

Statistical Thermodynamics of Nonideal Plasma

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Abstract

Based on the Debye model, the free energy of a nonideal electron-ion plasma is calculated for interaction parameters $0 < \gamma < \gamma_c$ below the critical solid state value γ_c ($\gamma = Ze^2n^{1/3}/KT$ is the ratio of mean Coulomb interaction energy to thermal energy), which takes into account the energy eigenvalues of (i) the thermal translational particle motions, (ii) the random collective electron and ion motions, and (iii) the static Coulomb interaction energy of the electrons and ions in their oscillatory equilibrium positions. From this physical model, the interaction part of the free energy is derived, which consists of a quasi-lattice energy, depending on the interaction parameter γ , and the free energies of the quantized electron and ion oscillations (long-range interactions). Depending on the degree of ordering, the Madelung 'constant' of the plasma is $\alpha(\gamma) = \bar{\alpha}$ for $\gamma \gg 1$, $\alpha(\gamma) \approx \bar{\alpha}$ for $\gamma > 1$ and $\alpha(\gamma) \propto \gamma^{1/2}$ for $\gamma \ll 1$, where $\bar{\alpha} \sim 1$ is a constant. The free energy of the high frequency plasmons (electron oscillations) is shown to be very small for $\gamma > 1$, whereas the free energy of the low frequency plasmons (ion oscillations) is shown to be significant for $\gamma > 1$, i.e. for proper nonideal conditions. From the general formula for the free interaction energy ΔF of the plasma for $0 < \gamma < \gamma_c$, simple analytical expressions are derived for ΔF in the limiting cases $\gamma \gg 1$, $\gamma \gtrsim 1$ and $\gamma \ll 1$.

1. Introduction

In the classical work of Debye and Hueckel (1923) on electrolytes, the total Coulomb interaction energy was calculated from the continuum theoretical picture of every ion interacting with its surrounding space charge cloud. With more sophisticated methods, similar results were obtained for weakly nonideal plasmas ($\gamma \ll 1$) by Mayer (1950, cluster expansion), Ichikawa (1958, collective variable approach), Vedenov and Larkin (1959, graphical density expansion) and Jackson and Klein (1964, hydrodynamic continuum interaction model). Based on different methods, further significant investigations of moderately ($\gamma \gtrsim 1$) and strongly ($\gamma \gg 1$) nonideal plasmas were given by Berlin and Montroll (1952), Theimer and Gentry (1962), Ecker and Kroell (1963), Ebeling *et al.* (1967), Vorobev *et al.* (1970) and Deutsch *et al.* (1981).

In spite of differences in the theoretical approaches, the leading terms of the analytical results for proper nonideal plasmas ($\gamma > 1$) give essentially the same formula for the free plasma energy, $\Delta F/NKT = -a\gamma + b \ln \gamma + c$, due to Coulomb interaction, where $\gamma = Ze^2n^{1/3}/KT$ is the ratio of the electron-ion interaction energy to the thermal energy and a, b, c are constants depending on the respective approximations and assumptions. The thermodynamic functions of strongly nonideal plasmas ($\gamma \gg 1$) were also determined with the help of Monte Carlo and computer methods by Brush *et al.* (1966), Hansen (1973), Vorobev *et al.* (1969) and Theimer and Theimer (1978).

For a more comprehensive review of the subject, the reader is referred to Norman and Starostin (1970), and the more recent, detailed treatise on strongly coupled plasmas by Deutsch *et al.* (1981).

At sufficiently high electron densities, for which $\gamma > 1$, classical statistical theories fail because of thermodynamic instabilities (Deutsch *et al.* 1981), which are inhibited by quantum mechanics. The classical plasma (pressure) would collapse for $\gamma > 1$ due to the negative electron-ion interaction energy, whereas in reality the pressure remains positive in a plasma due to the Fermi pressure (exclusion principle) of the electrons. For these reasons, we present here a quantum-statistical theory for non-ideal plasmas based on concepts similar to those used by Debye (1912) for solids.

The application of the Debye model to proper nonideal plasmas ($\gamma > 10^{-1}$) is justified since a plasma exhibits a quasi-crystalline structure for $\gamma \gtrsim 10^{-1}$ before it undergoes a diffuse transition into a solid metallic state at a critical value γ_c . The role of the longitudinal phonons of the Debye theory is played here by the quanta of the plasma oscillations (plasmons). The theory takes into consideration (i) the energy eigenvalues of the random collective electron and ion oscillations, and (ii) the static Coulomb interaction energy (quasi-lattice energy) of the electrons and ions. The results are applicable to nonideal plasmas, with interaction parameters $\gamma < \gamma_c$, in an approximation corresponding to the Debye theory.

In analogy to the Debye theory, the following idealizations are made. The dispersion equations $\omega_{e,i} = \omega_{e,i}(k)$ for the electron and ion sound waves are (a) extended to nonideal plasmas by redefining the specific heat ratios $\kappa_{e,i}$, and (b) extrapolated to large wave numbers $k \sim n_{e,i}^{1/3}$. In thermal equilibrium, the entire wave spectrum $0 < k \lesssim n_{e,i}^{1/3}$ exists as a result of microscopic excitation and deexcitation mechanisms (detailed balance). A more rigorous approach must be postponed until the theory of longitudinal waves in nonideal plasmas is developed.

The importance of non-ideal plasma phenomena has been recognized in astrophysics for a long time. As has been shown recently, the physics of nonideal plasmas is also very important in fusion and weapons research. Even electric ball lightning appears to be explainable as a low temperature ($T \approx 300$ K) multiply ionized ($n \approx 10^{19}$ cm⁻³) air plasma. Here the negative Coulomb interaction energy is larger than the thermal energy so that the plasma ball behaves like a Coulomb liquid, one which has a relatively long lifetime (Wilhelm 1980) since the nonideal state is energetically more favourable than the recombined gas phase.

In stellar atmospheres and in particular in dense stellar interiors, nonideal plasma phenomena due to Coulomb interactions occur which are of quantitative significance. The pressure in such systems deviates considerably from the ideal (classical or quantum-statistical) equation of state due to Coulomb interactions, where $\Delta p = -\partial \Delta F / \partial V$ and ΔF is the free energy contribution from the Coulomb interactions. The nonideal equation of state has been calculated for specific stellar models, for example by Salpeter (1961) for white dwarfs assuming a completely degenerate zero-temperature plasma state. In cooling stars, the Coulomb interactions become increasingly important, until the thermal motions are insufficient to prevent the ions from localizing in a lattice structure. As a result, the star freezes from the centre into a crystalline solid (van Horn 1968).

