Journal of Theoretical Physics

Founded and Edited by M. Apostol **302** (2019)

ISSN 1453-4428

Cohesive force between macro-, meso- and nanoscopic bodies, double layer and surface plasmons

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Abstract

The cohesive force acting between macro-, meso- and nanoscopic bodies is derived from the cohesion theory of matter. It is shown that it is much smaller than the van der Waals-London-Casimir force for all relevant distances. Heavy atoms are discussed in this context. Also, the surface double layer is derived, the surface tension, the work function and the surface plasmons are computed for half-spaces and spheres. The electron dynamics is described and applied to such finite bodies. The remanent effects of the cohesion of the macro-, meso- and nanoscopic bodies are associated with the surface double layers and their dynamics (surface plasmons).

Cohesion of matter. We consider N identical ions with charge q and N electrons with mass m and charge $-q$, all embedded in a volume V. We assume that the electrons are delocalized and form a Fermi sea with Fermi wavevector k_F and density $n = k_F^3/3\pi^2$. The kinetic energy is

$$E_{kin} = \frac{V\hbar^2 k_F^5}{10\pi^2 m} = \frac{3(3\pi^2)^{2/3}V\hbar^2}{10m}n^{5/3} \ ; \tag{1}$$

we introduce the notation $\varepsilon_{kin}(n) = \left[3(3\pi^2)^{2/3}\hbar^2/10m\right]n^{5/3}$ and write the total kinetic energy as

$$E_{kin} = V\varepsilon_{kin} \ . \tag{2}$$

We assume that the electron density n acquires small spatial variations ($n \longrightarrow n(\mathbf{r})$, $k_F \longrightarrow k_F(\mathbf{r})0$, such that the total kinetic energy becomes

$$E_{kin} = \int d\mathbf{r}\varepsilon_{kin}(n(\mathbf{r})) \ . \tag{3}$$

The interaction of the ensemble of ions and electrons is the potential energy

$$E_{pot} = -q^2\sum_i \int d\mathbf{r}\frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_i|} + \frac{1}{2}q^2\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}q^2\sum_{i\neq j}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|} \ , \tag{4}$$

where we recognize the ion-electron Coulomb attraction and the electron-electron and ion-ion Coulomb repulsion; $\mathbf{R}_{i,j}$ denote the positions of the $i(j)$-th ion.

At equilibrium the first-order variation of the total energy with respect to the electron density

$$\delta E^{(1)} = \int d\mathbf{r}\frac{\partial\varepsilon_{kin}}{\partial n}\delta n(\mathbf{r}) - q^2\sum_i\int d\mathbf{r}\frac{1}{|\mathbf{r}-\mathbf{R}_i|}\delta n(\mathbf{r}) + q^2\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\delta n(\mathbf{r}) \tag{5}$$

should be zero,

$$\frac{\partial \varepsilon_{kin}}{\partial n} - q^2 \sum_i \frac{1}{|\mathbf{r}-\mathbf{R}_i|} + q^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = 0 \ . \tag{6}$$

It is convenient to introduce the potential

$$\varphi(\mathbf{r}) = q \sum_i \frac{1}{|\mathbf{r}-\mathbf{R}_i|} - q \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{7}$$

which satisfies the Poisson equation

$$\Delta\varphi = -4\pi q \sum_i \delta(\mathbf{r}-\mathbf{R}_i) + 4\pi q n(\mathbf{r}) \ . \tag{8}$$

Equation (6) becomes

$$\frac{\partial \varepsilon_{kin}}{\partial n} - q\varphi(\mathbf{r}) = 0 \ , \tag{9}$$

or

$$\frac{(3\pi^2)^{2/3}\hbar^2}{2m} n^{2/3} - q\varphi(\mathbf{r}) = 0 \ , \ \frac{\hbar^2 k_F^2}{2m} - q\varphi(\mathbf{r}) = 0 \ ; . \tag{10}$$

hence,

$$n = \left[\frac{2mq}{(3\pi^2)^{2/3}\hbar^2}\right]^{3/2} \varphi^{3/2}(\mathbf{r}) \tag{11}$$

and equation (8) becomes

$$\Delta\varphi = -4\pi q \sum_i \delta(\mathbf{r}-\mathbf{R}_i) + 4\pi q \left[\frac{2mq}{(3\pi^2)^{2/3}\hbar^2}\right]^{3/2} \varphi^{3/2}(\mathbf{r}) \ . \tag{12}$$

Equation (12) is the starting point of the Thomas-Fermi model[1] and the density-functional theory.[2, 3] It should be solved for the potential φ, then the density would be computed by equation (11), then the total energy given by equations (3) and (4) would be computed and minimized with respect to the ion positions. Unfortunately, the Thomas-Fermi model has not a minimum of energy (it does not "bind", "no-binding theorem"),[4] while the density-functional theory introduces additional "quantum-mechanical" terms into the energy.

The difficulty originates in the abrupt variations of the potential and the electron density in the vicinity of the ions, which require, indeed, a quantum-mechanical treatment, but, at the same time, collapse matter into atoms. These abrupt variations should be left aside in describing the cohesion of matter. In matter the electrons behave quasi-classically.

