LAWRENCE LIVERMORE LABORATORY
University of California / Livermore, California / 94550

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**STATISTICAL MECHANICS OF REACTING GASES
WITH APPLICATIONS
TO THE EQUATION OF STATE OF HYDROGEN**

Forrest J. Rogers

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STATISTICAL MECHANICS OF REACTING GASES WITH APPLICATIONS TO THE EQUATION OF STATE OF HYDROGEN

Abstract

A method has been developed from fundamental statistical mechanics for systematically correcting the ideal gas equation of state (Saha equation) to take into account the interactions that occur in any real gas. At the current stage, all effective two-body interactions that can occur among the various species present in the system are taken into account. Because of the long-range nature of the coulomb potential, the problem is formulated from the point of view of many-body perturbation theory. It is necessary to use the quantum theory to avoid the short-range divergence of the classical cluster integrals. However, considerable insight into the form of the quantum-mechanical result is obtained from the classical perturbation theory. The result of the many-body perturbation theory is that the coulomb problem is replaced with a new problem involving the cluster coefficients of the screened coulomb potential and a large number of other terms which are associated with plasma interactions.

The work is primarily concerned with how atoms are formed out of a plasma as the temperature is lowered; however, ordinary gases are included in a natural way. The method has been used to calculate the equation of state of a neutral gaseous electron-proton (hydrogen) system at a moderate density. The corrections to the Saha equation were found to be significant.

For the application to hydrogen the second cluster coefficient, which is just the negative of the second virial coefficient, was calculated with the Beth-Uhlenbeck method. This involved detailed numerical calculations of the eigenvalues and phase shifts of the static screened coulomb potential. Calculations of the equation of state of He, Fe, and Xe are currently underway.

Chapter I. Introduction

The equation of state of a given amount of material is governed in varying degrees by a number of different effects. The relative importance of these various physical effects depends considerably on the temperature and density. At very low density and high temperature the equation of state is simply that of an ideal gas (at sufficiently high temperature the photon gas predominates). At very high density the equation of state is determined by electron degeneracy, relativistic effects, and nuclear reactions. As one lowers the temperature at moderate to low density two-body bound states will start to form out of the plasma, still further reduction in the temperature will result in a complicated mixture of molecules and atoms which because of the relatively large average separation (compared to a liquid) interact primarily through two composite particles at a time, three body interactions being less probable. At still lower temperatures the system will collapse into a liquid or a solid. It will be the purpose of this work to develop a consistent procedure for calculating the equation of state of a gas in the moderate density and moderate to high temperature region. This procedure will be applied to the calculation of the EOS of a neutral electron proton system.

In this chapter we will review some of the standard methods for calculating the EOS in the present region of interest. A detailed description of current procedures that extend well beyond this region can be found in Refs. (1-6).

The natural starting place for discussing the EOS of ionizing gases is the Saha equation. The assumption is that the constituents of the system can undergo associative-dissociative reactions but that no other interactions, i.e. scattering off of a potential, are important. This condition should be realized at very low densities. The grand partition function for a many-component system is given by

$$\Xi = e^{PV/kT} = \sum_{N_1, N_2, \dots} e^{\mu_1 N_1 + \mu_2 N_2 + \dots} Z_{N_1, N_2, \dots} \quad (1.1)$$

where $\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{V, T, \{N_j\}}$ is the chemical potential of component i

and $Z_{N_1, N_2, \dots}$ is the canonical partition

function for $N_1, N_2, \dots$ particles of type 1, 2, etc., respectively, in the volume V . The Helmholtz free energy is given by

$$F = E - TS = \sum_i N_i \mu_i - PV \quad (1.2)$$

When the Saha assumption is valid the energy levels of the system are just those of isolated atoms and molecules, so that

$$\frac{PV}{kT} = \sum_i N_i \mu_i + \ln \left(\frac{Z_1^{N_1}}{N_1!} \frac{Z_2^{N_2}}{N_2!} \dots \right) \quad (1.3)$$

The free energy is therefore

$$F = - \sum_i N_i kT \ln \left[\frac{eV}{N_i} \left(\frac{m_i kT}{2\pi\hbar^2} \right)^{3/2} \sum_j e^{-E_{ij}/kT} \right] \quad (1.4)$$

The condition for equilibrium is that the Helmholtz free energy be a minimum at constant T and P or that the Gibbs free energy, $G = F + PV$, be a minimum at constant V and P. The equation of state at constant T and V can be found by minimizing the free energy with respect to the concentrations of the $\{N_i\}$ consistent with the stoichiometric constraints. Or equivalently one can consider a condition of constant T and P and solve the system of simultaneous equations

$$\sum_i \mu_i N_i = 0 \quad (1.5)$$

which result from the requirement that the free energy be a minimum.

For ionization reactions of the type,

the usual procedure is to use only the ground state energy level to calculate the atomic partition function. The Saha equation in the one level approximation is given by

$$K_p^n(T) = \frac{1}{P} \frac{C_{n-1}}{C_n C_e} = \frac{1}{kT} \frac{g_{n-1}}{g_n g_e} \left(\frac{2\pi m_n kT}{h^2} \right)^{3/2} e^{I_n/kT} \quad (1.6)$$

where $K_p^n(T)$ is the equilibrium constant, p is the pressure, the g's are the statistical weight of the ground states, and I_n is the n th ionization potential of the atom. Equation (1.6) predicts that as the temperature

is increased the equilibrium is shifted in the direction of increased ionization. However, the n th electron is almost completely ionized at temperatures well below I_n . This is because of the competition between decreasing energy and increasing entropy to obtain the minimum free energy. The energy is lowered by formation of a bound state, whereas, the entropy is increased by the disorder associated with ionization. In general, the n th electron is removed from a large percentage of the atoms at temperatures of order $0.1 I_n$. This tendency to ionize at temperatures well below I_n shows up in Eq. (I.6) through the smallness of the factor multiplying the exponential. The Saha equation predicts that any atom will be completely ionized at very low density and that it will associate as the density is increased. However, the basic assumption in deriving Eq. (I.6) was low density and the effect of interactions must be included at moderate densities to obtain realistic results.

A more refined calculation of the EOS requires that proper account of higher energy states be included in the partition function. The assumption that the atomic energy levels are those of an isolated atom can only be exact in the zero density limit. The true energy levels of the system at any non-zero density will be perturbed from those of an isolated atom. The higher the state the greater the perturbation. Neglect of this perturbation, however slight, poses a dilemma; the partition function of an isolated hydrogenic atom,

$$Z = \sum_{n=1}^{\infty} 2n^2 e^{-\text{Ryd}/n^2 kT}, \quad (\text{I.7})$$

diverges. The usual procedure for avoiding this difficulty is to state that it is intuitively obvious that only a few of the lowest states can

by truly bound states and that any reasonable criteria for placing a limit on the sum (I.7) is sufficient.

Many procedures for limiting the sum have been suggested. These various methods have been discussed by McChesney⁷ and B. H. Armstrong, et al.⁸ have given an extensive list of references. The most common procedures are the following: (1) To assume that states whose mean radius is greater than the average interparticle distance are free. (2) To subtract from each exponential term in the partition function sum the terms $-1 - \beta E_{nl}$, where E_{nl} are the eigenvalues of the unperturbed atom.⁹ This removes all divergences from the sum over states. (3) To use the Inglis-Teller relation which relates the electron density to the maximum quantum number of resolvable lines due to Stark broadening in a plasma. (4) To consider the atoms to be confined to a spherical box whose volume is determined by the number of the other particles in the system.¹⁻³ The atomic energy levels are then taken to be those of an atom in a spherical box as given by DeGroot and ten Seldam.¹⁰ (5) To recognize that the coulomb potential is a long range potential such that each charged particle interacts simultaneously with all the other charged particles in the system, effectively shielding the interaction between pairs of particles. The resultant potential is referred to as the static screened coulomb potential and it has only a finite number of bound states.

A refinement to the Saha procedure that is in standard use at high temperature and moderate density is to assume that the charged particles interact according to the Debye-Huckel theory. Originally this theory was applied to electrolyte solutions and its derivation was somewhat ambiguous.¹¹ However, its use in plasmas has been rigorously justified from the classical virial expansion¹² and from the quantum-

mechanical many-body perturbation expansion of the grand partition function.¹⁴ In its original derivation it is assumed that the electrostatic potential can be calculated from Poisson's equation and that the density is low enough that the charge is spatially distributed according to Boltzmann's formula. Consistent with the low density assumption the exponential charge distribution is linearized giving the result

$$V_{ij}(r) = (\epsilon_i \epsilon_j) \frac{e^{-r/\lambda_D}}{r} \quad (I.8a)$$

$$\lambda_D \left(\frac{4\pi}{kT} \sum_j n_j \epsilon_j^2 \right)^{-1/2} \quad (I.8b)$$

$$E_{es} = - \frac{N\Lambda}{2} \quad (I.8c)$$

where

$$n = N/V = \sum_j n_j$$

and

$$\Lambda = \frac{1}{4\pi n \lambda_D^3}$$

V_{ij} is the potential, n_j is the number density of charged particles of type j , ϵ is the charge of the particle and E_{es} is the electrostatic energy. From thermodynamics there results

$$(P - P_I)/NkT = - \Lambda/3 \quad (I.9a)$$

$$P - P_I = \Lambda/6 \quad (I.9b)$$

When the interaction of charged particles is added to the ideal gas free energy as in Eq. (I.9a) one is assuming that the bound state part of the calculation is uncoupled from the electrostatic interaction. This again is consistent with the assumption of low density.

In what follows it will be shown that the bound state problem and the interaction of charged particles should be considered together.

The primary purpose of this study is to obtain a fairly precise description of how bound states are formed out of a plasma as the temperature is lowered. Most of the discussion will pertain to an electron-proton gas, but, the introduction of nuclei is straightforward. Because of the long range nature of the coulomb potential it is necessary to formulate the problem from the point of view of many-body perturbation theory. The problem is necessarily quantum mechanical because of the short range divergence of the classical integrals for the electron-proton interaction. However, considerable insight into the form of the quantum-mechanical problem can be obtained from the classical perturbation theory since it can be worked out at least formally, in complete detail. The result of perturbation theory is that the coulomb problem is replaced with a new problem involving the screened coulomb potential.

