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Direct linear term in the equation of state of plasmas

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We discuss a long-standing discrepancy in the equation of state of charge-neutral plasmas, the occurrence of an e^2 direct term. This e^2 term may appear in dependence of the way to determine the mean value of the potential energy. We show that such a contribution should not appear for pure Coulomb interaction.

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I. INTRODUCTION

The determination of thermodynamic functions for a strongly correlated plasma is an old task of many-body theory. New experimental measurements and numerical *ab initio* simulations that are nowadays accessible will not be discussed in this paper. We focus on analytic results which are obtained in limiting situations (only) using quantum statistical approaches such as the Green's function method. In particular, in the low-density limit exact results can be given for the virial expansion. For very high densities where the temperature does not play a deciding role, we can treat the strongly degenerate system. This means that the two limiting cases of very low and very high degeneracies are tractable by analytic means. Any exact result may serve as a benchmark to derive interpolation formulas that, using also the results of simulations, are applicable in a wide region of plasma parameters. We are not going to deal with the vast number of papers on numerical determinations of thermodynamic data; we mention only the review article by McMahan *et al.* [1] and references quoted therein.

Exact expressions for many-body systems with short-range interaction have long been known. In particular, the Beth-Uhlenbeck formula expresses the second virial coefficient in terms of two-particle binding energies and scattering phase shifts, see, e.g., Ref. [2]. For Coulomb systems several intricacies occur due to the long-range ($\propto 1/r$) character of the bare Coulomb interaction. The mean-field (Hartree) term is divergent in the thermodynamic limit. This is only resolved by considering charge-neutral plasmas where the sum of the Hartree terms is zero. Therefore we will consider here a charge-neutral hydrogen plasma. Furthermore, scattering phase shifts cannot be introduced in the standard way, and the intrinsic partition function of the hydrogen bound states diverges. This problem is resolved introducing the Planck-Larkin partition function. Despite these mathematical (not physical) problems, it is challenging to find exact results for the neutral hydrogen plasma because of the exceptional role of the Coulomb interaction in physics.

The pioneering work in the statistics of Coulomb systems began in the 1950s. We mention W. Macke, who overcame one of the typical Coulomb divergencies and found the logarithmic contribution to the thermodynamic functions [3]. One finds an essential step forward in the paper by Gellman and Brueckner [4], whose results were valid at zero temperature up to the order e^4 of the electron charge. In the 1960s, Kelbg found a way to construct an effective potential which accounts for the influence of quantum effects on the interaction between two charged particles [5]. Based on a systematic study of many-particle systems, a new field of research was devoted to find thermodynamic functions of plasmas containing all powers of the charge. Results were achieved by Ebeling, Hoffmann, and Kelbg [6] following a cluster approach given by Friedman [7]. Green's function calculations were given in Ref. [8]. In Coulomb systems, the lower orders with respect to e^2 have to be dealt with separately as they are subject to the well-known Coulomb divergencies. The higher orders of the direct contribution and all orders of the exchange contribution can be written as a series, see below Eqs. (3) and (4). These results were, in detail, again given in Ref. [9] in Eqs. (6.218) and (6.219).

In Sec. II we introduce the virial expansion of the pressure in terms of the densities, Eq. (5) at fixed temperatures that is the usual way to introduce virial coefficients. Alternatively, one considers the expansion with respect to the fugacities that are natural variables considering the pressure as thermodynamic potential, see Eq. (1). Both virial expansions are closely related, see Refs. [2,8]. In deriving the second virial coefficient for Coulomb systems, the different approaches that have been used are presented in Sec. III. The main topic of the present work is to discuss whether a direct linear term arises in different approaches. This question leads to consequences for calculating higher virial coefficients or $(ne^2)^{5/2}$ terms and is dealt with in Sec. IV, see also Ref. [10].

II. THERMODYNAMICS

We consider a two-component system, in particular a neutral hydrogen plasma consisting of electrons (e) and protons (p), interacting via the Coulomb potential $V_{ab}^{\rm Coul} = V_{ab}(r) = e_a e_b / r$. Here and subsequently we use Heaviside units. The equation of state $p(\{z_c\},T)$, which relates the pressure to the independent variables temperature T and the fugacities $z_a = (2s_a + 1)/\Lambda_a^3 \exp[\mu_a/(k_B T)]$, may be derived from the cluster expansion for the grand-canonical ensemble (see, e.g., Refs. [8,9,11–14]). The thermal wavelength is given by $\Lambda_a = h/(2\pi m_a k_B T)^{1/2}$, where μ_a is the chemical potential.

