

Virial theorem and some properties of the electron gas in metals

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Abstract. The status of the virial theorem in classical and quantum mechanics is discussed and the principal virial relationships are derived. A model of the electron Fermi gas in a metal is considered taking explicit account of the consequences of the virial theorem for a stable system of electrons and ions interacting in accordance with the Coulomb law. This model is used to obtain expressions for the total energy and the chemical potential of the conduction electrons in undeformed and deformed metals. These expressions are used to estimate the equilibrium concentrations of electrons and ions, the electron work function of a metal, and the contribution of the collective-state electrons to the bulk modulus of a metal. It is shown that an electric field appears in an inhomogeneously deformed metal and that this field is proportional to the gradient of the bulk strains. A space charge, which is compensated by a surface charge of opposite sign, also appears in such a metal.

1. Introduction

In the electron theory of metals the conduction electrons are regarded as a degenerate Fermi gas inside a potential well created by the field of ions. The electrons and ions in a metal interact in accordance with the Coulomb law and form a stable quantum system which, to some extent, resembles a single atom or a molecule†.

†This analogy was stressed by Frenkel' [1].

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Stable classical and quantum systems obey the 'virial theorem' first formulated by Clausius over 120 years ago (see, for example, Refs [2–4]). This theorem follows from the most general principles of classical and quantum mechanics. In particular, if particles interact in accordance with the Coulomb law, it follows from the virial theorem that

$$2\bar{T} = -\bar{U}, \quad (1)$$

where \bar{T} is the average kinetic energy of the particles and \bar{U} is the average potential energy.

We shall use the virial theorem to describe some properties of the electron gas in a metal. This theorem makes it possible to readily estimate the equilibrium concentrations of electrons and ions, the electron work function of a metal, and the contribution of collective-state electrons to the bulk modulus (compressibility) of a metal.

The Coulomb interaction leads to a significant renormalisation of the chemical potential of the electron gas in undeformed and deformed metals.

2. Virial theorem in classical and quantum mechanics

We shall consider a system of interacting particles which are moving in a bounded part of space. The total kinetic energy of these particles is

$$T = \frac{1}{2} \sum_i m_i v_i^2 = \frac{1}{2} \sum_i \mathbf{P}_i \cdot \frac{d\mathbf{r}_i}{dt}. \quad (2)$$

We shall rewrite Eqn (2) in the form

$$T = \frac{1}{2} \frac{d}{dt} \sum_i \mathbf{P}_i \cdot \mathbf{r}_i - \frac{1}{2} \sum_i \mathbf{r}_i \cdot \mathbf{F}_i. \quad (3)$$

Here, $\mathbf{F}_i = d\mathbf{P}_i/dt$ is a force acting on the i th particle.

We shall average Eqn (3) over a very long time. Since the momenta and coordinates of the particles in bounded motion are finite, it follows that

$$\overline{\frac{d}{dt} \sum_i \mathbf{P}_i \cdot \mathbf{r}_i} = 0. \quad (4)$$

This leads to the virial theorem

$$2\bar{T} = -\overline{\sum_i \mathbf{r}_i \cdot \mathbf{F}_i} . \quad (5)$$

The right-hand side of Eqn (5) is usually called the virial of the system (from the Latin 'vires', which means forces) [2]†.

If the system is conservative, then

$$\mathbf{F}_i = -\frac{\partial}{\partial \mathbf{r}_i} U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n) , \quad (6)$$

where $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n)$ is the potential energy of the interaction. Substitution of Eqn (6) into Eqn (5) gives

$$2\bar{T} = \overline{\sum_i \mathbf{r}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n)} . \quad (7)$$

We shall consider an important case when there are no external forces and the potential $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n)$ consists of pair potentials $\varphi(r_{ik})$ that depend only on the distance between the particles ($r_{ik} = |\mathbf{r}_i - \mathbf{r}_k|$). Then

$$U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n) = \frac{1}{2} \sum_{i \neq k} \sum \varphi_{ik}(r_{ik}) , \quad (8)$$

$$\frac{\partial}{\partial \mathbf{r}_i} U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n) = \sum_{k(\neq i)} \frac{\mathbf{r}_i - \mathbf{r}_k}{r_{ik}} \frac{d\varphi_{ik}(r_{ik})}{dr_{ik}} , \quad (9)$$

and Eqn (7) becomes

$$2\bar{T} = \frac{1}{2} \overline{\sum_{i \neq k} \sum r_{ik} \frac{d\varphi_{ik}(r_{ik})}{dr_{ik}}} . \quad (10)$$

If the pair potentials obey $\varphi_{ik} \propto r_{ik}^n$, we have

$$\frac{1}{2} \overline{\sum_{i \neq k} \sum r_{ik} \frac{d\varphi_{ik}(r_{ik})}{dr_{ik}}} = \frac{1}{2} n \overline{\sum_{i \neq k} \sum \varphi_{ik}(r_{ik})} . \quad (11)$$