Therefore, products of the type $[k_F(\mathbf{r})]^n$ must be replaced by $\overline{k}_F^{n-1} k_F(\mathbf{r})$ for any power $n > 1$, where $\overline{k}_F$ is a variational parameter. Thereby, a linearized Thomas-Fermi theory is obtained.[5]-[7] Making use of this procedure, we get

$$\begin{gathered} n = \tfrac{\overline{k}_F^2}{3\pi^2} k_F \ , \ \tfrac{\hbar^2 k_F^2}{2m} = \tfrac{\hbar^2 \overline{k}_F}{2m} k_F = q\varphi \ , \\ k_F = \tfrac{2mq}{\hbar^2 \overline{k}_F}\varphi \ , \ n = \tfrac{2mq\overline{k}_F}{3\pi^2\hbar^2}\varphi \ . \end{gathered} \tag{13}$$

We introduce the notation κ^2 given by

$$4\pi q n = \frac{8mq^2\overline{k}_F}{3\pi\hbar^2}\varphi = \kappa^2\varphi \tag{14}$$

and write equation (8) as

$$\Delta\varphi = -4\pi q \sum_i \delta(\mathbf{r}-\mathbf{R}_i) + \kappa^2\varphi(\mathbf{r}) \ . \tag{15}$$

The solution of this equation is the screened Coulomb potential

$$\varphi = \sum_i \frac{q}{|\mathbf{r}-\mathbf{R}_i|} e^{-\kappa|\mathbf{r}-\mathbf{R}_i|} \tag{16}$$

and the electron density is

$$n = \frac{\kappa^2}{4\pi q}\varphi = \frac{\kappa^2}{4\pi}\sum_i \frac{1}{|\mathbf{r}-\mathbf{R}_i|} e^{-\kappa|\mathbf{r}-\mathbf{R}_i|} \ . \tag{17}$$

By using the same linearization procedure we get the kinetic energy (equation (1))

$$E_{kin} = \frac{\hbar^2 \overline{k}_F^4}{10\pi^2 m}\int d\mathbf{r} k_F = \frac{27\pi^2\hbar^6}{640 m^3 q^4}\kappa^4 N \ . \tag{18}$$

For calculating the potential energy it is convenient to note that the potential φ given by equation (7) can be decomposed into an ion part

$$\varphi_i = q\sum_i \frac{1}{|\mathbf{r}-\mathbf{R}_i|} \tag{19}$$

and an electron part

$$\varphi_e = -q\int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ , \tag{20}$$

$\varphi = \varphi_i + \varphi_e$. The potential energy given by equation (4) can be written as

$$\begin{aligned} E_{pot} &= -q\int d\mathbf{r} n\left(\varphi - \tfrac{1}{2}\varphi_e\right) + \tfrac{1}{2}q^2 \textstyle\sum_{i\neq j}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|} = \\ &= -\tfrac{1}{2}q\int d\mathbf{r} n\left(\varphi+\varphi_i\right) + \tfrac{1}{2}q^2\textstyle\sum_{i\neq j}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|} = -\frac{\kappa^2}{8\pi}\int d\mathbf{r}\varphi\left(\varphi+\varphi_i\right) + \tfrac{1}{2}q^2\textstyle\sum_{i\neq j}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|} \ . \end{aligned} \tag{21}$$

The integral in equation (21) can be effected by using elliptic coordinates; we get

$$E_{pot} = -\frac{3}{4}Nq^2\kappa - \frac{1}{4}q^2\kappa\sum_{i\neq j}\left(1-\frac{2}{\kappa\left|\mathbf{R}_i-\mathbf{R}_j\right|}\right)e^{-\kappa|\mathbf{R}_i-\mathbf{R}_j|} \ . \tag{22}$$

The first term on the right in equation (22) is a self-energy, while the second term on the right is an ion-ion interaction. The potential energy is minimized with respect to the ion coordinates $\kappa\left|\mathbf{R}_i-\mathbf{R}_j\right|$ (the ion-ion interaction potential has a minimum for $\kappa\left|\mathbf{R}_i-\mathbf{R}_j\right| = 1+\sqrt{3}$); thereafter, the total energy is minimized with respect to the parameter κ. This procedure is applied to metallic clusters in Ref. [5, 6]. The contribution of the ion-ion interaction to the binding energy is very small; if we assume that the ions are continuously distributed (the continuum approximation), the ion-ion interaction is vanishing. We are left with the total energy

$$E = E_{kin} + E_{pot} = \frac{27\pi^2\hbar^6}{640 m^3 q^4}\kappa^4 N - \frac{3}{4}Nq^2\kappa \ ; \tag{23}$$

this energy has a minimum for $\kappa a_H = (40/9\pi^2)^{1/3} \simeq 0.77$, where $a_H = \hbar^2/mq^2$ is the Bohr radius. The energy is

$$E = E = -\frac{5^{1/3}(9/\pi)^{2/3}}{8}\frac{q^2}{a_H}N \simeq -0.43\frac{q^2}{a_H}N \ . \tag{24}$$

We note that in the continuum approximation the potential (equation (16)) is

$$\varphi = \frac{4\pi q}{a^3\kappa^2} \tag{25}$$

and the electron density is $n = \kappa^2\varphi/4\pi q = 1/a^3$, where a is the mean ion-ion and electron-electron separation distance.

