SOVIET PHYSICS JETP VOLUME 28, NUMBER 4 APRIL, 1969

SECOND VIRIAL COEFFICIENTS OF A PLASMA

V. P. KOPYSHEV

Submitted February 8, 1968

Zh. Eksp. Teor. Fiz. 55, 1304–1310 (October, 1968)

A general expression is obtained for the second virial coefficient of a plasma at any temperature. It is shown that the Coulomb corrections for an ideal gas are limited. For the pressure in light elements, the maximum correction is of the order of 5%.

A general quantum-mechanical formula for the second virial coefficient, expressed in terms of its phase, was first derived by Beth and Uhlenbeck[1] but is applicable directly only to short-range forces, and leads to divergences in the case of a Coulomb plasma.

Rigorously founded rules for the elimination of Coulomb divergences in the second virial coefficient were formulated in the papers of Vedenov and Larkin[2] and Larkin[3], where analytic formulas were obtained for this coefficient in the limits of high[2] and low[3] temperatures, where the Born and quasiclassical approximation are valid, respectively. In the present paper we carry out the calculation in the entire intermediate region of temperatures.

We use the following notation: i—number of the ion, and in the particular case of an electron it is assumed that i = e; $Q_i = Z_i e$—charge of ion, $Q_e = -e$; g_i—multiplicity of degeneracy of the ground state of the ion, $g_e = 2$, m_i—ion mass, $m_e = m$; m_{ij}—reduced mass of two ions, for heavy ions (i ≠ e) we put $m/m_i = 0$ throughout (adiabatic approximation); n_i—ion density, $\beta = 1/kT$; μ_i—chemical potential of the ion; C = 0.5772—Euler's constant, and

$$\xi_i = g_i (2\pi\hbar^2\beta/m_i)^{3/2} e^{\beta\mu_i}.$$

The second virial correction $\Delta\Omega$ to the thermodynamic Gibbs potential (per unit volume), which is proportional to ξ^2, equals[2]

$$-\beta\Delta\Omega = \frac{1}{2}\sum_{ij}\xi_i\xi_j\left(\frac{2\pi\hbar^2\beta}{m_{ij}}\right)^{3/2}[Z_{ij}(e^2) - Z_{ij}(0)], \tag{1}$$

$$Z_{ij}(e^2) = \frac{1}{g_i g_j}\sum_{\nu} e^{-\beta E_{ij\nu}}, \tag{2}$$

where ν are all the quantum numbers (including the spin) for the relative motion of the two ions, and $E_{ij\nu}$ are the corresponding energies; allowance for the identity of the electrons makes it necessary to take the odd states in the sum over ν (2) with weight 3/2 and the even ones with weight 1/2 when i = j = e. From dimensionality considerations we obtain the general form of the expansion of the statistical sum (2) in powers of e^2 for the relative motion of particles with Coulomb interaction:

$$Z_{ij}(e^2) = \sum_{s=0}^{\infty}\alpha_{ijs}x_{ij}^{s/2}, \tag{3}$$

$$x_{ij} = \frac{\beta m_{ij}Q_i^2 Q_j^2}{2\hbar^2} \sim \beta e^4. \tag{4}$$

For brevity we shall henceforth omit the indices ij.

We consider first only part of the sum (3), which begins with s = 4 (and contains no divergences[2]):

$$\Sigma(x) = \sum_{s=4}^{\infty}\alpha_s x^{s/2} = Z(e^2) - Z(0) - Z'(0)e^2 - \frac{1}{2}Z''(0)e^4 - \frac{1}{6}Z'''(0)e^6, \tag{5}$$

and break (2) up into two sums—over the states of the discrete (d) and continuous (c) spectra. A similar decomposition will occur also in the sum (5):

$$\Sigma = \Sigma_d + \Sigma_c. \tag{6}$$

The contribution from the discrete spectrum (it is present only when i = e, j ≠ e or i ≠ e, j = e) is[3]

$$\Sigma_d = \frac{1}{2g_i}\sum_{E_\nu<0}(e^{-\beta E_{ie\nu}} - 1 + \beta E_{ie\nu}), \quad i \neq e, \tag{7}$$

since $E_{ie\nu} \sim e^4$. We note that

$$\Sigma_d \sim (\beta e^4)^2 \sim x^2 \quad \text{as} \quad x \to 0. \tag{8}$$

The sum (7) is calculated from the experimental terms; it converges, since the states of the higher excitations are hydrogenlike.