For the diagnostics of astrophysical plasmas, spectroscopic methods are frequently used. The Coulomb interactions change not only the width of the spectral lines (Stark broadening) but also their intensity, which depends on the ionization and com-

position of the plasma. As a time-average effect, the binary and many-body Coulomb interactions annihilate the higher excited states of atoms and ions, and thus bring about an effective lowering $\Delta\varepsilon$ of the ionization energy, given by $\Delta\varepsilon = -\sum_s \nu_s \partial\Delta F/\partial N_s$, where N_s is the number and ν_s the stoichiometric coefficient of particles of type s . A comprehensive theory of preionization has been given by Stewart and Pyatt (1966) for plasmas with nondegenerate free electrons using a finite temperature Thomas-Fermi model, which gives the Debye-Hueckel and ion sphere limits of $\Delta\varepsilon$ as special cases.

At sufficiently high electron densities in stars, the electric field of the (negative) electrons effectively reduces the Coulomb field of the (positive) nuclei so that their Coulomb barrier is lowered and their thermonuclear reaction rates are increased (Salpeter 1954). The screening energy E_s of the electrons need not be large compared with the thermal energy KT in order to produce a significant effect, since E_s/KT enters exponentially into the reaction rates in which mainly nuclei from the tail of the Maxwell distribution are involved. The transport of current and heat in astrophysical plasmas (Hubbard 1966) is changed by nonideal effects which modify the (Maxwell or Fermi) distributions of the electrons.

2. Physical Foundations

The object of our theoretical considerations is a quasi-homogeneous high pressure plasma consisting of electrons of charge $-e$ and density $n = N/V$ and ions of charge $+Ze$ and density $n/Z = N/ZV$, with typical densities in the range $10^{20} \lesssim n \lesssim 10^{24} \text{ cm}^{-3}$ and temperatures of the order $T \sim 10^4 \text{ K}$. For these conditions, the Debye radius $D = \{4\pi n e^2(1+Z)/KT\}^{-\frac{1}{2}}$ is $6 \cdot 901 \{T/n(1+Z)\}^{\frac{1}{2}} \lesssim 10^{-8} \text{ cm}$, i.e. D is smaller than atomic dimensions and the number of particles in the Debye sphere would be $N_D = \frac{4}{3}\pi n D^3 \lesssim 1$ for $D < 10^{-8} \text{ cm}$ and this range of n . It is seen that the concept of Debye shielding completely breaks down, and statistical theories containing the Debye length as a characteristic parameter would be physically meaningless for high density plasmas.

The nonideal behaviour of plasmas is determined by the interaction parameter γ (see the Introduction), where

$$\gamma = Ze^2 n^{\frac{1}{3}}/KT = 1 \cdot 671 \times 10^{-3} Zn^{\frac{1}{3}}/T. \quad (1)$$

It follows that $0 \cdot 5Z \lesssim \gamma \lesssim 15Z$ for $10^{20} \lesssim n \lesssim 10^{24} \text{ cm}^{-3}$ and $T \sim 10^4 \text{ K}$. For $\gamma \approx 1$, the nature of the plasma changes from a 'thermally expanding' ($\gamma < 1$) to an 'electrostatically contracting' ($\gamma > 1$) plasma. For $\gamma > 1$, the collapse of the plasma due to Coulomb attraction between electrons and ions is inhibited by the Fermi pressure of the electrons, i.e. by the quantum mechanical exclusion principle. Thus, in the region $0 < \gamma < \gamma_c$ the plasma undergoes a diffuse transition from a nonideal classical plasma ($\gamma < 1$) to a quasi-crystalline plasma ($1 \lesssim \gamma < \gamma_c$), with an incomplete ordering comparable with that of a liquid.

An understanding of strongly nonideal plasmas has been attempted via the model of discrete interacting particles in a dense gas (Deutsch *et al.* 1981). For the above reasons, however, it appears to be more adequate to calculate the thermodynamic functions of proper nonideal plasmas from the picture of collective electron and ion oscillations. In this approach, the free interaction energy is due to the static Coulomb interaction of the electrons and ions in their 'equilibrium positions' (Madelung energy) and their oscillation energies about average equilibrium positions (plasmon energies).

Since the plasma volume V contains N electrons and N/Z ions, there exist N (high frequency branch) and N/Z (low frequency branch) characteristic frequencies ω_i of longitudinal oscillation. Each plasma oscillator of frequency ω_i can have the energies $E_n^i = (n + \frac{1}{2})\hbar\omega_i$, $n = 0, 1, 2, \dots$, so that the energy of a plasma state with $n = 1, 2, 3, \dots$ plasmons of frequency ω_i is

$$E\{i\} = \sum_n n\hbar\omega_i, \quad (2)$$

where $\{i\}$ refers to the entire set of given eigenfrequencies ω_i . Accordingly, the partition function Q of the longitudinal plasma oscillations is

$$Q = \prod_i \sum_n \exp(-n\hbar\omega_i/KT) = \prod_i \{1 - \exp(-\hbar\omega_i/KT)\}^{-1}. \quad (3)$$

From Q , the thermodynamic functions such as pressure, internal energy, entropy, etc. are derived in the usual way; for example, the free energy of the plasmons is

$$\tilde{F} = -KT \ln Q = KT \sum_i \ln\{1 - \exp(-\hbar\omega_i/KT)\}. \quad (4)$$

In the limit $V \rightarrow \infty$, the discrete eigenfrequencies ω_i are replaced by continuous ones, $\omega = \omega(k)$, in accordance with the dispersion law for space charge waves of wavelength $\lambda = 2\pi/k$, with $0 \leq k \leq \hat{k}$.

Electron Oscillations

The high frequency branch of the space charge waves is due to longitudinal electron oscillations. Their frequency ω for classical ($n \ll \tilde{n}$) and completely degenerate ($n \gg \tilde{n}$) electrons is given by (Sitenko 1967)

$$\omega^2 = \omega_p^2 \{1 + (\kappa_e/4\pi)Z\gamma^{-1}(k\bar{r}_e)^2\}, \quad n \ll \tilde{n} \quad (5)$$

$$= \omega_p^2 \{1 + \pi^{-1} \frac{9}{20} (\frac{1}{6}\pi)^{\frac{1}{2}} (n/\tilde{n})^{\frac{3}{2}} (Z/\gamma)(k\bar{r}_e)^2\}, \quad n \gg \tilde{n}, \quad (6)$$

where

$$\tilde{n} = 2(2\pi mKT/h^2)^{3/2}, \quad (7)$$

$$\omega_p = (4\pi ne^2/m)^{\frac{1}{2}}, \quad (8)$$

$$\bar{r}_e = n^{-\frac{1}{3}}, \quad (9)$$

are the critical electron density, the plasma frequency and the mean electron distance ($\kappa_e = (C_p/C_v)_e$ of the nonideal gas of electrons of mass m). Since $k_{\max} \sim 2\pi/\bar{r}_e$ (oscillations with $\lambda < \bar{r}_e$ are physically impossible), the electron oscillations propagate with $\omega = \omega(k) > \omega_p$ in nonideal plasmas.