We can assess the accuracy of the linearized Thomas-Fermi theory by computing the average parameter κ and comparing it with the variational parameter κ derived here. To this end we estimate first the average Fermi wavevector

$$k_{Fav} = \frac{1}{N}\int d\mathbf{r} n k_F \ , \tag{26}$$

where n is given by equation (17) and k_F is given by equation (13). For an ion we get

$$k_{Fav} = \frac{m\kappa_{av}^2}{2\pi\hbar^2 k_{Fav}}\int d\mathbf{r}\varphi_{av}^2 = \sqrt{\kappa_{av}/a_H} \tag{27}$$

and, making use of equation (14), $\kappa_{av}a_H = (8/3\pi)^2$; comparing this result with $\kappa a_H = (40/9\pi^2)^{1/3}$ derived above, we get $\kappa_{av}/\kappa = (8/5)^{1/3} \simeq 1.17$. The error (17%) arises from quantum-mechanical corrections. The quantum-mechanical corrections are computed for heavy atoms,[8] and they can also be computed for extended matter (global exchange energy included). By a similar procedure, we can say that the error may finally be reduced to $0.17 \times 17\% \simeq 3\%$. This figure may be taken as the upper limit of errors, caused by using one-particle wavefunctions (instead of multi-particle wavefunctions).

The above theory of cohesion of matter is valid for a large number of ions, from large macromolecules to supramolecular agrregates, clusters and condensed matter (for small molecules the quantum-mechanical behaviour dominates). Also, the theory is suitable for metallic cohesion, though the results are qualitatively valid for (directional, anisotropic) covalent binding. The theory is extended to classical plasmas, where it predicts the condensation into a succession of a liquid phase, a classical solid and a quantum-mechanical solid at high densities and low temperature.[9] Ionic solids can be understood qualitatively on simialar grounds.

Heavy atoms. The cohesion theory is applied to heavy atoms in order to estimate their binding energy and dynamics.[8] In heavy atoms we use a linearization scheme according to the substitution $[k_F(\mathbf{r})]^n \longrightarrow n\overline{k}_F^{n-1}k_F(\mathbf{r})$, $n > 1$, which is more appropriate for the large regions with small density. The screened potential is $\varphi = Ze\cdot e^{-\kappa r}/r$, where $Z \gg 1$ is the atomic number and $-e$ is the electron charge. The quasi-classical theory is valid for distances r in the range a_H/Z (radius of the first Bohr orbit) and a_H ("extension" of the electron cloud); the electron density $n = (\kappa^2/4\pi e)\varphi$ is concentrated at a distance of the order $a_H/Z^{1/3}$. The minimum of the total energy is realized for $\kappa a_H = (6/\pi^2)^{1/3}Z^{1/3}$. Including the quantum-mechanical corrections we get the binding energy $-15.84Z^{7/3}eV$, which agrees well with the empirical value $-16Z^{7/3}eV$.[10] The exchange energy is $-(1.21 - 1.27) \times 18.12Z^{5/3}eV$. The electron cloud may oscillate as a whole with respect to the central nucleus. The radial giant-dipole frequency is

$$\omega_0 = \left(\frac{27}{2\pi^2}\right)^{1/2}\frac{Ze}{\sqrt{ma_H^3}} \simeq 4.5Z \times 10^{16}s^{-1} \tag{28}$$

($\hbar\omega_0 \simeq 28ZeV$; this frequency is slightly changed by numerical factors for forced oscillations or waves propagating in the electron cloud)).

The charge density of a heavy atom placed at $\mathbf{R}$ is

$$\rho = Ze\delta(\mathbf{r}-\mathbf{R}) - \frac{\kappa^2}{4\pi} Ze \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}|}}{|\mathbf{r}-\mathbf{R}|} \; ; \tag{29}$$

the interaction energy of this atom with an identical atom placed at the origin is

$$U = \int d\mathbf{r}\rho\varphi = Z^2e^2\frac{e^{-\kappa R}}{R} - \frac{Z^2e^2\kappa^2}{4\pi}\int d\mathbf{r}\frac{e^{-\kappa r}}{r}\frac{e^{-\kappa|\mathbf{r}-\mathbf{R}|}}{|\mathbf{r}-\mathbf{R}|} \; . \tag{30}$$

The calculation of the integral in equation (30) leads to

$$U = Z^2e^2\left(1-\frac{1}{2}\kappa R\right)\frac{e^{-\kappa R}}{R} \tag{31}$$

and an interaction force

$$F = Z^2e^2\left(1+\kappa R-\frac{1}{2}\kappa^2R^2\right)\frac{e^{-\kappa R}}{R^2} \; . \tag{32}$$

The two atoms attract each other at large distance, have an equilibrium position at $\kappa R = 1+\sqrt{3}$ and repel each other at shorter distance. Actually, the equilibrium distance is of the order $R \simeq a_H/Z^{1/3}$, which shows that the two atoms collapse in fact into a bound state. Similar results hold for distinct atoms and for ions.[8]