It is convenient for us to represent (7) in an identical form, separating the ground state $E_0 = -I$ of the ion-electron system, where I is the ionization potential of one electron,

$$\Sigma_d = e^{\beta I} + \Delta\Sigma_d. \tag{9}$$

In general, the contribution from the discrete spectrum is significant only at low temperatures, when the ionization is incomplete, and then the first term of (9) is large compared with the second, since usually the minimum energy of excitation is of the order of I.

In the continuous spectrum, for a pure Coulomb interaction, the phase at large distances r equals

$$\varphi_l = kr + \frac{1}{ak}\ln 2kr - \frac{l\pi}{2} + \arg\Gamma\left(l + 1 - \frac{i}{ak}\right), \quad kr \gg 1, \tag{10}$$

where $a = a_{ij} = -\hbar^2/m_{ij}Q_iQ_j$, and the level density in k-space dn/dk is obtained from the requirement that the wave function vanish at a distance r, i.e.,

$$\frac{dn}{dk} = \frac{g_i g_j}{\pi}\sum_l (2l+1)\frac{d\varphi_l}{dk}, \quad k \gg \frac{1}{r}. \tag{11}$$

We introduce the notation u = ak, yu = 1, and

$$\Phi_l(y) = -d\arg\Gamma(l + 1 - iy)/dy. \tag{12}$$

The function (12) is even (see below). Using the definitions (6), (5), (2), (11), (10), (12), and (4) we get

$$\Sigma_c(x) = \pm\frac{1}{\pi}\int_0^{\infty}\frac{du}{u^2}e^{-xu^2}\sum_l(2l+1)\left[\Phi_l\left(\frac{1}{u}\right) - \Phi_l(0) - \frac{1}{2}\Phi_l''(0)\left(\frac{1}{u}\right)^2\right]. \tag{13}$$

In (13) and subsequently, the upper sign corresponds to attraction ($a > 0$) and the lower to repulsion ($a < 0$). To calculate (12) we use the well known relation

$$\Phi_l(y) = \operatorname{Re} \frac{d \ln \Gamma(z)}{dz} \Big|_{z=l+1-iy} = \Big(\sum_{n=1}^{l} \frac{1}{n} - C \Big) + \sum_{n=l+1}^{\infty} \frac{y^2}{n(n^2+y^2)};$$

and then

$$\Sigma_c(x) = \mp \frac{1}{\pi} \sum_{l} \sum_{n=l+1}^{\infty} \int_0^{\infty} \frac{du}{u^4} \frac{(2l+1) e^{-xu^2}}{n^3(u^2n^2+1)}. \tag{14}$$

The integral (14) diverges at small values of u, but in the region $u = ak \lesssim a/r$ the level density is no longer expressed in terms of the asymptotic phase shift, since formula (10) is not valid in this region. However, there is no need to make φ_l more precise. Indeed, the integral for the second derivative Σ_c'' converges and is bounded when $x = 0$, so that the unknown contribution to the integral (14) from the region of small u determines only the integration constants A and B:

$$\Sigma_c = A + Bx + O(x^2). \tag{15}$$

On the other hand, it follows from (6), (8), and (5) that $\Sigma_c = \Sigma - \Sigma_d \sim x^2$ as $x \to 0$, i.e., $A = 0$ and $B = 0$. These considerations remain in force also for the part of the sum (3) which begins with $s = 3$. In Larkin's paper[3], the sum (3) began with $s = 3$, and the quasiclassical expression was used for dn/dk.

