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F. J. Rogers

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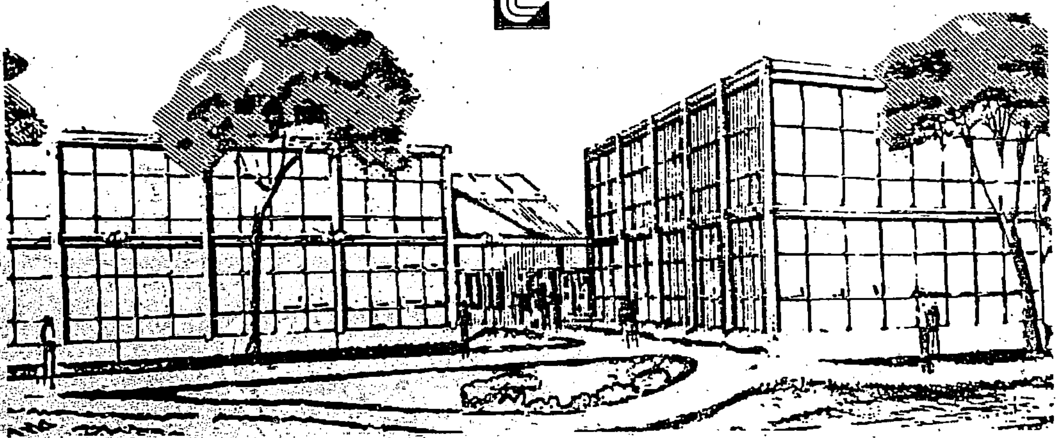

EQUATION OF STATE OF REACTING STRONGLY COUPLED PLASMAS

F. J. Rogers

University of California, Lawrence Livermore Laboratory

P. O. Box 808, Livermore, California 94550

ABSTRACT

A brief review is given of the quantum statistical theory of strongly coupled many component reacting plasmas. It is shown that three distinct renormalizations of the many component activity series are required to obtain an expansion, which can properly handle strongly coupled reacting plasmas, for all states of ionization when $Z > 1$. Compensation between bound and scattering state contributions to the partition function is shown to be an important consideration and leads automatically to a convergent internal partition function.

I. INTRODUCTION

The equation of state of complex reacting mixtures of partially ionized gases is almost always obtained from a free energy model. Typically this is a pseudo ideal gas free energy minimization calculation in which a particular aspect of the interaction of an atom (or ion) with its surroundings is invoked to cut off the divergence of the atomic partition function.[1] This results in some uncertainty in the equation of state even in the zero coupling limit. The Debye Hückel electrostatic free energy is often added to the ideal gas free energy to account for ionic coupling. In more sophisticated calculations additional additive free energy terms to account for the finite size of the atoms (and ions) and other effects are also included.[2] These model approaches grew out of a need to obtain the equation of state of astrophysical mixtures at a time when a consistent fundamental theory was not available.

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Considerable progress on the theory has been made in recent years. But even now most of the work is concerned with hydrogen plasmas. The recent monograph of Ebeling, Kraeft, and Kremp gives an excellent review of this literature.[3] In the present paper we give a brief review of the theory for plasmas having $Z > 1$. A more detailed description of most of the material can be found in references 4 and 5.

II. PLASMA ACTIVITY EXPANSION

A. Renormalization to Account for the Formation of Composites

The general starting place of this work is an activity expansion of the grand partition function. Several important features of the problem can be demonstrated by way of a simple example. Consider the most basic ionization problem of electrons (e) and nuclei (α) in equilibrium with one-electron composites (c), i.e.

$$e + \alpha \rightleftarrows c. \tag{1}$$

Truncation of the activity series at two-body terms gives

$$P/kT = z_e + z_\alpha + z_e^2\, b_{ee} + 2 z_e z_\alpha b_{e\alpha} + z_\alpha^2\, b_{\alpha\alpha}, \tag{2}$$

subject to the conditions,

$$\rho_i = N_i/V = z_i \frac{\partial(P/kT)}{\partial z_i} \quad , \; i = (e,\alpha) \tag{3}$$

where,

$$z_i = (2s_i+1)e^{\mu_i/kT} . \tag{4}$$

is the activity,

$$\lambda_i = (2\pi\hbar^2/M_i kT)^{1/2} \tag{5}$$

is the deBroglie wavelength, and the b_{ii} are second cluster coefficients. Classical approximations to b_{ee} and $b_{\alpha\alpha}$ are sufficient for the present discussion, i.e.