Then, subject to Eqn (8), a simple relationship applies between the average kinetic energy \bar{T} and the average potential energy \bar{U} :

$$2\bar{T} = n\bar{U} . \quad (12)$$

If the particles interact in accordance with the Coulomb law ($n = -1$), then Eqn (1) applies. In quantum mechanics the initial expression of Eqn (3) is still valid, but it should be regarded as an operator relationship. In quantum mechanics the bounded motion corresponds to stationary states of a many-body system with a discrete energy spectrum. For a stationary state the average value of a time-derivative operator vanishes. This means that the virial theorem also remains valid in quantum mechanics:

$$2\langle \hat{T} \rangle = \sum_i \left\langle \mathbf{r}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n) \right\rangle . \quad (13)$$

The symbol $\langle \dots \rangle$ denotes quantum-mechanical average and

$$\hat{T} = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2$$

†Virial is sometimes defined as the quantity

$$\sum_i \mathbf{r}_i \cdot \mathbf{F}_i ,$$

i.e. the right-hand part of Eqn (5) without the minus sign [5], or as half this value.

is the kinetic energy operator. If the particles interact in accordance with the Coulomb law, we find that

$$2\langle T \rangle = -\langle U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n) \rangle . \quad (14)$$

The total energy of a stationary state is then equal to the average kinetic energy with its sign reversed:

$$E = -\langle T \rangle . \quad (15)$$

Since all the atomic and molecular systems (including solids!) consist of particles interacting in accordance with the Coulomb law, the relationships (14) and (15) should apply to them. The source of the exchange energy, which ensures chemical binding, is also the Coulomb interaction. Consequently, in Eqn (14) the quantity $\langle T \rangle$ should be regarded as the average kinetic energy of all the electrons and nuclei, and the quantity $\langle U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n) \rangle$ includes also the exchange energy, which is due to antisymmetrisation of the wave function of identical electrons. In particular, it follows from Eqn (15) that the dissociation energy of the hydrogen molecule is equal to the average sum of the kinetic energies of two electrons and two protons (in a reference system in which the centre of mass of the molecule is at rest).

It should be stressed that the virial theorem—represented by Eqns (7), (10), (14), and (15)—remains valid also in the case of complex microscopic systems: it is then necessary to carry out an additional averaging over a statistical ensemble. From now on we shall use a bar to denote the averages, irrespective of the nature of the averaging process.

We have assumed so far that no external forces act on the system and, in particular, that there is no external pressure. Let us now consider the case when the pressure is $P \neq 0$. The total external force is still zero because otherwise the motion of the system would not have been bounded. Also, Eqn (5) is valid under these conditions: the right-hand side of Eqn (17) should be supplemented by the virial of the 'walls'. We must now write

$$2\bar{T} = \overline{\sum_i \frac{\partial}{\partial \mathbf{r}_i} U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n)} + P \oint_S d\mathbf{S} \cdot \mathbf{r}_i . \quad (16)$$

Here, $d\mathbf{f} = -P d\mathbf{S}$ is the force acting on an element of a closed surface S which is the boundary of the volume V of a body, and $d\mathbf{S} = \mathbf{n} dS$, where \mathbf{n} is a unit vector along the direction of the outer normal to the surface S .

It follows from the Gauss theorem that

$$\oint_S d\mathbf{S} \cdot \mathbf{r} = \int_V \text{div} \mathbf{r} dV = 3V . \quad (17)$$

Substitution of Eqn (17) into Eqn (16) yields the equation of state

$$PV = \frac{2}{3} \bar{T} - \frac{1}{3} \overline{\sum_i \mathbf{r}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n)} . \quad (18)$$

If the potential energy has the structure of Eqn (7) with $\varphi_{ik} \propto r_{ik}^n$, then [4]

$$PV = \frac{1}{3} \bar{T} - \frac{n}{3} \bar{U} \quad (19)$$

or

$$PV = -\frac{nE}{3} + \frac{n+2}{3} \bar{T} , \quad (20)$$

where $E = \bar{T} + \bar{U}$ is the total energy of the system. In the Coulomb interaction case ($n = -1$) Eqns (19) and (20) give

$$PV = \frac{2\bar{T} + \bar{U}}{3} = \frac{E + \bar{T}}{3}. \quad (21)$$

Consequently, in the absence of pressure we have

$$E + \bar{T} = 0$$

in full agreement with Eqn (15).