Ion Oscillations

The low frequency branch of the space charge waves is essentially due to ion sound waves. Since the ions are presumed to be nondegenerate, the frequency of the ion oscillations is given by (Sitenko 1967)

$$\omega = \delta(k)(\kappa_i KT/M)^{\frac{1}{2}} k, \quad (10)$$

where

$$\delta(k) \approx \left(1 + \frac{Z\kappa_e/\kappa_i}{1 + (\kappa_e/4\pi)Z\gamma^{-1}(k\bar{r}_e)^2}\right)^{\frac{1}{2}}, \quad n \ll \tilde{n} \quad (11)$$

$$\approx 1, \quad n \gg \tilde{n} \quad (12)$$

is a correction factor of order 1, which shows the influence of the electrons on the ion oscillations ($\kappa_i = (C_p/C_v)_i$ of the nonideal gas of ions of mass M).

In weakly nonideal plasmas ($\gamma \ll 1$) the electron sound waves are strongly damped for wavelengths $\lambda < D$ due to trapping of the resonance electrons with thermal speeds comparable with the wave speed. For proper nonideal plasmas ($\gamma \gtrsim 1$) the number of particles in the Debye sphere $\frac{4}{3}\pi D^3$ is no longer large compared with one and $D < 10^{-8}$ cm is smaller than atomic sizes, so that ordinary Landau damping is no longer possible.

The ions are nondegenerate since $n_i \ll g_i(2\pi MKT/h^2)^{3/2}$ for the n - T region under consideration. The electrons are considerably degenerate for $n > \tilde{n}$ by equation (7), i.e. their kinetic energy is essentially given by the Fermi energy $E_F = \hbar^2(3\pi^2 n)^{2/3}/2m$ for $n > \tilde{n}$. For this reason, the nonideal behaviour of the electrons increases with increasing n as long as $n < \tilde{n}$, but then decreases with increasing n as soon as $n \gtrsim \tilde{n}$. From the condition $Ze^2 n^{2/3} = E_F$ it follows that the electrons again form an ideal gas for $n \gg 10^{23} Z^3$. This anomalous behaviour is explained by the stronger increase of $E_F \propto n^{2/3}$ with n , compared with the increase of Coulomb energy $E_C \propto n^{1/3}$.

It is recognized that the effects of degeneracy and nonideal behaviour on the dispersion of the ion sound waves (equation 10) are small. Similarly, the effect of nonideal behaviour on the dispersion of the sound waves of the degenerate electrons (equation 6) is negligible. But in the dispersion equation for classical electrons (equation 5), κ_e has to be interpreted as a polytropic coefficient, where to order of magnitude $\kappa_e(\gamma) \sim \kappa_e(0)$.

3. Statistical Thermodynamics

In the plasma under consideration, the electrons and ions interact through their longitudinal Coulomb fields (transverse electromagnetic interactions are negligible for $KT \ll mc^2$). The electrons ($s = e$) and ions ($s = i$) have thermal velocities \mathbf{c}_s and random collective mean mass velocities $\tilde{\mathbf{v}}_s$ due to their oscillatory wave motions about the equilibrium positions, so that their local velocity is $\mathbf{v}_s = \tilde{\mathbf{v}}_s + \mathbf{c}_s$, with $\langle \mathbf{c}_s \rangle = \mathbf{0}$ and $\langle \mathbf{v}_s \rangle = \tilde{\mathbf{v}}_s$, where we define $\langle \mathbf{u}_s \rangle = \int \mathbf{u}_s f_s d\mathbf{v}_s$ as the average of \mathbf{u}_s with respect to the normalized velocity distribution f_s of the species s . The resulting Hamilton function with Coulomb interaction gives for the free energy of the plasma the ideal (F_0) and nonideal (ΔF) contributions:

$$F_0 = \sum_{s=e,i} F_s^{(0)}, \quad \Delta F = \sum_{s=e,i} \tilde{F}_s + E_M. \quad (13a, b)$$

Here $F_s^{(0)}$ is the ideal free energy of the noninteracting plasma components s , E_M is the Coulomb interaction energy of the electrons and ions in their equilibrium positions, and $\tilde{F}_{e,i}$ is the free energy of the electron and ion oscillations, i.e. of the high and low frequency plasmons (equation 4).

It should be noted that equations (13) take into consideration the most significant short- and long-range Coulomb interactions by means of the Madelung energy E_M

and the plasmon energies \tilde{F}_s . As is evident from the derivation of equations (5), (6) and (10), in which terms of order m/M are neglected, equations (13) contain the e-e, e-i and i-i Coulomb interactions at distances $\lambda \gtrsim n^{-1/3}$.

Free Energy $F_s^{(0)}$

In high pressure plasmas, the electrons are partially degenerate for densities $n > \tilde{n}$, with $\tilde{n} = 4.828 \times 10^{15} T^{3/2} \text{ cm}^{-3}$, whereas the ions behave in general classically. Fermi statistics give for the free energy of the ideal electron gas (Tolman 1938)

$$F_e^{(0)} = -NKT U_{3/2}(\mu/KT)/U_{3/2}(\mu/kT), \quad (14)$$

where

$$U_\rho(\mu/KT) = \frac{1}{\Gamma(\rho+1)} \int_0^\infty \frac{x^\rho dx}{\exp(x - \mu/KT) + 1}, \quad \rho = \frac{1}{2}, \frac{3}{2}, \quad (15)$$

$$n = 2(2\pi mKT/h^2)^{3/2} U_{3/2}(\mu/KT), \quad (16)$$

define the Sommerfeld (1928) integrals and determine the chemical potential $\mu = \mu(n, T)$ of the electrons respectively. The free energy of the translational degrees of freedom of the classical ideal ion gas is (Tolman 1938)

$$F_i^{(0)} = -(N/Z)KT \ln\{(2\pi MKT/h^2)^{3/2} Z/n\}. \quad (17)$$

Quasi-lattice Energy E_M

The equilibrium positions of the electrons and ions, about which the electrostatic oscillations occur, form an electron 'lattice' and an ion 'lattice', with an incomplete ordering. In the Wigner-Seitz approximation, the Coulomb interaction energy of the electron-ion lattice is, independent of the lattice type,

$$E_M = -\alpha\gamma NKT; \quad \alpha \approx \bar{\alpha} = \frac{9}{10}(4\pi/3Z)^\dagger, \quad \gamma > 1. \quad (18)$$

As the ordering of the plasma increases with γ , $\alpha(\gamma)$ is a weak function of γ such that asymptotically $\alpha = \bar{\alpha}$ for $\gamma \gg 1$. Equation (18) indicates that $-E_M/N \sim Ze^2/\bar{r}_i$ is of the order of the average e-i interaction energy. For weak ordering ($\gamma \ll 1$) it will be shown that $\alpha \propto \gamma^{1/2}$.