$$b_{ii} = 2\pi \int_0^\infty dr\, r^2 (e^{-z_i^2 e^2 r/kT} - 1) \tag{6}$$

which diverges in the first three orders of perturbation theory as $r \to \infty$. The strong attraction of the electron-ion term always requires a quantum mechanical treatment. A useful expression for $b_{e\alpha}$ was obtained by Beth and Uhlenbeck[4]:

$$b_{e\alpha} = b_{e\alpha}^b + b_{e\alpha}^f \tag{7}$$

where,

$$b_{e\alpha}^b = \sqrt{2}\, \lambda_{e\alpha}^3 \sum_{n\ell} (2\ell+1) e^{-E_{n\ell}/kT} \tag{8}$$

is the bound state contribution and

$$b_{e\alpha}^f = \frac{\sqrt{2}\, \lambda_{e\alpha}^3}{\pi} \int_0^\infty dp \sum_\ell (2\ell+1) \frac{d\delta_\ell}{dp} e^{-p^2/2\mu_{e\alpha}} \tag{9}$$

is the scattering state contribution. In eqs. (8-9) $\lambda_{e\alpha}$ is the deBroglie wavelength for particles of reduced mass $\mu_{e\alpha}$, δ_ℓ is the phase shift and p is the relative momentum.

$b_{e\alpha}$ has divergences for large r similar to those of b_{ee} and $b_{\alpha\alpha}$. However it can be shown that the divergences in the bound state sum are completely compensated by the continuum state terms and have nothing to do with the large r divergence.[7-11] After compensation the result for large r is

$$\begin{aligned} b^b_{e\alpha} &= \sqrt{2}\,\lambda^3_{e\alpha}\sum_{n\ell}^{n_{\max}\,\ell_{\max}} (2\ell+1)(e^{-\beta E_{n\ell}} - 1 + \beta E_{n\ell}) \\ b^f_{e\alpha} &= \pi(\beta Ze^2)r^2 + \pi(\beta Ze^2)^2 r - \frac{\pi(\beta Ze^2)}{3}\,\log\left(\frac{\lambda_{e\alpha}}{r}\right) \\ &\quad + O(\lambda^3_{e\alpha}\,\beta E_{1s}) \end{aligned} \tag{10}$$

where $E_{n\ell}$, $n_{\max}$, and $\ell_{\max}$ are functions of r for states whose Bohr radius is of order r, but are hydrogenic over the range of $(n\ell)$ that contributes to $b^b_{e\alpha}$. The r^2 divergence in the cluster coefficients cancels out due to electrical neutrality. The second order term is the lowest order ring diagram. The classical sum over these diagrams gives the Debye-Hückel result. A quantum statistical mechanical evaluation of the ring diagrams has been given by DeWitt.[12] Summation of the latter diagrams starting at third order gives an expression that resembles the third cluster coefficient of the dynamic screened Coulomb potential.[13] In the limit $\lambda/\lambda_D \to 0$ this potential goes over to the Debye-Hückel form and the latter sum gives

$$s_{ij} = b_{ij}(\lambda_D) - b^1_{ij}(\lambda_D) - b^2_{ij}(\lambda_D) \ , \tag{11}$$

where $b_{ij}(\lambda_D)$ is the second cluster coefficient for a Debye potential, $b^1_{ij}(\lambda_D)$ and $b^2_{ij}(\lambda_D)$ are the first and second order perturbation terms. In this limit the many body plasma part of the problem remains classical while the few body part displays the necessary uncertainty principle effects at short distances. Alternatively we can obtain the same result by replacing the Boltzmann factors of the classical theory by Slater sums. This is the method used in the formal development.