Interchanging the order of summation in (14) and calculating the sums, we get

$$\Sigma_c'' = \mp \frac{1}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \int_0^{\infty} \frac{e^{-xu^2} du}{u^2n^2+1}, \tag{16}$$

where for an electron pair it is necessary to replace the factor 1/n in (16), owing to the difference in the weights with respect to the even and odd l, by $1/n + (-1)^n/2n^2$. This difference, due to the exchange interaction of the electron pair, is more conveniently taken into account in the sum (3) by starting it not with $s = 4$ but with $s = 3$; for such a sum we obtain the expression

$$\frac{1}{2\pi} \sum_{n=1}^{\infty} \int_0^{\infty} \frac{(-1)^n u^2 e^{-xu^2} du}{u^2n^2+1} = -\frac{\pi}{24} \sqrt{\frac{\pi}{4x}} + \Sigma_{c \cdot \mathrm{exc}}''. \tag{17}$$

The first term in (17) corresponds to the term with $s = 3$, and the second to the sum beginning with $s = 4$. The integrals (16) and (17) are expanded in a Taylor series with respect to $\sqrt{x}$ at the point $x = 0$:

$$\mp P'' \equiv \Sigma_c''(x) = \mp \frac{1}{2} \sum_{m=0}^{\infty} \Big[\frac{1}{m!} \Big(\sum_{n=1}^{\infty} \frac{1}{n^{2m+2}} \Big) - \frac{2^m}{(2m+1)!!} \Big(\sum_{n=1}^{\infty} \frac{1}{n^{2m+3}} \Big) \sqrt{\frac{4x}{\pi}} \Big] x^m, \tag{18}$$

$$Q'' \equiv \Sigma_{c \cdot \mathrm{exc}}''(x) = \frac{1}{4} \sum_{m=0}^{\infty} \Big[\frac{1}{m!} \Big(\sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n^{2m+3}} \Big) - \frac{2^m}{(2m+1)!!} \Big(\sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n^{2m+4}} \Big) \sqrt{\frac{4x}{\pi}} \Big] x^m. \tag{19}$$

On the other hand, the principal terms of the asymptotic form at large values of x are equal to

$$\mp P'' \equiv \Sigma_c''(x) = \mp \frac{1}{\sqrt{4\pi x}} \Big[\Big(\ln \sqrt{4x} + \frac{3C}{2} \Big) + \frac{1}{24x} \Big], \tag{20}$$

$$Q'' = \Sigma_{c \cdot \mathrm{exc}}''(x) = \frac{1}{\sqrt{4\pi x}} \Big[\frac{\pi^2}{24} - \frac{1}{8x} + \frac{\pi}{\sqrt{3}} \Big(\frac{\pi}{2x} \Big)^{1/3} \exp\Big(-3 \Big(\frac{\pi^2 x}{4} \Big)^{1/3} \Big) \Big]. \tag{21}$$

For practical purposes it suffices to retain in the sums (18) and (19) six terms (up to $m = 5$) in the region $x < 1$, and to change over to the asymptotic relations (20) and (21) in the region $x > 1$. The exponential in (21) is best interpolated by the term Bx^{-2}. The assumed error does not exceed 1%. The integration with respect to x of the functions P'' and Q'' is then elementary.

Let us consider the low-temperature limit $x \gg 1$, when the region of small u is significant in the integral (16). If $u \ll 1$, then $ƛ \gg |a|$, i.e., the quasiclassical approximation is valid (the motion of heavy ions in the adiabatic approximation is always quasiclassical, since x is proportional to their mass). Using the principal term of (20), we obtain

$$-\beta \Delta\Omega(s \geqslant 4) = \frac{\pi}{3} \sum_{ij} \xi_i \xi_j (\beta Q_i Q_j)^3 \Big[\ln \sqrt{4x_{ij}} + \frac{3C}{2} - \frac{4}{3} \Big], \quad \frac{1}{\beta} \to 0. \tag{22}$$

On the other hand, the contribution from the sum (3), when started from $s = 3$, was calculated in the quasiclassical approximation (taking into account the compensation of the divergence in the term with $s = 3$ by Debye screening) by Larkin[3]; it is equal to

$$-\beta \Delta\Omega(s \geqslant 3) = \frac{\pi}{3} \sum_{ij} \xi_i \xi_j (\beta Q_i Q_j)^3 \Big[\ln |3\varkappa \beta Q_i Q_j| + 2C - \frac{11}{6} \Big], \tag{23}$$

where

$$\varkappa^2 = 4\pi\beta \sum_i Q_i^2 \xi_i. \tag{24}$$

The third-order term ($s = 3$) at arbitrary temperature is of the form

$$\frac{\pi}{3} \sum_{ij} \xi_i \xi_j (\beta Q_i Q_j)^3 (\ln \varkappa \sqrt{\beta} + D_{ij})$$

(see[2]), so that the constant D_{ij} in this expression is already determined by the asymptotic form at $\beta \to \infty$, for which it is sufficient to subtract (22) from (23).