High Frequency Contribution \tilde{F}_e

Since the number of longitudinal modes with wave numbers between k and $k+dk$ in volume V is $V4\pi k^2 dk/(2\pi)^3$, equation (4) gives for the free energy \tilde{F}_e of the high frequency electron oscillations of energy $\hbar\omega(k)$

$$\tilde{F}_e/KT(V/2\pi^2) = \int_0^{\tilde{k}_e} \ln[1 - \exp\{-\hbar\omega(k)/KT\}]k^2 dk, \quad (19)$$

where

$$\omega(k) = \omega_p(1 + a^2k^2)^\dagger, \quad (20)$$

$$a^2 \equiv c_m^2/\omega_p^2 = (\kappa_e/4\pi)(Z/\gamma)\bar{r}_e^2, \quad n \ll \tilde{n} \quad (21)$$

$$\equiv \frac{3}{5}v_F^2/\omega_p^2 = \frac{9}{20}\pi^{-1}(\frac{1}{6}\pi)^\dagger(n/\tilde{n})^\dagger(Z/\gamma)\bar{r}_e^2, \quad n \gg \tilde{n} \quad (22)$$

by equations (5) and (6). The speed of sound c_m and the Fermi speed v_F of the electrons are

$$c_m = (\kappa_e KT/m)^{\frac{1}{2}}, \quad v_F = \hbar(3\pi^2 n)^{\frac{1}{3}}/m. \quad (23a, b)$$

The number of modes in $(0, \hat{k}_e)$ and V equals the number N of longitudinal degrees of freedom of the electron gas, i.e.

$$(2\pi)^{-3} V \int_0^{\hat{k}_e} 4\pi k^2 dk = N; \quad \hat{k}_e = (6\pi^2 n)^{\frac{1}{3}}. \quad (24)$$

Integration of equation (19) by parts, under consideration of the equation $\hat{k}_e^3 KTV/6\pi^2 = NKT$, yields for the free energy of the high frequency plasmons

$$\tilde{F}_e = NKT \left[\ln \left\{ 1 - \exp \left(-\frac{\hbar\omega_p}{KT} (1 + a^2 \hat{k}_e^2)^{\frac{1}{2}} \right) \right\} - \mathcal{F} \left(\frac{\hbar\omega_p}{KT}, a\hat{k}_e \right) \right], \quad (25)$$

where

$$\mathcal{F} \left(\frac{\hbar\omega_p}{KT}, a\hat{k}_e \right) = \frac{\hbar\omega_p}{KT} (a\hat{k}_e)^{-3} \int_0^{a\hat{k}_e} \frac{x^4 (1+x^2)^{-\frac{1}{2}} dx}{\exp\{(\hbar\omega_p/KT)(1+x^2)^{\frac{1}{2}}\} - 1}, \quad (26)$$

$$\hbar\omega_p/KT = (4\pi)^{\frac{1}{2}} (\lambda_e/\bar{r}_e)(\gamma/Z)^{\frac{1}{2}}; \quad \lambda_e = \hbar/(mKT)^{\frac{1}{2}}, \quad (27)$$

$$a\hat{k}_e = \kappa_e^{\frac{1}{2}} (\frac{3}{4}\pi^{\frac{1}{2}})^{\frac{1}{2}} (Z/\gamma)^{\frac{1}{2}}, \quad n \ll \tilde{n} \quad (28)$$

$$= 6^{1/6} \pi^{\frac{1}{2}} \frac{3}{2} 5^{-\frac{1}{2}} (n/\tilde{n})^{\frac{1}{2}} (Z/\gamma)^{\frac{1}{2}}, \quad n \gg \tilde{n}. \quad (29)$$

By means of the successive substitutions (i) $x = \sinh \xi$, $dx = \cosh \xi d\xi$ and (ii) $\varepsilon = (\hbar\omega_p/KT) \cosh \xi$, $d\varepsilon = (\hbar\omega_p/KT) \sinh \xi d\xi$, the integral (26) is transformed to

$$\mathcal{F}(\varepsilon_p, a\hat{k}_e) = (a\hat{k}_e \varepsilon_p)^{-3} \int_{\varepsilon_p}^{\hat{\varepsilon}_e} (\varepsilon^2 - \varepsilon_p^2)^{3/2} (\varepsilon^e - 1)^{-1} d\varepsilon, \quad (30)$$

where

$$\varepsilon_p = \hbar\omega_p/KT, \quad \hat{\varepsilon}_e = \varepsilon_p \{1 + (a\hat{k}_e)^2\}^{\frac{1}{2}}. \quad (31a, b)$$

Since the leading expression in equation (25) is the logarithmic term, it is sufficient to give for $\mathcal{F}(\varepsilon_p, a\hat{k}_e)$ the series approximation (see the Appendix)

$$\begin{aligned} \mathcal{F}(\varepsilon_p, a\hat{k}_e)/2^{3/2} (a\hat{k}_e)^3 \varepsilon_p^{-3/2} = \\ \sum_{m=1}^{\infty} \exp(-m\varepsilon_p) \sum_{n=0}^{\infty} \left(\frac{3}{2}\right) (2\varepsilon_p)^{-n} m^{-(5/2+n)} \gamma\left(\frac{5}{2} + n, (\hat{\varepsilon}_e - \varepsilon_p)m\right); \quad \hat{\varepsilon}_e < 3\varepsilon_p, \end{aligned} \quad (32)$$

where

$$\gamma\left(\frac{5}{2} + n, (\hat{\varepsilon}_e - \varepsilon_p)m\right) = m^{5/2+n} \int_0^{\hat{\varepsilon}_e - \varepsilon_p} u^{3/2+n} \exp(-mu) du \quad (33)$$

is the incomplete gamma function (Abramowitz and Stegun 1965). Since $\gamma/Z \leq 1$ for $\varepsilon_p < \hat{\varepsilon}_e < 3\varepsilon_p$, the expansion (32) is useful where simple approximate relations do not exist.

