INTERACTION OF ATOMS WITH ELECTRONS AND IONS IN A PLASMA

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The contribution made to the thermodynamic potential of a plasma by the dipole and quadrupole interactions of the atoms with the electrons and the ions is calculated. The derived expression is used to calculate the decrease of the ionization energy of negative ions.

IN a fully ionized plasma, an important role may be played, besides the Coulomb interaction of the charged particles, also by the interaction between the atoms and the electrons or the ions. In the multipole expansion of the operator of the interaction of the atom with the electron (ion), dipole $(1/r^2)$ and quadrupole $(1/r^3)$ terms are important. The dipole and quadrupole interactions, which do not vanish in the first order of perturbation theory, vanish when summed over the states of the atom. However, these types of interaction make a finite contribution to the thermodynamic quantities, owing to the correlation between the atoms and the electrons (ions). If the first-order effects of perturbation theory vanish, then the dipole interaction in the second order of perturbation theory comes to the foreground.

1. The potential energy of the interaction of the atom with the electron (ion) at a distance that is large compared with the radius of the atom, is given by

$$U(r) = \frac{b_s z^k e^2 a^{s-1}}{r^s}, \quad s = 2, 3, 4, \quad (1)$$

where b_s is a coefficient that depends on the state of the atom, z is the charge number of the ion $(z_e = -1)$, k is the order of perturbation theory, and a is the Bohr radius. The constants k and s determine the type of interaction.

The contribution made to the thermodynamic potential by an interaction of the type (1) between the atoms and the electrons (ions) can be calculated by means of the formula of Bethe and Uhlenbeck for the second virial coefficient[1]

$$-\beta\Delta\Omega_{ae} = \zeta_a \zeta_e \left(\frac{2\pi\hbar^2\beta}{m_e}\right)^{3/2} \left[\sum_n e^{-\beta\varepsilon_n} \right.$$
$$\left. + \frac{1}{\pi}\int_0^\infty \sum_l (2l+1)\frac{\partial\delta_l(K)}{\partial K}\exp\left\{-\frac{\beta\hbar^2 K^2}{2m_e}\right\}dK \right], \quad (2)$$

where the activity ζ_a is determined by the formula

$$\zeta_a = e^{\beta\mu_a}\left(\frac{m_a}{2\pi\hbar^2\beta}\right)^{3/2} Z_a, \quad (3)$$

β is the reciprocal temperature, μ is the chemical potential, and Z is the partition function relative to the internal states of the particle. For atom-ion interaction, the electron mass must be replaced by the reduced mass $m = m_a m_i/(m_a + m_i)$. The partition function of the discrete spectrum for an interaction on the type (1) is meaningless, and therefore the quantity $Z_a Z_e \sum_n \exp(-\beta\varepsilon_n)$ in the first term of formula (2) must be replaced by the partition function Z_a^- of the negative

ion a^- (or the molecular ion for interactions between the atom and the ion). Noting that $\mu_a + \mu_b = \mu_a^-$, we find that the first term in (2) becomes

$$\zeta_a\zeta_e\left(\frac{2\pi\hbar^2\beta}{m_e}\right)^{3/2}\frac{Z_{a-}}{Z_a Z_e} = \zeta_{a-}, \quad (4)$$

i.e., it represents the contribution to the thermodynamic potential from the free negative ions a^- (or molecular ions). For this reason, we shall henceforth denote by $\Delta\Omega_{ae}$ the second term in formula (2).

Assume that the continuous spectrum satisfies the quasiclassical criterion

$$s\hbar\beta^{1/2}/2^{3/2}m_e^{1/2}\,|b_s\beta e^2 a^{s-1}|^{1/s} \ll 1; \quad (5)$$