Due to the rearrangement just mentioned, which summed certain types of diagrams from all cluster coefficients, Eq. (2) is replaced by a properly behaved activity series. It is

$$\frac{P}{kT} = z_e + z_\alpha + S_R + z_e^{\,2}\; s_{ee} + 2z_e z_\alpha s_{e\alpha} + z_p^{\,2} s_{\alpha\alpha} \tag{12}$$

where

$$S_R = 1/12\pi\ \lambda_D{}^3, \quad \lambda_D = [kT/4\pi e^2(z_e+Z^2z_p{}^2)]^{1/2},$$

is the Debye-Hückel correction obtained by a sum over the ring diagrams. Eq. (12) includes the possibility of the formation of composites. To see how this comes about assume zero coupling to the ideal gas, so that, eq. (12) reduces to

$$\begin{aligned} P/kT &= z_e + z_\alpha + 2z_e z_\alpha\, s^b_{e\alpha} \qquad (13) \\ &= \rho_e{}^* + \rho_\alpha{}^* + \rho_{e\alpha}, \end{aligned}$$

where $s^b_{e\alpha}$ is the non-compensating part of the bound state sum similar to eq. (10), but, now involving the Debye energy levels. $\rho_e{}^*$, $\rho_p{}^*$ and $\rho_{e\alpha}$ are the equilibrium numbers of free electrons, free protons, and one electron composites, respectively. Due to electrical neutrality

$$\rho_e{}^* = (Z-1)\ \rho_\alpha + \rho_\alpha{}^*,\ \rho_{e\alpha} = \rho_\alpha - \rho_\alpha{}^*\ , \qquad (14)$$

For the special case Z = 1 symmetry requires that $z_e = z_\alpha$ and it follows from eqs. (3) and (12), that

$$z_e = z_p = (-1 + \sqrt{1 + 8\rho_e\, s^b_{e\alpha}})/4s^b_{e\alpha} \qquad (15)$$

and

$$\begin{aligned} P/kT &= 2[-1 + \sqrt{1 + 8\rho_e s^b_{e\alpha}}\ ]/4s^b_{e\alpha} \qquad (16) \\ &\quad + [-1 + \sqrt{1 + 8\rho_e s^b_{e\alpha}}\ ]^2/8s^b_{e\alpha}\ . \end{aligned}$$

At high temperature $s^b_{e\alpha} \to 0$ so that $PV/N_ekT \to 2$ indicating complete ionization. As $T \to 0$ $s^b_{e\alpha} \to \infty$ and $PV/N_ekT \to 1$ indicating the formation of one electron composites. The important point is that the product $2z_ez_\alpha\ s^b_{e\alpha}$ plays the role of an activity, $z_{e\alpha}$, for one electron composites, so that eq. (12) takes the form

$$P/kT = z_e + z_\alpha + z_{e\alpha} + S_R(z_e + Z^2 z_\alpha) + z_e^{\,2} s_{ee} + 2z_e z_\alpha s^f_{e\alpha} + z_\alpha^{\,2} s_{\alpha\alpha} \qquad (17)$$

Since there are no two body terms involving electrons on nuclei scattering from composite ions, it is apparent that eq. (17) is short of terms. These terms come from the third cluster coefficients which are composed of three conceptually different parts corresponding to: (1) the formation of two electron composites; (2) scattering of electrons & nuclei from one electron composites; (3) scattering between three unbound particles. These parts enter the activity expansion at first, second, and third order in powers of the activity, respectively. The entire activity series must be renormalized on this basis. The first order terms in the revised series correspond to the Saha equation. Scattering states enter only in higher order terms. Because of this natural separation of bound and scattering state terms it is essential that effective compensations be taken into account before the separation is made. Otherwise the high temperature term will not be properly ordered, i.e. the Saha term will predict too many composites.