Chapter II. Development of the Problem

A. Difficulties Encountered With Standard Procedures

Further refinement of the Saha procedure outlined in Ch. I requires that we make explicit use of the fact that the energy levels of the system are perturbed from those of an isolated atom. There we were only interested in terminating the partition function sum over the states of isolated atoms. At moderate densities even low lying states can be significantly shifted from their isolated atom positions, and at sufficiently high density there may be no bound states at all. (Provided crystallization does not occur.) This perturbation of low lying bound states has been obtained from the confined atom model and by calculating the energy levels of the static screened coulomb potential (SSCP) Eq. (I.8a) from perturbation theory.^{1-3,15,16} The partition function now becomes a sum over a finite number of perturbed bound states. The number of bound states in the first case depends on the density of composite particles and in the second case on the density of charged particles and the temperature.

The use of the SSCP is on much firmer theoretical grounds than is the potential which becomes infinite for $r \geq r_0$, at least at moderate density. It is the use of the SSCP in calculating the EOS that we wish to analyze further. Consider a system composed of electrons, protons, and hydrogen atoms. The usual procedure is to write the free energy as a sum of terms,¹⁶

$$\begin{aligned}
F = & - N_e kT \ln \frac{eV}{N_e} (2\pi m_e kT)^{3/2} - N_p kT \ln \frac{eV}{N_p} (2\pi m_p kT)^{3/2} \\
& - N_H kT \ln \frac{eV}{N_H} (2\pi m_H kT)^{3/2} \sum_{n,l} (2l+1) e^{-E_{nl}/kT} \\
& - kTV/12\pi\lambda_D^3
\end{aligned} \tag{II.1}$$

where the E_{nl} are the eigenvalues of the SSCP. The numbers of e , p , and H can be found by minimizing the free energy. Other thermodynamic properties are then obtained through the relations

$$P = - \left(\frac{\partial F_{\text{equil}}}{\partial V} \right) \{N_i\}_{\text{equil}}, T \tag{II.2a}$$

$$S = - \left(\frac{\partial F_{\text{equil}}}{\partial T} \right) \{N_i\}_{\text{equil}}, V \tag{II.2b}$$

The Debye length, λ_D , that goes into the calculation of the eigenvalues, E_{nl} , depends only on the number of unbound electrons and protons in the system. So here again we are treating the bound state problem and the coulomb gas problem as separable. Since the number of bound states in the SSCP is finite the partition function does not diverge, however it is a discontinuous function of the screening length (see Fig. B-2) and hence, of V and T . This can be seen by noticing that when V or T are such that incremented changes in their values produce or destroy a bound state the partition function changes discontinuously by the amount $2l+1$. This has the undesired result that the free energy and pressure are discontinuous functions of V and T .

B. The Importance of Continuum States

What are the approximations that have produced this unphysical discontinuity in the thermal properties? First, we note that we have taken the partition function to be a sum over bound states, whereas, the complete partition function is defined as

$$Z = \text{Tr} e^{-\beta H}, \quad (\text{II.3})$$

which is a sum over continuum (scattering) states as well as bound states. Beth and Uhlenbeck^{17,18} and Gropper¹⁹ have shown that the partition function can be written as a sum over bound states and a momentum integral over the phase shifts of the potential. For two-body interactions the result for Boltzmann particles is

$$Z_{\text{int}} = \lambda_{\text{ab}}^{-3} (\text{Tr} e^{-\beta(H_0 + u)} - \text{Tr} e^{-\beta H_0}) = \sum_l (2l + 1) \left(\sum_n e^{-E_{nl}/kT} + \frac{1}{\pi} \int_0^\infty dp \frac{d\delta_l(p)}{dp} e^{-p^2/2\mu kT} dp \right) \quad (\text{II.4a})$$

where H_0 is the operator $p^2/2\mu$ (relative motion),

$$\lambda_{\text{ab}} = \sqrt{2\pi\hbar^2 / (m_a + m_b)kT}, \quad (\text{II.4b})$$

p is the momentum, and $\delta_l(p)$ is the phase shift due to the potential.

At low temperature for a potential having bound states the probability that a two-body bound pair is formed, becomes very large and the ground state term dominates Z_{int} , so that one can safely ignore the phase shift contribution to the two-body partition function (depending on the temperature and density, three-body bound states and energy levels may or may not be important). At sufficiently high temperature

the probability that bound pairs exist becomes very small and Z_{int} is dominated by the integral of Eq. (II.4a).

If one retains only the first term of Eq. (II.4a) for an attractive potential $gu(r)$, as g is decreased the bound states, E_{nl} , below zero energy move up into the continuum. As each state reaches zero energy, a partition function which includes only the bound-state sum will be discontinuous. These discontinuities would extend to all the thermal properties, such as pressure and specific heat. However, if we integrate Eq. (II.4a) by parts an interesting fact becomes apparent.^{20,21} From Levinson's theorem we know that the phase shift $\delta_l(p)$ at $p = 0$ is given by $n_l\pi$, where n_l is the number of bound states of angular momentum l . Thus Eq. (II.4) becomes

$$Z_{\text{int}} = \sum_l (2l+1) \sum_n (e^{-E_{nl}/kT} - 1) + \frac{2\mu kT}{\pi} \int_0^\infty \sum_l (2l+1) p \delta_l(p) e^{-p^2/2\mu kT} dp \quad (\text{II.5})$$

where the double sum in the first term ranges only over bound states.

Equation (II.5) gives the complete interaction partition function of the system and can be used to demonstrate two points. First, the zero energy part of the phase-shift contribution to the partition function exactly cancels the zero-energy part of the bound state sum, removing the discontinuity, so Z_{int} remains continuous as a function of the interaction strength. Second, there is an additional important contribution from non-zero energy phase shifts.

This full form of the interacting-particle partition function is essential to a complete and correct calculation of the thermodynamic functions of the system. Obviously, current methods which include only

the bound state sum in Eq. (II.4a) are in error, and introduce discontinuities into the thermodynamic state function at those points where the bound state levels pass into the continuum. Accurate thermodynamic results for such a system require that the bound-state levels E_{nl} and the phase shifts δ_l both be calculated in the same manner and to the same degree of accuracy.

For an ordinary gas we could just replace the sum over bound states appearing in Eq. (II.1) with the total partition function (II.4a). However, the coulomb gas presents some special problems. The bound state sum for the coulomb potential is undefined since it has an infinite number of bound states. If we use the SSCP, the partition function exists, but, two difficulties remain. One is the way the plasma electrostatic interaction is added to Eq. (II.1). This term in some sense must come out of the phase shift part of the partition function so that we are including an approximation to it in the partition function which is different from the last term of the equation. In addition to this, the screening length that we need to know to calculate the eigenvalues and phase shifts requires that we know the number of free charges in the system. If we substitute Eq. (II.4a) in Eq. (II.1) then N_H is the total number of electron-proton pairs that are interacting i.e. all those electrons that are within the effective range of the potential, r_D , to a proton including both bound and scattering states. If we adopt the usual convention of defining particles in states of negative energy as bound, then the number of bound states is given by

$$N_H^{bs} = N_H \sum_{n,l} (2l+1) e^{-E_{nl}/kT} / Z_{int} \quad (II.6)$$

However, this function is discontinuous and the thermal properties are still discontinuous. Of course, if one could justify associating the -1 of Eq. (II.5) with the exponential, this discontinuity would disappear. Rather than putting further effort into justifying the present approach to the problem, we will take these difficulties as being symptomatic of additional fundamental errors in the procedure. In fact, if we work from the grand partition function these difficulties do not arise.

C. The Quantum-Mechanical Partition Function and the Formation of Bound Pairs

Consider a one-component gas and assume

$$\frac{p}{kT} = b_1 z + b_2 z^2 + b_3 z^3 + \dots \quad (II.7a)$$

where the b's are undetermined constants and

$$z = (2s+1)\lambda^{-3} e^{\mu/kT} \quad (II.7b)$$

is called the activity,*

$$\lambda = \sqrt{2\pi\hbar^2/mkT} \quad (II.7c)$$

is the deBroylie wavelength, and s is the spin. If Eq. (II.7) is substituted in Eq. (I.1) there results

$$\Xi = e^{pV/kT} = e^V \sum_{j=1}^{\infty} b_j z^j = 1 + \sum_{N \geq 1} \left(\frac{Z_N V^N}{Z_1^N} \right) z^N \quad (II.8)$$

where Z_N is the canonical partition function for N particles in the Volume V. If like coefficients are equated the following relations between the b's and the Z_N 's are obtained:

* Actually the standard definition of the activity is the ratio Z/n , which is unity for an ideal gas.

$$b_1 = 1 \quad (II.9a)$$

$$b_2 = \frac{1}{2V} \lambda^6 [2Z_2 - Z_1^2] / (2s + 1)^2 \quad (II.9b)$$

$$b_3 = \frac{1}{3V} \lambda^9 [3Z_3 - 3Z_2 Z_1 + Z_1^3] / (2s + 1)^3 \quad (II.9c)$$

$$b_4 = \frac{\lambda^{12}}{4V} [4Z_4 - 4Z_3 Z_1 - 2Z_2^2 + 4Z_1^2 Z_2 - Z_1^4] / (2s + 1)^4 \quad (II.9d)$$

⋮

The activity can be eliminated from Eq. (II.8) through the relations

$$N = z \left(\frac{\partial \ln Z}{\partial z} \right)_{V,T} \quad (II.10a)$$

$$n = \frac{N}{V} = z \frac{\partial}{\partial z} \left(\frac{p}{kT} \right) = z + 2b_2 z^2 + \dots \quad (II.10b)$$

The usual procedure for doing this is to assume that the activity can be expanded in a power series of the density, the solution of which is the virial expansion in powers of the density

$$\frac{p}{kT} = n + \sum_{j=2}^{\infty} B_j n^j \quad (II.11a)$$

where $B_2 = -b_2 \quad (II.11b)$

$$B_3 = 4b_2^2 - b_3 \quad (II.11c)$$

⋮

This expansion works very well for gases whose potential is weak such as a gas of H_2 molecules. However, if we consider a hydrogen gas at a temperature of 7000°C, the system is composed almost entirely of hydrogen atoms. If we now apply Eq. (II.11a) to this gas through terms

in n^2 , expanding in the initial density of atoms, and lower the temperature, bound states start to form and B_2 begins to increase exponentially with temperature. At sufficiently low temperature the pressure given by Eq. (II.11a) becomes negative, whereas, at low density (and at temperatures of a few hundred degrees) we expect that only molecules are present and the pressure should be an expansion in the density of molecules. Temporarily assume that b_3, b_4 , etc., are zero.* This is equivalent to truncating Eq. (II.9a) at the quadratic term. A summation of all the terms in Eq. (II.11a) gives

$$\frac{P}{KT} = \frac{1}{2} \{n_H - \frac{1}{4B_2} [\sqrt{1 - 8n_H B_2} - 1]\} \quad (\text{II.12})$$

Eq. (II.12) is interesting. It gives the usual virial expansion in terms of N_H at high T and noting that at low temperature the Saha equation (obtained from the conditions $2\mu_H = \mu_{H_2}$) gives $B_2 = N_{H_2} N_H^2 = -1/K$, where K is the equilibrium constant, Eq. (II.12) becomes

$$\frac{P}{KT} = \frac{1}{2} \{n_H + \frac{K}{4} [\sqrt{1 + 8n_H K} - 1]\} \quad (\text{II.13})$$

This is just the pressure expression²² for a two component ideal gas that can undergo associative-dissociative reactions. The activity in this approximation obtained by inverting Eq. (II.10b) and retaining the + sign since the activity must be real and positive is

$$z = \left\{ -1 + \sqrt{1 + 8n_H b_2} \right\} / 4b_2 \quad (\text{II.14})$$

* Although the $b_j = 0$ for $j \geq 3$, the $B_j \neq 0$ i.e., $B_3 = 4b_2^2$, etc.

