is, the energy is field-independent. A body that does not possess the magnetic moment in the absence of the field, will not acquire it in the presence of the field. However, such a result holds only in the classical case and fails when particles move according to quantum mechanical laws.

Let electrons in atoms move with velocity v_a . When a field *H* is applied, 1.16 each electron undergoes Larmor precession with the angular velocity Ω_{I} = -eH/2mc (Problem I.4.102) and acquires an additional velocity

(1)
$$\Delta \boldsymbol{v}_a = \boldsymbol{\Omega}_L \times \boldsymbol{r}_a$$

A change in the kinetic energy of the electrons is given by

(2)
$$\Delta K = \frac{m}{2} \sum_{a} [(\boldsymbol{v}_{a} + \Delta \boldsymbol{v}_{a})^{2} - \boldsymbol{v}_{a}^{2}] \approx m \sum_{a} \boldsymbol{v}_{a} \cdot \Delta \boldsymbol{v}_{a} = m \boldsymbol{\Omega}_{L} \cdot \sum_{a} \boldsymbol{r}_{a} \times \boldsymbol{v}_{a},$$

where the second-order term in small velocity Δv is omitted.

Using the evident expression $\mu = \sum_{a} \mu_{a}$ for the total magnetic moment of an atom, and the coupling Equation (I.4.76) for the mechanical and magnetic orbital moments, $\mu_a = er_a \times p_a/2mc$, we obtain the relation given in the statement of the problem. Note that, conceptually, it would be more reasonable to write **B** instead of **H** in the expression for Ω_L . However, since the magnetic susceptibility of gases is small, the error introduced in this case is negligible.

Further calculations of the magnetization and magnetic susceptibility can be carried out in the same manner as for the electric polarization in Example 1.3, that is, with the aid of the Boltzmann distribution. In the

general case, the magnetization is expressed in terms of the Langevin function

(3)
$$M = N\mu L\left(\frac{\mu H}{T}\right).$$

At $\mu H \ll T$, the dependence between M and H is linear, and the magnetic susceptibility is given by

(4)
$$\chi = \frac{N\mu^2}{3T} \propto \frac{1}{T}$$

(the **Curie**⁸⁾ **law for paramagnetics**). The results obtained are not at variance with the Bohr–Van Leeuween theorem since the model considered in the present problem is not purely classical: the assumption on the existence of stationary orbits of electrons in atoms is inconsistent with classical mechanics and electrodynamics.

1.17 The operator of interaction between an atom and a field in the approximation, which is linear in the field has the form

$$\hat{V} = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{H}.$$

In the absence of the external field, the energy levels at given L, S, J, and M_J degenerate in M_J with multiplicity 2J + 1, but the degeneracy is removed in the magnetic field. In order to solve the problem, one needs to find corrections to the energy levels based on the perturbation theory and thereafter calculate the average magnetic moment of the atom in a magnetic field making use of the density matrix in the energy representation (Equations (I.C43) and (I.C44)).

Let the direction of the field H be the quantization axis *Oz*. Hence, in accordance with the stationary perturbation theory, the corrections to the energy levels must be calculated as

(2)
$$\Delta \mathcal{E}_{LSIM_{I}} = -\langle LSJM_{I} | \hat{\mu}_{z} | LSJM_{I} \rangle H.$$

In order to calculate this matrix element, it is convenient to present the magnetic moment operator in the form

$$\hat{\mu} = \hat{G}\hat{J},$$

where \hat{G} is a certain scalar operator. Using the explicit form of $\hat{\mu}$, given in the statement of the problem, we have

(4)
$$\hat{G}\hat{J} = \mu_B(\hat{J} + \hat{S}),$$

and consider the scalar product of this equation and the operator \hat{J} . Then, we calculate the diagonal matrix elements of both sides of the obtained equation:

(5)
$$\langle LSJM_J | \hat{G} \hat{J}^2 | LSJM_J \rangle = \mu_B \langle LSJM_J | \hat{J}^2 + \hat{S} \cdot \hat{J} | LSJM_J \rangle.$$

Curie Pierre (1859–1906), outstanding French physicist, studied magnetism, physics of crystals, radioactivity; Nobel Prize laureate.