B. Renormalization to Account for the Plasma Coupling of Composite Particles

Eq. (12) has another obvious shortcoming. The ring term and the Debye length that appears in the s_{ij} only involve the activities of electrons and nuclei, whereas, it is apparent that one electron composites must somehow be included. The resolution of this problem is complicated and involves finding a Taylor series expansions of functions of $\lambda_D(z_e + Z^2 z_\alpha + (Z-1)^2 z_{e\alpha})$ in the complete expansion (17). A result of this second type of renormalization the energy levels of the Debye potential that enter $s^b_{e\alpha}$ are shifted, to first order, back to their isolated atom (ion) values, i.e.

$$E_{n\ell}(\lambda_D) = E_{n\ell}(\lambda_D) - Ze^2/\lambda_D \qquad (18)$$

This is consistent with a result of Jackson and Klein.[14] The result of this renormalization which includes all terms through 5/2 powers in the activity, allowing the possibility of the formation of many particle composites, is given in ref. 5. Composite particles enter this expansion similar to fundamental particles although, due to the fact that composite particle activities are coupled to the many body system through their λ_D dependence, there are some differences. If terms of type $b_{e\alpha}^{b}$ of Eq. (10) are not included in the resummation required to eliminate the scattering state divergences, an expansion in which composite activities enter exactly like fundamental particles is obtained. This will be discussed in detail elsewhere.

C. Renormalization to Account for Strong Ion Coupling

When Z >> 1 eq. (12) has an additional shortcoming. This is easily seen by truncating P/kT at the Debye Hückel term and assuming there are no composites. The activities are given by[4]

$$z_e = \rho_e \, e^{-\partial S/\partial \rho_e} = \rho_e e^{-\Lambda/2} \tag{19}$$

$$z_\alpha = \rho_\alpha \, e^{-\partial S/\partial \rho_e} = \rho_\alpha \, e^{-Z^2\Lambda/2} \tag{20}$$

where S is the Mayer S function and

$$\Lambda = \beta e^2/kT\lambda_D(\rho_e + z^2\rho_\alpha) \tag{21}$$

corresponds to the approximation $S = S_R(\rho_e + Z^2\rho_\alpha)$.

In general eq. (19-20) cannot be used to obtain z_e and z_α since, as already discussed, when composites are formed $S_R = S_R\,(\rho_e{*} + Z^2\rho_2{*} + (Z-1)^2\rho_{e\alpha})$ where $\rho_e{*}, \rho_\alpha{*}$, and $\rho_{e\alpha}$ depend on (V,T). Eqs. (19-20) show that for sufficiently large values of Z, $z_\alpha/\rho_\alpha << 1$ when $\Lambda << 1$. The expansion in powers of the activity given by eq. (12) is only valid when $z_\alpha/\rho_\alpha \gtrsim 1/2$ and is not applicable to this situation. In fact it predicts that the nuclei fall out of the interaction terms altogether, whereas, the density expansion predicts the electrons fall out of the problem, i.e. the Debye-Huckel pressure correction in the cononical formulism is given by

$$P_{DH} = \frac{-1}{24\pi\lambda_D^3} = \frac{-1}{24\pi} \left[4\pi\beta e^2(\rho_e + Z^2\rho_\alpha)\right]^{3/2} \tag{22}$$

$$= \frac{-1}{24\pi} (4\pi\beta e^2 Z^2 \rho_\alpha)^{3/2} \left(1 + \frac{3}{2} \frac{\rho_e}{Z^2\rho_\alpha} ---\right)$$

Neither result is entirely correct. The difficulty is that the Debye-theory only applies to weakly correlated motion, whereas, due to the high Z the nuclear motion is strongly correlated even at very low density. By adding higher S_n corrections[5] in the density expansion it is possible to show that the electron part decreases in importance as Z is increased and goes over to the result for ion mixtures in a neutralizing electron background. As a first approximation to the interaction correction at high temperature we can use the multi-component fitting formula for the Monte-Carlo results worked out by H. E. DeWitt.[15] In order to account for the formation of composites it is convenient to express this formula in terms of activities. To accomplish this we equate the canonical expression for the pressure to that given by the grand canonical theory,

$$\frac{P}{kT} = \rho_e^* + \rho_I + S(Z_{ef}^2\Lambda) - \rho_I \partial S(Z_{ef}^2 \Lambda)/\partial\rho_I \tag{23}$$

$$= z_e + z_I\, g(Z_{ef}^2 \Lambda_z) \tag{24}$$

where the electrons are uncoupled from the ions which are treated by a one fluid model, i.e.