Then the scattering phase $\delta_l(K)$ in formula (2) can be replaced by their quasiclassical expression

$$\delta_l(K) = \int\left(\sqrt{K^2 - \frac{l(l+1)}{r^2} - \frac{2mU}{\hbar^2}} - \sqrt{K^2 - \frac{l(l+1)}{r^2}}\right)dr, \quad (6)$$

and the summation over l can be replaced by integration. The integration is carried out in the classically accessible region, where the radicands in (6) are positive. In the calculation it is convenient to integrate first over l, and then differentiate and integrate with respect to K. The result of the calculation depends on the sign of the potential. For $U > 0$ (repulsion) we have

$$-\beta\Delta\Omega_{ae} = \zeta_a\zeta_e\cdot 4\pi\int_0^\infty (e^{-\beta U} - 1)r^2\,dr. \quad (7)$$

For $U < 0$ (attraction)

$$-\beta\Delta\Omega_{ae} = \zeta_a\zeta_e\cdot 4\pi\int_0^\infty\left(e^{-\beta U}\frac{\Gamma(3/2, -\beta U)}{\Gamma(3/2)} - 1\right)r^2\,dr, \quad (8)$$

where

$$\Gamma(3/2, -\beta U) = \int_{-\beta U}^\infty x^{1/2}e^{-x}\,dx$$

is the incomplete Γ function.

The integral in (7) coincides with the classical integral, but the integral in (8) differs from the classical group integral by a factor containing the incomplete Γ function. This difference is a result of a separation of the contribution from the discrete spectrum of negative energies, a contribution corresponding to the bound states in the two-particle system. It is easy to see that for an attraction potential of the type (1) the integral in (8) converges when $r \rightarrow 0$ (unlike the classical group integral). Since a potential in the form (1) contains a coefficient b_s that depends on the state of the atom, it is necessary also to sum over the states. Changing the variables in the integrals, we obtain

ultimately

$$- \beta \Delta \Omega_{ae} = \zeta_a \zeta_e \frac{1}{Z_a} \sum_{nJM} e^{-\beta \varepsilon_n} (\beta e^2 a^{s-1} |z_i{}^k b_s|)^{3/s} \cdot 4\pi C_s, \quad (9)$$

where J and M are the values of the total angular momentum and its projection,

$$C_s = \theta(-z_i{}^k b_s) A_s + \theta(z_i{}^k b_s) B_s, \quad A_s = \int_0^\infty \left(e^{x-s} \frac{\Gamma(3/2, x^{-s})}{\Gamma(3/2)} - 1 \right) x^2 \, dx,$$

$$B_s = \int_0^\infty (e^{-x-s} - 1) x^2 \, dx, \quad \theta(z_i{}^k b_s) = \begin{cases} 1, & z_i{}^k b_s > 0 \\ 0, & z_i{}^k b_s < 0 \end{cases} \quad (10)$$

2. Assume that the condition $\beta e^2/a \gg 1$ is satisfied (low temperatures). Then, for each level of the atom we can separate the principal type of interaction, making the largest contribution to the thermodynamic potential, namely, the interaction that has the lowest s and does not vanish at this level. Let us consider different types of interaction between the atom and the electron (ion)[2].

A. Dipole interaction k = 1, s = 2. This type of interaction is peculiar to the hydrogen atom (but it vanishes in the ground state) and to low-excited levels of atoms. Here $b_2 = -(3/2)n(n_1 - n_2)$, where $n = n_1 + n_2 + |m| + 1$ is the principal quantum number, m is the projection of the angular momentum, and n_1 and n_2 are parabolic quantum numbers. The integrals A_2 and B_2 diverge linearly at the upper limits, but this divergence is cancelled out upon summation over the states of the atom differing in the orientation of the dipole moment. At fixed n and $|m|$, n_1 varies from 0 to $n - |m| - 1$. The coefficients b_2 for the values of n_1 and n_1', under the condition $n_1 + n_1' = n - |m| - 1$, differ only in sign, so that the result of the summation over n_1 does not change if one adds to C_2 the term $\text{const} \cdot \text{sign}(z_ib_2)$. We choose the constant such that the coefficient C_2 is independent of the sign of z_ib_2. We obtain

$$C_2 = \frac{A_2 + B_2}{2} = \int_0^\infty \left[\frac{1}{2} \left(e^{x-2} \frac{\Gamma(3/2, x^{-2})}{\Gamma(3/2)} + e^{-x-2} \right) - 1 \right] x^2 \, dx. \quad (11)$$