1.4 Answers and Solutions 27

It is clear that

(6)
$$\hat{J}^2 |LSJM_J\rangle = J(J+1)|LSJM_J\rangle, \quad \hat{L}^2 |LSJM_J\rangle = L(L+1)|LSJM_J\rangle,$$

 $\hat{S}^2 |LSJM_J\rangle = S(S+1)|LSJM_J\rangle.$

Finally, we square both sides of the equality $\hat{J} - \hat{S} = \hat{L}$ and use Equation (6) to find

(7)
$$2\hat{S}\cdot\hat{J}|LSJM_J\rangle = [J(J+1) - L(L+1) + S(S+1)]|LSJM_J\rangle.$$

With the aid of Equations (6) and (7) we obtain the matrix element

(8)
$$\langle LSJM_J | \hat{G} | LSJM_J \rangle = g\mu_B$$

and calculate the energy levels

(9)
$$\Delta \mathcal{E}_{LSJM_I} = -g\mu_B H M_J,$$

where

(10)
$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

is the gyromagnetic factor or Landé g-factor.

The magnetization can be calculated with the aid of the probability (I.C44) by substituting the values of the energy levels given by Equation (9):

(11)
$$M = Ng\mu_B \frac{\sum_{m=-J}^{m=J} me^{am}}{\sum_{m=-J}^{m=J} e^{am}} = Ng\mu_B \frac{d}{da} \ln\left(\sum_{m=-J}^{m=J} e^{am}\right).$$

where $a = g\mu_B H/T$, and the sum over *m* under the logarithm is a statistical sum for an individual atom. Its calculation with the aid of the formula for a finite geometric progression yields

(12)
$$M = M_0 L_J(aJ)$$
, where

$$L_{J}(x) = \left(1 + \frac{1}{2J}\right) \operatorname{coth}\left[\left(1 + \frac{1}{2J}\right)x\right] - \frac{1}{2J}\operatorname{coth}\left(\frac{x}{2J}\right)$$

is the quantum Langevin function or **Brillouin**⁹ **function**). The quantity $M_0 = Ng\mu_B J$ is the saturation magnetization which is reached at low temperatures ($aJ \gg 1$). If the opposite inequality is satisfied, then the magnetization is proportional to the magnetic field, and the paramagnetic susceptibility is expressed in the form

(13)
$$\chi = \frac{Ng^2\mu_B^2 J(J+1)}{3T}$$

At $J \gg 1$ we pass to the semi-classical model considered in Problem 1.16. In this case, the atomic magnetic moment is expressed in the form $\mu \approx g\mu_B J$,

⁹⁾ Brillouin Léon (1889–1969), French physicist, worked mainly in quantum mechanics, radiophysics, physics of solids.

and the quantum Langevin function becomes the classical one, $L_J(x) \rightarrow L(x)$ as $J \rightarrow \infty$.

The paramagnetic susceptibility of gases under normal conditions is very low. Substituting $N \approx 3 \times 10^{19}$ cm⁻³ and $T \approx 10^{-14}$ erg in Equation (13), we obtain $\chi \approx 10^{-7}$. For comparison, the dielectric susceptibility under the same conditions is $\alpha \approx 10^{-3}$. The difference arises from the fact that the magnetization is related to the motion of particles, owing to which the magnetic susceptibility possesses an additional small factor $(v/c)^2 \approx 10^{-4}$, where v is the velocity of atomic electrons.

1.18 Due to Larmor precession, each electron acquires an additional velocity Δv which is given by Equation (1) of the solution of Problem 1.16. Introducing the volume charge density of the electron shell $\rho(r)$, we calculate the atomic magnetic moment induced by the Larmor precession:

(1)
$$\boldsymbol{\mu} = \frac{1}{2c} \int \boldsymbol{r} \times \rho \Delta \boldsymbol{v} \, dV = \frac{1}{2c} \int \rho \boldsymbol{r} \times [\boldsymbol{\Omega}_L \times \boldsymbol{r}] \, dV.$$

In view of spherical symmetry of $\rho(r)$, the vector μ is parallel to Ω_L :

(2)
$$\boldsymbol{\mu} = \frac{1}{2c} \boldsymbol{\Omega}_L \int \rho(x^2 + y^2) \, dV,$$

where the *Ox-* and *Oy-*axes are perpendicular to the vector *H*. Evidently, it is possible to write down

(3)
$$\int \rho(x^2 + y^2) \, dV = \frac{2}{3} Zea^2,$$

where Ze is the total charge of the electron shell and a^2 is the squared distance of electrons from the nucleus averaged over all electrons. As a result, from Equations (2) and (3) we get

(4)
$$M = N\mu = \chi H$$
, where $\chi = -\frac{NZe^2a^2}{6mc^2} < 0$

is the diamagnetic susceptibility. The diamagnetic atomic moment is opposite to the magnetic field, and the diamagnetic susceptibility is negative.

