THERMODYNAMIC FUNCTIONS OF A LOW-TEMPERATURE PLASMA

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We have evaluated the thermodynamic functions of a plasma at temperatures below the ionization temperature. We have shown that if the interaction of the ions with the electrons of the continuous spectrum is properly taken into account, this will partially compensate the contribution from the excited states of the atoms and the complex ions.

THE thermodynamic potential of an electron-ion plasma is usually defined by the formula

$$-\beta\Omega = \sum_i \zeta_i, \tag{1}$$

where $\beta = 1/kT$ and where the summation is over all the types of particles, while the quantities ζ_i are expressed in terms of the corresponding chemical potentials

$$\zeta_i = (m_i / 2\pi\hbar^2\beta)^{3/2} \exp[\beta(\mu_i + I_i)]. \tag{2}$$

Here I_i is the energy for the complete ionization of the i-th ion. The conditions for equilibrium and neutrality lead to the following relations between the chemical potentials

$$\mu_z + \mu_e = \mu_{z-1}, \qquad \sum Q_i\, \partial\Omega_i / \partial\mu_i = 0. \tag{3}$$

Equation (1) is the first term in an expansion of the thermodynamic potential in powers of ζ. One must in the next approximation add to expression (1) the Debye term $\kappa^3/12\pi$, where

$$\varkappa^2 = 4\pi\beta \sum Q_i^2 \zeta_i. \tag{4}$$

Moreover, one must replace in Eq. (2) the last factor by a sum $\Sigma_m \exp(\beta I_{im})$ over all excited states of the i-th ion. This sum is formally equal to infinity. If we restrict the summation, as is done in the papers by Fermi and others,[1] only to those states where the ionic dimensions are less than the interparticle distance, we get the result that the contribution from the excited ions to the thermodynamic potential is proportional to $\zeta^{3/2}$ and is of the same order of magnitude as the Debye term.

If one, however, takes the interaction between an ion with charge Q_i and the electrons of the continuous spectrum properly into account, one is led to an expression which compensates the divergence of the sum over the bound states of the ion with charge $Q_i - e$. After separating the Debye term, there remains thus an expression which is proportional to $\zeta^2 \ln \zeta$, ζ^2, and higher powers of ζ.

Let us consider the interaction between an ion with charge Q_i and an electron. The correct magnitude of the term of order ζ^2 (see reference 2) is obtained by subtracting from the quantum mechanical expression for the virial coefficient the infinite terms: the term

$$\zeta_i\zeta_e \int \frac{\beta Q_i Q_e}{r}\, dV,$$

leading to the neutrality of the plasma, and the term

$$\frac{1}{2}\zeta_i\zeta_e \int \left(\frac{\beta Q_i Q_e}{r}\right)^2 dV,$$

were already taken into account when the Debye term was evaluated. The remaining expression

$$\zeta_i\zeta_e \left\{\left(\frac{2\pi\hbar^2\beta}{m}\right)^{3/2} \sum_k \exp(-\beta E_k) - \int \left[1 + \frac{\beta Q_i Q_e}{r} + \frac{1}{2}\left(\frac{\beta Q_i Q_e}{r}\right)^2\right] dV\right\} \tag{5}$$

diverges logarithmically, and to remove this divergence one must replace at large distances from the ion its Coulomb potential by the Debye potential $(Q_i/r)\exp(-\kappa r)$, where κ is defined by Eq. (4). The sum in the first term of Eq. (5) is taken over all states of both the continuous and the discrete spectrum. The contribution from the largest term in that sum, which corresponds to the ground state of the ion (or atom) with charge $Q_i - e$, is equal to ζ_{i-1} and was already taken into account in Eq. (1), so that we shall assume that the summation is only over the excited states. If the ion is not a nucleus, we must take for the energies of the first levels experimental or approximately evaluated values, but at higher excitation energies the spectrum is a Coulomb one, i.e., the levels are n^2-fold degenerate and have an energy $E_n = -\frac{1}{2} m (Q_i Q_e/\hbar n)^2$. Let the condition for quasi-classical behavior $\beta m (Q_i Q_e/\hbar)^2 \gg 1$ be fulfilled; only in that case will there be an appreciable contribution from the bound states. The opposite limiting case was considered in the paper by Vedenov and Larkin.[2] We take for n_0 such a quantum number that $\beta |E_n| \ll 1$; we can then replace the sum over the bound states with $n > n_0$ and over the states of the continuous spectrum by an integral, using for the density of states the quasi-classical expression $dn = (2\pi)^{-3} d\mathbf{p} d\mathbf{r}$. For large n_0 the remaining sum is proportional to n_0^3, but the integral term contains a compensating term. In the calculation it is convenient to differentiate twice with respect to β the expression within the braces in (5), after which one can put $n_0 = \infty$ and evaluate separately the sum and the integral.