The force given by equation (32) may be called a cohesive force. It should be compared with the van der Waals-London-Casimir forces acting between atoms, molecules and macroscopic bodies.[11]-[16] For all distances of interest a heavy atom may be appproximated by a pointlike dipole. The electromagnetic field generated by this dipole induces charges and currents in the other atom, which oscillate with a characteristic frequency close to the the plasma frequency (plasmon-polariton modes); for a heavy atom the role of the plasma frequency is played by the frequency ω_0 given above. Similar oscillations occur in the first atom, under the effect of the field generated by the second atom. The equation of motion of these coupled oscillations exhibit eigenfrequencies which give a zero-point energy, by which the force can be computed (London-Casimir dispersion forces).[15] There are two characteristic parameters which govern these equations: a coupling constant given by the ratio of the volume v of the atom to the third power of the distance (R^3) and the ratio of the distance to the "plasma wavelength" $\lambda_0 = c/\omega_0$ (where c is the speed of light in vacuum). For distances R much smaller than λ_0 we get the non-retarded (static) van der Waals forces; for distances R much longer than the plasma wavelength λ_0 we get the retarded Casimir forces (the temperature effects are given by a small correction factor $e^{-\hbar c/RT}$, where T denotes the temperature).[17] The coupling constant is much smaller than unity, so we may find the solution for the eigenfreqencies as a perturbations series. Making use of equation (28), we get the plasmon wavelength for a heavy atom $\lambda_p = c/\omega_0 \simeq (0.66/Z)\times 10^{-6}cm$, such that the whole region of interest is dominated by the Casimir force. This force is repulsive (specific to point-like approximation). Its magnitude is of the order $3\hbar\omega_0^5v^2/32\pi^2c^4R^3$; compared with the cohesive force $Z^2e^2\kappa^2e^{-\kappa R}/2$ (equation (32)), we get the inequality $4\times 10^{-2}Z^3\alpha^4a_H^3 < R^3e^{-\kappa R}$, where $\alpha = e^2/\hbar c$ is the fine-structure constant. We can see that the cohesive force dominates the repulsion force.

Dynamics of the electrons. Let us consider the ensemble of bound ions and electrons under the action of an electromagnetic field. The ions are too heavy for being set in motion, so we may consider them at rest. But the electrons will get a displacement field $\mathbf{u}(t,\mathbf{r})$, which generates a polarization change in electron density $\delta n = -ndiv\mathbf{u}$ and a polarization current density $-qn\dot{\mathbf{u}}$. The electromagnetic field is sufficiently small to induce a small displacement $\mathbf{u}$, which varies

slowly in space and time. Therefore, we may leave aside the effects of the magnetic field (since $\dot{u}/c \ll 1$). It follows that $\mathbf{u}$ moves only under the action of the electric field. For a radiation electromagnetic field in an ensemble with an infinite spatial extension the displacement field $\mathbf{u}$ is transverse ($div\mathbf{u} = 0$); in these conditions there is no polarization charge (there exist only conserved polarization currents). These currents generate a perfectly compensating field which cancels out the external radiation field. This is the Ewald-Oseen extinction theorem. In finite ensembles, or in ensembles with spatial variations, or for external electromagnetic fields with a longitudinal component the polarization charge $qndiv\mathbf{u}$ is not vanishing and it generates an internal (polarization) electric field $4\pi qn\mathbf{u}$ (bulk field), which gives rise to a characteristic frequency $\omega_0 = (4\pi nq^2/m)^{1/2}$ (corresponding to the restoring force). This is the (bulk) plasma frequency. A similar frequency can appear from surfaces or from spatial variations of the density, as those appearing in cohesion. According to our assumptions the frequency ω of the external field should be much lower than the characteristic frequency ω_0 ($\omega \ll \omega$), such that $\omega = \frac{c}{\lambda} \ll \omega_0 = \frac{c}{\lambda_0}$, *i.e.* the wavelegths λ should be much longer than the plasma wavelength λ_0 (this inequality ensures negligible contributions from the magnetic field). We note that the density n is an average (uniform) density. Its small spatial variations generate a second-order effect when combined with the small displacement $\mathbf{u}$, so we may negect them. The dynamics of these variations can be treated separately.

The dynamis of the electrons is given by the second-order variation of the energy (equation (5))

$$\delta E^{(2)} = \frac{1}{2}\int d\mathbf{r}\frac{\partial^2\varepsilon_{kin}}{\partial n^2}[\delta n(\mathbf{r})]^2 + \frac{1}{2}q^2\int d\mathbf{r}d\mathbf{r}'\frac{\delta n(\mathbf{r})\delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\delta n(\mathbf{r}) \ , \tag{33}$$

or

$$\delta E^{(2)} = \frac{1}{2}\int d\mathbf{r}\frac{\partial^2\varepsilon_{kin}}{\partial n^2}n^2(div\mathbf{u})^2 + \frac{1}{2}q^2\int d\mathbf{r}d\mathbf{r}'n^2\frac{div\mathbf{u}(\mathbf{r})div\mathbf{u}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ , \tag{34}$$

where the derivatives should be taken at equilibrium. However, if these equilibrium values imply small spatial variations, we may limit ourselves to the leading contributions. The lagrangian is obtained by adding to the second-order variation of the energy the kinetic term