1.19 If the orbital and spin moments of an electron shell of an atom are zero, then the operator (1.43) will give the zero value of the magnetic moment in all orders of the perturbation theory while the nonzero value will be associated with the term quadratic in vector-potential in the interaction operator (I.6.57). Since we deal with the constant but non-quantized external field, we can substitute $A = H \times r/2$ in Equation (I.6.57) and write the operator of interaction of the electron shell with the magnetic field in the form

(1)
$$\hat{V} = \frac{e^2}{8mc^2} \sum_a [H \times r_a]^2.$$

The correction to the atomic energy in the first order of the perturbation theory is expressed by the integral

(2)
$$\Delta \mathcal{E} = \int \psi^*(q) \hat{V} \psi(q) \, dq,$$

where q is a set of coordinates of all atomic electrons. Owing to spherical symmetry of the electron shell, in integrating over the angles, the quantity $\sin^2 \vartheta_a$ entering the vector product may be substituted by its average value which is equal to 2/3. The final result is

(3)
$$\Delta \mathcal{E} = \frac{e^2}{12mc^2} H^2 \sum_a \langle \psi | r_a^2 | \psi \rangle.$$

The atomic magnetic moment can be calculated as $\mu = -\partial \Delta \mathcal{E} / \partial H$ (see Section 3.3 below). For the number density of atoms N, the calculation of the magnetization yields

(4)
$$M = N\mu = \chi H$$
, where $\chi = -\frac{Ne^2}{6mc^2} \sum_a \langle \psi | r_a^2 | \psi \rangle$.

The sum of r_a^2 for atomic electrons in Equation (4), averaged over the quantum state of the atom, may be replaced by the product Za^2 , where a^2 is the mean squared distance for all electrons. Thereafter the quantum formula for the diamagnetic susceptibility will coincide with the semi-classical formula obtained in Problem 1.18. The numerical values of the diamagnetic susceptibility of gases are very small. An estimate can be made by substituting the squared Bohr radius (4). Under normal pressure, we will have $\chi \approx 10^{-10}$. For condensed matter, where number density of particles is four orders of magnitude higher, we will obtain $\chi \approx 10^{-6}$.

1.21 The total magnetic susceptibility is equal to the sum of the paramagnetic and diamagnetic susceptibilities (Problems 1.16, 1.18, 1.19*):

(1)
$$\chi = \frac{N\mu^2}{3kT} - \frac{Ne^2}{6mc^2}\overline{r^2}$$

The magnetic moment μ of an individual rotator entering this formula can be calculated in the following way. Based on the well-known theorem (Equation (I.2.61)), we have

(2)
$$\mu = \frac{e}{2mc}K$$

where *K* is the angular momentum of the particle. In the case of a rotator, the *K* is related to the kinetic energy through the formula

$$W_k = \frac{K^2}{2ma^2}$$

The statistical average $\overline{K^2}$ is therefore expressed in terms of the average kinetic energy

(4)
$$\overline{K^2} = 2ma^3 \overline{W}_k.$$

The average kinetic energy \overline{W}_k can be found from the theorem on uniform energy distribution over degrees of freedom. Since the rotator has two degrees of freedom, $\overline{W}_k = T$. Substituting Equations (4) and (2) in Equation (1), we find $\chi = 0$. This result is consistent with the general

Bohr–Van Leeuween theorem (Problem 1.15) according to which the total magnetic moment of a body obeying the classical statistics is zero. A nonzero magnetic moment will only be obtained assuming discrete electron orbits in atoms. However, such an assumption goes beyond the scope of the classical theory.