The relationship (16) can readily be generalised to the case of arbitrary inhomogeneous strains created by bulk and surface external forces. The virial theorem then becomes

$$2\bar{T} = \overline{\sum_i \mathbf{r}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n)} - \int_V \mathbf{f} \cdot \mathbf{r} dV - \oint_S \sum_{\alpha=1}^3 \sum_{\beta=1}^3 t_{\alpha\beta} dS_{\beta} x_{\alpha}. \quad (22)$$

Here, $t_{\alpha\beta}$ are elements of the stress tensor [5] and \mathbf{f} is the external force acting on a unit volume. The second term on the right-hand side of Eqn (22) describes the virial of the bulk external forces and the third term represents the virial of the surface forces. Application of the Gauss theorem gives

$$-\oint_S \sum_{\alpha=1}^3 \sum_{\beta=1}^3 t_{\alpha\beta} dS_{\beta} x_{\alpha} = - \int_V \left(\sum_{\alpha=1}^3 \sum_{\beta=1}^3 \frac{\partial t_{\alpha\beta}}{\partial x_{\beta}} x_{\alpha} \right) dV - \int_V \left(\sum_{\alpha=1}^3 t_{\alpha\alpha} \right) dV. \quad (23)$$

On the other hand, under equilibrium conditions we have

$$\mathbf{f}_{\alpha} = - \sum_{\beta=1}^3 \frac{\partial t_{\alpha\beta}}{\partial x_{\beta}}, \quad (24)$$

so that

$$\mathbf{f} \cdot \mathbf{r} = - \sum_{\beta=1}^3 \sum_{\alpha=1}^3 \frac{\partial t_{\alpha\beta}}{\partial x_{\beta}} x_{\alpha}. \quad (25)$$

Substituting Eqns (23) and (25) into Eqn (22), we obtain

$$2\bar{T} = \overline{\sum_i \mathbf{r}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)} - \int_V \left(\sum_{\alpha=1}^3 t_{\alpha\alpha} \right) dV. \quad (26)$$

In the case of a homogeneous hydrostatic strain, when $t_{\alpha\beta} = -PS_{\alpha\beta}$, Eqn (26) reduces to Eqn (16).

3. Virial theorem and the energy of the electron gas in metals. Equilibrium condition

In the absence of an external pressure the average kinetic and potential energies of electrons and ions in a metal should be related by Eqn (1). Then

$$2(\bar{T}_e + \bar{T}_i) = -\bar{U}, \quad (27)$$

where \bar{T}_e is the average kinetic energy of the electrons, \bar{T}_i is the average kinetic energy of the ions, and \bar{U} is the average potential energy.

If we take into account the external pressure, which creates hydrostatic compressive or tensile strains, we find from the expressions in Eqn (21) that

$$\frac{2(\bar{T}_e + \bar{T}_i) + \bar{U}}{V} = 3P. \quad (28)$$

Eqn (28) remains valid also in the case of inhomogeneous strains provided T/V and U/V are replaced with the appropriate local densities of the kinetic and potential energies†.

It should be stressed that, strictly speaking, the initial equation (1) applies to a completely isolated system of all the electrons and nuclei in a metal, interacting in accordance with the Coulomb law. However, in the first approximation, we can consider the subsystems of free and bound electrons independently and we can therefore apply the virial theorem for the Coulomb interaction separately to the motion of the conduction electrons and charged ions, and to the internal motion of the bound electrons and nuclei (some of the bound electrons are in a collective state under the influence of the neighbouring ions, which ensures binding of the lattice).

We shall be interested only in the properties of the conduction-electron gas. It is important to stress that, in view of the large mass of the ions, their kinetic energy can be ignored compared with the kinetic energy of electrons. If $\bar{T}_i \ll \bar{T}_e$, Eqn (3) gives

$$2\bar{T}_e + \bar{U} = 3P_e V, \quad (29)$$

where P_e is the partial pressure of the electron gas. The relationship given by Eqn (29) is obviously the equation of state of the electron gas in a metal.

We shall assume, as usual, that the conduction electrons are inside a certain effective potential well. In this model under degeneracy conditions, i.e. at temperatures much lower than $10^4 - 10^5$ K, the average kinetic energy of the electrons is described by the familiar expression

$$\bar{T}_e = \frac{3}{5} N z E_F, \quad (30)$$

where N is the number of the ions, z is the charge of an ion, and E_F is the Fermi energy.

We then have

$$E_F = (3\pi^2)^{2/3} \frac{\hbar^2}{2m} (nz)^{2/3}, \quad (31)$$

where $n = N/V$ is the concentration of the ions, nz is the concentration of the electrons, and m is the mass of an electron.

It is worth noting that if we take into account the virial theorem, the potential energy of the system of free electrons and ions and the effective depth of the potential well for one electron cannot be arbitrary: they should be in one-to-one relationship with the average kinetic energy of the electrons and proportional to the Fermi energy E_F .