From the determination of the mean value of the potential energy $\langle V^{\rm Coul}\rangle$ we derive thermodynamic quantities in the usual manner. We mention here that we consider the mean value of the *Coulomb potential* thus restricting the consideration to Coulomb systems. We have then for the pressure up to the order z^2 in the weakly degenerate case $(a,b,c = e,p)$

$$\frac{p(\{z_c\}T)}{k_BT} = \sum_a z_a + \frac{\tilde{\kappa}^3}{12\pi} + \sum_{ab} z_a z_b \bigg[\frac{\pi}{2}(\beta e_a e_b)^3 \ln(\tilde{\kappa}\lambda_{ab}) + \frac{\pi}{2}\beta^3 e_a^2 e_b^4 + 2\pi\lambda_{ab}^3\, K_0(\xi_{ab},s_a) \bigg] + \mathcal{O}\big(\{z_c^{5/2}\ln z_c\}\big). \tag{1}$$

Here z is the "modified" fugacity, approaching the number density in the low-density limit, and it differs from the usual fugacity $\tilde{z}_a = \exp(\beta\mu_a)$. The thermal wavelengths are given by $\lambda_{ab} = \hbar/(2m_{ab}k_BT)^{1/2}$, where $m_{ab} = m_a m_b/(m_a + m_a)$ is the reduced mass, $\beta = 1/(k_BT)$, and $\xi_{ab} = -e_a e_b/(k_BT\lambda_{ab})$ is the Born parameter. The "modified" screening quantity (Debye) is given by $\tilde{\kappa}^2 = \sum_a 4\pi z_a e_a^2/(k_BT)$. The functions occurring in Eq. (1) are given by

$$K_0(\xi_{ab},s_a) = Q(\xi_{ab}) \pm \delta_{ab}\frac{(-1)^{2s_a}}{2s_a+1}E(\xi_{ab}), \tag{2}$$

$$Q(\xi) = -\frac{\sqrt{\pi}\xi^2}{8} - \frac{\xi^3}{6}\left(\frac{C}{2} + \ln 3 - \frac{1}{2}\right) + \sum_{n=4}^{\infty}\frac{\sqrt{\pi}\zeta(n-2)}{\Gamma\left(\frac{n}{2}+1\right)}\left(\frac{\xi}{2}\right)^n, \tag{3}$$

$$E(\xi) = \frac{\sqrt{\pi}}{4} + \frac{\xi}{2} + \frac{\sqrt{\pi}}{4}\ln 2\,\xi^2 + \frac{\pi^2}{72}\xi^3 + \sum_{n=4}^{\infty}\frac{\sqrt{\pi}(1-2^{2-n})\zeta(n-1)}{\Gamma\left(\frac{n}{2}\right)}\left(\frac{\xi}{2}\right)^n. \tag{4}$$

The term $E(\xi)$ represents exchange contributions for identical particles and contains the degeneracy contribution (virial expansions at finite temperatures starting with the limit of the ideal gas), while $Q(\xi)$ stands for the direct ones. Here C is Euler's number, Γ is Euler's Gamma function, and ζ is Riemann's Zeta funtion. In addition to the lower orders, the contributions to the second virial coefficient are given as power series with respect to the Born paramen ξ_{ab}. In contrast to the exchange contribution $E(\xi)$ which contains a linear term in ξ, no linear term arises in the direct contribution $Q(\xi)$ as well as in the lower order terms in Eq. (1). The separate Hartree terms are divergent and compensate each other for charge-neutral Coulomb systems.

The thermodynamic equation of state, i.e., the pressure as a function of the temperature T and the particle densities n_c may be derived from Eqs. (1)–(4) excluding the fugacities z_a using $n_a = \beta z_a \frac{\partial p}{\partial z_a}|_{T,z_c \neq z_a}$. The result of such procedure reads up to the order ξ_{ab}^3 (cf. Ref. [8]),

$$\frac{p(\{n_c\}T)}{k_BT} = \sum_a n_a - \frac{\kappa^3}{24\pi} - \sum_{ab} n_a n_b \bigg\{ -\frac{\pi}{3}(\beta e_a e_b)^3 \ln(\kappa\lambda_{ab}) + \frac{\pi}{2}\beta^3 e_a^2 e_b^4$$

$$+ 2\pi\lambda_{ab}^3 \bigg[-\frac{\xi_{ab}^2}{8}\sqrt{\pi} - \frac{\xi_{ab}^3}{6}\left(\frac{C}{2} + \ln 3 - \frac{1}{2} + 1\right) \pm \delta_{ab}\frac{(-1)^{2s_a}}{2s_a+1}\left(\frac{\sqrt{\pi}}{4} + \frac{\xi_{ab}}{2} + \frac{\sqrt{\pi}}{4}\xi_{ab}^2 \ln 2 + \frac{\pi^2}{72}\xi_{ab}^3\right) \bigg] \bigg\}, \tag{5}$$

Here we use $\kappa^2 = \sum_a 4\pi n_a e_a^2/k_BT$. We find that also this version of a second virial coefficient (with respect to the density expansion) does not deliver direct contributions of the order ξ.