$$\rho_I = \rho_\alpha^* + \rho_{e\alpha} + \rho_{ee\alpha} + --- \tag{25}$$

$$z_I = z_\alpha + z_{e\alpha} + z_{ee\alpha} + --- \tag{26}$$

$$Z_{ef}^2 = \langle Z\rangle^{1/3} \langle Z^{5/3}\rangle \tag{27}$$

$$\langle Z^n\rangle = (z_\alpha Z^n + z_{e\alpha} (Z-1)^n + ---)/z_I \tag{28}$$

$$\Lambda_Z = \beta_e{}^2/\lambda_D(z_e + Z^2 z_\alpha + (Z-1)^2 z_{e\alpha} + ---) \tag{29}$$

By using the relation

$$z_I = \rho_I \, e^{-\partial S/\partial \rho_I} \tag{30}$$

to eliminate z_I from Eq. (24), and since the electrons are uncoupled $z_e = \rho_e^*$, the function g can be tabulated from

$$g(Z_{ef}^2 \Lambda_z) = -1 + \frac{\rho_I + S - \rho_I \partial S/\partial \rho_I}{\rho_I \, e^{-\partial S/\partial \rho_I}} \tag{31}$$

Eq. (24) can now be solved in the usual way through the relation

$$\rho_e = z_e \frac{\partial(\rho/kT)}{\partial z_e}, \quad \rho_\alpha = z_\alpha \frac{\partial(\rho/kT)}{\partial z_\alpha} \tag{32}$$

The composite activities are also involved in Eq. (32) since they are built up from products of z_e and z_α. Since the ions are now strongly coupled to the ideal gas they have a significant effect on the ionization equilibrium and always increase the state of ionization from that obtained in a Saha calculation.

Going beyond Eq. (24) to obtain an expression that includes electron corrections as the temperature is reduced for a given Z, or for intermediate values of Z, is complicated. The addition of any electron coupling invalidates the relation $z_e = \rho_e^*$ and would require the tabulation of g as a function of many variables. The difficulty can be removed by a third renormalization in which the most important part of each term in the expansion of P/kT in terms of the Mayer S function, i.e.

$$\frac{P}{kT} = z_e + z_\alpha + z_{e\alpha} + \ldots + S(z_e, z_\alpha, z_{e\alpha} \ldots)$$

$$+ \frac{1}{2} \sum_{i=(e,\alpha,e\alpha,\ldots)} z_i \left(\frac{\partial S}{\partial z_i}\right)^2 + \ldots \tag{33}$$

are first summed together, the second most important terms summed, etc. This results in an expansion of the following form,

$$\frac{p}{kT} = z_e + z_\alpha + z_{e\alpha} + \ldots + P_1 + P_2 + \ldots \qquad (34)$$

where

$$P_1 = S + \sum_i z_i \left(e^{\frac{\partial S}{\partial z_i}} - 1 - \frac{\partial S}{\partial z_i} \right)$$

$$P_2 = \frac{1}{2} \sum_{ij} z_i z_j \frac{\partial S}{\partial z_i \partial z_j} \left(e^{\frac{\partial S}{\partial z_i}} - 1 \right) \left(e^{\frac{\partial S}{\partial z_j}} - 1 \right) \qquad (35)$$

Eq. (34) is valid over the entire range of Z and T and for all densities in the fluid phase provided phase transition or phase separation is not taking place. A full description of the results of this section including calculation for silicon at all stages of ionization will be given elsewhere

III. CONCLUDING REMARKS

This paper has given a brief review of the current state of theoretical procedures for calculating the equation of state of complex mixtures of reacting plasmas under various conditions. No mention was made of electron degeneracy and exchange effects, diffraction corrections for λ/λ_D finite, or relativistic effects for high Z. These effects can be very important, but, only quantitatively effect the discussion here. A more detailed description of much of the material can be found in the cited literature. The procedures described all start from a rigorous basis, but require approximations along the way whose effect can be evaluated. The resultant calculations are much more involved than those in the models mentioned in the beginning, but, at the least they can be used to improve these models. This work is by no means complete and much remains to be done. A very important test of the theory, for instance, can be made by attempting to explain recent conductivity measurements of P. P. Kulik and his collaborators.[16] A study of the possibility of phase separation in high Z plasmas is another interesting problem.

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