$$T = \frac{1}{2}\int d\mathbf{r}mn\dot{\mathbf{u}}^2 \ . \tag{35}$$

Therefore, the equation of motion for the field $\mathbf{u}$ is

$$mn\ddot{\mathbf{u}} - grad\left[\left(\frac{\partial^2\varepsilon_{kin}}{\partial n^2}\right)n^2div\mathbf{u}\right] - q^2grad\left[n\int d\mathbf{r}'\frac{n(\mathbf{r}')div[\mathbf{u}(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}\right] = n\mathbf{F}_{ex} \ , \tag{36}$$

where $\mathbf{F}_{ex}$ is the external force; or

$$m\ddot{\mathbf{u}} - \frac{(3\pi^2)^{2/3}\hbar^2}{3mn}grad\left[n^{5/3}div\mathbf{u}\right] - \frac{q^2}{n}grad\left[n\int d\mathbf{r}'\frac{n(\mathbf{r}')div[\mathbf{u}(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}\right] = \mathbf{F}_{ex} \ . \tag{37}$$

We note that equation (36) indicates a hydrodynamic behaviour of the (interacting) electrons, while equation (37) defines an interaction (potential) energy. For a uniform density n and an external plane-wave force $\mathbf{F}_{ex} = \mathbf{F}^0_{ex}e^{-i\omega t+i\mathbf{kr}}$ the displacement is $\mathbf{u} = \mathbf{u}^0e^{-i\omega t+i\mathbf{kr}}$, where the amplitude $\mathbf{u}^0$satisfies the equation

$$\omega^2\mathbf{u}_0 - \omega_0^2\frac{(\mathbf{k}\mathbf{u}_0)\mathbf{k}}{k^2} - v^2(\mathbf{k}\mathbf{u}_0)\mathbf{k} = e\mathbf{E}_0 \ , \tag{38}$$

where v is one-third of the Fermi velocity ($v = \frac{1}{3}v_F$). The waves are longitudinal with eigenfrequency given by

$$\omega^2 = \omega_0^2 + v^2k^2 \ . \tag{39}$$

These modes are dispersive (bulk) plasmons. For being consistent with our assumption we require $vk \ll \omega_0$. We note that for higher fields the velocity can be higher, and the magnetic field cannot be left aside (even in infinite ensembles); then, the propagation is governed by polaritons with the dispersion relation given by $\omega^2 = \omega_p^2 + c^2k^2$, where $ck \gg \omega_0$.[18]

Half-space. For a uniform distribution of ions with density n the potential (equation (16)) is a constant,

$$\varphi = n\int d\mathbf{R}\frac{q}{|\mathbf{r}-\mathbf{R}|}e^{-\kappa|\mathbf{r}-\mathbf{R}|} = \frac{4\pi nq}{\kappa^2} \ , \tag{40}$$

as expected, and the electron density is $n_e = \kappa^2\varphi/4\pi q = n$, equal with the ion density; the interaction energy in equation (3) is zero in this case. For finite bodies, the potential φ exhibits a surface charge double layer.

Let us consider a uniform distribution of ions in the half-space $x < 0$ with a plane surface at $x = 0$. The potential φ given by equation (16) is

$$\varphi = \begin{cases} \frac{4\pi nq}{\kappa^2}\left(1 - \frac{1}{2}e^{\kappa x}\right) \ , \ x < 0 \ , \\ \frac{2\pi nq}{\kappa^2}e^{-\kappa x} \ , \ x > 0 \end{cases} \tag{41}$$

and the potential energy is

$$E_p = -\frac{3}{4}Nq^2\kappa + \frac{\pi nq^2}{2a\kappa^3}N_s \ , \tag{42}$$

where N_s is the number of surface ions (and a is the mean inter-ion distance, $n = 1/a^3$; the kinetic energy is not affected). The minimization of the energy with respect to κ brings a correction proportional to $N_s/N \ll 1$ which may be neglected.

Since the density of electric charge ρ is given by $\Delta\varphi = -4\pi\rho$, we get from equations (41)

$$\rho = -\frac{1}{2}nq \cdot sgn(x)e^{-\kappa|x|} \ . \tag{43}$$

Making use of $4\pi n_e q = \kappa^2\varphi$, we get the electron density

$$n_e = \begin{cases} n\left(1 - \frac{1}{2}e^{\kappa x}\right) \ , \ x < 0 \ , \\ \frac{1}{2}ne^{-\kappa x} \ , \ x > 0 \end{cases} \tag{44}$$

We can see that the internal face of the surface ($x < 0$) is depleted of electrons, which spill over its external face ($x > 0$). This is a surface double layer. The surface energy in equation (6) is the surface tension.