Both expressions (1) and (5) may be considered as exact results that are useful to give benchmarks for the low-density limit of the equation of state of neutral Coulomb systems.

III. $\xi/6$ TERM IN THERMODYNAMICS

A. Slater sum scheme

We discuss the question of the existence of $\xi/6$ in connection with papers by Angel Alastuey [15] and Lowell Brown [16]. A more recent statement is given in Ref. [10]. In the three papers just mentioned, the existence of a $\xi/6$ term is assumed.

The classical pair distribution function for a Coulomb system expressed in terms of the Debye function g_{ab} according to Meeron and other researchers [17–19] reads

$$F_{ab} = \exp(-\beta\, V'_{ab} + g_{ab}) \times \left\{ 1 + \sum_c n_c \int \left(\frac{1}{2}g_{ac}g_{bc}^2 + \frac{1}{2}g_{ac}^2 g_{bc}\right) d\mathbf{q}_c + \sum_{cd} n_c n_d \int \frac{1}{2} g_{ac} g_{cd}^2 g_{bd}\, d\mathbf{q}_c d\mathbf{q}_d \right\}. \tag{6}$$

Here

$$g_{ab}(r) = -\beta e_a e_b \frac{1}{r} e^{-\kappa r} \tag{7}$$

is the Debye function. The short-range potential V'_{ab} is now expressed in terms of the two-particle Slater sum $S_{ab}(r)$ for Coulomb systems, and we write according to the idea of Morita [20] and thus getting results quantum statistically correct in the range of low degeneracy (we see later that $V' = V^{\text{Kelbg}} - V^{\text{Coul}}$) [see Eq. (17)],

$$F_{ab} = \exp(g_{ab} + \beta V_{ab}) S_{ab} \times \left\{ 1 + \sum_c n_c \int \left(\frac{1}{2}g_{ac}g_{bc}^2 + \frac{1}{2}g_{ac}^2 g_{bc}\right) d\mathbf{q}_c + \sum_{cd} n_c n_d \int \frac{1}{2} g_{ac} g_{cd}^2 g_{bd}\, d\mathbf{q}_c d\mathbf{q}_d \right\}. \tag{8}$$

The two-particle Slater sum is given using momentum eigenfunctions (see, e.g., Ref. [21]),

$$S_{ab}(\mathbf{r}_1,\mathbf{r}_2) = \int d\mathbf{k}_1 d\mathbf{k}_2 \sum_{\sigma_1\sigma_2} \big\{ \psi^*_{\mathbf{k}_1\mathbf{k}_2 ab}(\mathbf{r}_1\mathbf{r}_2) \exp(-\beta H_{ab}) \times \psi_{\mathbf{k}_1\mathbf{k}_2 ab}(\mathbf{r}_1\mathbf{r}_2) \big\}. \tag{9}$$

The wave functions account for the symmetry

$$\begin{aligned}\psi_{\mathbf{k}_1\mathbf{k}_2ab}(\mathbf{r}_1\mathbf{r}_2) = C\{&\exp(i\mathbf{k}_1\mathbf{r}_1 + i\mathbf{k}_2\mathbf{r}_2)\chi_a(\sigma_1)\chi_b(\sigma_2)\\ &+(-1)^{2s_a}\delta_{ab}\exp(i\mathbf{k}_1\mathbf{r}_2 + i\mathbf{k}_2\mathbf{r}_1)\\ &\times\chi_a(\sigma_2)\chi_b(\sigma_1)\}.\end{aligned} \tag{10}$$

The Hamiltonian has the usual shape with V_{ab} being the Coulomb potential

$$H_{ab} = -\frac{\hbar^2}{2m_a}\Delta_a - \frac{\hbar^2}{2m_b}\Delta_b + V_{ab}\,. \tag{11}$$

We are going to determine the correlation energy via

$$E_{\mathrm{corr}} = \frac{1}{2}\sum_{ab} n_a N_b \int V_{ab}(r)F_{ab}(r)d\mathbf{r}\,. \tag{12}$$

Here, again, $V_{ab}(r)$ is the Coulomb potential and *not* some effective potential and N_b is the particle number. Any influence caused by the existence of other particles influences the binary distribution function F_{ab}; we will apply here Eq. (8), and, therefore, formula (12) accounts for quantum diffraction and exchange effects. The expression (12) is another version of $E_{\mathrm{corr}} = \frac{n^2}{2}\mathrm{Tr}_{12}(V_{12}F_{12})$, and, again, V_{12} is the Coulomb potential (only). The Slater sum has to be determined [9,22,23], and with the first terms of the Born series, we get from Eq. (8)

$$\begin{aligned}F_{ab} = &\left(1+g_{ab}+\beta V_{ab} + \tfrac{1}{2}g_{ab}^2 + g_{ab}\beta V_{ab} + \tfrac{1}{2}\beta^2V_{ab}^2+\cdots\right)\\ &\times\left(1 + S^0_{\mathrm{exch}} + S^1_{\mathrm{dir}} + S^1_{\mathrm{exch}} + \cdots\right).\end{aligned} \tag{13}$$

As we are interested in the lowest-order terms only, we did not have to take into account the integral terms in the curly brackets of (8) (leading to n^2e^6 terms in Eq. (12) as shown in Refs. [22,23]). We will see later that the contribution S^1_{dir} corresponds to the Kelbg potential [5].