Let us examine this problem in greater detail. The potential energy of this system of electrons and ions includes the contributions of the following components: the Coulomb interaction of electrons with one another (including the exchange energy), the Coulomb interaction of ions and electrons, and the Coulomb interaction of ions with one another. Calculations show that in this case the average potential energy is [6]

$$\bar{U} = -C(z)e^2(Nz)(nz)^{1/3}, \quad (32)$$

where $C(z)$ is a coefficient which is of the order of unity and depends on the lattice structure; e is the electron

†For arbitrary strains we must also make the substitution $3P \rightarrow -(t_{xx} + t_{yy} + t_{zz})$, where t_{ii} are the diagonal elements of the stress tensor [see Eqn (26)].

charge. Consequently, the total energy of electrons and ions is given by the expression

$$E = \bar{T}_e + \bar{U} = \frac{3}{5}(3\pi^2)^{2/3} \frac{\hbar^2}{2m} (nz)^{2/3} Nz - C(z)Nze^2(nz)^{1/3}. \quad (33)$$

It should be noted that the total energy of Eqn (33) is independent of temperature and is identical with the free energy F .

We shall demonstrate that the dependence of the average potential energy on the concentration of ions

$$\bar{U} \propto n^{1/3}$$

is a rigorous consequence of the virial theorem for the Coulomb interaction. Let us represent \bar{U} in the general form

$$\bar{U} = N\varphi(n), \quad (34)$$

which satisfies the requirement of additivity. According to Eqn (29), we have

$$P_e = P_0 + \frac{1}{3}n\varphi(n), \quad P_0 = \frac{1}{3V}\bar{T}_e. \quad (35)$$

Here, P_0 is the pressure related to the kinetic energy of the electrons and P_e is the total pressure of the electron gas. On the other hand, if we allow for the temperature independence of the total energy, we can define the pressure by

$$P_e = -\frac{\partial E}{\partial V}, \quad (36)$$

which gives

$$P_e = P_0 + n^2 \frac{d\varphi(n)}{dn}, \quad n = \frac{N}{V}. \quad (37)$$

A comparison of Eqns (35) and (37) leads to the equation

$$\varphi(n) = 3n \frac{d\varphi(n)}{dn}. \quad (38)$$

Hence, we find that

$$\varphi(n) = \text{const} \times n^{1/3}$$

in full agreement with Eqn (32).

According to the virial theorem, in the absence of an external pressure the average potential energy of electrons and ions is equal to twice the average kinetic energy of the conduction electrons taken with the reversed sign:

$$\bar{U} = -2(\bar{T}_e + \bar{T}_i) \cong -2\bar{T}_e.$$

It follows from Eqn (30) that

$$\bar{U} = -\frac{6}{5}NzE_F, \quad (39)$$

$$E = \bar{T}_e + \bar{U} = -\frac{3}{5}NzE_F. \quad (40)$$

For real metals Eqns (39) and (40) represent a satisfactory approximation provided the external pressure is $P \ll 10^{10}$ Pa.

The virial theorem can be used to find the equilibrium ion concentration n_0 in an undeformed metal, i.e. at zero external pressure. In fact, it follows from Eqns (30)–(32) that in the case of a stable equilibrium of the system of electrons and ions we have

$$\frac{6}{5}(3\pi^3)^{2/3} \frac{\hbar^2}{2m} (n_0z)^{2/3} = C(z)e^2(n_0z)^{1/3}. \quad (41)$$

Hence,

$$n_0 = \frac{125}{243\pi^4} \left(\frac{1}{a_0}\right)^3 C^3(z) \frac{1}{z}, \quad (42)$$

where

$$a_0 = \frac{\hbar^2}{me^2} = 0.53 \times 10^{-8} \text{ cm}$$

or

$$n_0 \cong 3.5C^3(z) \frac{1}{z} 10^{22} \text{ cm}^{-3}.$$

This result is in order-of-magnitude agreement with the real values of the density of metals. Similar estimates had been obtained by Frenkel' within the framework of the 'diatomic model' of a solid [1].

We shall use $E_F^{(0)}$ to denote the Fermi energy for an equilibrium concentration of ions $n = n_0$. According to Eqns (30) and (31), if there is a finite external pressure resulting in compressive ($P > 0$, $n > n_0$) or tensile ($P < 0$, $n < n_0$) strains, the average kinetic energy of the electron gas is

$$\bar{T}_e = \frac{3}{5}NzE_F^{(0)} \left(\frac{n}{n_0}\right)^{2/3}. \quad (43)$$

Bearing in mind that, according to Eqn (32), $U \propto n^{1/3}$, and that the equality $\bar{U} = -2\bar{T}_e$ should be obeyed for $n = n_0$, we readily obtain the following expressions for the average potential energy and the total energy of electrons and ions in a deformed metal:

$$\bar{U} = -\frac{6}{5}NzE_F^{(0)} \left(\frac{n}{n_0}\right)^{1/3}, \quad (44)$$

$$E = -\frac{3}{5}NzE_F^{(0)} \left[2\left(\frac{n}{n_0}\right)^{1/3} - \left(\frac{n}{n_0}\right)^{2/3} \right]. \quad (45)$$

It is clear that if $n = n_0$, then

$$\frac{dE}{dn} = 0, \quad \frac{d^2E}{dn^2} = \frac{2}{15}Nz \frac{E_F^{(0)}}{n_0^2} > 0. \quad (46)$$

As expected, we can see that in an equilibrium state defined by the virial theorem the total energy E is minimal, which ensures stability of the binding of electrons and ions.