The integral in formula (11) diverges logarithmically at the upper limit and it must be cut off at the Debye radius. We then obtain

$$C_2 \approx 0.67 - \frac{2}{3\sqrt{\pi}} \left[c - \ln \left(4\pi \beta e^2 \sum_i \zeta_i z_i^2 \right)^{1/2} (|z_ib_2| \beta e^2 a)^{1/2} \right],$$

$$\left[\left(4\pi \beta e^2 \sum_i \zeta_i z_i^2 \right)^{1/2} (|z_ib_2| \beta e^2 a)^{1/2} \ll 1 \right], \quad (12)$$

where c = 0.577 is Euler's constant.

B. Quadrupole interaction k = 1, s = 3. Here

$$b_3 = Q_0 \frac{J(J+1) - 3M^2}{2J(2J-1)}$$

where Q_0 is the quadrupole moment (in atomic units), J is the total angular momentum, and M is the projection of the total angular momentum. This type of interaction vanishes in states with J = 0 and $1/2$. The integrals A_3 and B_3 diverge logarithmically at the upper limit, but the divergence is completely cancelled in summation over states having different momentum orientations. The result of the summation over M does not change if one adds to C_2 the term $\text{const} \cdot \text{sign}(z_ib_3)$.

Indeed

$$\sum_{M=-J}^{J} \text{sign}(z_ib_3) |z_ib_3| = \frac{Q_0 z_i}{2J(2J-1)} \sum_{M=-J}^{J} [J(J+1) - 3M^2] = 0.$$

Redefining C_3 in the same manner as C_2, we obtain

$$C_3 = \int_0^\infty \left[\frac{1}{2} \left(e^{x-3} \frac{\Gamma(3/2 x^{-3})}{\Gamma(3/2)} + e^{-x-3} \right) - 1 \right] x^2 \, dx \approx -0.11. \quad (13)$$

C. Dipole interaction k = 2, s = 4. An interaction of this type in the ground state is always an attraction. Here $b_4 = -\alpha/2$, where α is the polarizability of the atom (in atomic units). Calculation of the integrals yields $A_4 \approx 1.61$ and $B_4 \approx -1.21$.

We have used throughout potentials describing the interaction at distances that are large compared with the radius of the atom. This apparently leads to an overestimate of the contribution made to the integrals by small distances, and its justification may be the smallest of the contribution made to the integrals by distances smaller than the Bohr radius. This leads to the condition

$$|b_s \beta e^2 / a| \gg 1. \quad (14)$$

We note that both the quasiclassical criterion (5), and the less restrictive condition (14), are the easier to satisfy, the larger $|b_s|$, i.e., the stronger the interaction and the larger the contribution to the thermodynamic potential.

If the interaction of the atom with the electron is weak, condition (5) is not satisfied. In the important case of polarization interaction, at low energies, we can use for the scattering phase shifts an expansion in terms of the wave vector, the phases with $l \neq 0$ turning out to be small compared with the s-scattering phase[3]. If the atom has a negative ion with low binding energy $|\epsilon| = \hbar^2\kappa^2/2m_e$, then the principal term of the expansion equals

$$K \, \text{ctg} \, \delta_0 = -\varkappa. \quad (15)$$

Substituting δ_0 from (15) in (2), we obtain

$$- \beta \Delta \Omega_{ae} = -\frac{1}{2} \zeta_a \zeta_e \left(\frac{2\pi\hbar^2\beta}{m_e} \right)^{3/2} e^{\beta|\epsilon|} (1 - \Phi(\sqrt{\beta|\epsilon|})), \quad (16)$$

where

$$\Phi(\sqrt{\beta|\epsilon|}) = \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{\beta|\epsilon|}} e^{-x^2} \, dx$$

is the error integral. The condition for the applicability of formula (16) is the opposite of the quasiclassical condition (5).