In Eq. (12), we need terms from (13) multiplied by the Coulomb potential. We write only the lowest-order terms of the integrand I of (12)

$$\begin{aligned}I = &V_{ab} + V_{ab}S^0_{\mathrm{exch}} + V_{ab}g_{ab}\\ &+\left[V_{ab}S^1_{\mathrm{dir}} + \beta V_{ab}^2\right] + V_{ab}S^1_{\mathrm{exch}} + \cdots,\end{aligned} \tag{14}$$

where the right-hand side terms represent the following: (1) the Hartree contribution, separately diverging, but canceling in a two-component neutral plasma; (2) Fock (exchange) of order n^2e^2; (3) limiting law, order $(ne^2)^{3/2}$; (4) (square brackets) diffraction terms, order n^2e^4; and (5) the exchange term, order n^2e^4.

This finding is in agreement with Refs. [22,23] and with Eq. (5.85) in Ref. [21]. Equation (5.86) of this paper, however, leads to the expansion

$$\begin{aligned}I_1 = &\mathcal{O}((ne^2)^{3/2}) + \left(1 + S^0_{\mathrm{exch}} + S^1_{\mathrm{dir}} + S^1_{\mathrm{exch}} + \cdots\right)\\ &\times\left(1 + g_{ab} + \beta V_{ab} + \tfrac{1}{2}g_{ab}^2 + \tfrac{1}{2}\beta^2V_{ab}^2 + \cdots\right)\\ &-1 - g_{ab} - \tfrac{1}{2}g_{ab}^2.\end{aligned} \tag{15}$$

The essential difference between (15) and (14) is the occurrence of the bare term S^1_{dir} in Eq. (15) leading (in combination with βV_{ab}) to the occurrence of the $\xi/6$ contribution in thermodynamic functions. The origin is due to the fact that, from the beginning, in (5.86) in Ref. [21], the interaction potential was taken to be $V_{ab} + V'_{ab}$ instead of the "bare" Coulomb potential V_{ab}, see Ref. [6]. In Ref. [6], Eqs. (74) and (78) contain the direct contribution of the order ξ; there is, however, an exchange term of the same order. In the electrolyte theory, e.g., the single particles are ions having, as a model, a hard core, and so they do not represent a pure Coulombic system. On the other hand, the potential is assumed to occur in the pair distribution function and prevents two particles from coming close to each other. The short-range potential occurs, in this sense, at two places, see the appendix. The essential integral producing the term linear in ξ reads (constants are omitted)

$$\begin{aligned}&\int_0^\infty dr\int_0^\infty ds\int_0^1 dx\\ &\times\left\{\frac{r}{s}\sin(rs)\{\exp[-As^2(1-x^2)]-1\}\right\} = -\frac{\pi A}{3}.\end{aligned} \tag{16}$$

For the determination of (3), the integral (16) does not occur [9]; the constant A is zero if the linear term in $Q(\xi)$ does not exist. The integral (16) represents the difference between the Coulomb and the Kelbg potentials, i.e., it represents the short-range potential, while the long-range (divergent) contributions are compensated. Up to a constant and the factor $1/s^2$, the curly brackets of (16), $(1/s^2)\{\exp[-As^2]\int_0^1 dx\exp[As^2x^2] - 1\}$, represent the difference between the Fourier transforms of the Kelbg and Coulomb potentials. The Kelbg potential and its Fourier transform are given by the following two formulas in position (r) and momentum (k) spaces, respectively [5]:

$$\begin{aligned}V^{\mathrm{Kelbg}}_{ab}(r) = \frac{e_ae_b}{r}\Bigg[&1 - \exp\left(-\frac{r^2}{\lambda_{ab}^2}\right)\\ &+\sqrt{\pi}\frac{r}{\lambda_{ab}}\left(1-\Phi\left(\frac{r}{\lambda_{ab}}\right)\right)\Bigg],\end{aligned} \tag{17}$$

$$\tilde{V}^{\mathrm{Kelbg}}_{ab}(k) = 4\pi e_ae_b\,\frac{1}{k^2}\,{}_1F_1\left(1,\frac{3}{2};-\frac{\lambda_{ab}^2k^2}{4}\right). \tag{18}$$

B. Starting from grand partition function

In this subsection, we will derive the results of Sec. III A by use of another method.