1.22 In the absence of a field, each pair of electrons of equal energy has, according to the Pauli principle, the opposite spin projections, and the microscopic magnetic moment of the system equals zero. In the presence of the field, each of the electrons acquires an additional energy $\pm \mu_B B$ depending on the direction of its spin projection. In other words, the Fermi levels of electrons with different spin projections shift by $2\mu_B B$. However, in a statistically equilibrated system there must be a single Fermi level for all particles. It means that some electrons will change the spin projection. The number density N' of spin-flip electrons can be determined from the condition $\epsilon_{F+} = \epsilon_{F-}$, or

(1)
$$\frac{\hbar^2}{2m}(6\pi)^{2/3}\left(\frac{N}{2}-N'\right)^{2/3}+\mu_B B=\frac{\hbar^2}{2m}(6\pi)^{2/3}\left(\frac{N}{2}+N'\right)^{2/3}-\mu_B B.$$

The same condition ensures minimum of internal and free energies at T = 0.

For a weak field $(\mu_B B \ll \epsilon_F)$ we will have $N' \ll N$, and from Equation (1) we obtain

(2)
$$N' = \frac{3\mu_B B}{4\epsilon_F} N.$$

The magnetization is calculated from the formula $M = 2\mu_B N'$, and the paramagnetic susceptibility of a completely degenerate electron gas (T = 0) is given by

(3)
$$\chi_{para} = \frac{3\mu_B^2 N}{2\epsilon_F}.$$

The temperature corrections to the quantity (Equation (3)) are of the order of $(T/\epsilon_F)^2 \approx 10^{-4}$ for the majority of metals at room temperature. For this reason, the "Pauli paramagnetism" (Equation (3)) unlike the Curie law [see Equation (4) in Problem 1.16 and Equation (13) in Problem 1.17] is almost independent of temperature.

A degenerate electron gas exhibits also the diamagnetic susceptibility (Landau diamagnetism):

(4)
$$\chi_{dia} = -\frac{1}{3}\chi_{para}, \qquad \chi = \chi_{para} + \chi_{dia} = \frac{2}{3}\chi_{para}$$

(see Landau and Lifshitz (1980) and Problem 1.23).

1.23 In order to calculate the magnetization, we use the formulas of statistical physics for the free energy: $F = -T \ln Z$ ((I.C46)) and $M = -\partial F/\partial B$ (Section 3.3). Since the gas is rarefied and homogeneous, we ignore the electron-electron interaction and calculate the free energy per unit

volume from the formula $F = -NT \ln z$, where z is the statistical sum of an individual electron regarded as a quasi-independent equilibrium subsystem. With the aid of the data given in the statement of the problem, we find

(1)
$$z = z_s z_{orb}, \quad z_s = \sum_{m_s = -1/2}^{m_s = 1/2} \exp\left(-\frac{2\mu_B B m_s}{T}\right) = 2\cosh\left(\frac{\mu_B B}{T}\right),$$
$$z_{orb} = \sum_{n=0}^{\infty} \exp\left(-\frac{\hbar\omega_B}{2T}(2n+1)\right) \int \exp\left(-\frac{p_z^2}{2mT}\right) \frac{eBVdp_z}{(2\pi\hbar)^2 c}$$
(2)
$$= \sqrt{2\pi mT} \frac{eBV}{(2\pi\hbar)^2 c} \frac{1}{2\sinh(\hbar\omega_B/2T)},$$

where z_s relates to the spin states and z_{orb} to the states of orbital motion. Further on, we take into consideration that $\hbar \omega_B/2 = \mu_B B$ and $\mu_B B \ll T$. Carrying out the small-argument expansion of the hyperbolic functions, we find

(3)
$$M = NT\left(\frac{\partial z_s}{\partial B} + \frac{\partial z_{orb}}{\partial B}\right) = \frac{N\mu_B^2 B}{T} - \frac{N\mu_B^2 B}{3T}$$

The first and second terms in the right-hand side describe the paramagnetic and diamagnetic effects, respectively. Now the corresponding susceptibilities depend on temperature; however the relation between them remains the same as for degenerate gas:

(4)
$$\chi_{para} = \frac{N\mu_B^2}{T}, \qquad \chi_{dia} = -\frac{1}{3}\chi_{para}$$