Thus, we have found all the terms of the sum (3) at $s \geq 3$. In[2] are calculated the terms of the sum at $s = 1$ and $s = 2$ (some coefficients have been corrected in[4]), in which the divergences were eliminated in a consistent manner. We present the final expression for the free energy:

$$F = F_B + F_{DH} + (F_d + F_{ee} + F_{ei} + F_{ii} + F_{sh}). \tag{25}$$

Here

$$-\beta F_Б = \sum_i n_i \Big[\ln \frac{g_i}{n_i} \Big(\frac{m_i}{2\pi\hbar^2\beta} \Big)^{3/2} + 1 + \beta I_i \Big] \tag{26}$$

is the main contribution from the Boltzmann ideal gas: I_i—ionization potential of all the electrons of the given ion, $I_e = 0$, and for bare nuclei also $I_i = 0$;

$$-\beta F_{DH} = \varkappa^3/12\pi \tag{27}$$

is the Debye-Huckel correction, which is proportional to $n^{3/2}$ and is due to the elimination of the divergence in the term with $s = 2$ (see[2,3]). The remaining terms of (25), enclosed in the parentheses, are proportional to n^2 (second virial correction) with accuracy to $\ln \kappa$, which is due to the elimination of the divergence in the term with s = 3;

$$-\beta F_{\mathrm{d}}=\left(\frac{2\pi\hbar^2\beta}{m}\right)^{3/2}\sum_i{}' n_e n_i \Delta\Sigma_{\mathrm{d}ie}, \quad i\neq e \tag{28}$$

is the remnant of the contribution from the discrete spectrum; the energy in formula (26) is reckoned from its principal part (see (9); see also[3]).

We note that in[3], the remnant of the contribution made to $\Delta\Sigma_{\mathrm{d}}$ from the ground state (ν = 0), due to the last two terms in (7), has been incorrectly omitted;

$$-\beta F_{\mathrm{ee}}=\frac{1}{2}\left(\frac{4\pi\hbar^2\beta}{m}\right)^{3/2} n_e^2\left\{-\frac{1}{16}+\frac{1}{8\sqrt{\pi}}\eta-\frac{1+\ln 2}{16}\eta^2\right.$$
$$\left.+\frac{1}{12\sqrt{\pi}}\left[\ln(3\varkappa\eta)+\frac{C-1}{2}-\frac{\pi^2}{24}\right]\eta^3+Q\left(\frac{\eta^2}{4}\right)+P\left(\frac{\eta^2}{4}\right)\right\}, \tag{29}$$

where $\eta = (\beta me^4/\hbar^2)^{1/2}$ is the contribution due to the interaction between the electrons. The first term in the curly brackets takes into account the degeneracy in the ideal gas of the electrons and does not depend on the charge; the second, third, and fourth terms take into account the remainder of the terms with s = 1, s = 2, s = 3 after compensation of the divergences in them, and the fifth and sixth term are proportional at high temperature to η^4, whereas at low temperature the principal contribution is proportional to $\eta^3(\ln \eta + \mathrm{const})$, and in this order there is no contribution from exchange, as should be the case in the quasiclassical approximation;

$$-\beta F_{\mathrm{ei}}=-\left(\frac{2\pi\hbar^2\beta}{m}\right)^{3/2}\sum_i{}' n_e n_i\left\{\frac{Z_i^2\eta^2}{8}+\frac{Z_i^3\eta^3}{3\sqrt{2\pi}}\right.$$
$$\left.\times\left[\ln\left(\frac{3}{\sqrt{2}}\varkappa\eta\right)+\frac{C-1}{2}\right]+P\left(\frac{Z_i^2\eta^2}{2}\right)\right\} \tag{30}$$

is the contribution from the interaction between the electrons of the continuous spectrum and the heavy ions;

$$-\beta F_{\mathrm{ii}}=\frac{\pi}{3}\sum_{ij}{}'' n_i n_j(\beta Q_i Q_j)^3\left[\ln|3\varkappa\beta Q_i Q_j|+2C-\frac{11}{6}\right], \quad i\neq e, \quad j\neq e \tag{31}$$