In Ref. [8], some expressions, e.g., Eq. (6.3), contain the term $\xi/6$, which should not show up, while Eqs. (3.21), (3.25), (3.85), and (5.90) do not have such a contribution. The appearance of the $\xi/6$ term is seen in Ref. [21], in Eqs. (5.86) and (5.94), while there is no such term in Eqs. (5.85) and (6.14).

We repeat some equations from Refs. [8,9,21–24] in order to show that the different approaches described in this and the preceding subsection give identical results, i.e., they especially do *not* give a $\xi/6$ term for charge-neutral H-plasmas. The grand partition function reads

$$Z_g = \mathrm{Tr}[\exp(-\beta(H-\mu N))] \tag{19}$$

with $H = H_{id} + \lambda V$, where λV is the Coulomb potential and λ is a formal coupling parameter, which is finally identified with e^2. The mean value of the potential is then

$$\frac{\partial}{\partial \lambda} \ln Z_g = -\beta \langle V \rangle. \tag{20}$$

The pressure p is then (Ω volume)

$$\beta p \Omega = [\ln Z_g]_{\lambda=1}, \tag{21}$$

or, with the charging procedure,

$$p - p_{\rm id} = -\frac{1}{\Omega} \int_0^1 \frac{d\lambda}{\lambda} \langle \lambda V \rangle_\lambda, \tag{22}$$

where the potential energy may be expressed in terms of Green's functions,

$$\langle \lambda V \rangle = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \lambda V(\mathbf{r}_1 - \mathbf{r}_2) G_2(12, 1^{++}2^{+}, \lambda)_{t_2 = t_1^+}. \tag{23}$$

In the integrand of (23), the two-particle Green's function may be replaced by the single-particle Green's function and the self-energy Σ,

$$\int d\mathbf{r}_2 V(\mathbf{r}_1 - \mathbf{r}_2) G_2(12, 1^{++}2^{+}, \lambda)_{t_2 = t_1^+} = i \int_0^{-i\beta} d\bar{1} \Sigma'(1 - \bar{1}) G_1(\bar{1} - 1^+). \tag{24}$$

The evaluations of (23) and (24) carried out in Refs. [4,8,9,11,22–24] do not find a "direct" contribution of the type $\xi/6$. We remark that the sum over the species vanishes, i.e., $\sum_{ab} \lambda_{ab}^3 \xi_{ab} = -\sum_{ab} \lambda_{ab}^2 e_a e_b/(k_B T) = 0$, i.e., the term in question does not contribute to thermodynamics. This fact could lead to the opinion that in thermodynamics it does not really matter whether such a term linear in ξ exists. However, products with ξ_{ab} prior to summation can lead to $\sum_{ab} e_a^2 e_b^2 \neq 0$. This is the problem occurring in Refs [15,16], leading to questionable results of the order $(ne^2)^{5/2}$.

C. Comparison

In deriving the relations given so far, different approaches have been used. Whereas in the Green-function approach [9] no direct contributions of the order ξ occur at all, the special approach using the mean value of the potential energy [6] introduces a slightly different expression,

$$Q_1(\xi_{ab}) = Q(\xi_{ab}) - \frac{\xi_{ab}}{6}, \tag{25}$$

as shown in Fig. 1. The quasiclassical approach using a cluster expansion and taking into account the quantum effects by an appropriately chosen additional short-range interaction term, that leads to the expression (25), has been introduced in such a manner that it gives the exact second virial coefficient (see Ref. [6]). However, this approach cannot be used to evaluate higher orders in the virial expansion or other thermodynamic properties.

In Ref. [6], the occurrence of a contribution $\xi_{ab}/6$ originates from the fact that the mean value of the potential energy of a plasma is taken using the Coulomb potential plus a short-range one instead of the Coulomb potential only. [Equation (A9)–(A12) below are the relevant integrals for the mean value of Coulomb potential plus short-range correction.] The two functions $Q(\xi_{ab})$ and $Q_1(\xi_{ab})$ give the same results in thermodynamics if one considers approximations up to z^2 only; if one wants to go beyond, then there is a diffence, see below, Sec. IV A.

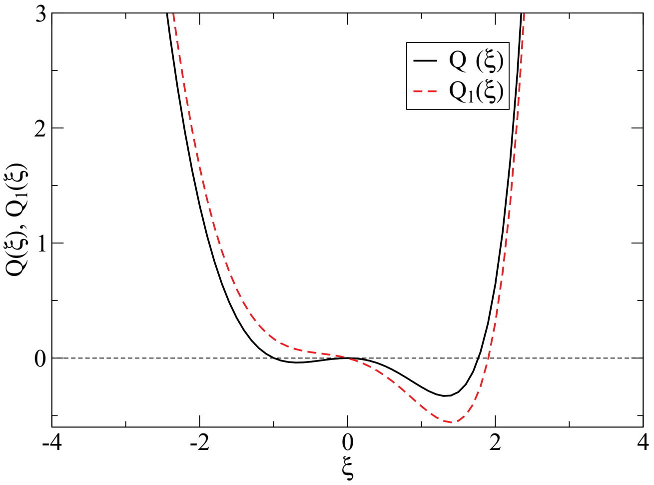

FIG. 1. (Color online) Function $Q(\xi)$ according to Eq. (3) and $Q_1(\xi) = Q(\xi) - \xi/6$.