At low T , $z \rightarrow \sqrt{n_H/2b_2}$ so that $z \ll n_H$. Equation (II.12) can also be derived from the canonical partition function. This is described in Appendix A.

D. The Classical Partition Function

Now consider the relations (II.9) in greater detail. We first discuss the classical theory. Mayer²³ has studied the cluster coefficients in great generality for classical systems. The partition function can be written as

$$Z_N = \frac{\lambda^{3N}}{N!} \int_V \dots \int e^{-U/kT} d\vec{r}_1 \dots d\vec{r}_N \quad (\text{II.15})$$

Where U is the potential energy which is assumed to be pair-wise additive so that

$$U = \sum_{1 \leq i < j \leq N} U(r_{ij}) \quad (\text{II.16})$$

He defines the function

$$f_{ij} \equiv e^{-U(r_{ij})/kT} - 1 \quad (\text{II.17})$$

where $U(r_{ij})$ is the potential between particles i and j .

Using this definition the partition function can be written

$$Z_N = \frac{\lambda^{3N}}{N!} \int_V \dots \int (1 + \sum_{ij} f_{ij} + \sum_{ijkl} f_{ij} f_{kl} + \dots) d\vec{r}_1 \dots d\vec{r}_N \quad (\text{II.18})$$

If for example, there are three particles in the volume V , the connected terms of Eq. (II.18) can be represented diagrammatically as in Fig. II.1. These diagrams are mathematical rather than physical.

Fig. II-1

The diagram labeled d is referred to as an irreducible cluster. These ^{at least} are all those diagrams for k particles which have/two entirely independent paths which do not cross at any circle. The irreducible cluster integrals, β_k , are that part of the configurational integral in Eq. (II.15) for k particles which includes only the irreducible clusters. The b_j are related to the β_k through the relation

$$b_j = \frac{1}{j^2} \sum_m \sum_{k=1}^{j-1} \left(\frac{j\beta_k}{m_k!} \right)^{m_k} \quad (\text{II.19})$$

where the summation is over all sets m subject to the condition

$$\sum_{k=1}^{j-1} k m_k = j - 1 \quad (\text{II.20})$$

The factorization of the cluster coefficients fails with terms of order $\hbar^4$ in the quantum mechanical theory.²⁴

The first few b_j 's are explicitly

$$b_2 = \beta_1/2 \quad (\text{II.21a})$$

$$b_3 = \frac{\beta_1^2}{2} + \frac{\beta_2}{3} \quad (\text{II.21b})$$

$$b_4 = \frac{2}{3} \beta_1^3 + \beta_1 \beta_2 + \frac{1}{4} \beta_3 \quad (\text{II.21c})$$

Substitution of (II.19) into (II.11) results in

$$\frac{PV}{NkT} = 1 - \sum_{k \geq 1} \frac{k}{k+1} \beta_k n^k \quad (\text{II.22})$$

The pressure depends only on the irreducible diagrams, all other diagrams have cancelled out. The classical virial coefficient is given by

$$B_k = - \frac{k-1}{k} \beta_{k-1} \quad (\text{II.23})$$

It is apparent that the neglect of b_3 , b_4 , etc. when $b_2 \gg 1$, if the relations (II.21) were valid, could not be justified since using the result $z \approx \sqrt{n/2b_2}$ gives

$$\begin{aligned} \frac{P}{kT} &\approx \sqrt{\frac{n}{2b_2}} + \frac{1}{2} n + \sqrt{\frac{b_2}{2}} n^{3/2} + \dots \\ &\approx \frac{1}{2} n [1 + 2\sqrt{\frac{b_2}{2}} n + \dots] \end{aligned} \quad (\text{II.24})$$

The correction term to the ideal gas pressure becomes large at low T unless the density is very low. However, there is no reason to take these relations very seriously in this region, since we are specifically considering a quantum mechanical situation where a bound-pair is formed in a potential which has only a few strong binding states. The classical approximation in such a case would predict much larger virial coefficients than the quantum theory, in fact, for a purely attractive potential the classical virial coefficients would be undefined.

E. Factorization of the Quantum-Mechanical Cluster Coefficients

The quantum mechanical evaluation of b_2 has been worked out for the Leonard-Jones potential and for hard spheres.²⁵ Procedures for calculating b_3 have been worked out from several points of view and only

recently has a procedure similar to that of Beth-Uhlenbeck been given for calculating b_3 from the phase shifts²⁶ (bound states are not included as yet). A very general procedure for calculating all the virials using the S-matrix has been given by Dashen, Ma, and Bernstein,²⁷ but it has not been applied in actual calculations. However, the moderate density we are assuming allows some approximation to be made.

At high temperature where the system has dissociated into its basic components the virial expansion in terms of the density of these components is useful. If the series is terminated at the second virial coefficient, the approximation is that only two-body interactions are important, i.e., three-body, four-body, etc. phase shifts can be ignored. This should be a good approximation at moderate density for short range potentials, since the probability that three particles are within a sphere of radius r_0 (the effective range of the potential) is small compared to the probability that two particles are in the sphere. At lower temperatures where many of the component particles are bound into the various allowed composite particles we expect that to the same approximation the two-body eigenvalues and phase shifts between all possible pairs of component, and composite particles should be sufficient.

To show how this comes out of the activity expansion consider Eq. (II.9). For Boltzmann particles, after changing to relative coordinates, Eq. (II.9b) becomes in the limit $s \rightarrow \infty$

$$b_2 = 4\pi^{3/2} \chi_\mu^3 Z_{\text{int}} \quad (\text{II.25})$$

where

$$\chi_\mu = h/\sqrt{2\mu kT}$$

where Z_{int} is given by Eq. (II.4). Equation (II.9c) can be rewritten in the form

$$b_3 = \frac{\lambda^9}{V} \left[\left(Z_3 - \frac{Z_1^3}{3!} \right) - Z_1 \left(Z_2 - \frac{Z_1^2}{2!} \right) \right] \quad (\text{II.26})$$

Remembering that Z_N is the canonical partition function for N particles in the volume V , we note that Z_3 can be written diagrammatically as,

$$Z_3 = \begin{array}{c} \text{O} \text{---} \text{O} \\ | \\ \text{O} \end{array} + \begin{array}{c} \text{O} \text{---} \text{O} \\ | \\ \text{O} \end{array} + \begin{array}{c} \text{O} \text{---} \text{O} \text{---} \text{O} \\ | \\ \text{O} \end{array} \quad (\text{II.27})$$

where the first diagram indicates all states for which three particles are simultaneously interacting, the second diagram indicates all states for which two-particles are interacting but the third is beyond the range of the potential, and the third diagram indicates states for which all three particles are separated by a distance greater than r_0 . The partition function for three particles in a box, that do not interact, is just $Z_1^3/3!$. The partition function for three particles in a box, if only two particles interact at a time is just $Z_1(Z_2 - Z_1^2/2!)$. The only effect of these diagrams in Eq. (II.27) is to cancel out the one and two-body partition function terms in Eq. (II.26). The term that remains involves all those states for which three of the component particles interact,* i.e. all those states for which three particles are in a microscopic sphere of radius r_0 . At high temperature this is just the third virial coefficient which involves three-body phase shifts of the component particles. This term is being ignored in the present study. At low

* In many-body perturbation theory this results in the linked cluster expansion. ²⁸

temperature two of the component particles are very likely to form a bound state if the potential is attractive. This bound pair then interacts with the third particle as an effective two-body interaction, with the possibility of a three particle bound state being formed at still lower temperature if the potential has a sufficiently deep well.

The interaction potential for a great variety of conditions is discussed in Hirschfelder, Curtiss, and Bird.²⁹ Since a bound-pair will in general dissociate at temperatures well below the ionization energy, the formation of excited states is not very likely, i.e., the dissociation occurs before the temperature is high enough to excite a higher state. For this reason it will be assumed that the interaction potential between the bound pair and the third particle (in the case of b_3) is the same for all states of the bound pair.

The idea here is that the density is low enough that b_3 , b_4 , etc., do not contribute appreciably to the equation of state unless at least A_2 pairs are formed, in which case, in the temperature regions where association is occurring, the b 's are much larger than they would be for a potential that has no bound states. For example, b_3 is much larger at low temperature than it would be if the attractive part of the A-A interaction were multiplied by a minus sign, which in the present approximation is assumed to be small enough that it can be ignored. This A-A bound pair is then (in the case of b_3) assumed to interact with the other A particle in the volume V (essentially infinite) as an ordinary two-body interaction. The same reasoning can be applied

for higher clusters A_3 , A_4 , etc., that can occur for the higher b 's. At low temperature the partition function is dominated by the lowest states and the approximation should become very good at least for b_3 and b_4 . For b_5 and higher cluster coefficients there are three or more unbound clusters of component particles if only an A_2 state can be formed. If A_3 or higher bound states can be formed then the approximation considered here gives essentially correct values for some of the higher coefficients at low temperature. Of course the claim that some of the higher cluster coefficients are known is not terribly interesting in itself, since at low density these are just the experimentally observed energy levels for the various atoms and molecules that can be formed in the system. The same information is included in the Saha equation. What is interesting about the present approach is that it looks at the system only in terms of its basic components and consistently calculates the equation of state from the grand partition function. This will result at the level of the current discussion in a consistent first order correction to the Saha equation.