3. Taking into account the Coulomb interaction and the interaction of the atoms with the electrons and ions, the thermodynamic potential of the plasma is given by the following expression (for concreteness we assume that the quasiclassical criterion is satisfied; in addition, we assume that the plasma is sufficiently rarefied and that the electron gas is far from degenerate):

$$- \beta \Omega = \sum_d \zeta_d + \frac{1}{12\pi} \left(4\pi \beta e^2 \sum_i \zeta_i z_i^2 \right)^{3/2} + \sum_{i, a} \zeta_i \zeta_a \frac{1}{Z_a} \sum_{nJM} e^{-\beta r_n}$$

$$\times (\beta e^2 a^{s-1} |z_i{}^k b_s|)^{3/s} \cdot 4\pi C_s, \quad (17)$$

where the index d numbers all the plasma components, i are the charged components and a the atomic components. The first term is the contribution from the free particles, the second the Debye term, and the

third the contribution from the interaction of the atoms with the electrons or ions. The constants k and s correspond to the principal type of interaction for each level of the given atom. The particle density is calculated by the formula

$$n_k = \zeta_k \left(\frac{\partial}{\partial \zeta_k} \right)_{\beta, V} (-\beta \Omega).$$

For the atomic component we have

$$n_a = \zeta_a \left[1 + \sum_i \zeta_i \frac{1}{Z_a} \sum_{nJM} e^{-\beta \varepsilon_n} (\beta e^2 a^{s-1} |z_i^k b_s|^{3/s} 4\pi C_s \right]. \qquad (18)$$

For the charged component

$$n_i = \zeta_i \left[1 + \frac{1}{2} \gamma_\zeta z_i^2 + \sum_a \zeta_a \frac{1}{Z_a} \sum_{nJM} e^{-\beta \varepsilon_n} (\beta e^2 a^{s-1} |z_i^k b_s|)^{3/s} \cdot 4\pi C_s \right], \qquad (19)$$

where

$$\gamma_\zeta = \left(4\pi (\beta e^2)^3 \sum_i \zeta_i z_i^2 \right)^{1/2}.$$

Equations (17)—(19) determine the equation of state in parametric form.

If the Coulomb interaction is more significant than the interaction of the atoms with the electrons or ions, the last term of (19) can be neglected. We put $z_i^2 = 1$. Multiplying (19) by $4\pi (\beta e^2)^3 z_i^2$ and summing over the charged components, we get $\gamma^2 = \gamma_\zeta^2 + (1/2)\gamma \zeta^3$, where γ differs from γ_ζ in that ζ_i is replaced by n_i. We solve this equation with respect to γ_ζ: $\gamma_\zeta = \gamma \varphi(\gamma)$, where $\varphi(\gamma)$ is the positive root of the equation

$$\varphi^3 + \frac{2}{\gamma} \varphi^2 - \frac{2}{\gamma} = 0.$$

Expressing by means of (18) and (19) the activities in terms of the densities, and substituting in (4), we obtain the equilibrium equation for the ionization of the negative ion, with the correction to the ionization energy:

$$-\beta \Delta I_{a^-} = \ln \left[1 + \sum_i \frac{n_i}{1 + 1/2 \gamma \varphi(\gamma)} \frac{1}{Z_a} \sum_{nJM} e^{-\beta \varepsilon_n} \right.$$
$$\left. + (\beta e^2 a^{s-1} |z_i^k b_s|)^{3/s} 4\pi C_s \right] \qquad (20)$$

A similar calculation yields for the decrease of the ionization energy of the atom

$$-\beta \Delta I_a = 2\ln [1 + 1/2 \gamma \varphi(\gamma)] + \beta \Delta I_{a^-}, \qquad (21)$$

where the first term is due to the Coulomb interaction and the second to the interaction of the atoms with the electrons and ions.

Mal'nev and Pekar[4] calculated the classical second virial coefficient for the dipole-dipole interaction in the first order of perturbation theory $(1/r^3)$ of identical atoms in different states. This yielded integrals that diverged strongly at small distances, and were cut off, from qualitative considerations, at a distance on the order of double the atomic radius. The result, naturally, depends strongly on the cut off parameter. The method employed here makes it possible to avoid divergence of the integrals, and the use of incorrect potentials at small distances does not lead to large errors in the integrals. We note, however, that for the van der Waals interaction $(1/r^6)$ a logarithmic divergence does remain, and it is necessary to correct the potential at small distances.

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