We remark that the structure of the lower orders of (1) is in agreement with that of Ref. [11], i.e., the occurrence of the direct terms of the orders $(ne^2)^{3/2}$, n^2e^4, $n^2e^6 \ln n$, and n^2e^6 and exchange terms of the orders n^2e^2, n^2e^4, and n^2e^6. The ideal pressure contains quantum effects, too, represented by the contribution $\sqrt{\pi}/4$ of Eq. (4).

IV. SPECIAL FEATURES OF THE EQUATION OF STATE

A. Thermodynamics up to $(ne^2)^{5/2}$

We now stress once more that the proper determination of the mean value of the potential energy is crucial.

The Kelbg potential does not give the proper result for the mean value of the potential energy of Coulomb systems if applied in the following frame:

$$\begin{aligned}\langle V \rangle &= \frac{1}{2} \int d\mathbf{r} V^{\rm Coul}(r) F^{\rm quant}(r) \\ &= 0 + \mathcal{O}((e^2)^{3/2}) + \text{exch.} + \cdots, \\ &\neq \frac{1}{2} \int d\mathbf{r} V^{\rm Kelbg}(r) F^{\rm quant}(r) \\ &= c \times e^2 + \mathcal{O}((e^2)^{3/2}) + \text{exch.} + \cdots\end{aligned}$$

with some finite constant c. In this example, the Coulomb potential is the right choice for Coulomb systems, while the application of $V^{\rm Kelbg}$ leads to the linear term in question.

In papers by Alastuey and Perez [15] and by Brown and Yaffe [16], the contribution linear in e^2 is used leading to contributions of order $\mathcal{O}(ne^2)^{5/2}$ that are not justified (see Ref. [25]).

Thermodynamic functions up to the order $n^{5/2}$, or $z^{5/2}$, respectively, are given by [26–28]

$$\begin{aligned}\beta p &= \sum_a z_a + \frac{\tilde{\kappa}^3}{12\pi} \\ &\quad + \sum_{ab} z_a z_b \lambda_{ab}^3 \left[K_0(\xi_{ab}) - \frac{\xi_{ab}^3}{6} \ln \tilde{\kappa}\lambda_{ab} \right] \\ &\quad + \frac{\tilde{\kappa}^3}{12\pi} \sum_a \left[\frac{1}{8}\tilde{\kappa}_a^2\lambda_{aa}^2 + \frac{3}{2(2s_a+1)} \left(\tilde{\kappa}_a^2\lambda_{aa}^2 - \frac{z_a\Lambda_a^3}{\sqrt{2}} \right) \frac{\tilde{\kappa}_a^2}{\tilde{\kappa}^2} \right].\end{aligned} \tag{26}$$

Here we have, again, $\tilde{\kappa}^2 = \sum_a 4\pi z_a e_a^2/(k_B T)$, but $\tilde{\kappa}_a^2 = 4\pi z_a e_a^2/(k_B T)$. For λ_{ab}, Λ_a see near Eq. (1). However, there is no agreement between [27] on one hand and Alastuey and Perez [15], Brown and Yaffe [16], and Alastuey and Ballenegger [29] on the other; in Refs. [15,16,29], the existence of $\xi/6$ is assumed.

As outlined in Ref. [25], in the latter papers, a function $Q_1(\xi_{ab}) = Q(\xi_{ab}) - \xi_{ab}/6$ is used and multiplied by some expression proportional to $e_a e_b$, leading to $\sum_{ab} e_a e_b \xi_{ab} \neq 0$. In this sense, in Refs. [15,16], contributions to the equation of state of the order $n^{5/2}$ are produced. Such terms cannot be produced this way, since, for the Coulomb system, the contribution in question $\xi/6$ does not arise. Results of the order $n^{5/2}$ are also included in Eq. (6.5) in Ref. [8] and in Eqs. (2.50)– (2.57) in Ref. [21]; the latter have to be considered to be unjustified. For details, see Ref. [27].