At moderate density, where atoms and molecules are still separated by distances relatively large compared to the effective range of typical potentials, it is still a good approximation to use the unperturbed energy levels. If the temperature is high enough that appreciable numbers of ions and free electrons are present this would not be true. In this situation it is necessary to consider the internal atomic states. For hydrogen atoms, at least, it is known how to calculate the shift

of the energy levels. This will be discussed in Ch. IV. As long as the energy levels of the atoms and molecules are not density and temperature dependent the discontinuities encountered with the SSCP do not arise. The high lying levels of higher Z atoms should be treated in a manner somewhat similar to hydrogen in a more extensive study.

Returning now to Eq. (II.26) we have that

$$b_3 = \frac{\lambda^9}{V} \left[\begin{array}{c} \circ \text{---} \circ \\ | \\ \circ \end{array} \right] \quad (\text{II.28})$$

Assuming that only the A_2 -A interaction is important and that the A_2 -A potential is independent of the state of A_2 Eq. (II.28) is given, in relative co-ordinates, by

$$b_3 = \frac{\lambda^9}{V} \left(\frac{3m_A kT}{2\pi\hbar^2} \right)^{3/2} \frac{Z_{int}^{A-A}}{Z_{int}^{A_2-A}} \quad (\text{II.29})$$

where Z_{int}^{A-A} is the partition function for the A-A interaction, $Z_{int}^{A_2-A}$ is the total partition function for the A_2 -A two-body interaction. Equation (II.29) can be recast in the form

$$\begin{aligned} b_3 &= \left[\frac{2\pi\hbar^2(m_A + m_A)}{m_A m_A kT} \right]^{3/2} \left[\frac{2\pi\hbar^2(m_{A_2} + m_A)}{m_A m_{A_2} kT} \right]^{3/2} \frac{Z_{int}^{A-A}}{Z_{int}^{A_2-A}} \\ &= b_2^{A-A} b_2^{A_2-A} \end{aligned} \quad (\text{II.30})$$

where b_2^{A-A} the second virial coefficient for the A-A interaction, and $b_2^{A_2-A}$ is the second virial coefficient for the two-body A_2 -A interaction. Therefore $b_3 \ll b_2^2$ at low temperature for an attractive potential since

the interaction potential between A_2-A is in general much weaker than the interaction between $A-A$, so that $b_2^{A-A} \gg b_2^{A_2-A}$. The quantum result is much different than the classical theory in this low temperature region.

Now consider the next term b_4 . It can be written

$$b_4 = \frac{\lambda^{12}}{V} \left[\left(Z_4 - \frac{Z_1^4}{4!} \right) - Z_1 \left\{ \left(Z_3 - \frac{Z_1^3}{3!} \right) - Z_1 \left(Z_2 - \frac{Z_1^2}{2!} \right) \right\} - \frac{Z_1^2}{2} \left(Z_2 - \frac{Z_1^2}{2!} \right) - \left(Z_2 - \frac{Z_1^2}{2!} \right)^2 / 2 \right] \quad (\text{II.31})$$

Following the procedure for Z_3 we represent Z_4 diagrammatically as

$$Z_4 = \begin{array}{c} \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} \\ \text{Diagram 4} + \text{Diagram 5} \end{array} \quad (\text{II.32})$$

The diagrams represent various ways of connecting four particles (represented by circles) with lines (representing interactions). Diagram 1 shows two horizontal lines with vertical lines connecting them. Diagram 2 shows a horizontal line with a diagonal line. Diagram 3 shows two horizontal lines with a vertical line connecting them. Diagram 4 shows two horizontal lines with a vertical line connecting them. Diagram 5 shows two horizontal lines with a vertical line connecting them.

This can be written as

$$Z_4 = \left[\text{Diagram 1} \right] + Z_1 b_3 + \frac{b_2^2}{2} + \frac{Z_1^2}{2} b_2 + \frac{Z_1^4}{4!} \quad (\text{II.33})$$

The only term that survives when (II.33) is substituted in (II.31) is the term for which all particles are interacting (not necessarily with all the other particles)

$$b_4 = \frac{\lambda^{12}}{V} \left[\text{Diagram 1} \right] \quad (\text{II.34})$$

In relative co-ords this can be written

$$b_4 = \frac{\lambda^{12}}{V} \left(\frac{u_{AA} kT}{2\pi h^2} \right)^{3/2} \left(\frac{z_{int}^{A-A}}{z_{int}} \right)^2 z_{int}^{A_2-A_2} \quad (II.35)$$

The four-body interaction term has been factored into the sum over the internal states of two non-interacting atoms multiplied by their interaction states. This can be written as

$$\begin{aligned} b_4 &= \left[\frac{m_{A_2} kT}{2\pi h^2 m_A m_A} \right]^2 \left[\frac{(m_{A_2} + m_{A_2}) kT}{m_{A_2} m_{A_2}} \right] \left(\frac{z_{int}^{A-A}}{z_{int}} \right)^2 z_{int}^{A_2-A_2} \\ &= \left(\frac{z_{int}^{A-A}}{b_2} \right)^2 z_{int}^{A_2-A_2} \end{aligned} \quad (II.36)$$

Whenever there are an even number of particles in the cluster the b_n contains the factor $(z_{int}^{A-A})^{N/2}$. When one additional particle is added to the cluster the power of b_2^{A-A} remains the same, since an additional A-A pair cannot be formed.

Now consider the effect of including additional terms in Eqs. (II.7) and (II.10) using the above approximation. For terms beyond the second, the direct inversion of Eq. (II.10) becomes undesirable. In general, a numerical root solving method will be necessary. We start with the low temperature form of Eq. (II.10) and substitute the approximation

$$z \approx \sqrt{\frac{n_A}{2b_2^{A-A}}}$$

This gives

$$\frac{P}{kT} \approx \sqrt{\frac{n_A}{2b_2}} + \frac{n_A}{2} + \frac{1}{4} \frac{b_2^{A_2-A_2}}{\sqrt{2b_2}} n_A^{3/2} + n_A^2 b_2^{A_2-A_2} + \dots \quad (II.37)$$

where the A-A superscript has been dropped

Now $b_2 \gg 1$ and $\sqrt{b_2} \gg b_2^{A_2-A}$ so that the odd terms in this expansion are very small and can be ignored. Keeping terms through b_4 the next correction term to Eq. (II.37) is

$$z^2 \approx \left(-2b_2 \pm 2b_2 \sqrt{1 + \frac{4b_4}{b_2^2} n_A} \right) / 8b_4 \quad (\text{II.38})$$

$$z \approx \sqrt{\frac{n_A}{2b_2} - \frac{1}{2} \frac{b_4}{b_2^3} n_A^2} \quad (\text{II.39})$$

and

$$\begin{aligned} \frac{P}{kT} &\approx b_2 z^2 + b_4 z^4 \\ &= \frac{n_A}{2} - \frac{1}{2} b_2^{A_2-A} n_A^2 + \frac{b_2^{A_2-A}}{4} n_A^2 - \frac{1}{2} b_2^{A_2-A} n_A^3 \dots \\ &\approx n_{A_2} + n_{A_2}^2 \frac{b_2^{A_2-A}}{2} \end{aligned} \quad (\text{II.40})$$

provided the density is not too high. The low temperature form of Eq. (II.7) in the present approximation is just the virial expansion in terms of molecules to terms through the second virial coefficient. This is the expected result since at low temperature (but not too low!) the atoms should essentially all be bound into molecules. The virial expansion for molecules results at low temperature even though we considered the system from the atomic point of view. At high temperature (≈ 7000 degrees for an H_2 gas) the system should be in its decomposed state (provided ionization does not occur) so that in the present approximation to terms linear in the density, the result is the usual virial expansion for atoms.

From the above arguments it is clear that the usual method of looking at the equilibrium properties of a system that can undergo dissociative reactions in terms of explicit numbers of the various reactants

is unnecessary. In fact one never needs to know explicitly how the composite particles are distributed into the various bound states available to them. This procedure offers a systematic way to improve the low density Saha equation. When one looks at the system as composed as various numbers of atoms, molecules, ions, and electrons, such a systematic procedure is apparently not available. The procedure seems clear for ordinary gases at moderate density where the potential is not density and temperature dependent. When the temperature is high enough that there are free electrons in the system, then we are dealing with the SSCP for which the quantity N_A^{bs} given by Eq. (II.6) is discontinuous. This problem will be dealt with in chapters III and IV.

Chapter III. Density Expansion of the Classical Coulomb Gas

A. Introduction

At the current stage we have shown that the activity expansion provides a consistent procedure for calculating corrections to the Saha equation of ordinary gases provided the density is not too high. It has been shown that as a function of the interaction strength, the phase shift contribution to the partition function has a discontinuity which just cancels out a discontinuity in the bound state sum. This causes no difficulty at moderate density for ordinary gases, since the strength of the potential is constant. In the case of the coulomb gas, where, the potential is density and temperature dependent it is necessary that one take account of this fact. However, removal of this difficulty still leaves a discontinuity because the density of free charges that determines the screening length (which is related to the strength of the potential) is, according to the usual definition, a discontinuous function. In this chapter the classical many-body perturbation density expansion for the coulomb gas, which results from a rearrangement of the virial expansion, is reviewed.

It is clear at the outset that the formation of bound states out of a plasma can only be calculated from quantum mechanics. The classical second virial coefficient for a coulomb gas has a divergence at large r due to the long range nature of the potential and a divergence at small r due to the fact that there is no minimum energy state

and the integral diverges. The long range divergence is removed by considering the many-body shielding effects on the two-body interaction. The short range divergence is removed by quantum mechanics which introduces the uncertainty principle so that the electron-proton pair cannot coalesce. In equilibrium a coulomb gas must be electrically neutral, otherwise the charge density near the walls would be higher than at the center and a true equilibrium situation would not exist. It is the polarization of the medium rather than the effect of unbalanced charge that is of interest.

Each of the β_k in the Mayer classical development for the pressure contains a diagram in which all $k+1$ particles are connected in a ring. These diagrams are referred to as ring diagrams. The o-o diagram for B_2 is taken to be the first of these. The diagram labeled d in Fig. 1 is the next such term. Mayer¹² has shown that these diagrams give the leading terms in the coulomb correction to a classical ideal gas. This is the linearized Debye-Hückel term Eq. (1.9). In the high density limit these diagrams give the correlation energy for an ideal Fermi gas. Further progress for terms beyond the rings has been made by Meeron,³⁰ Friedman,³¹ Abe,¹³ and Brush, et al.³² The procedure due to Abe seems the most useful for the present study. He expanded the Mayer f function in powers of $u(r)$ and rearranged the virial expansion into a true perturbation expansion. The result is an infinite series of terms that resemble the classical virial coefficients for an ordinary gas interacting through the SSCP. For the coulomb gas the

virial coefficients for an electron-proton interaction diverge at small r so that the classical theory does not work. However, one can imagine a one-component system in a continuous neutralizing background, as would exist if the electrons were very degenerate and thus possessed very large kinetic energy.