is the contribution from the classical interaction of the heavy ions (see[3]);

$$-\beta F_{\mathrm{sh}}=\frac{1}{2}\sum_{ij} n_i n_j\left(\frac{2\beta\pi\hbar^2}{m_{ij}}\right)^{3/2}\frac{1}{\pi}\sum_l(2l+1)\int_0^\infty\frac{d\delta_l}{dp}\exp\left\{-\frac{\beta p^2}{2m_{ij}}\right\}dp \tag{32}$$

is the contribution due to the additional phase shift $\delta_{ijl}(p)$ resulting from the presence of electron shells that distort the Coulomb field near the nucleus (see[5]); this term of the order of $(na_0^3)^2$, and becomes leading at high densities.

The ion concentrations $n_i = c_i n$ are calculated from the conditions of the chemical equilibrium

$$\frac{\partial F}{\partial n_e}+\frac{\partial F}{\partial n_i}=\frac{\partial F}{\partial n_{i-1}}, \quad i=1,\ldots,Z; \tag{33}$$

The index i indicates here the multiplicity of ionization, Z_i = i. In the zeroth approximation ($F = F_B$), (33) reduce to the Saha equations.

Let us consider hydrogen by way of an example. The Saha equation for the concentrations in the zeroth approximation yields

$$na_0^3=\frac{1-\alpha}{\alpha^2}(4\pi\beta I)^{-3/2}e^{-\beta I},$$

where α is the degree of ionization. The equation for the corrections to the concentrations in the Debye-Huckel approximation yield

$$\Delta\alpha=\frac{\alpha(1-\alpha)}{2-\alpha}\sqrt{8\pi\alpha n\beta^3 e^6}.$$

The ratio of the pressure correction to the pressure of an ideal gas is

$$\zeta=\frac{\Delta P_{\mathrm{DH}}}{P_{\mathrm{id}}}=-\frac{16}{3}\left(\frac{2}{\pi}\right)^{1/4}x^{3/4}e^{-x}\frac{y\sqrt{1-4y^2}}{9-4y^2},$$

where $x = \beta I/2$, $y = \alpha - 1/2$. At a fixed temperature, the limit of the total ionization $\alpha \rightarrow 1$ corresponds to a low density $n \rightarrow 0$. Both functions of x and y are bounded. With increasing density, ζ decreases, reaching a minimum at α = 0.8635, after which it increases and vanishes at α = 0.5. The absolute minimum is $\zeta_{\min} = -0.0534$ at T = 9.06 eV and $\rho = 5.6 \times 10^{-3}$ g/cm^3. The virial corrections shift the minimum.

Numerical calculations (without allowance for F_{sh}) yielded $\zeta_{\min} = -0.0438$ at T ≈ 5 eV, $\rho \approx 1 \times 10^{-3}$ g/cm^3. In general they are of the same order of magnitude as the Debye-Huckel corrections, in a broad vicinity of the minimum. Obviously, a similar minimum should exist also for any substance, since $\zeta \rightarrow 0$ in both limits $n \rightarrow 0$ and $n \rightarrow \infty$. In the former case the ionization is complete, but the charges are far from each other; in the latter case, the recombination is complete and there is no Coulomb interaction, since the charge is equal to zero. The sharp increase of pressure will be due to repulsion of the electron shells, i.e., to the term F_{sh}.

A general conclusion can be drawn that apparently the Coulomb interaction is small (for hydrogen, helium, and lithium $\lesssim 5\%$), and that the corresponding perturbation-theory series in terms of the density converges poorly.

In conclusion, the author is deeply grateful to N. A. Dmitriev and A. I. Larkin for valuable discussions.

---

[1] E. Beth and G. Uhlenbeck, Physica 4, 915 (1937).

[2] A. A. Vedenov and A. I. Larkin, Zh. Eksp. Teor. Fiz. 36, 1133 (1959) [Sov. Phys.-JETP 9, 806 (1959)].

[3] A. I. Larkin, ibid. 38, 1896 (1960) [11, 1363 (1960)].

[4] B. A. Trubnikov and V. F. Elesin, ibid. 47, 1279 (1964) [20, 866 (1965)].

[5] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Fizmatgiz, 1964 (Addison-Wesley 1959).

Translated by J. G. Adashko
146