As a result we get

$$-\beta\Omega_{ie} = \zeta_i \zeta_e \left\{ \left(\frac{2\pi\hbar^2\beta}{m}\right)^{3/2} \sum_m [\exp(\beta E_m) - 1 - \beta E_m] + \frac{2\pi}{3} (\beta Q_i Q_e)^3 \left(\ln \frac{1}{3\beta Q_i Q_e \varkappa} - 2C + \frac{11}{6}\right) \right\}. \quad (6)$$

Here C is Euler's constant, which is equal to 0.577; the sum is over all bound states and converges.

The contribution to the thermodynamical potential from the interactions between ions with charge Q_i and Q_j is evaluated from the classical formula for the second virial coefficient

$$-\beta\Omega = \zeta_i \zeta_j \int (e^{-\beta u} - 1)\, dV.$$

As the ions repel one another, there is no divergence at small distances apart and the divergence at large distances is removed in the way described above. When one evaluates this integral, as in the evaluation of the term with the integral in Eq. (6), the important distances are of the order $\beta Q_i Q_j$; at these distances the interaction even between complex ions can be assumed to be a Coulomb one. As a result we get

$$-\beta\Omega_{ij} = -\frac{2\pi}{3} (\beta Q_i Q_j)^3 \left(\ln \frac{1}{3\beta Q_i Q_j \varkappa} - 2C + \frac{11}{6}\right). \quad (7)$$

The interaction between electrons and between ions of the same kind leads to an expression which differs from Eq. (7) only by a factor $\frac{1}{2}$.

To evaluate the Debye term we must bear in mind that the screening occurs not for free particles but for particles in the field of other particles. Using the diagram technique, described in the paper by Vedenov and the author,[2] to evaluate the correction term, we find a contribution to $-\beta\Omega$ equal to

$$\frac{\pi}{2} \beta^3 \left(\sum Q_i^4 \zeta_i\right) \left(\sum Q_i^2 \zeta_i\right).$$

If the plasma is weakly ionized, we must take into account the interaction between the atoms. If, however, the number of atoms is of the same order of magnitude as the number of ions the interaction between the atoms is less important and we shall not take it into account here. We have thus

$$-\beta\Omega = \sum \zeta_i + \frac{\varkappa^3}{12\pi} + \left(\frac{2\pi\hbar^2\beta}{m}\right)^{3/2} \zeta_e \sum_i \zeta_i \sum_m [\exp(\beta E_m) - 1 - \beta E_m] - \frac{\pi}{3} \beta^3 \sum_{ij} (Q_i Q_j)^3 \zeta_i \zeta_j \left(\ln \frac{1}{3\beta Q_i Q_j \varkappa} - 2C + \frac{11}{6}\right) + \frac{\pi}{2} \beta^3 \left(\sum Q_i^4 \zeta_i\right) \left(\sum Q_i^2 \zeta_i\right).$$

If the interelectronic interaction is not quasi-classical but must be described in the Born approximation, we must substitute for the corresponding term the analogous expression from a previous paper.[2] The interaction between the electrons and the ions can be treated in the Born approximation only when the plasma is fully ionized and in that case we must use the equations of reference 2.

In a recently published paper by Abe[3] only the interactions between the electrons were taken into account. The expression obtained there was the same as Eq. (7). The classical method used in that paper made it impossible to consider the interaction between the electrons and the ions.

[1] H. C. Urey, Astrophys. J. **59**, 1 (1924); E. Fermi, Z. Physik **26**, 54 (1924); R. H. Fowler, Phil. Mag. **1**, 845 (1926).

[2] A. A. Vedenov and A. I. Larkin, JETP **36**, 1133 (1959), Soviet Phys. JETP **9**, 806 (1959).

[3] R. Abe, Progr. Theoret. Phys. (Kyoto) **22**, 213 (1959).

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