B. Kinetic energy at low temperatures

After discussing of the problem of the linear term, we mention still another special feature of Coulomb systems. One may observe an unexpected behavior of the kinetic energy in interacting quantum systems, see Kraeft *et al.* [26] and Militzer and Pollock [30]. By those authors, the *kinetic and correlation energies* and distribution functions of dense plasmas were considered. The internal energy U has to be decomposed as

$$U = \langle K \rangle^{\mathrm{id}} + \langle K \rangle^{\mathrm{corr}} + \langle V \rangle = \langle K \rangle^{\mathrm{id}} + U^{\mathrm{corr}}.$$

The mean value of the potential energy $\langle V \rangle$ differs from the correlation energy U^{corr} due to the fact that, in quantum systems, the mean value of the kinetic energy has a correlation part $\langle K \rangle^{\mathrm{corr}}$. For classical systems the correlation energy is equal to the mean value of the potential energy, i.e., we have $\langle K \rangle^{\mathrm{corr}} = U^{\mathrm{corr}} - \langle V \rangle = 0$. For quantum systems at $T = 0$ and *in most cases* also for $T \neq 0$ we find $\langle K \rangle > \langle K \rangle^{\mathrm{id}}$. However, for quantum systems at $T \neq 0$ we have temperature regions where the mean value of the kinetic energy is smaller than the ideal kinetic energy, $\langle K \rangle < \langle K \rangle^{\mathrm{id}}$; this means $\langle K \rangle^{\mathrm{corr}} < 0$, see Refs. [26,30].

Recent publications on thermodynamic functions of dense plasmas are found, e.g., in Refs. [31,32]. In those papers, special attention is paid to the role of the protons or ions, respectively. For results from numerical work, see, again Ref. [1].

V. CONCLUDING REMARKS

In a short formulation, the direct linear ξ term appears if and only if, in Eq. (19), instead of the bare Coulomb potential, the sum of the Coulomb potential and an additional short-range potential is taken, i.e., $V^{\mathrm{short}} + V^{\mathrm{Coul}}$ instead of V^{Coul}. Most notably, the difference between the Kelbg potential and the Coulomb potential is such a short-range potential leading to the $\xi/6$ term in thermodynamics. *For a pure Coulomb system, such as a charge-neutral hydrogen plasma, no direct linear term occurs in the thermodynamic functions.*

The question of the existence of a direct ξ term is of interest as the proper determination of orders like $n^{5/2}$ is of relevance for applications in helioseismology [33–39]. There exists an exchange term of the order ξ; however, there is no direct term linear in ξ for charge-neutral plasmas, e.g., in Refs. [4,9,11,22–24]. See also Ref. [25].

Up to the linear direct term $\xi/6$, the two ways discussed (mean value of the Coulomb potential and mean value of the Kelbg potential) give *identical results* in the limiting case of very low degeneracy.

The introduction of the linear direct term leads to unjustified results for Coulomb systems, among them our own ones in Ref. [8], Eq. (6.3), and [21], Eqs. (2.52) and (2.53), if it is applied in the derivation of terms higher than n^2 or z^2, respectively. The more general case away from hydrogen leads, again, to the nonexistence of an e^2 term if the potential in question remains of Coulomb type. If the internal structure of the corresponding ion is taken into account, the *effective potential* deviates from the Coulomb one. This question will not be considered here.

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APPENDIX

We discuss the role of an additional short-range potential in deriving the virial expansion, i.e., if, instead of the bare Coulomb potential, the Coulomb potentila *plus* a short-range potential is used. To determine the equation of state, we may start from the free energy, which is then given by

$$F - F_{id} = \frac{1}{2} \sum_{ab} n_a N_b \iint_0^1 \frac{d\lambda}{\lambda} [\lambda U_{ab}(r) F_{ab}(r)] d\mathbf{r}\,. \tag{A1}$$

Here $U_{ab}(r) = V_{ab}(r) + \mathcal{V}_{ab}(r)$, where V_{ab} is the Coulomb potential and $\mathcal{V}_{ab}$ is the short-range potential, which is assumed, for our discussion, to have the same factor λ. The binary distribution function is given by

$$\begin{aligned}F_{ab}(r) &= \exp\left(g_{ab}(r) - \beta V'_{ab}(r)\right)\{1 + \cdots\} \\ &= \exp\left(-\beta V'_{ab}(r)\right)\left\{1 + g_{ab}(r) + \tfrac{1}{2} g_{ab}^2(r) + \cdots\right\}.\end{aligned} \tag{A2}$$

Here we introduced, again, a short-range potential $V'_{ab}(r)$. So far, we have a different notation for the short-range potentials, according to the place in which they occurred in this section. The Debye function reads $g_{ab}(r) = -\frac{e_a e_b}{k_B T r}\exp(-\kappa r)$.

We now give a (new) derivation of the final result including the Slater sum, Eq. (A12).