Low Frequency Contribution \bar{F}_i

With the number of modes in the interval dk at k and volume V given by $V4\pi k^2 dk/(2\pi)^3$, equation (4) yields for the free energy \bar{F}_i of the low frequency ion oscillations of energy $\hbar\omega(k)$

$$\bar{F}_i/KT(V/2\pi^2) = \int_0^{\hat{k}_i} \ln[1 - \exp\{-\hbar\omega(k)/KT\}]k^2 dk, \tag{34}$$

where

$$\omega(k) = \delta(k)c_M k, \tag{35}$$

$$c_M = (\kappa_i KT/M)^{\frac{1}{2}} \tag{36}$$

by equations (10) and (12). The number of modes in $(0, \hat{k}_i)$ and V equals the number N/Z of longitudinal degrees of freedom of the ion gas, i.e.

$$(2\pi)^{-3}V \int_0^{\hat{k}_i} 4\pi k^2 dk = N/Z, \quad \hat{k}_i = (6\pi^2 n/Z)^{\frac{1}{3}}. \tag{37}$$

Partial integration of equation (34), under consideration of the equation $\hat{k}_i^3 KTV/6\pi^2 = (N/Z)KT$, gives for the free energy of the low frequency plasmons

$$\bar{F}_i = (N/Z)KT (\ln[1 - \exp\{-(\hbar c_M/KT)\delta(\hat{k}_i)\hat{k}_i\}] - \mathcal{G}(\hat{k}_i)), \tag{38}$$

where

$$\mathcal{G}(\hat{k}_i) = \frac{\hbar c_M}{KT} \hat{k}_i^{-3} \int_0^{\hat{k}_i} \frac{\{\delta(k) + k\delta'(k)\}k^3 dk}{\exp\{(\hbar c_M/KT)\delta(k)k\} - 1}. \tag{39}$$

Since the dispersion factor $\delta(k)$ is a bounded function varying very little with k , such that $1 \leq \delta(k) \lesssim (1+Z)^{\frac{1}{2}}$ for $k \in (0, \hat{k}_i)$, it can be approximated by an average value:

$$\delta(k) = \bar{\delta} \sim 1, \quad n \lesssim \bar{n}. \tag{40}$$

Since in addition the logarithmic expression is the dominant term in (38), the integral (39) can be approximated by

$$\mathcal{G}(\hat{\varepsilon}_i) \approx \hat{\varepsilon}_i^{-3} \int_0^{\hat{\varepsilon}_i} \varepsilon^3 (e^\varepsilon - 1)^{-1} d\varepsilon, \tag{41}$$

where

$$\varepsilon = \hbar c_M \bar{\delta} k/KT, \quad \hat{\varepsilon}_i = \hbar c_M \bar{\delta} \hat{k}_i/KT. \tag{42a, b}$$

Here $\mathcal{G}(\hat{\varepsilon}_i)$ has the semi-convergent series expansions (Abramowitz and Stegun 1965)

$$\mathcal{G}(\hat{\varepsilon}_i) = \frac{1}{3}(1 - \frac{3}{8}\hat{\varepsilon}_i + \frac{1}{20}\hat{\varepsilon}_i^2 + \dots), \quad \hat{\varepsilon}_i \ll 1 \tag{43}$$

$$= \frac{1}{15}\pi^4 \hat{\varepsilon}_i^{-3} + O\{\exp(-\hat{\varepsilon}_i)\}, \quad \hat{\varepsilon}_i \gg 1. \tag{44}$$

This completes the formal mathematical aspects of the theory, the physical implications of which require further discussion.

4. Applications

For applications of the theory to strongly, intermediate and weakly nonideal plasmas, it should be noted that the dimensionless parameters γ/Z , $\hbar\omega_p/KT$, $a\hat{k}_e$ and n/\bar{n} occurring in equation (25) for the free energy \bar{F}_e of the high frequency plas-

mons cannot be varied independently. Since both γ/Z and λ_e/\bar{r}_e increase with increasing n and decreasing T , $\hbar\omega_p/KT \sim (\lambda_e/\bar{r}_e)(\gamma/Z)^{\frac{1}{2}}$ varies over a large n - T region similar to $(\gamma/Z)^{\frac{1}{2}}$ (see equation 7).

Numerically, we have

$$\gamma/Z = 1.670 \times 10^{-3} n^{\frac{1}{2}}/T, \quad \hbar\omega_p/KT = 4.328 \times 10^{-7} n^{\frac{1}{2}}/T, \quad (45a, b)$$

$$n/\tilde{n} = 2.071 \times 10^{-16} nT^{-3/2}, \quad (45c)$$

$$a\hat{k}_e = 1.100 \kappa_e^{\frac{1}{2}}(\gamma/Z)^{-\frac{1}{2}}, \quad n \ll \tilde{n} \quad (46a)$$

$$= 2.294(n/\tilde{n})^{\frac{1}{2}}(\gamma/Z)^{-\frac{1}{2}}, \quad n \gg \tilde{n}. \quad (46b)$$

For example, for $T = 10^4$ K, $\gamma/Z \geq 1$ if $n \geq 10^{21}$ cm⁻³ and $\hbar\omega_p/KT \geq 1$ if $n \geq 5 \times 10^{20}$ cm⁻³, as to order of magnitude. Thus, for typical conditions of nonideal plasmas, γ/Z and $\hbar\omega_p/KT$ are of the same order of magnitude. It is also recognized that in general $n/\tilde{n} \gg 1$ if $\gamma/Z \gg 1$, and $n/\tilde{n} \ll 1$ if $\gamma/Z \ll 1$.

In equation (38) for the free energy \tilde{F}_i of the low frequency plasmons, only one characteristic parameter $\hat{\epsilon}_i$ occurs since $\delta(k) \sim \delta \sim 1$. By equation (42b), this parameter is

$$\begin{aligned} \hat{\epsilon}_i &= \hbar c_M \delta \hat{k}_i / KT = (6\pi^2)^{\frac{1}{2}} \kappa_i^{\frac{1}{2}} \delta \lambda_i / \bar{r}_i \\ &= 1.496 \times 10^{-5} Z^{-\frac{1}{2}} (m/M)^{\frac{1}{2}} (n^{\frac{1}{2}}/T^{\frac{1}{2}}) \delta \ll 1, \end{aligned} \quad (47)$$

where

$$\lambda_i = \hbar/(MKT)^{\frac{1}{2}}, \quad \bar{r}_i = (n/Z)^{-\frac{1}{2}}. \quad (48a, b)$$

Accordingly, for typical nonideal plasma conditions, we have $\hat{\epsilon}_i \ll 1$ since $\lambda_i/\bar{r}_i \ll 1$ (classical ions), although in general $\lambda_e/\bar{r}_e > 1$ (degenerate electrons) for $\gamma/Z > 1$ or $\hbar\omega_p/KT > 1$.

The deviation ΔF of the free energy of a nonideal plasma from ideal behaviour is due to the quasi-lattice energy E_M and the plasmon energies $\tilde{F}_{e,i}$ (see equation 13b). Since the theory of electron oscillations has not yet been developed for arbitrary degrees of degeneracy ($n \lesssim \tilde{n}$), the contributions of the electron oscillations to ΔF in the cases $n \lesssim \tilde{n}$ and $n \gtrsim \tilde{n}$ have to be estimated from the dispersion equations for $n \ll \tilde{n}$ (equation 5) and $n \gg \tilde{n}$ (equation 6) respectively. Fortunately, it turns out that $|\tilde{F}_e| \ll |\Delta F|$ for $\gamma/Z \gtrsim 1$, so that quantitatively reliable approximations for ΔF can be derived.