To establish the uniform background consider the free energy, given by cluster integral theory, for a two-component gas of electrons and protons³²

$$\beta F = N_e F_{oe} + N_p F_{op} + V(B_{2ee} n_e^2 + 2B_{2ep} n_e n_p + B_{2pp} n_p^2) + \dots \quad (\text{III.1})$$

where $\beta = \frac{1}{kT}$, F_{oe} , F_{op} are the respective ideal gas free energies for electrons and protons, and

$$B_{2AB} = \frac{1}{2V} \iint d\tau_1 d\tau_2 (e^{-\beta U_{AB}} - 1), \quad (\text{III.2})$$

is the classical second virial coefficient. The potentials for e-e, e-p, and p-p interactions are given by

$$U_{ee} = \frac{e^2}{r}, \quad U_{ep} = -\frac{Z_p e^2}{r}, \quad U_{pp} = \frac{Z_p^2 e^2}{r}, \quad \text{respectively.} \quad (\text{III.3})$$

If the exponential in Eq. (III.2) is expanded in a Taylor series, Eq.

(III.1) can be written as

$$\begin{aligned} F = & N_e F_{oe} + N_p F_{op} - \frac{\beta}{2V^2} \left(N_e^2 - 2N_e N_p Z_p + N_p^2 Z_p^2 \right) \iint d\tau_1 d\tau_2 \frac{e^2}{r_{12}} \\ & + \left(\frac{\beta}{2 \cdot 2! V^2} \right) \left(N_e^2 + 2N_e N_p Z_p^2 + N_p^2 Z_p^4 \right) \iint d\tau_1 d\tau_2 \left(\frac{e^2}{r_{12}} \right)^2 \\ & - \left(\frac{\beta^2}{2 \cdot 3! V^2} \right) \left(N_e^2 - 2N_e N_p Z_p^3 + N_p^3 Z_p^6 \right) \iint d\tau_1 d\tau_2 \left(\frac{e^2}{r_{12}} \right)^3 \end{aligned} \quad (\text{III.4})$$

The first integral in Eq. (III.4) falls out because of electrical neutrality. Now imagine that $Z_p \rightarrow 0$ as $N_p \rightarrow \infty$ in such a way as to keep the product $Z_p N_p$ constant. All the terms involving $Z_p^2 N_p$, $Z_p^3 N_p$, etc. vanish. In addition, since the background has been converted into a fixed continuum, the ideal-gas free energy, $N_p F_{op}$, also must vanish. The result is

$$N_p F_{os} = N_p^2 \left(\frac{e^2}{2 \cdot 2! V} \right) \int d\tau \left(\frac{e}{r} \right)^2 + \frac{N_p^2}{2V} \sum_{m=3}^{\infty} \frac{(-1)^m}{m} \int d\tau \left(\frac{e e^2}{r} \right)^m + \dots \quad (\text{III.5})$$

Eq. (III.5) now involves only one-component in a fixed continuum neutralizing background.

For use in the following discussion make the definition

$$S = \sum_{j=2}^{\infty} \frac{B_{j-1} n^j}{j}, \text{ where } n = N/V. \quad (\text{III.6})$$

The free energy and pressure in terms of S are given by the cluster integral theory as

$$\frac{F}{NkT} = \ln \frac{n}{e} \left(\frac{2\pi n^2}{NkT} \right)^{3/2} - S/n \quad (\text{III.7})$$

$$\frac{P}{kT} = n + S - n \frac{\partial S}{\partial n} \quad (\text{III.8})$$

B. The Abs Density Expansion

A brief discussion of how the EOS, of a one-component gas in a uniform background, is obtained from the classical virial expansion is now given. In this model it is only the divergence at large r that needs to be eliminated, the short range divergence only occurs for particles of opposite charge. The discussion is similar to that given by Brush, DeWitt, and Trulio.³²

One can show using a screened potential,

$$u(r) = e^{-\epsilon r}/r, \quad (\text{III.9})$$

that the ring term in each β_{j-1} is divergent as r^{2j-3} as $r \rightarrow \infty$, $\epsilon \rightarrow 0$. All the other terms diverge less rapidly. In addition, Eq. (III.5) shows that the leading term in the expansion of β_1 in powers of u for a coulomb potential is more divergent than any of the other terms at large r . The next higher term is logarithmically divergent and higher terms are convergent. In a similar way it is found that the leading term in the expansion of the ring term of each β_{j-1} is the most divergent at large r . Now replace each β_{j-1} by its most divergent part, which involves j coulomb potentials interacting in a ring, and calculate the sum of Eq. (II.6). If this sum exists it is expected that it gives the leading correction term to an ideal gas. Other correction terms are expected to be obtained by summing less divergent types of terms. The correctness of this procedure can only be verified by working out additional terms to verify that an ordered expansion in some characteristic parameters is obtained.

The most divergent part of the β_{j-1} is given by

$$\beta_{j-1} = \frac{(-1)^j j[(j-1)!/2]}{j!V(kT)^j} \int \dots \int d\vec{r}_1 \dots d\vec{r}_j u(r_{12})u(r_{23}) \dots u(r_{j1}) \quad (\text{III.10})$$

where $u(r_{ij}) = e^2/r_{ij}$, the quantity $(j-1)!/2$ is the number of ways the j particles can be placed on a ring, and the factor $(kT)^j$ arises from the expansion of the f function. The integral of Eq. (III.10) can be

obtained by Fourier analysis. If the Fourier integral is defined as

$$u(\mathbf{r}) = \frac{V}{(2\pi)^3} \int d\mathbf{k} u(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}} \quad (\text{III.11})$$

then for the screened potential, Eq. (III.9),

$$u_{\epsilon}(\mathbf{k}) = \frac{1}{V} \int d\mathbf{r} u_{\epsilon}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} = \frac{4\pi e^2}{V(k^2 + \epsilon^2)} \quad (\text{III.12})$$

Substitution of Eq. (III.11) and Eq. (III.12) into Eq. (III.10) gives

$$\beta_{j-1} = \frac{(-1)^j V}{4\pi^2} \left(\frac{4\pi e^2}{kT} \right)^j \int_0^{\infty} \frac{dk k^2}{(k^2 + \epsilon^2)^j}, \quad (\text{III.13})$$

where the delta function,

$$\delta(\mathbf{k}) = \frac{1}{(2\pi)^3} \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (\text{III.14})$$

has been used.

Substitution of Eq. (III.13) into Eq. (III.6) gives

$$\frac{S}{N} = \frac{F_{\text{ring}}}{NkT} = \frac{V}{4\pi^2} \sum_{j=2}^{\infty} \frac{(-1)^j \lambda_D^{-2j}}{2^j} \int_0^{\infty} \frac{dk k^2}{(k^2 + \epsilon^2)^j} \quad (\text{III.15})$$

where $\lambda_D = \left(\frac{4\pi e^2 N}{kT} \right)^{-1/2}$.

If the summation is performed before the integration, it can be shown that in the limit $\epsilon \rightarrow 0$, i.e., for the coulomb potential, that

$$S = \frac{1}{12\pi\lambda_D^3} = \frac{n\lambda}{3} \quad (\text{III.16})$$

The one-component result for the ring terms can be generalized to many components by use of the multinomial expansion. For a two-component

gas, for instance, Eq. (III.4) gives the term $(N_e + Z_p^2 N_p)^2$ multiplying $f(e/r)^2$. The similar term from $\beta_{2,ees}, \beta_{2,eep}, \beta_{2,pep}, \beta_{2,ppp}$ would be $(N_e + Z_p^2 N_p)^3$. The multicomponent S is related to the screening length through Eq. (III.16), however, the screening length now involves many components and is given by Eq. (II.8b). The "ring sum" gives the same correction to the ideal gas as the linearized Debye-Huckel theory.

A general procedure for summing the remaining terms in the expansion in powers of u has been given by Abe.¹³ The terms in the expansion for each β_k involve integrals which diverge as $r \rightarrow 0$. This is a result of the expansion procedure and Abe collects terms in such a manner as to avoid this difficulty. The next correction beyond the "ring term" is

$$S_2 = 2\pi^2 \int_0^\infty r^2 dr [e^{-\beta u_s} - 1 + \beta u_s - \frac{(\beta u_s)^2}{2}] \quad (\text{III.17})$$

where u_s is the SSCP. This is related to the second virial coefficient of the SSCP according to

$$\begin{aligned} \frac{S_2}{n} &= -B_2 + 2\pi \int_0^\infty (\beta u_s - \beta^2 \frac{u_s^2}{2}) r^2 dr \\ &= -B_2 + \frac{2\pi(\epsilon_1 \epsilon_1) \lambda_D^2}{kT} - \frac{\pi}{2} \left(\frac{\epsilon_1 \epsilon_1}{kT} \right)^2 \lambda_D \end{aligned} \quad (\text{III.18})$$

where the term in λ_D is subtracted off because of the assumption of electroneutrality (this is unnecessary for many component systems) and the second term was already included in the ring sum. The integral in Eq. (III.17) has not been obtained in closed form. For $\Lambda \ll 1$ it can be expanded in powers of Λ and $\Lambda \log \Lambda$ according to

$$\frac{S_2}{n} = \Lambda^2 \left(\frac{\log 3}{12} + \frac{\gamma}{6} - \frac{11}{72} \right) + \frac{\Lambda^2 \log \Lambda}{12} + o(\Lambda^3), \quad (\text{III.19})$$

where $\gamma = 0.5772$ is Euler's constant. This term is higher order than the ring term. For $\Lambda \gg 1$ the expansion becomes

$$\frac{S_2}{n} = -\frac{\Lambda}{8} + \frac{1}{2} + \text{smaller terms} \quad (\text{III.20})$$

In this limit S_2/n is of the same order as the ring term but the constant multiplying Λ is only 3/8 as large.