The energy needed for taking an electron from the surface ($x = 0$) to infinity, $q\varphi(x = 0^+) = 2\pi nq^2/\kappa^2$, is the work function of the material.[19, 20]

According to the cohesion theory κa is of the order of unity. We can see that the changes brought about by the surface vanish rapidly over distances of the order a. In the continuum limit we may view these changes as being localized on the surface. We may discard the surface contributions, and view them as indeterminacies. Indeed, variations over distances of the order of the mean inter-ion separation distance a are affected by errors in the cohesion theory. For instance, the interaction energy $\delta e = -\frac{1}{2}q\delta\varphi\delta n_e/n$ for an electron may be viewed as an indeterminacy in energy. It is given by $\delta e \simeq \pi q^2 n/4a\kappa^3$. We can see that it is half the surface energy per ion. Indeed, it includes

half the electron-ion energy, such that, adding the other half and the ion-ion energy, we get twice δe, which is the surface energy. Such an indeterminacy in energy may contribute to the electron lifetime, as a consequence of the presence of the surface. It is limited to electron scattering by the surface. If we view δe as an uncertainty, we can estimate it as the square root of $\sum_i \delta e_i^2/N$, for N intervals, $N \to \infty$. This uncertainty vanishes in the limit $N \to \infty$. We can see that the surface scattering is a very limited concept.

Let us compute now the interaction energy between two (identical) half-spaces with parallel surfaces separated by distance R. We write the potential generated by the first half-space as

$$\varphi = \frac{4\pi nq}{\kappa^2}\theta(-x) + \frac{2\pi nq}{\kappa^2} sgn(x) e^{-\kappa|x|} \tag{45}$$

and the charge density of the second half-space as

$$\rho = -\frac{1}{2} nq \cdot sgn(R-x) e^{-\kappa|R-x|} \ ; \tag{46}$$

the interaction energy is

$$U = \int d\mathbf{r}\varphi(\mathbf{r})\rho(\mathbf{r}) = -\frac{\pi n^2 q^2 S}{\kappa^3}\left(1+\kappa R\right) e^{-\kappa R} \tag{47}$$

and the force acting between the two bodies is

$$F = -\frac{\pi n^2 q^2 S}{\kappa} R e^{-\kappa R} \ , \tag{48}$$

where S is the area of the surface. We can see that the force is attractive, with a minimum for $R = 1/\kappa \simeq a$, which indicates the tendency of the two bodies to collapse into one body.

The Casimir force between two identical (metallic) half-spaces is $F_C = -\pi^2 \hbar c S/240 R^4$, valid for $R \gg c/\omega_0$ (where ω_0 is the plasma frequency); the van der Waals-London force is $F_W = -\hbar\omega_0 S/32\pi\sqrt{2}R^3$ (for dielectrics small correction factors may appear).[13, 14] For macro-, meso- and even nanoscopic bodies the plasma wavelength $\lambda_0 = c/\omega_0$ ($\simeq 10^3$Å) is much longer than the mean inter-ion separation distance, such that the van der Waals-London-Casimir force dominates the cohesive force for all distances of interest. (Macroscopic bodies are defined as having linear dimensions larger than 10^4Å ($1\mu m$), mesoscopic bodies have linear dimensions in the range than 10^3Å $- 10^4$Å and nanoscopic bodies have linear dimensions in the range 10Å $- 10^3$Å). Indeed, the maximum value of the cohesive force (equation (48)) is of the order q^2/a^2 per surface ion ($\kappa \simeq 1/a$), reached for distances of the order $R \simeq a$, while the van de Waals force for this distance is of the order $\hbar\omega_0//a \simeq q^2/a^2$ (a is of the order of the Bohr radius); at these distances the two forces are comparable. However, at larger distance we should compare e^{-x} with $1/x^3$, where $x = R/a$; we can see that the inverse power dominates the exponential for all relevant distances.

The motion of the electrons in a half-space, as described by equation (37), requires a special treatment. Equation (37) and the cohesion theory assume that the electron density is extended to the whole space. We note that the displacement $\mathbf{u}$ extends to the whole space. On the other hand, since the surface double layer is limited to a small region with thickness of the order of the small distance a and the electron density and the potential fall off rapidly to zero for $x > 0$ (κ is large), we may limit ourselves to the half-space $x < 0$ with a uniform density n. The most convenient way of doing this is to solve equation (37) for the whole space and take the restriction of the solution to $x < 0$. However, in doing so, we should include the contribution of the double layer, because, although the direct contribution of its high derivatives may be neglected, since they are localized,

their contribution to the Coulomb integral (interaction) are large. Such a special treatment is suitable for the integral equation (37). Therefore, first we write equation (37) for uniform density as

$$m\ddot{\mathbf{u}} - \frac{1}{3}mv_F^2 grad\, div\mathbf{u} - q^2 n \cdot grad \int d\mathbf{R}' \frac{div[\mathbf{u}(\mathbf{R}')]}{|\mathbf{R}-\mathbf{R}'|} = \mathbf{F}_{ex} \quad , \tag{49}$$

where $\mathbf{R} = (x, \mathbf{r})$, $\mathbf{r}$ being the position vector parallel with the surface (in-plane position vector). Thereafter, we note that the existence of the double layer implies a displacement v, directed along the x-axis and localized at $x = 0$. This displacement describes the motion of the double layer. Therefore, we may replace the $div\mathbf{u}$ in equation (49) by

$$div\mathbf{u} \longrightarrow div\mathbf{u} - v\delta(x) \ ; \tag{50}$$

indeed the displacement in a half-space can be written as $\mathbf{u}\theta(-x)$, such that $div[\mathbf{u}\theta(-x)] = div\mathbf{u} \cdot \theta(-x) - u_x\delta(x)$. Since $\mathbf{u}$ is extended to the whole space we may omit $\theta(-x)$ and get equation (50) with $v = u_x$.