Strongly Nonideal Plasmas

By equation (6) the spectrum $\omega(k)$ of electron oscillations extends over a band $\Delta\omega \sim \omega_p$ above the plasma frequency for $\gamma/Z \gg 1$, since $k\bar{r}_e \leq \hat{k}_e \bar{r} \sim 1$ and $(n/\tilde{n})^{\frac{1}{2}} \gamma^{-1} \sim 1$. Application of the mean value theorem for integrals to equation (25) shows that the free energy \tilde{F}_e of the high frequency plasmons vanishes exponentially for $\epsilon_p \rightarrow \infty$, i.e. $\gamma/Z \rightarrow \infty$:

$$\begin{aligned} \tilde{F}_e/NKT &= \left(\ln[1 - \exp\{-\epsilon_p(1 + a^2 \hat{k}_e^2)^{\frac{1}{2}}\}] \right. \\ &\quad \left. - \frac{\epsilon_p (a\hat{k}_e)^{-3}}{\exp\{\epsilon_p(1 + \tilde{x}^2)^{\frac{1}{2}}\} - 1} \int_0^{a\hat{k}_e} x^4 (1 + x^2)^{-\frac{1}{2}} dx \right) \rightarrow 0, \quad \epsilon_p \rightarrow \infty; \end{aligned} \quad (49)$$

with $0 \leq \tilde{x} \leq a\hat{k}_e$. Accordingly, we get $|\tilde{F}_e|/NKT \ll 1$ for $\varepsilon_p \gg 1$, i.e. $\gamma/Z \gg 1$. On the other hand, the free energy of the low frequency plasmons is by equation (38) for nondegenerate ions

$$\begin{aligned} \tilde{F}_i &\approx (N/Z)KT(\ln \hat{\varepsilon}_i - \frac{1}{3}) \\ &= (N/Z)KT[\ln \gamma + \ln\{(6\pi^2/Z^4)^{\frac{1}{3}}\delta(\kappa_i KT/M)^{\frac{1}{2}}/(e^2/\hbar)\} - \frac{1}{3}], \quad \hat{\varepsilon}_i \ll 1. \end{aligned} \quad (50)$$

It is noted that $\gamma/Z \gg 1$ is compatible with $\hat{\varepsilon}_i = \hbar c_M \hat{k}_i \delta / KT \ll 1$ as explained above.

Equations (49) and (50) demonstrate that the contribution of the electron oscillations to the free energy is negligible in strongly nonideal plasmas with $\gamma/Z \gg 1$. In this limit, the nonideal part of the free energy is due to the quasi-lattice energy E_M and the ion oscillations:

$$\Delta F/NKT = -\bar{\alpha}\gamma + (1/Z)\ln \gamma + (1/Z)\ln(\beta c_M/v_B) - 1/3Z, \quad \gamma/Z \gg 1, \quad (51)$$

where

$$v_B = e^2/\hbar, \quad \beta = (6\pi^2 Z^{-4})^{\frac{1}{3}}\delta. \quad (52a, b)$$

Note that $\ln \gamma$ depends on both n and T , whereas $\ln(\beta c_M/v_B)$ depends only on T , where the Bohr speed is $v_B = 2 \cdot 118 \times 10^8 \text{ cm s}^{-1} \gg c_M = (\kappa_i KT/M)^{\frac{1}{2}}$.

It is remarkable that the electron oscillations contribute little to the free energy compared with the ion oscillations for $\gamma/Z \gg 1$. This result holds even for moderately nonideal conditions ($\gamma/Z > 1$). Thus, we disagree with the formula

$$F = n\varepsilon_0 + 3NKT \ln(\hbar\omega_0/KT)$$

stated without derivation (for $3N$ degrees of freedom!) by Norman and Starostin (1970), according to whom 'all the vibrations have exactly the same frequency ω_0 near the plasma frequency ω_p '. The derivation of this formula requires $\hbar\omega(k)/KT \ll 1$ for the electron oscillations, which implies $\gamma/Z \ll 1$. But the latter inequality contradicts their assumption $\omega(k) \approx \omega_0 \approx \omega_p$, since the frequency spectrum extends over a large band $\Delta\omega > \omega_p$ above ω_p for $\gamma/Z \ll 1$. For these reasons, the free energy proposed by them is not applicable to proper nonideal plasmas ($\gamma/Z > 1$), nor is it correct for less nonideal conditions ($\gamma/Z < 1$).

Intermediate Nonideal Plasmas

For intermediate nonideal conditions ($1 \lesssim \gamma/Z < 10$), the spectrum $\omega(k)$ of electron oscillations extends over a region $\Delta\omega < O(\omega_p)$ above ω_p by equation (6), since $(n/\tilde{n})^{\frac{2}{3}}Z\gamma^{-1} < 1$ and $k\bar{r}_e \leq \hat{k}_e \bar{r}_e \sim 1$. Also in this case, a relatively simple formula can be devised for the free energy. The logarithmic term in \tilde{F}_e (see equation 25) is negligible compared with that in \tilde{F}_i (see equation 38) for $\gamma/Z > 1$, since $\varepsilon_p \gg \hbar c_M \delta \hat{k}_i / KT$ for $\gamma/Z > 1$ by equations (45) and (47). Accordingly, the nonideal part (13b) of the free energy is for intermediate nonideal plasmas ($\gamma/Z \gtrsim 1$)

$$\Delta F/NKT = -\bar{\alpha}\gamma + (1/Z)\ln \gamma + (1/Z)\ln(\beta c_M/v_B) - (1/Z)\mathcal{G}(\hat{\varepsilon}_i) - \mathcal{F}(\varepsilon_p, a\hat{k}_e). \quad (53)$$

For $\gamma/Z \gtrsim 1$, the ions can be assumed to be non-degenerate, $\hat{\varepsilon}_i = \hbar c_M \delta \hat{k}_i / KT \ll 1$ by equation (47), so that the ion integral (41) reduces to

$$\mathcal{G}(\hat{\varepsilon}_i) = \frac{1}{3}, \quad \hat{\varepsilon}_i \ll 1. \quad (54)$$

Since $\hat{\epsilon}_e > \epsilon_p \gtrsim 1$ and $a\hat{k}_e \epsilon_p \gtrsim 1$ (equations 46) for $\gamma/Z \gtrsim 1$, the electron integral (30) is significantly smaller than $\mathcal{G}(\hat{\epsilon}_i) = \frac{1}{3}$:

$$0 < \mathcal{F}(\epsilon_p, a\hat{k}_e) < (\hat{\epsilon}_e^2 - \epsilon_p^2)^{3/2} (a\hat{k}_e \epsilon_p)^{-3} \ln[\{1 - \exp(-\hat{\epsilon}_e)\} / \{1 - \exp(-\epsilon_p)\}] \ll 1, \quad \gamma/Z \gtrsim 1. \tag{55}$$