The next term in the series resembles the third virial coefficient for the SSCP. It is

$$\begin{aligned} \frac{S_3}{n} = & \frac{n^2}{3!V} \iiint d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \{ \mathcal{W}_0(x_{12}) \mathcal{W}_2(x_{23}) \mathcal{W}_2(x_{31}) \\ & + \mathcal{W}_2(x_{12}) \mathcal{W}_2(x_{23}) \mathcal{W}_2(x_{31}) \} \end{aligned} \quad (\text{III.21a})$$

where

$$x_{ij} = r_{ij}/\lambda_D, \quad (\text{III.21b})$$

$$\mathcal{W}_0 = -\beta u_S = -\Lambda e^{-X}/X \equiv -q(X) \quad (\text{III.21c})$$

$$\mathcal{W}_2 = e^{-q} - 1 + q \quad (\text{III.21d})$$

This nine-fold integration can be immediately reduced to six by changing to the variables $\vec{r}_1/\lambda_D$, $\vec{x}_{12} = (\vec{r}_1 - \vec{r}_2)/\lambda_D$, $\vec{x}_{13} = (\vec{r}_1 - \vec{r}_3)/\lambda_D$. Integration over $\vec{r}_1/\lambda_D$ gives a factor V so that

$$\begin{aligned} \frac{S_3}{n} = & \frac{1}{3\Lambda^2} \iint \frac{d\vec{x}_{12} d\vec{x}_{13}}{(\pi\Lambda)^2} \{ \mathcal{W}_0(x_{12}) \mathcal{W}_2(x_{23}) \mathcal{W}_2(x_{13}) \\ & + \mathcal{W}_2(x_{12}) \mathcal{W}_2(x_{23}) \mathcal{W}_2(x_{13}) \} \end{aligned} \quad (\text{III.22})$$

Substitution of Eqs. (III.21c) and (III.21d) into (III.22) shows the S_3 is related to B_3 according to

$$\begin{aligned} \frac{S_3}{n} = & -\frac{B_3}{2} - \frac{3}{3!n^2 A^2} \iint d\vec{x}_{12} d\vec{x}_{13} q(x_{12})q(x_{31})(e^{-q(x_{23})} - 1) \\ & - \frac{2}{3!n^2 A^2} \iint d\vec{x}_{12} d\vec{x}_{13} q(x_{12})q(x_{23})q(x_{31}) \end{aligned} \quad (\text{III.23})$$

The Abe procedure can also be generalized to multicomponent gases. The two-component result for the free energy with terms through S_2 is

$$F = F_{\text{os}} + F_{\text{op}} - \frac{kTV}{12\pi\lambda_D^3} - kTV(S_{2ee} + 2S_{2ep} + S_{2pp}) \quad (\text{III.24})$$

where S_{2ee} , S_{2ep} , S_{2pp} are the S_2 contributions for e-e, e-p, and p-p interactions as given by Eq. (III.18). However, as already pointed out S_{2ep} is undefined. This divergence can be removed by replacing the classical virial coefficient with its quantum counterpart as given by Eqs. (II.25) and (II.4). With the eigenvalues and phase shifts of the SSCP we can calculate a value for S_{2ep} which is always finite, although very large at low temperature. This will lead to unphysical negative pressures if the density expansion is used. However, it presents no difficulty for the activity expansion since the arguments of Ch. II indicate that for a large S_{2ep} the activity expansion will recognize that most of the free-charges in the system have combined into hydrogenic bound states. The activity expansion for an electron-proton gas will be developed in Chapters IV and V.

C. Use of the SSCP in EOS Calculations

The use of the SSCP is rigorously justified in regions where the classical approximation is valid, which in general means at high temperature where a large number of states contribute to the partition function so that it can be replaced by an integral. However, for a coulomb gas, the classical approximation is not justified at temperatures $> R_{yd}$. This is because the classical distance of closest approach becomes less than the de Broyle wavelength and wave-mechanical corrections are present. However, the moderate density of the present study, this is not important since the total correction to an ideal gas is small at these temperatures.

At high temperatures the screening length will decrease with decreasing temperature according to Eq. (I.8b) until atoms start to form in which case the screening length should increase very rapidly with further decrease of the temperature. When this happens even fairly high states are essentially unperturbed from their hydrogenic positions. Since there is always some free charge present, S_{2ep} remains a well defined quantity even though very high levels are essentially those of the isolated hydrogen atom.

There is one aspect of the problem that the static potential cannot account for; that is

the finite lifetime of excited states. A more rigorous potential would have imaginary parts that account for this effect. This has been investigated by Nakayama and DaWitt³³ who express the dynamic screened coulomb potential as a four-dimensional Fourier transform. In

the static limit this potential becomes the SSCP. In addition, they derive the quantum mechanical form of S_2 . Their result resembles the quantum-mechanical second virial coefficient for the SSCP. The use of the SSCP and the quantum generalization of the Abe S_2 , therefore, seems well justified. A more rigorous calculation would be much more involved.

The quantum-mechanical generalization of the Abe classical perturbation expansion has been worked out for the ring terms and for a few additional terms. A more extensive discussion is given in Ch. V. This work has been done almost exclusively by H. E. DeWitt³⁴⁻³⁶ and W. Ebeling.³⁷⁻³⁹ However, a complete calculation that will take into account the formation of atoms and molecules has not been given. Ebeling obtains some terms in the perturbation expansion which include the effect of bound states. In Appendix D the second virial coefficient for the SSCP, obtained by calculating eigenvalues and phase shifts, is compared with these calculations.

D. Summary

It has been shown thus far how to generalize the Abe procedure so that it is well behaved for multi-component coulomb gases, in the range where the virial expansion in terms of the basic components is useful, i.e., very few bound pairs exist. The screening length in this case only depends, in the case of a hydrogen plasma, on the total number of electrons and protons in the system. When many atoms are formed the screening length must be modified to account for the fact that bound pairs contribute very little to the screening. However, the discontinuity associated with the screening length, pointed out in Ch. II, appears in this case.

Chapter IV. Activity Expansion of the Classical Coulomb Gas

A. Introduction

In Ch. II it was shown that the formation of bound aggregates of the component particles is naturally accounted for in the activity expansion of $\ln \mathcal{Z}$. The classical $\ln \mathcal{Z}$ is obtained by substituting Eq. (II.19) into Eq. (II.8). However for the coulomb gas, as discussed in Ch. III, each of the β_k is divergent and it is necessary to sum over them in such a way that the result is finite. The density expansion for the coulomb gas was obtained by expanding the Mayer f functions, that appear in the virial expansion, in powers of the potential and then collecting terms in such a manner as to obtain a true perturbation expansion. The virial expansion in terms of the irreducible cluster diagrams was obtained from the ordinary activity expansion using the assumption that the activity is a power series in the density. One could question whether the Mayer and Abe procedure for removing the long range divergence of the cluster integrals, by proper reordering of the virial expansion, gives the same result as a similar reordering of the ordinary activity expansion into a true perturbation expansion in the activity, prior to eliminating the activity.

It is shown in Ch. III that the sum

$$S(z) = \sum_{j=2}^{\infty} \frac{\beta_{j-1} z^j}{j} \quad (\text{IV.1})$$

is finite and a perturbation procedure for evaluating S is given. In

addition to the irreducible diagrams, $\ln \Xi$ involves a very large number of reducible diagrams i.e., those terms that involve various numbers of β_k multiplied together. In this chapter it will be shown that the entire $\ln \Xi$ can be generated from the function $S(z)$. The result of this is that the perturbation expansion of $S(n)$, which is described in Ch. III, can be taken over without change to obtain the perturbation expansion of $\ln \Xi$. All the summation procedures discussed above are applicable, the only change being that the density is everywhere replaced by the activity. As a consequence the screening length is now given by

$$\lambda_D = \left[\frac{4\pi e^2}{kT} \sum_j \epsilon_j^2 z_j \right]^{-1/2} \quad (\text{IV.2})$$

where z_j is the activity of component j . At high temperature $z_j \rightarrow n_j$, so that the screening length defined by either Eq. (I.8b) or (IV.24) are the same. At low temperature $z \approx \sqrt{n/2b_2}$ so that the screening length becomes very large, as expected. Equation (IV.2) has the important result that the screening length is a continuous function of V and T since the cluster coefficients involve the total Z_{int} which is a continuous function.

B. A Generating Function for $\ln \Xi$

Consider all those terms in the expansion of $\ln \Xi$ that involve two cluster integrals multiplied together. Their contribution to $\ln \Xi$ is

$$\chi_2 = \sum_{j=3}^{\infty} b_{j,2} z^j \quad (\text{IV.3a})$$

where

$$2b_{3,2} = \beta_1 \beta_1 \quad (\text{IV.3b})$$

$$2b_{4,2} = \beta_2 \beta_1 + \beta_1 \beta_2 \quad (\text{IV.3c})$$

$$2b_{5,2} = \beta_3 \beta_1 + \beta_2 \beta_2 + \beta_1 \beta_3 \quad (\text{IV.3d})$$

$$2b_{6,2} = \beta_4 \beta_1 + \beta_3 \beta_2 + \beta_2 \beta_3 + \beta_1 \beta_4 \quad (\text{IV.3e})$$

$\vdots$

The $b_{j,2}$ have been written in a form which makes the sum χ_2 readily apparent. The outermost diagonal terms of each $b_{j,2}$ has a β_k in common and their contribution to χ_2 is

$$\chi_2^* = \frac{1}{2} \beta_1 z \sum_{j=2}^{\infty} \beta_{j-1} z^j \quad (\text{IV.4})$$

Summation of the similar terms from all the other diagonals gives the result

$$\chi_2 = \frac{1}{2} \left(\sum_{j=2}^{\infty} \beta_{j-1} z^j \right)^2 = \frac{z}{2} \left(\frac{\partial S}{\partial z} \right)^2 \quad (\text{IV.5})$$

Therefore, the contribution to $\ln \Xi$ of all the terms which involve two β_k multiplied together is given by the square of the derivative of the sum over those terms which involve only the reducible diagrams.