It is worth noting in this context that the change brought about by the double layer in the electron density is a

$$\delta n_e = \frac{1}{2} n \cdot sgn(x) e^{-\kappa|x|} \tag{51}$$

(equation (44)). Since

$$\begin{aligned} \textstyle\int dx f e^{-\kappa|x|} &= \textstyle\int_0^\infty dx[f(x>0) + f(x<0)]e^{-\kappa x} = \\ &= \textstyle\int_0^\infty dx[2f(0) + x^2 f^{(2)}(0) + ...]e^{-\kappa x} = \frac{2}{\kappa} f(0) + \frac{2}{\kappa^3} f^{(2)}(0) + ... \end{aligned} \tag{52}$$

for any (differentiable) function f, and similarly for $sgn(x)e^{-\kappa|x|}$, we may use the approximations

$$e^{-\kappa|x|} = \frac{2}{\kappa}\delta(x) \ , \ sgn(x)e^{-\kappa|x|} = -\frac{2}{\kappa^2}\delta'(x) \tag{53}$$

for large κ. Therefore, we can see that

$$\delta n_e = \frac{1}{2} n \cdot sgn(x) e^{-\kappa|x|} = -\frac{1}{\kappa^2} n \delta'(x) = -n\frac{\partial u_x}{\partial x} \quad , \tag{54}$$

i.e. $u_x = \frac{1}{\kappa^2}\delta(x)$. Since the support of $\delta(x)$ is $1/\kappa$ within this approximation, we have also $\delta n_e = \frac{1}{\kappa} n\delta(x)$ from equation (54), such that $\delta n_e = vn\delta(x)$, where $v = 1/\kappa$, *i.e.* v is of the order a.

The contribution of the term $-v\delta(x)$ (equation (50)) to $grad\, div\mathbf{u}$ (equation (49)) may be neglected. The remaining equation in $\mathbf{u}$ is the same as the equation for the bulk; it gives the bulk plasmons (equations (39)). The contribution of the term $-v\delta(x)$ to the Coulomb integral in equation (49) is

$$\int d\mathbf{R}' \frac{-v(\mathbf{r}')\delta(x')}{|\mathbf{R}-\mathbf{R}'|} = -ve^{i\mathbf{kr}} \int d\mathbf{r}' \frac{e^{-i\mathbf{kr}'}}{\sqrt{r'^2 + x^2}} = -\frac{2\pi v}{k} e^{i\mathbf{kr}} e^{-k|x|} \tag{55}$$

for $v(\mathbf{r}') = ve^{i\mathbf{kr}'}$ (Sommerfeld integral[21]) and

$$-q^2 n \cdot grad \int d\mathbf{R}' \frac{-v(\mathbf{r}')\delta(x')}{|\mathbf{R}-\mathbf{R}'|} = 2\pi n q^2 v \left(-sgn(x), i\frac{\mathbf{k}}{k}\right) e^{i\mathbf{kr}} e^{-k|x|} \ . \tag{56}$$

In this result $\mathbf{k} \longrightarrow 0$ and $x = 0^-$; the frequency is given by

$$-m\omega^2 v + 2\pi n q^2 v = 0 \ , \ \omega^2 = \frac{2\pi n q^2}{m} = \frac{1}{2}\omega_0^2 \tag{57}$$

which is the frequency of the surface plasmons ($\omega_0^2 = 4\pi n q^2/m$). The in-layer motion remains undetermined. Actually, $\mathbf{k}$ serves only as a cutoff parameter for the divergent integral in equation (55); if we use a cutoff $R \longrightarrow \infty$ in this integral, we get equation (57). Surface plasmons of two coupled half-spaces and surface plasmons in a slab with finite thickness are derived in Ref. [13]. The surface plasmons are associated with the motion of the double layer.

Sphere. A spherical uniform distribution of ions in equation (16) gives the potential

$$\varphi = \begin{cases} \frac{4\pi n q}{\kappa^2}\left[1 - (1+\kappa r_0)\, e^{-\kappa r_0}\frac{\sinh \kappa r}{\kappa r}\right] \ , \ r < r_0 \ , \\ \frac{4\pi n q}{\kappa^2}\left(\kappa r_0 \cosh \kappa r_0 - \sinh \kappa r_0\right)\frac{e^{-\kappa r}}{\kappa r} \ , \ r > r_0 \ , \end{cases} \tag{58}$$

where r_0 is the radius of the sphere. This potential is continuous at $r = r_0$ with continuous derivative. The electron density is given by $4\pi q n_e = \kappa^2 \varphi$ and the charge density

$$\rho = \begin{cases} n q\,(1+\kappa r_0)\, e^{-\kappa r_0}\frac{\sinh \kappa r}{\kappa r} \ , \ r < r_0 \ , \\ -n q\,(\kappa r_0 \cosh \kappa r_0 - \sinh \kappa r_0)\frac{e^{-\kappa r}}{\kappa r} \ , \ r > r_0 \end{cases} \tag{59}$$