4. Chemical potential of the electrons in a metal and the work function

We shall describe the number of electrons in a metal by

$$N_e = Nz = nVz \quad (47)$$

and rewrite Eqn (45) in the form

$$E = -\frac{3}{5}N_e E_F^{(0)} \left[2\left(\frac{N_e}{zVn_0}\right)^{1/3} - \left(\frac{N_e}{zVn_0}\right)^{2/3} \right]. \quad (48)$$

As pointed out already, in the adopted approximation the total energy E is equal to the free energy. The general definition of the chemical potential (see, for example, Ref. [5]) readily yields, on the basis of Eqn (48), an explicit expression for the chemical potential of electrons in a metal:

$$\mu_e = \left(\frac{\partial F}{\partial N_e}\right)_V = \left(\frac{\partial E}{\partial N_e}\right)_V = E_F^{(0)} \left[\left(\frac{n}{n_0}\right)^{2/3} - \frac{8}{5} \left(\frac{n}{n_0}\right)^{1/3} \right]. \quad (49)$$

A direct calculation of the thermodynamic potential of a metal per electron leads to Eqn (49). In fact, if we take account of Eqn (28), the thermodynamic potential is found to be a linear combination of the total and potential energies:

$$\Phi = F + PV = E + PV = \frac{5}{3}E - \frac{1}{3}\bar{U}. \quad (50)$$

Substitution of Eqns (45) and (44) on the right-hand side of Eqn (50) and division of the result by the number of electrons Nz gives Eqn (49).

If $n \approx n_0$, the chemical potential of electrons in a metal is

$$\mu_e = -\frac{3}{5}E_F^{(0)}. \quad (51)$$

We can see that the chemical potential μ_e is negative relative to vacuum. A positive quantity

$$W = -\mu_e = \frac{3}{5}E_F^{(0)} \quad (52)$$

is the ‘work function’ which is the work that has to be done in breaking the binding of an electron to ions and removing this electron from a metal to vacuum. Therefore, in our model of the electron gas the electron work function of a metal represents three-fifths of the Fermi energy. The surface effects are ignored here, but they can significantly affect the work function.

The contribution of the kinetic energy of the electron gas to the chemical potential is equal to the Fermi energy. We shall represent the chemical potential of an electron in the form [7]

$$\mu_e = -W = E_F^{(0)} + u.$$

Here, u is the effective self-consistent potential of one electron. It follows from Eqn (51) that the depth of the potential well containing an electron in a metal is

$$u = -\frac{8}{5}E_F^{(0)}. \quad (53)$$

The quantity $\phi = u/e$ determines the jump in the electrostatic potential across a double layer at the vacuum–metal interface.

Eqn (31) for the Fermi energy and Eqns (52) and (53) allow us to express readily the work function and the depth of the potential well in terms of the density of a metal ρ and the mass number of the element:

$$W = 15.6 \left(\frac{\rho z}{A} \right)^{2/3}, \quad (54)$$

$$u = -41.6 \left(\frac{\rho z}{A} \right)^{2/3}. \quad (55)$$

Here, W and u are in electron volts, and ρ is in grammes per centimetre.

In the case of some metals such as Ca, Sr, Cu, and Hg the experimental values of the work function are almost identical with the results of calculations based on Eqn (54). In the case of other metals the agreement is poorer, but the ratio of the theoretical and experimental values $W_{\text{th}}/W_{\text{exp}}$ lies within the interval 0.5–1.75 (Fig. 1).

The quantity z in Eqns (31), (54), and (55) gives the number of conduction electrons per nucleus. It is usual to assume that z is identical with the valence of an element.

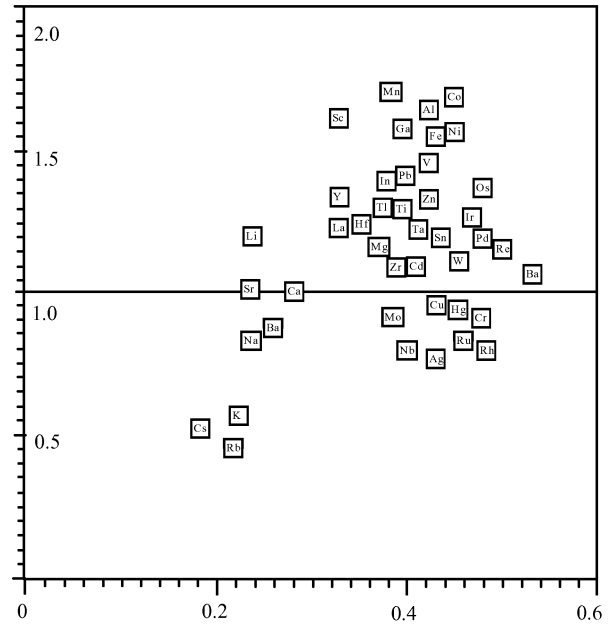


Figure 1. Work function calculated from Eqn (52) and the experimental values obtained for various metals. The ordinate gives the value of $3E_F/5W_{\text{exp}}$ and the abscissa represents the experimental values of the work function W_{exp} in electron volts.