Continuing this summation procedure consider next those terms involving three cluster integrals multiplied together. Their contribution to $\ln \Xi$ is

$$\chi_3 = \sum_{j=4}^{\infty} b_{j,3} z^j \quad (\text{IV.6a})$$

where

$$b_{4,3} = \frac{2}{3} \beta_1^3 \quad (\text{IV.6b})$$

$$b_{5,3} = \frac{5}{2} \beta_1^2 \beta_2 \quad (\text{IV.6c})$$

$$b_{6,3} = 3 \beta_1 \beta_2^2 + 3 \beta_1^2 \beta_3 \quad (\text{IV.6d})$$

$$b_{7,3} = \frac{7}{2} \beta_1^2 \beta_4 + \frac{7}{6} \beta_2^3 + 7 \beta_1 \beta_2 \beta_3 \quad (\text{IV.6e})$$

⋮

At this point a more systematic procedure than that used for the previous set of terms seems desirable. This will be to subtract from χ_3 terms like

$$\chi'_{3,1} = C \beta_1^2 z^3 \sum_{j=2}^{\infty} \beta_{j-1} z^{j-1} = C \beta_1^2 z^3 \left(\frac{\partial S}{\partial z} \right) \quad (\text{IV.7})$$

where C is chosen such that remainder in χ_3 of the term corresponding to the first term of $\chi'_{3,1}$ is zero. If $C = 2/3$, then the β_1^3 term of $\chi_3 - \chi'_{3,1}$ is identically zero and

$$\chi_3 - \chi'_{3,1} = \frac{11}{6} \beta_1^2 \beta_2 z^5 + 3 \beta_1 \beta_2^2 z^6 + \frac{14}{6} \beta_1^2 \beta_3 z^6 + \dots \quad (\text{IV.8})$$

Next subtract the terms

$$\chi'_{3,2} = \frac{11}{6} \beta_1 \beta_2 z^4 \sum_{j=2}^{\infty} \beta_{j-1} z^{j-1} = \frac{11}{6} \beta_1 \beta_2 z^4 \left(\frac{\partial S}{\partial z} \right) \quad (\text{IV.9})$$

This process is repeated until all terms have been subtracted from χ_3 .

The result is

$$\begin{aligned} \chi_3 &= \chi'_{3,1} + \chi'_{3,2} + \dots \\ &= \frac{1}{6} (48 \beta_1 \beta_1 z^3 + 11 \beta_1 \beta_2 z^4 + 7 \beta_2 \beta_2 z^5 \\ &\quad + 14 \beta_1 \beta_3 z^5 + 17 \beta_1 \beta_4 z^6 + 17 \beta_2 \beta_3 z^6 \\ &\quad + 10 \beta_3 \beta_3 z^7 + 20 \beta_1 \beta_5 z^7 + 20 \beta_2 \beta_4 z^7 + \dots) \left(\frac{\partial S}{\partial z} \right) \quad (\text{IV.10}) \end{aligned}$$

The terms in Eq. (IV.10) can be further summed. In exactly the same manner as the $(\partial S/\partial z)$ terms were subtracted out of χ_3 terms like

$$\chi_{3,1}'' = \frac{4}{6} \beta_1 \left(\frac{\partial S}{\partial z} \right)^2 \quad (\text{IV.11})$$

can also be subtracted. This gives

$$\begin{aligned} \chi_3 - \chi_{3,1}'' = \frac{1}{6} (& 7\beta_1\beta_2 z^3 + 7\beta_2\beta_2 z^4 \\ & + 10\beta_1\beta_3 z^4 + \dots) \left(\frac{\partial S}{\partial z} \right) \end{aligned} \quad (\text{IV.12})$$

Repetition of this process results in

$$\begin{aligned} \chi_3 &= \chi_{3,1}'' + \chi_{3,2}'' + \dots \\ &= \left[\frac{4}{6} \beta_1 + \frac{7}{6} z\beta_2 + \frac{10}{6} z^2\beta_3 + \dots \right] \left(\frac{\partial S}{\partial z} \right)^2 \end{aligned} \quad (\text{IV.13})$$

At this point higher derivatives of S start to appear. To see this subtract from χ_3 the terms

$$\chi_{3,1}''' = \frac{z}{6} \left(\frac{\partial S}{\partial z} \right)^3 \quad (\text{IV.14})$$

This gives

$$\chi_3 - \chi_{3,1}''' = \frac{z^2}{2} (\beta_1 + 2z\beta_2 + 3z^2\beta_3 + \dots) \left(\frac{\partial S}{\partial z} \right)^2 \quad (\text{IV.15})$$

The final result is

$$\chi_3 = \frac{z}{6} \left(\frac{\partial S}{\partial z} \right)^3 + \frac{z^2}{2} \left(\frac{\partial^2 S}{\partial z^2} \right) \left(\frac{\partial S}{\partial z} \right)^2 \quad (\text{IV.16})$$

It is noted that Eq. (IV.16) can be written in more compact form according to

$$\chi_3 = \frac{z}{3!} \frac{\partial}{\partial z} z \left(\frac{\partial S}{\partial z} \right)^3 \quad (\text{IV.17})$$

This summation process can be continued for higher terms involving four β_k , five β_5 , etc. This has been done for χ_4 and χ_5 . Because the number of manipulations increases rapidly for each additional χ_n , it is impractical to carry this summation any further. However, the terms χ_4 and χ_5 can be written in the compact form

$$\chi_4 = \frac{z}{4!} \frac{\partial}{\partial z} z \frac{\partial}{\partial z} z \left(\frac{\partial S}{\partial z} \right)^4 \quad (\text{IV.18a})$$

$$\chi_5 = \frac{z}{5!} \frac{\partial}{\partial z} z \frac{\partial}{\partial z} z \frac{\partial}{\partial z} z \left(\frac{\partial S}{\partial z} \right)^5, \quad (\text{IV.18b})$$

so that, we can say with some confidence that the general result is

$$\chi_m = \frac{z}{m!} \left(\frac{\partial}{\partial z} z \right)^{m-2} \left(\frac{\partial S}{\partial z} \right)^m \quad (\text{IV.19})$$

Therefore, the entire activity series can be generated from the function $S(z)$ and its derivatives.

C. Some General Relations

The pressure can be expressed in terms of $S(z)$ according to

$$\frac{P}{kT} = z + S + \sum_{m=2}^{\infty} \frac{z}{m!} \left(\frac{\partial}{\partial z} z \right)^{m-2} \left(\frac{\partial S}{\partial z} \right)^m \quad (\text{IV.20})$$

Equation (II.10b) which relates the activity to the density becomes

$$n = z + \sum_{m=1}^{\infty} \frac{z}{m!} \left(\frac{\partial}{\partial z} z \right)^{m-1} \left(\frac{\partial S}{\partial z} \right)^m \quad (\text{IV.21})$$

The fluctuations in particle number are given by

$$\langle N^2 \rangle - \langle N \rangle^2 = z \left(\frac{\partial N}{\partial z} \right)_{V,T} = z + \sum_{m=1}^{\infty} \frac{z}{m!} \left(\frac{\partial}{\partial z} z \right)^m \left(\frac{\partial S}{\partial z} \right)^m \quad (\text{IV.22})$$

Using the relation $G = N\mu = F + PV$ we have from Eqs. (III.7) and (III.8) that

$$N\mu = NkT \ln \left[n \left(\frac{2\pi h^2}{mkT} \right)^{3/2} \right] - kT V n \frac{\partial S}{\partial n} \quad (\text{IV.23})$$

The activity is, therefore, given by

$$\begin{aligned} z &= \left(\frac{mkT}{2\pi h^2} \right)^{3/2} e^{\beta\mu} = n e^{-(\partial S(n)/\partial n)} \\ &= n e^{-(\partial S(n)/\partial n)} \end{aligned} \quad (\text{IV.24})$$

Equation (IV.24) can also be verified to be a solution of Eqs. (IV.20) and (IV.21). From Eq. (IV.24) we have that

$$dz = dn \left(1 - n \frac{\partial S(n)}{\partial n} \right) e^{-\partial S(n)/\partial n} \quad (\text{IV.25})$$

Using Eq. (IV.22) the density fluctuations are

$$\frac{\langle n^2 \rangle - \langle n \rangle^2}{\langle n \rangle^2} = \frac{1}{\left(1 - n \frac{\partial^2 S}{\partial n^2} \right)} = kT k \quad (\text{IV.26a})$$

where

$$k = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{N,T} \quad (\text{IV.26b})$$

The χ_m appearing in Eq. (IV.19) involve the operation $z \frac{\partial}{\partial z} z$ $m-2$ times on the $\left(\frac{\partial S}{\partial z} \right)^m$. The result of applying this operator repeatedly gives

$$\frac{z}{m!} \frac{\partial}{\partial z} z \left(\frac{\partial S}{\partial z} \right)^m = \frac{z}{m!} \left[\left(\frac{\partial S}{\partial z} \right)^m + m z \left(\frac{\partial S}{\partial z} \right)^{m-1} \left(\frac{\partial^2 S}{\partial z^2} \right) \right] \quad (\text{IV.27a})$$

$$\begin{aligned} \frac{z}{m!} \frac{\partial}{\partial z} z \frac{\partial}{\partial z} z \left(\frac{\partial S}{\partial z} \right)^m &= \frac{z}{m!} \left[\left(\frac{\partial S}{\partial z} \right)^m + 3m z \left(\frac{\partial S}{\partial z} \right)^{m-1} \frac{\partial^2 S}{\partial z^2} \right. \\ &\quad \left. + m(m-1) z^2 \left(\frac{\partial S}{\partial z} \right)^{m-2} \left(\frac{\partial^2 S}{\partial z^2} \right)^2 + m z^2 \left(\frac{\partial S}{\partial z} \right)^{m-1} \frac{\partial^3 S}{\partial z^3} \right] \end{aligned} \quad (\text{IV.27b})$$

$$\begin{aligned}
\frac{z}{n!} \frac{\partial}{\partial z} z \frac{\partial}{\partial z} z \frac{\partial}{\partial z} z \left(\frac{\partial S}{\partial z}\right)^n &= \frac{z}{n!} \left[\left(\frac{\partial S}{\partial z}\right)^n \right. \\
&+ 7n z \left(\frac{\partial S}{\partial z}\right)^{n-1} \frac{\partial^2 S}{\partial z^2} + 6n(n-1) z^2 \left(\frac{\partial S}{\partial z}\right)^{n-2} \left(\frac{\partial^2 S}{\partial z^2}\right)^2 \\
&+ 6n z^2 \left(\frac{\partial S}{\partial z}\right)^{n-1} \frac{\partial^3 S}{\partial z^3} + n(n-1)(n-2) z^3 \left(\frac{\partial S}{\partial z}\right)^{n-3} \left(\frac{\partial^2 S}{\partial z^2}\right)^3 \\
&\left. + 3n(n-1) z^3 \left(\frac{\partial S}{\partial z}\right)^{n-2} \frac{\partial^2 S}{\partial z^2} \frac{\partial^3 S}{\partial z^3} + n z^3 \left(\frac{\partial S}{\partial z}\right)^{n-1} \frac{\partial^4 S}{\partial z^4} \right] \quad (\text{IV.27c})
\end{aligned}$$