The lower and upper bounds of $\mathcal{F}(\epsilon_p, a\hat{k}_e)$ have been obtained by means of the mean value theorem for the integral (30):

$$\mathcal{F}(\epsilon_p, a\hat{k}_e) = (a\hat{k}_e \epsilon_p)^{-3} (\tilde{\epsilon}^2 - \epsilon_p^2)^{3/2} \int_{\epsilon_p}^{\tilde{\epsilon}_e} (e^\epsilon - 1) d\epsilon, \quad \epsilon_p \leq \tilde{\epsilon} \leq \hat{\epsilon}_e. \tag{56}$$

While for strongly nonideal conditions the contribution of the electron oscillations to the free energy is completely negligible, this contribution is still insignificant for intermediate nonideal conditions ($\gamma/Z \gtrsim 1$) by equation (55). For more exact evaluations, the small term $\mathcal{F}(\epsilon_p, a\hat{k}_e)$ in equation (53) can be computed from (30) or (32).

Weakly Nonideal Plasmas

Although the theory of weakly nonideal systems is well understood, it is interesting to investigate whether the present model for proper nonideal plasmas gives reasonable results in the limit $\gamma/Z \ll 1$. For $\gamma/Z \ll 1$ we get $a\hat{k}_e \gg 1$ by equations (46), and the spectrum $\omega(k)$ of electron oscillations extends over a large region $\Delta\omega \gg \omega_p$ above ω_p by equation (5). The electron integral then becomes

$$\mathcal{F}(\epsilon_p, a\hat{k}_e) = \epsilon_p (a\hat{k}_e)^{-3} \int_0^{a\hat{k}_e} \{\exp(\epsilon_p x) - 1\}^{-1} x^3 dx, \quad \gamma/Z \ll 1, \tag{57}$$

i.e.

$$\mathcal{F}(\epsilon_p, a\hat{k}_e) = \frac{1}{3} \{1 - \frac{3}{8}(\epsilon_p a\hat{k}_e)^1 + \frac{1}{20}(\epsilon_p a\hat{k}_e)^2 - \dots\}, \quad \epsilon_p a\hat{k}_e \ll 1. \tag{58}$$

Although $\epsilon_p a\hat{k}_e$ is independent of γ/Z by (27) and (28), the expansion (58) is valid since the electrons are certainly nondegenerate, as $\lambda_e/\bar{r}_e \ll 1$ for $\gamma/Z \ll 1$, and

$$\epsilon_p a\hat{k}_e = (4\pi\kappa_e)^{\frac{1}{2}} (\frac{3}{4}\pi^{\frac{1}{2}})^{\frac{1}{2}} \lambda_e/\bar{r}_e \ll 1, \quad \lambda_e/\bar{r}_e \ll 1. \tag{59}$$

For nondegenerate ions, the integral (41) is $\mathcal{G}(\hat{\epsilon}_i) = \frac{1}{3}$ by equation (43), since $\hat{\epsilon}_i \ll 1$. Thus, one obtains from equations (18), (25) and (38) for the interaction part of the free energy of weakly nonideal plasmas:

$$\begin{aligned} \Delta F/NKT &= -\alpha(\gamma)\gamma + (1/Z)\ln \gamma + (1/Z)\ln(\beta c_M/v_B) \\ &+ \ln(\epsilon_p a\hat{k}_e) - \frac{1}{3}(1 + Z^{-1}), \quad \gamma/Z \ll 1, \end{aligned} \tag{60}$$

where the logarithmic term in (25) has been expanded for $\epsilon_p a\hat{k}_e \ll 1$.

In equation (60), $\alpha(\gamma)$ is the Madelung constant of the weakly nonideal plasma with weak electron and ion ordering, with $\alpha(\gamma) \rightarrow 0$ for $\gamma \rightarrow 0$. Comparison of the term $-\alpha(\gamma)\gamma(NKT)$ in (60) with

$$\Delta F = -(NKT)^{\frac{2}{3}} \pi^{\frac{1}{2}} (1 + Z)^{3/2} e^3 n^{\frac{1}{2}} (KT)^{-3/2}$$

of the Debye–Hueckel (1923) theory (weakly nonideal plasmas) yields the result

$$\alpha(\gamma) = \frac{2}{3}\pi^{\frac{1}{2}}(1 + Z^{-1})^{3/2}\gamma^{\frac{1}{2}}, \quad \gamma/Z \ll 1. \quad (61)$$

The previous theories of weakly nonideal plasmas do not lead to the logarithmic terms in (60) since they do not take into account the effects of electron and ion oscillations.

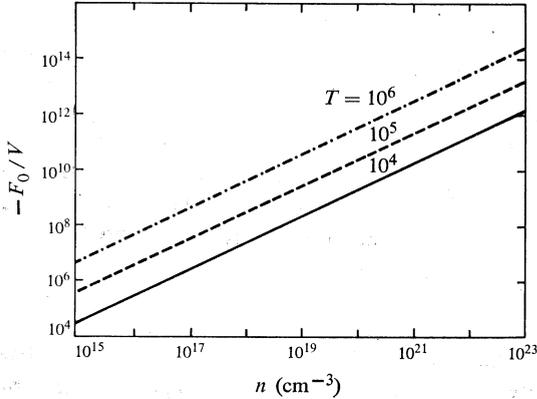


Fig. 1. Free energy $F_0 < 0$ per unit volume of an ideal plasma as a function of n for three values of T (K) ($Z = 1$).

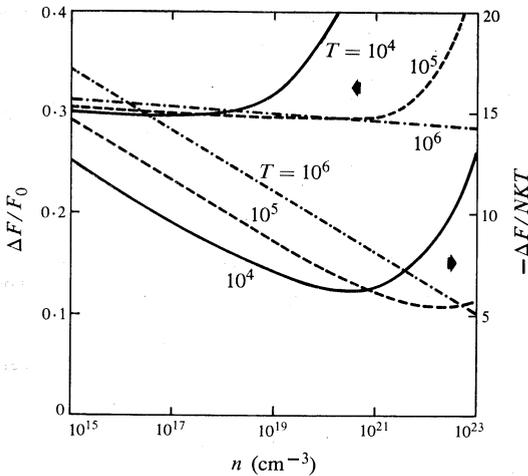


Fig. 2. Deviation $\Delta F < 0$ of the free energy from both $F_0 < 0$ (left) and the thermal energy NKT (right) as a function of n for three values of T (K) ($Z = 1$).

Numerical Illustrations

Fig. 1 shows the (negative) free energy F_0 per unit volume of an ideal $Z = 1$ plasma versus n for three values of T based on equations (14)–(17). Here F_0 serves as a reference quantity, relative to which the quantitative significance of the nonideal contributions are measured. It is seen that $|F_0|$ increases with increasing n and T .