But an element may have several valences and the problem of the number of collective-state electrons does not have an unambiguous solution. Ions in a metal may carry different charges and in particular some of them may be in the form of neutral atoms. Therefore, we shall replace z by ‘effective valence’ \tilde{z} which need not be an integer. Moreover, a correction is necessary for the finite volume of an ion which is inaccessible to the collective-state electrons because of the Pauli principle. If we take into account the finite volume of an ion, we find that the Fermi energy is proportional to $\tilde{n}^{2/3}$, where

$$\tilde{n} = n(1 - v_0 n)^{-1} = \frac{N}{V - v_0 N} \quad (56)$$

and v_0 is the characteristic volume of an ion[†].

Consequently, the expressions for the work function and the depth of the potential well become

$$W = 15.6 \left(\frac{\rho}{A} \frac{\tilde{z}}{1 - v_0 n} \right)^{2/3} \text{ eV}, \quad (57)$$

$$U = -41.6 \left(\frac{\rho}{A} \frac{\tilde{z}}{1 - v_0 n} \right)^{2/3} \text{ eV}, \quad (58)$$

5. Elastic properties of metals

We shall now find the contribution of the conduction electrons to the bulk modulus (compressibility) of a metal. By definition, the bulk modulus is

$$K_e = -V \frac{dP_e}{dV} = n_e \frac{dP_e}{dn_e} = n \frac{dP_e}{dn}. \quad (59)$$

[†]If $v_0 \neq 0$, Eqn (42) defines the concentration \tilde{n}_0 and the ‘true’ equilibrium concentration of ions is given by

$$n_0 = \frac{\tilde{n}_0}{1 + v_0 \tilde{n}_0}.$$

Here, P_e is the pressure, n_e and $n = n_e/z$ are the concentrations of electrons and ions, respectively. If we combine Eqns (29), (43), and (44), we obtain the following expression for the electron gas pressure

$$P_e = \frac{2}{5} z n E_F^{(0)} \left[\left(\frac{n}{n_0} \right)^{2/3} - \left(\frac{n}{n_0} \right)^{1/3} \right]. \quad (60)$$

Hence,

$$K_e = \frac{2}{5} z n E_F^{(0)} \left[\frac{5}{3} \left(\frac{n}{n_0} \right)^{2/3} - \frac{4}{3} \left(\frac{n}{n_0} \right)^{1/3} \right]. \quad (61)$$

As pointed out already, the equilibrium concentration of ions n_0 corresponds to zero pressure. According to Eqn (61), under equilibrium conditions (when $n = n_0$), the bulk modulus of the electron gas in a metal is

$$K_e = \frac{2}{15} z n_0 E_F^{(0)} \quad (62)$$

and is related to the work function, given by Eqn (28), by the simple expression

$$K_e = \frac{2}{5} z n_0 W. \quad (63)$$

We shall now find the correction for the finite volume of an atom. The expression for the pressure becomes

$$P_e = \frac{2}{5} z \tilde{n} E_F^{(0)} \left(\frac{\tilde{n}_0}{n_0} \right)^{2/3} \left[\left(\frac{\tilde{n}}{\tilde{n}_0} \right)^{2/3} - \left(\frac{\tilde{n}}{\tilde{n}_0} \right)^{1/3} \right], \quad (64)$$

where $E_F^{(0)}$ is still the Fermi energy corresponding to the equilibrium concentration $n = n_0$, and

$$\tilde{n} = \frac{n}{1 - v_0 n}, \quad \tilde{n}_0 = \frac{n_0}{1 - v_0 n_0}. \quad (65)$$

Since

$$\frac{d\tilde{n}}{dn} = \frac{1}{(1 - v_0 n)^2}, \quad (66)$$

we find that

$$K_e = \frac{2}{5} z n_0 E_F^{(0)} (1 - v_0 n_0)^{-8/3}, \quad (67)$$

i.e. the result of Eqn (31) is multiplied by the coefficient

$$\beta = (1 - v_0 n_0)^{-8/3} > 1. \quad (68)$$

It follows from Eqn (31) that the bulk modulus obeys $K_e \propto z^{5/3}$. If the role of z is played by the effective valence \tilde{z} , then $K_e \propto \tilde{z}^{5/3}$. The relationship between the bulk modulus and the work function thus becomes

$$K_e = \frac{2}{5} n_0 \tilde{z} W (1 - v_0 n_0)^{-2}. \quad (69)$$

Calculation of the bulk modulus of a metal without allowance for the finite-volume correction [Eqn (63)] gives underestimated values for all metals. It should be noted that there are two groups of metals (Fig. 2).