1.24 The number densities of ions (N) and electrons (n) can be determined from the Boltzmann formula (1.31)10)

(1)
$$N = N_0 \exp\left(-\frac{Ze\varphi}{T}\right), \quad n = n_0 \exp\left(\frac{e\varphi}{T}\right),$$

where $k_B \approx 1.38 \times 10^{-16}$ erg/K is the Boltzmann constant and $\varphi(x, y, z)$ is the electric potential. The pre-exponents are chosen so that as $T \rightarrow \infty$ (when the interaction between the particles dies out) N and n become N_0 and n_0 . With Equation (1), the charge density becomes

(2)
$$\rho = ZeN - en = eZN_0 \exp\left(-\frac{Ze\varphi}{k_BT}\right) - en_0 \exp\left(\frac{e\varphi}{k_BT}\right)$$

The potential φ should be determined by solving the Poisson equation:

(3)
$$\Delta \varphi = -4\pi \rho = -4\pi e Z N_0 \exp\left(-\frac{Ze\varphi}{k_B T}\right) + 4\pi e n_0 \exp\left(\frac{e\varphi}{k_B T}\right).$$

¹⁰⁾ In this and next three problems, the quantities being considered are averaged over statistical ensemble but not over volume.

To do this, we take into account that the interaction energy is small compared with the thermal energy:

$$\left|\frac{Ze\varphi}{k_BT}\right| \ll 1, \qquad \left|\frac{e\varphi}{k_BT}\right| \ll 1.$$

Expanding the exponents into a series to within the terms linear in φ , and using the condition of electrical neutrality of the gas, $ZN_0 = n_0$, we obtain

(4)
$$\rho = -\frac{\kappa^2}{4\pi}\varphi, \qquad \kappa^2 = \frac{4\pi e^2 (Z^2 N_0 + n_0)}{k_B T}.$$

Equation (3) can therefore be written in the form

$$(5) \qquad \qquad \bigtriangleup \varphi = \kappa^2 \varphi.$$

The potential φ can depend only on distance *r* to the ion under consideration. The spherically symmetric solution of Equation (5) is

$$\varphi = C_1 \frac{e^{-\kappa r}}{r} + C_2 \frac{e^{\kappa r}}{r}.$$

The potential cannot grow up at infinity, and hence, $C_2 = 0$. The constant C_1 is determined from the condition that at $r \ll 1/\kappa$ it must become the purely Coulomb potential of the considered ion:

$$\varphi|_{r\ll 1/\kappa} = \frac{Ze}{r} = \frac{C_1}{r}, \qquad C_1 = Ze.$$

Thus, the ion is surrounded by a "cloud" of electrons and other ions. The density of the cloud exponentially decreases. The lower the temperature, the less the average radius $1/\kappa = r_D$.

The presented method for calculating the potential was proposed by Debye¹¹⁾ and Hückel¹²⁾ and was employed by them in the theory of strong electrolytes. The constant $1/\kappa = r_D$ is referred to as the Debye–Hückel radius.

1.25 The electric induction inside the plate is described by the formula

$$D(x) = E_0 \, \frac{\cosh \kappa x}{\cosh \kappa h},$$

where $\kappa = \sqrt{4\pi e^2 n_0/\epsilon T}$. At $\kappa h \gg 1$, for the region near the surfaces $x = \pm h$, we have

$$D(x) = E_0 e^{-\kappa(h-|x|)};$$

hence, as $|x - h| \gg 1/\kappa$ we have $D(x) \to 0$, that is, the field penetrates into the conductor at a depth of about $1/\kappa$. The charge is concentrated in the

- 11) Debye Peter (1884–1966), outstanding European scientist who worked in Switzerland, Holland, Germany, and United States, had a wide range of scientific interests: theory of crystal lattice, diffraction of X-rays, quantum theory of atoms, Compton effect, theory of strong electrolytes, and so on. Nobel Prize laureate in chemistry.
- Hückel Erich (1896–1980), German physicist-theorist. Worked mainly in the field of quantum mechanics, quantum chemistry and electrochemistry.

layer of the same thickness,

$$\rho = \frac{1}{4\pi} \frac{\partial D}{\partial x} = \pm \frac{\kappa E_0}{4\pi} e^{-\kappa (h - |x|)}$$

The "surface" charge density, which is considered in the macroscopic theory, is determined by integrating ρ . On the boundary x = h, we obtain

$$\sigma = \int \rho \, dx = -\frac{\kappa E_0}{4\pi} \int_0^\infty e^{-\kappa x'} \, dx' = \frac{E_0}{4\pi},$$

which is the same as the usual boundary condition on the surface of a conductor.