is obtained from $\Delta\varphi = -4\pi\rho$. This charge distribution indicates the presence of a surface double layer. Since $\kappa r_0 \gg 1$ for macro-, meso- and nanoscopic bodies, equations (58) and (59) can be simplified to

$$\varphi \simeq \begin{cases} \frac{4\pi n q}{\kappa^2} - \frac{2\pi n q}{\kappa^2}\frac{r_0}{r} e^{-\kappa(r_0 - r)} \ , \ r \lesssim r_0 \ , \\ \frac{2\pi n q}{\kappa^2}\frac{r_0}{r} e^{-\kappa(r - r_0)} \ , \ r > r_0 \end{cases} \tag{60}$$

and

$$\rho \simeq -\frac{1}{2} n q \frac{r_0}{r} sgn(r - r_0) e^{-\kappa|r - r_0|} \ ; \tag{61}$$

except for the factor r_0/r these expressions are similar with those corresponding to a half-space (equations (41) and (43)), as expected. Within the same approximation ($\kappa r_0 \gg 1$) the potential energy (surface tension) is the same as that of a half-space (equation (42)).

Making use of the potential and the charge density we can compute the interaction energy of two spheres separated by distance R (equation (47)); for two identical spheres ($R > 2r_0$), within the approximation $\kappa r_0 \gg 1$, we get approximately

$$U \simeq -\frac{\pi^2 q^2 n^2 r_0^2}{\kappa^3}\left(2 - \frac{3r_0}{R}\right) e^{-\kappa(R - 2r_0)} \tag{62}$$

and the force

$$F \simeq -\frac{\pi^2 q^2 n^2 r_0^2}{\kappa^2}\left(2 - \frac{3r_0}{R}\right) e^{-\kappa(R - 2r_0)} \ . \tag{63}$$

This is an attractive force with a maximum value of the order $F_{max} \simeq \pi q^2 n^2 S/8\kappa^2$; for $\kappa \simeq 1/a$, $F_{max} \simeq (q^2/a^2) N_s$, where N_s is the number of ions on the surface S. It is of the same order of magnituide as the maximum force acting between two half-spaces (per unit area of the surface, equation (48)). Similarly, the maximum energy is of the order $U_{max} \simeq (q^2/a) N_s$. We can see that under the action of this cohesive force the spheres tend to collapse into one body. The van der Waals-London-Casimir force dominates the cohesive force for all relevant distances.

We include here the interaction energy of a half-space and a sphere separted by distance R,

$$U \simeq -\frac{2\pi^2 n^2 q^2}{\kappa^3} r_0 (R - r_0) e^{-\kappa(R - r_0)} \ , \tag{64}$$

and the corresponding force

$$F \simeq -\frac{2\pi^2 n^2 q^2}{\kappa^3} r_0 \left[\kappa(R-r_0)-1\right] e^{-\kappa(R-r_0)} \tag{65}$$

for $\kappa r_0 \gg 1$ (where r_0 is the radius of the sphere and $R > r_0$).

We pass now to estimate the electron dynamics of a spherical double layer. According to equations (49) and (56) this dynamics is governed by the Coulomb integral

$$-q^2 n \cdot grad \int d\mathbf{r}' \frac{-v\delta(r'-r_0)}{|\mathbf{r}-\mathbf{r}'|} \ . \tag{66}$$

The *grad* should be taken along the z-direction, which is also the direction of the displacement v; equation (66) becomes

$$vq^2 n \int d\mathbf{r}' \frac{r - r'\cos\theta}{|\mathbf{r}-\mathbf{r}'|^3} \frac{z'}{r'} \delta(r'-r_0) \ . \tag{67}$$

This integral should be computed for $r = r'$; we get

$$2\pi v q^2 n \int d\theta \sin\theta \frac{\cos\theta}{[2(1-\cos\theta)]^{1/2}} = \frac{4\pi n q^2}{3} v \ ; \tag{68}$$

therefore, according to equation (49), the frequency of the spherical plasmons is given by $\omega^2 = \omega_0^2/3$, $\omega_0^2 = 4\pi n q^2/m$ (bulk plasmons). We note that there exists also a radial surface plasmon with frequency ω_0.

Conclusion. The cohesion theory of matter predicts an electron distribution extended in the whole space, even for finite bodies. However, for finite bodies, this extension is in fact relevant only in a surface region with thickness of the order of the mean separation distance between ions (electrons); this is the surface double layer, which gives the surface tension and work function; its dynamics is associated with the surface plasmons. In addition, the infinite extension of the electron distribution gives a cohesive force acting between heavy atoms, macro-, meso- and nanoscopic bodies, which tends to collapse the bodies into one body. The cohesive force is high at atomic distances, but it is much lower than the van der Waals-London-Casimir force at any relevant (macro-, meso- and nanoscopic) distance. These points (including electron dynamics) are examined here for heavy atoms, half-spaces and spheres.

Acknowledgements. The author is indebted to the members of the Laboratory of Theoretical Physics at Magurele-Bucharest for many fruitful discussions. This work has been supported by the Scientific Research Agency of the Romanian Government through Grants 04-ELI / 2016 (Program 5/5.1/ELI-RO), PN 16 42 01 01 / 2016, PN 19 09 01/2018 and PN (ELI) 16 42 01 05 / 2016.

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