Metals belonging to the first group (for example, noble metals, metals of the platinum group, and transition metals) all have a rigid ion lattice and the bulk modulus of the electron gas calculated without the finite-volume correction is approximately an order of magnitude less than the experimental value. The bulk modulus of a metal is then dominated by the lattice contribution, i.e. by the exchange coupling between the neighbouring ions because of an overlap of the wave functions of electrons that are not 'free' but are partly in a collective state. The contribution of the conduction electrons does not exceed 10%.

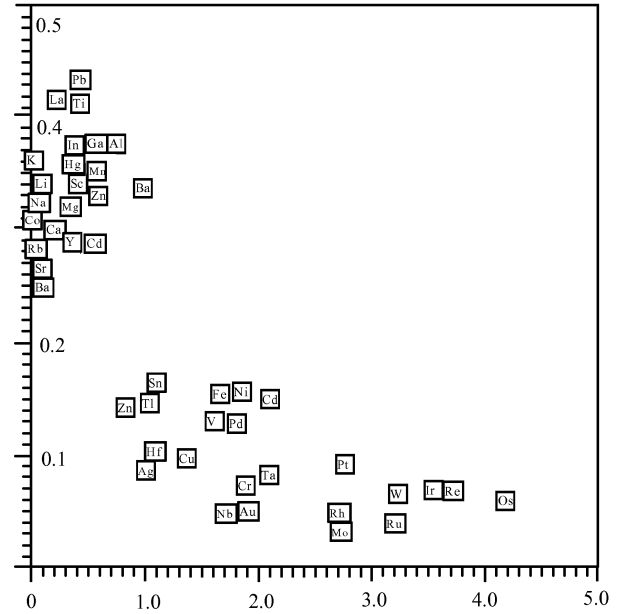


Figure 2. Bulk modulus calculated from Eqn (63) and the experimental values obtained for various metals. The ordinate gives the value of $2zn_0W_{\text{exp}}/9K_{\text{exp}}$, and the abscissa represents the experimental values of the bulk modulus K_{exp} in units of 10^{12} dyn cm^{-2} .

The second group of metals includes, for example, alkali and alkaline-earth elements whose compressibility calculated without the finite-volume correction is smaller by not more than a factor of 2–3 than the experimental values (Fig. 2). In any case, the elastic properties of metals cannot be explained entirely within the framework of our model of the electron gas if no allowance is made for additional factors.

6. Electrostatic phenomena in inhomogeneously deformed metals

The concentrations of electrons and ions and, consequently, the chemical potential μ_e (regarded as a function of the concentrations) in an inhomogeneously deformed metal are functions of the coordinates. Under thermodynamic equilibrium conditions the total ('electrostatic') potential of electrons should be constant. As shown below, this gives rise to a space charge inside a metal. It follows from the electrical neutrality condition that this space charge should be compensated by a surface charge concentrated in a narrow layer whose thickness is equal to the Debye radius of screening in a degenerate plasma. The surface and space charges create an electric field both inside and outside an inhomogeneously deformed metal†.

We shall now consider in greater detail the electrostatic phenomena that occur in inhomogeneously deformed metals and we shall do this with an aid of an explicit

†The question of the appearance of an electric field in an inhomogeneously deformed metal has been discussed earlier [8]. However, no allowance has been made for the dependence of the self-consistent potential inside a metal on the electron concentration, which follows from the virial theorem. This has led to expressions different from ours. In particular, the right-hand side of Eqn (10) in Ref. [8] should be multiplied by the coefficient 1/5.

expression for the chemical potential of electrons that follows from the virial theorem.

We shall use $\varphi(\mathbf{r})$ for the additional electrostatic potential. The condition of constancy of the electrochemical potential gives†

$$\mu_e(\mathbf{r}) + e\varphi(\mathbf{r}) = \text{const}, \quad (70)$$

where $e = -|e|$ is the electron charge and the chemical potential (with account taken of the relative smallness of the space charge) is described by Eqn (25) where the concentration of ions is $n = n(\mathbf{r})$.