1.26

$$\varphi = \varphi_0 \frac{\sinh \kappa x}{\sinh \kappa h}, \qquad \kappa = \sqrt{\frac{8\pi e^2 n_0}{\varepsilon T}}$$

In the present case the value of κ^2 is twice larger than in Problem 1.24 since there are mobile ions of two species.

1.27 Unlike Problem 1.24, this one deals with the electrons obeying the Fermi distribution. We start from the assumption that the states of the electrons in the vicinity of the ion are semi-classical. The origin is chosen at the point of the ion location and the electron number density is denoted by n(r). Far from the ion the boundary conditions are given by $n(r)|_{r\to 0} \to n_0, \ \varphi(r)|_{r\to 0} \to 0$, where $\varphi(r)$ is the electrostatic potential. At temperature $T \rightarrow 0$ all electron energy levels from the zero-level to the Fermi level ϵ_F are occupied. Far from the ion the Fermi level is determined by the conditions

(1)
$$\frac{2}{(2\pi\hbar)^3} \cdot \frac{4}{3}\pi p_F^3 = n_0, \qquad \epsilon_F = \frac{p_F^2}{2m} = \frac{(3\pi^2 n_0)^{2/3}\hbar^2}{2m}.$$

Here, the Fermi momentum p_F is calculated from the fact that the number of occupied states $p_F^3/3\pi^2\hbar^3$ is equal to the number of the electrons n_0 per unit volume.

The Fermi energy retains the value given by Equation (1) throughout space, since, otherwise, the electrons will move to the sites with lower ϵ_F . However, at finite *r* the Fermi energy ϵ_F should be regarded as a sum of the kinetic and potential energies,

(2)
$$\epsilon_F = \frac{(3\pi^2)^{2/3}\hbar^2}{2m} n^{2/3}(r) - e\varphi(r).$$

Expressing n(r) from Equations (1) and (2), we have

(3)
$$n(r) = n_0 \left[1 + \frac{e\varphi(r)}{\epsilon_F} \right]^{3/2} \approx n_0 \left[1 + 3\frac{e\varphi(r)}{2\epsilon_F} \right].$$

Using the last equation, we find the charge density distribution in the vicinity of the ion, $\rho(r) = -(3e^2n_0/2\epsilon_F)\varphi(r)$. For the potential we obtain

Equation (5) from the solution of Problem 1.24, where the screening constant is given by

(4)
$$\kappa^2 = \frac{4me^2}{\hbar^2} \left(\frac{3n_0}{pi}\right)^{1/3} = \frac{8}{a_B \lambda_F}$$

Here, $a_B = \hbar^2/me^2$ is the Bohr radius, and $\lambda_F = 2\pi\hbar/p_F$ is the De Broglie wavelength of the electron at the Fermi level.

1.28 Let us use the kinetic equation as in Example 1.5. For the equilibrium distribution function, we substitute the Fermi step-function $f_0(\epsilon)$ ($f_0(\epsilon) = 1$, $\epsilon \le \epsilon_F$; $f_0(\epsilon) = 0$, $\epsilon > \epsilon_F$, where ϵ_F is the Fermi energy expressed through particle number density – see the statement of Problem 1.22). Using the relation $\boldsymbol{v} = \partial \epsilon / \partial \boldsymbol{p}$, we write

(1)
$$\delta f = -e(\boldsymbol{E} \cdot \boldsymbol{v})\tau(\epsilon)\frac{\partial f_0}{\partial \epsilon},$$

and obtain the expression for the current density

(2)
$$\mathbf{j} = -e^2 \int \tau(\epsilon) \mathbf{v}(\mathbf{E} \cdot \mathbf{v}) \frac{\partial f_0}{\partial \epsilon} \frac{2 \, d^3 p}{(2\pi\hbar)^3},$$

where the last fraction under the integral presents the number of the quantum states including two spin projections.