Fig. 2 shows the deviation $\Delta F < 0$ of the free energy of a $Z = 1$ plasma from its ideal value $F_0 < 0$ versus n for three values of T based on equations (13b), (25) and (38). In the n – T region under consideration, $|\Delta F|$ is less than the magnitude $|F_0|$, but is considerably larger than the thermal energy $\sim NKT$. Here $\Delta F/F_0$ only exhibits a significant T dependence at large densities $n > 10^{19} \text{ cm}^{-3}$.

Fig. 3 shows the free energies \tilde{F}_e and \tilde{F}_i of the high (e) and low (i) frequency plasmons of a $Z = 1$ plasma based on equations (25) and (38). Here $|\tilde{F}_i|$ is considerably larger than $|\tilde{F}_e|$, in particular at higher densities. The T dependence of $\tilde{F}_{e,i}/F_0$ increases with increasing density n . Comparison of Figs 2 and 3 indicates that $\Delta F \approx \tilde{F}_e + \tilde{F}_i$, i.e. the quasi-lattice energy E_M (equations 18 and 61) is not the dominant nonideal effect.

Figs 2 and 3 demonstrate the quantitative importance of the nonideal effects $\Delta F = E_M + \tilde{F}_e + \tilde{F}_i$, in particular of the low (i) and high (e) frequency plasmon contributions \tilde{F}_i and \tilde{F}_e ($\tilde{F}_i > \tilde{F}_e$), for the evaluation of the free energy $F = F_0 + \Delta F$ of high density plasmas.

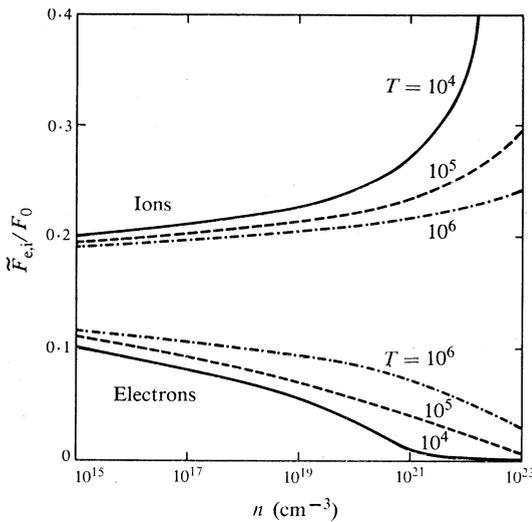


Fig. 3. Free energies $\tilde{F}_{e,i} < 0$ of high (electrons) and low (ions) frequency plasmons as a function of n for three values of T (K) ($Z = 1$).

For quantitative calculations, it is noted that the free energy ΔF is hardly affected by inaccuracies in the large maximum wave numbers \hat{k}_e and \hat{k}_i , which have been determined in accordance with the Debye theory which implies strong coupling ($\gamma \gg 1$). For weakly nonideal plasmas ($\gamma \ll 1$), it appears to be more meaningful to determine $k_s = 2\pi/\hat{\lambda}_s$ from the minimum wavelength $\hat{\lambda}_s \approx 2r_s$, where $r_s = (\frac{4}{3}\pi n_s)^{-\frac{1}{3}}$ is the mean particle radius and $s = e, i$. Both models give, however, essentially the same result since $\hat{k}_s^D/\hat{k}_s^\lambda \sim 1$. The theory presented does not contain the Debye length D , which no longer exists for nonideal plasmas with $\gamma \gtrsim 1$. Also, in this respect, our theory differs from most of the previous nonideal plasma theories, which are extensions of the weakly nonideal plasma limit.

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Appendix. Expansion of $\mathcal{F}(\varepsilon_p, a\hat{k}_e)$

The integral (26) is conveniently rewritten in the form

$$\mathcal{F}(\varepsilon_p, a\hat{k}_e) = (a\hat{k}_e \varepsilon_p)^{-3} I(\varepsilon_p, \hat{\varepsilon}), \quad (\text{A1})$$

where

$$I(\varepsilon_p, \hat{\varepsilon}) = \int_{\varepsilon_p}^{\hat{\varepsilon}} (\varepsilon^2 - \varepsilon_p^2)^{3/2} (\varepsilon^{\varepsilon} - 1)^{-1} d\varepsilon, \quad 0 < \varepsilon_p < \hat{\varepsilon} < \infty. \quad (\text{A2})$$

Since $\varepsilon > 0$, i.e. $e^{-\varepsilon} < 1$, there exists the series expansion

$$(e^{\varepsilon} - 1)^{-1} = \sum_{m=1}^{\infty} e^{-m\varepsilon}, \quad \varepsilon > 0. \quad (\text{A3})$$

The substitutions $u = \varepsilon - \varepsilon_p$ and $du = d\varepsilon$, together with equation (A3), transform (A2) into

$$I(\varepsilon_p, \hat{\varepsilon}) = \sum_{m=1}^{\infty} \exp(-m\varepsilon_p) \int_{u=0}^{\hat{\varepsilon}-\varepsilon_p} u^{3/2} (u+2\varepsilon_p)^{3/2} e^{-mu} du. \quad (\text{A4})$$

For $u < 2\varepsilon_p$, i.e. $\hat{\varepsilon} < 3\varepsilon_p$, the binomial expansion

$$(u+2\varepsilon_p)^{3/2} = (2\varepsilon_p)^{3/2} \sum_{n=0}^{\infty} \binom{\frac{3}{2}}{n} \left(\frac{u}{2\varepsilon_p}\right)^n, \quad u/2\varepsilon_p < 1 \quad (\text{A5})$$

is used, which reduces (A4) to the double series

$$I(\varepsilon_p, \hat{\varepsilon}) = (2\varepsilon_p)^{3/2} \sum_{m=1}^{\infty} \exp(-m\varepsilon_p) \sum_{n=0}^{\infty} \binom{\frac{3}{2}}{n} (2\varepsilon_p)^{-n} m^{-(5/2+n)} \gamma\left(\frac{5}{2}+n, (\hat{\varepsilon}-\varepsilon_p)m\right), \quad (\text{A6})$$

for $\hat{\epsilon} < 3\epsilon_p$, where

$$\gamma\left(\frac{5}{2} + n, (\hat{\epsilon} - \epsilon_p)m\right) = m^{5/2+n} \int_0^{\hat{\epsilon} - \epsilon_p} u^{3/2+n} e^{-mu} du \quad (\text{A7})$$

is the incomplete gamma function (Abramowitz and Stegun 1965). In an analogous way, the integral (A2) can be solved for $u > 2\epsilon_p$, i.e. $3\epsilon_p < \hat{\epsilon}$.

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