The free energy is then decomposed as

$$\begin{aligned} F - F_{\rm id} = \frac{1}{2}\sum_{ab} n_a N_b \iint_0^1 \frac{d\lambda}{\lambda}[\lambda V_{ab}(r)(1+g_{ab}(r)) \\ +\lambda V_{ab}(1+g_{ab})(\exp(-\beta V'_{ab})-1) \\ +\lambda V_{ab}[\exp(g_{ab})-1-g_{ab}]\exp(-\beta V'_{ab}) \\ +\lambda \mathcal{V}_{ab}F_{ab}]d\mathbf{r}. \end{aligned} \qquad \text{(A3)}$$

The first line of the right-hand side of Eq. (A3) corresponds to the well-known limiting law. The second line contains orders of $V_{ab}V'_{ab}$ and higher which will not be considered here. The third line is rewritten using the first step of an iteration of the screening equation (see Schmitz [40]) $V_{ab} = -k_B T g_{ab} + \cdots$ and neglecting terms of the order $V'_{ab}g^2_{ab}$. We get for the third line of the right-hand side of Eq. (A3), I_3,

$$I_3 = -\lambda k_B T g_{ab}[F_{ab} - 1 - g_{ab}]. \qquad \text{(A4)}$$

We write the following derivative:

$$H' = -k_B T\frac{\partial}{\partial\lambda}\left\{\exp(g_{ab} - \beta V'_{ab}) - 1 - g_{ab} - \tfrac{1}{2}g^2_{ab}\right\}. \qquad \text{(A5)}$$

The result is

$$H' = -k_B T\left(\frac{\partial g}{\partial\lambda} - \beta\frac{\partial V'}{\partial\lambda}\right)F_{ab} + k_B T\frac{\partial g_{ab}}{\partial\lambda}(1+g_{ab}). \qquad \text{(A6)}$$

We rewrite Eq. (A6) and get

$$H' = -k_B T\frac{\partial g}{\partial\lambda}[F_{ab} - 1 - g_{ab}] + \frac{\partial V'}{\partial\lambda}F_{ab}. \qquad \text{(A7)}$$

If one wants to perform a simple integration from Eq. (A5) inserted in Eq. (A1), one has to identify the corresponding outcome of Eq. (A2) with Eq. (A7), i.e., one has to make the following identification:

$$\mathcal{V}_{ab}(r) = V'_{ab}(r). \qquad \text{(A8)}$$

Only under this assumption can one make the final statement for the free energy [6],

$$\begin{aligned} F - F_{\rm id} = -\frac{k_B T V}{12\pi}\kappa^3 - \frac{k_B T V}{2}\sum_{ab} n_a n_b \int d\mathbf{r} \\ \times\left\{\exp[g_{ab}(r) - \beta V^{\rm short}_{ab}(r)] - 1 - g_{ab} - \frac{1}{2}g^2_{ab}\right\}. \end{aligned} \qquad \text{(A9)}$$

The short-range potential is now indicated by $V^{\rm short}_{ab}$, as its origin is somehow between $V'_{ab}(r)$ and $\mathcal{V}_{ab}(r)$. Equation (A9) originates from the mean value of the Kelbg potential instead of the mean value of the Coulomb one and is in agreement with Eqs. (16) and (17) of [6] where, in Eq. (17) of Ref. [6], the Slater sum according to Eq. (8) of this paper was introduced to replace the short-range potential, i.e., by $V^{\rm Kelbg} - V^{\rm Coul}$. If, in Eq. (A9), the short-range potential $V^{\rm short}_{ab}$ is substituted in the manner outlined above, the final result for the thermodynamic functions contains the contribution in question $\xi/6$. This term does *not* show up, however, if and only if $\mathcal{V}_{ab} = 0$. The conclusion is that one cannot use expression (A9) if, as for Coulomb systems, $\mathcal{V}_{ab}$ has to be taken to be zero in Eq. (A1).

We give the shape of three formulas. We write the integral occurring in Eq. (16) of Ref. [19], which was already given above [see Eq. (A9)],

$$\int d\mathbf{r}\left[\exp(-\beta V'_{ab} + g_{ab}) - 1 - g_{ab} - \frac{1}{2}g^2_{ab}\right], \qquad \text{(A10)}$$

while the integral of Eq. (17.14) of Ref. [7] reads

$$\begin{aligned} 4\pi\left[\int_{a_{ij}}^{\infty}\left[\exp g_{ij} - 1 - g_{ij} - \frac{1}{2}g^2_{ij}\right]r^2 dr \right. \\ \left. -\int_0^{a_{ij}}\left(1 + g_{ij} + \frac{1}{2}g^2_{ij}\right)r^2 dr\right]. \end{aligned} \qquad \text{(A11)}$$

This expression was derived for particles interacting via the Coulomb potential *plus* a short-range potential. In the special shape of Eq. (A11), hard spheres with the parameter a_{ij} were assumed to produce the potential V'_{ab} occurring in (A10), i.e., $V'_{ij}(r) = \infty, r < a_{ij};\ = 0, r > a_{ij}$. One more expression of the identical contents is given in Eq. (5.87) of Ref. [21], and looks like Eq. (A10), if V'_{ab} is expressed in terms of the Slater sum $S_{ab}(r)$, namely

$$\int d\mathbf{r}\left[S_{ab}(r)\exp(g_{ab} + \beta V_{ab}) - 1 - g_{ab} - \frac{1}{2}g^2_{ab}\right]. \qquad \text{(A12)}$$

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