For a degenerate electron gas, we have $\partial f_0 / \partial \epsilon = -\delta(\epsilon - \epsilon_F)$. Substituting the required quantities into Equation (2) and integrating over the energy with the aid of the delta-function, we obtain the electric conductivity, which is the coefficient of proportionality between the current and the electric field strength:

(3)
$$\kappa = \frac{ne^2\tau(\epsilon_F)}{m}.$$

This result coincides with the Drude formula (1.42).

In real metals, an electron gas interacts with a crystal lattice. As a result, the energy dependence of the particle on its momentum, $\epsilon(\mathbf{p})$, becomes more complicated, the effective mass of charge carriers may be anisotropic, and the Fermi surface in momentum space non-spherical. In this case, the simple model considered above is inapplicable.

1.29 A nonequilibrium additive correction to the electron distribution function, produced by weak electric and magnetic fields in the first order, is calculated from the kinetic equation and has the form

(1)
$$\delta f = \left(-e(\boldsymbol{E}\cdot\boldsymbol{v})\tau + \frac{e^2\tau^2}{mc}[\boldsymbol{E}\times\boldsymbol{B}]\cdot\boldsymbol{p}\right)\frac{\partial f_0}{\partial\epsilon}.$$

Using this distribution function, we find the current density

(2)
$$\mathbf{j} = \kappa \mathbf{E} + \mathbf{E} \times \mathbf{a},$$

where

(3)
$$\kappa = \frac{ne^2\tau}{m}, \qquad a = \frac{ne^3\tau^2}{m^2c}B.$$

The electric conductivity, under the action of the magnetic field, becomes anisotropic,

(4)
$$\kappa_{\alpha\beta} = \kappa \delta_{\alpha\beta} - e_{\alpha\beta\gamma} a_{\gamma},$$

and the electric current perpendicular to the magnetic field is induced (the Hall¹³⁾ current). The inverse dependence between the current and the electric field in the same approximation is of the form

(5)
$$E = \frac{1}{\kappa} \boldsymbol{j} - R[\boldsymbol{j} \times \boldsymbol{B}],$$

where R = 1/cen is the Hall constant.

1.30 We write down the stationary kinetic equation with allowance for the firstorder terms in *E*, but without restriction on values of *B*:

(1)
$$eE \cdot \frac{\partial f_0}{\partial p} + \frac{e}{c} [v \times B] \cdot \frac{\partial \delta f}{\partial p} = -\frac{\delta f}{\tau}$$

Multiply both parts of Equation (1) by ev, integrate over momenta, and transform this equation into the algebraic equation for the current $\mathbf{i} = e \int \mathbf{v} \delta f d^3 p$. Multiplying the result by τ , we obtain

(2)
$$\kappa E = j - \tau j \times \omega_B,$$

where κ is given by Equation (3) of Problem 1.29, and $\omega_{\rm B} = eB/mc$ is the cyclotron frequency. Resolving Equation (2) with respect to the components of **j**, we find $j_{\alpha} = \kappa_{\alpha\beta} E_{\beta}$, where the electric conductivity tensor is

(3)
$$\kappa_{\alpha\beta} = \begin{pmatrix} \kappa_{\perp} & \kappa_{H} & 0\\ -\kappa_{H} & \kappa_{\perp} & 0\\ 0 & 0 & \kappa_{\parallel} \end{pmatrix}, \text{ where } \kappa_{\perp} = \frac{\kappa}{1 + (\omega_{B}\tau)^{2}},$$
$$\kappa_{H} = \frac{\kappa(\omega_{B}\tau)}{1 + (\omega_{B}\tau)^{2}}, \quad \kappa_{\parallel} = \kappa.$$

The subscripts \perp and \parallel denote the directions perpendicular and parallel to the magnetic field, respectively. The component $\kappa_{\!H}$ is responsible for the Hall current.

The quantity $\omega_{\rm B}\tau$ is the rotation angle of the transverse momentum of the particle during relaxation time, when it is moving along a spiral trajectory. If $\omega_B \tau \ll 1$, the effect of the magnetic field is insignificant and the electric conductivity is almost isotropic. In the opposite case, when $\omega_B \tau \gg 1$, the conductivity is strongly anisotropic: $\kappa_{\parallel} \gg \kappa_H \gg \kappa_{\perp}$.