According to Eqn (70), the electric field inside an inhomogeneously deformed metal can be expressed in terms of the gradient of the chemical potential:

$$\mathbf{E} = -\nabla\varphi(\mathbf{r}) = \frac{1}{e}\nabla\mu_e(\mathbf{r}). \quad (71)$$

Let us now apply the Laplace operator to Eqn (70). It follows from the Poisson equation that

$$\nabla^2\varphi(\mathbf{r}) = -4\pi eb(\mathbf{r}), \quad (72)$$

where the function $eb(\mathbf{r})$ represents the density of the space charge inside the metal. This leads to

$$\nabla^2\mu_e(\mathbf{r}) = 4\pi^2 e^2 b(\mathbf{r}). \quad (73)$$

Eqn (49) leads to

$$\mathbf{E} = \frac{E_F^{(0)}}{e} \left[\frac{2}{3} \frac{1}{[n(\mathbf{r})]^{1/3} n_0^{2/3}} - \frac{8}{15} \frac{1}{[n(\mathbf{r})]^{2/3} n_0^{1/3}} \right] \nabla n(\mathbf{r}), \quad (74)$$

$$b(\mathbf{r}) = \frac{E_F^{(0)}}{4\pi e^2} \left\{ \left[\frac{2}{3} \frac{1}{[n(\mathbf{r})]^{1/3} n_0^{2/3}} - \frac{8}{15} \frac{1}{[n(\mathbf{r})]^{2/3} n_0^{1/3}} \right] \nabla n(\mathbf{r}) - \left[\frac{2}{9} \frac{1}{[n(\mathbf{r})]^{4/3} n_0^{2/3}} - \frac{16}{45} \frac{1}{[n(\mathbf{r})]^{5/3} n_0^{1/3}} \right] [\nabla n(\mathbf{r})]^2 \right\}. \quad (75)$$

We can readily see from Eqn (75) that

$$|b(\mathbf{r})| \sim \frac{1}{aL^2} \ll n_0. \quad (76)$$

Here, $a \approx e^2/E_F^{(0)} \approx 10^{-8}$ cm and L is the macroscopic length. Therefore, the density of the space charge inside a metal is very small compared with the ion concentration n_0 . If deformations are weak, we can substitute $n(\mathbf{r}) \approx n_0$ in front of the differentiation symbols. We then obtain

$$\mathbf{E} = \frac{2}{15} \frac{E_F^{(0)}}{e} \frac{\nabla n(\mathbf{r})}{n_0}, \quad (77)$$

$$b(\mathbf{r}) = \frac{E_F^{(0)}}{30\pi e^2} \left[\frac{\nabla^2 n(\mathbf{r})}{n_0} + \left(\frac{\nabla n(\mathbf{r})}{n_0} \right)^2 \right]. \quad (78)$$

We shall now represent the concentration of ions in the form

$$n(\mathbf{r}) = n_0 \frac{1}{1 + \tilde{u}} \cong n_0 (1 - \tilde{u} + \tilde{u}^2 \dots), \quad (79)$$

where \tilde{u} is the sum of the diagonal elements of the strain tensor [5].

Substitution of Eqn (79) into Eqns (77) and (78), gives, with an accuracy to within terms of the order of u ,

$$\mathbf{E} = -\frac{2}{15} \frac{E_F^{(0)}}{e} \nabla \tilde{u}, \quad (80)$$

$$b(\mathbf{r}) = \frac{E_F^{(0)}}{30\pi e^2} \left[(3\nabla \tilde{u})^2 - \nabla^2 \tilde{u} \right]. \quad (81)$$

It follows from Hooke's law that the bulk strain \tilde{u} is related to the sum of the diagonal elements of the stress tensor $t = t_{zz} + t_{xx} + t_{yy}$ by

$$u = \frac{t}{3K}, \quad (82)$$

where K is the bulk modulus of a deformed body [5].

Taking account of Eqn (82), and using Eqn (62) for the contribution of the conduction electrons K_e to the bulk modulus, we can write the expression for the electric field inside a deformed metal in the form

$$\mathbf{E} = \frac{1}{3} \frac{\nabla t}{n_0 z |e|} \frac{K_e}{K}. \quad (83)$$

In particular, in the hydrostatic compression case when $t_{ik} = -P\delta_{ik}$ and $t = -3P$, Eqn (83) gives

$$\mathbf{E} = -\frac{f}{z|e|n_0} \frac{K_e}{K}, \quad (84)$$

where $f = \nabla P$ is the external force acting on a unit volume of the deformed metal‡.

For simple tension or compression in a metallic rod ($t_{zz} = -P$, all the other components of the tensor vanish) the right-hand side of Eqn (84) is to be multiplied by 1/3.

In conclusion, we would like to stress that the adopted approach is far from complete and in no way can it replace a detailed analysis based on a rigorous theory. Powerful mathematical tools are available in the modern theory of metals. Nevertheless, it is interesting from both the methodological and practical points of view that some of the problems dealt with in the theory of metals can be understood and described approximately from first principles, one of which is the virial theorem.

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†In view of the smallness of the electron mass, we are ignoring here the contribution of the gravitational potential.

‡In the gravitational field of the Earth we have $f/n_0 \approx Mg$, where M is the mass of an ion and g is the acceleration due to gravity.