Putting $n = 3$ in Eq. (IV.27a) gives the contribution to Eq. (IV.20) due to terms involving three cluster integrals. Putting $n = 4$ in Eq. (IV.27b) gives the contribution of all terms involving four cluster integrals, etc. The terms of Eqs. (IV.27) that are summed in Eq. (IV.20) have characteristics that allow the sum of certain types of terms to be written in closed form. For example, the sum of all the leading terms gives

$$C_1 = \frac{\partial S}{\partial z} - 1 - \frac{\partial S}{\partial z}. \quad (\text{IV.28})$$

All the second terms appearing in the brackets of Eqs. (IV.27) have the sum

$$C_2 = \frac{\partial^2 S}{\partial z^2} \left(e^{\frac{\partial S}{\partial z}} - e^{\frac{\partial S}{\partial z}} - \frac{\partial S}{\partial z} \right). \quad (\text{IV.29})$$

Rather than summing down columns one could sum in a diagonal direction, including all those terms involving a constant power of $(\partial S/\partial z)^n$. The sum of all those terms involving $(\partial S/\partial z)^2$ and increasing powers of $(\partial^2 S/\partial z^2)$ give

$$n_1 = \frac{z}{2!} \frac{\left(\frac{\partial S}{\partial z}\right)^2}{1 - z \frac{\partial^2 S}{\partial z^2}} \quad (\text{IV.30})$$

The sum of all terms involving $(\partial S/\partial z)^3$ and increasing powers of $(\partial^2 S/\partial z^2)$ give

$$D_2 = \frac{z}{3!} \frac{\left(\frac{\partial S}{\partial z}\right)^3}{\left(1 - z \frac{\partial^2 S}{\partial z^2}\right)^3} \quad (\text{IV.31})$$

It is not explicitly displayed here but a continuation of this process indicates that one can continue to sum in this way obtaining terms which involve increasingly higher poles of $(1 - z (\partial^2 S/\partial z^2))$. This places a limit on the range of convergence of the activity series. However, there could be additional singularities inside this pole due to the terms appearing in the numerator. These terms, in general, involve more complex forms than those appearing in D_1 and D_2 . Note from Eq. (IV.26) that the fluctuations become infinite due to the singularity $1/(1 - n \partial^2 S(n)/\partial n^2)$. Therefore, the virial expansion ceases to be meaningful at the pole $1/(1 - n \partial^2 S(n)/\partial n^2)$ and the activity expansion ceases to be meaningful at the pole $1/(1 - z \partial^2 S(z)/\partial z^2)$. Since $z < n$ for an attractive potential, the virial expansion breaks down (assuming that it must eventually) before the activity expansion could possibly reach its pole. For a repulsive potential the opposite is true.

D. Comparison of the Activity and the Density Expansions for the Ring Terms

With the results given in Eqs. (IV.20-IV.22) it is now possible to directly eliminate the activity to check the virial result. For simplicity, only the ring terms will be considered. The expected result, therefore, is just the ring term given by Eq. (III.16). Only the one-component gas is discussed, but the many-component generalization is straightforward.

In this case

$$S(Z) = \frac{1}{12\pi\lambda_D^3} = \frac{1}{12\pi} \left(\frac{4\pi e^2 Z}{kT} \right)^{3/2} \quad (\text{IV.32})$$

Because of the simple Z dependence the general term is easily obtained and

$$\frac{PV}{kT} = \ln Z = VZ \sum_{m=0}^{\infty} \frac{(1 + \frac{m}{2})^{m-2}}{m!} \left(\frac{\lambda_Z}{2} \right)^m \quad (\text{IV.33a})$$

$$n = Z \sum_{m=0}^{\infty} \frac{(1 + \frac{m}{2})^{m-1}}{m!} \left(\frac{\lambda_Z}{2} \right)^m \quad (\text{IV.33b})$$

$$\frac{\langle n^2 \rangle - \langle n \rangle^2}{\langle n \rangle^2} = \frac{1}{1 - \Lambda/4} \quad (\text{IV.33c})$$

$$\lambda_Z = \frac{\beta e^2}{\lambda_D} = \left(\frac{Z}{n} \right)^{1/2} \Lambda \quad (\text{IV.33d})$$

$$\lambda_D = \left(\frac{kT}{4\pi e^2 Z} \right)^{1/2} \quad (\text{IV.33e})$$

It is apparent right away that these equations cannot always agree with the density expansion since the coefficients in the pressure series are all positive, whereas, Eq. (I.9b) predicts that $P < 0$ for $\Lambda > 6$. Also there is at most one positive root of Eq. (IV.33b) since there is only one change of sign (Descartes rule). Applying the ratio test to the series (IV.33b) and use of the Stirling approximation,

$$m! = \sqrt{2\pi m} m^m e^{-m} \quad (\text{IV.34})$$

gives

$$\frac{u_{m+1}}{u_m} = \frac{(1 + \frac{m+1}{2})^{m-1} e^{m+1} \sqrt{2\pi m} m^m (\lambda_Z/2)}{\sqrt{2\pi(m+1)} (m+1)^{m+1} (1 + \frac{m}{2})^{m-2} e^m} \quad (\text{IV.35})$$

The approximation³⁵

$$\left(1 + \frac{x}{n}\right)^n = e^x \left(1 - \frac{x^2}{2n} + \frac{x^3}{3n^2} + \dots\right) \quad (\text{IV.36})$$

is of use here. With this approximation Eq. (IV.35) becomes for large n

$$\frac{u_{n+1}}{u_n} = \frac{e^3 (1 - 3^2/2n + \dots) e(\Lambda_z/2)}{2e^2 (1 - 2^2/2n + \dots) e(1 - 1/2n + \dots)} \quad (\text{IV.37})$$

The series converges for

$$\begin{aligned} \Lambda_z &< \frac{\frac{4}{e} (1 - 2^2/2n + \dots)(1 - 1/2n + \dots)}{(1 - 3^2/2n + \dots)} \\ &= \frac{4}{e} (1 + 5/2n - \dots) \end{aligned} \quad (\text{IV.38})$$

Any truncation of the series (IV.33b) will appear to converge for Λ_z slightly greater than $4/e$. As more and more terms are included in the series this interval decreases. Because of the lower power of $(1 + n/2)$ the pressure series converges fairly rapidly.

The relation (IV.24) gives

$$z = n e^{-\Lambda/2} \quad (\text{IV.39})$$

The pressure given by Eq. (III.8) is

$$\frac{P}{kT} = n(1 - \Lambda/6) \quad (\text{IV.40})$$

This is just the Debye-Huckel result. However, Eq. (IV.33c) shows that the fluctuations become infinite at $\Lambda = 4$, i.e., $(\partial P/\partial V)_T = 0$. Eq. (IV.40) predicts, that beyond $\Lambda = 4$, $(\partial P/\partial V)_T > 0$. From (IV.33d)

$$\Lambda_z = \Lambda e^{-\Lambda/4} \quad (\text{IV.41})$$

Λ_2 has a maximum at $\Lambda = 4$ at which $\Lambda_2 = 4/e$. The fluctuations are thus found to be infinite at the point where the series (IV.33b) is at its convergence limit.

A direct numerical solution of Eq. (IV.33a and b) verifies that Eqs. (IV.39) and (IV.40) are valid for $\Lambda \leq 4$. For $\Lambda > 4$ this is no longer the solution. Instead of decreasing as predicted by Eq. (IV.39) the activity increases slowly to values greater than $4/e$. As more and more terms are added to the sum the activity increases more slowly for $\Lambda > 4$. For a very large number of terms (10^{23}) the activity will be greater than $4/e$ by a very small amount. $PV/N_0 kT$ for various numbers of terms in the sum is shown as a function of Λ in Fig. IVa. The pressure is seen to disagree with the density expansion for $\Lambda > 4$ for all values of m . The number of terms necessary to obtain the converged pressure increases with Λ . In Fig. IVa the pressure is very close to its $m = \infty$ value for the curve labeled $m = 800$. For this curve the pressure agrees with the virial expansion for $\Lambda < 4$ but for $\Lambda > 4$ the pressure is given by

$$\frac{P}{kT} = \frac{16n}{3\Lambda^2} \quad (\text{IV.4})$$

Therefore, for $\Lambda > 4$, $\partial P / \partial V = 0$. The nearly constant value of the activity for $\Lambda > 4$ means that the chemical potential is constant for all densities for which $\Lambda > 4$. The activity expansion thus predicts that a first order gas-liquid phase transition occurs at $\Lambda = 4$. Since there is no repulsive interaction to limit the compressibility the system simply collapses to zero volume so that $V_{\text{critical}} = 0$, $T_{\text{critical}} = \infty$, $P_{\text{critical}} = \infty$. Some isotherms as given by the density expansion and by the activity

Fig. IV-1. Comparison of the ring approximation given by a proper summation of the virial expansion with that obtained by a summation of the activity series prior to elimination of the density. n is the number of terms kept in Eq. (IV-33a).

Fig. IV-2. Comparison of some isotherms given by the ring approximation to the virial expansion (Debye-Huckel) with those given by the activity expansion using the ring approximation to S . The solid line corresponds to the $S = S_{\text{Ring}}$ approximation to $\ln I$.

expansion are given in Fig. IVb.

Also plotted in Fig. IVa is the Monte Carlo calculation of Brush, Sahlin, and Teller⁴⁰ (BST) for the one-component coulomb gas in a uniform background. It is essentially an exact result. It shows that the ring terms are sufficient only for $\Lambda < 0.5$ and that they give much to large net attraction near $\Lambda = 4$. It will be shown in Ch. V that the S_j are all negative and will move the pressure up toward BST. As each S_j is added the gas-liquid transition predicted here, using just the ring terms, will move out to larger Λ . If S_2 is added, the predicted value of the transition moves out to $\Lambda = 6$. Apparently, if all the S_j are included the transition will disappear since the BST calculation predicts only a gas-solid transition at $\Lambda = 2465$. Evidence of this is given by the fact that in the high density limit the sum of the leading terms of all S_j can be shown to cancel the Debye-Huckel term exactly.³² This analysis of the ring terms is also valid for the many component gas.

Chapter V. Formulation of the Problem and Results

A. Introduction

Chapters II-IV together with the many-body quantum-mechanical perturbation theory to be described in this chapter provide the basis for formulating the gaseous EOS of a given number of electrons, protons and nuclei in a specified volume. Chapter II has shown how the activity expansion, for ordinary gases, accounts for the formation of bound aggregates. Chapter III reviewed the classical many-body density expansion, which results in the replacement of the coulomb potential with the SSCP. Chapter IV showed that the classical activity expansion in terms of cluster integrals, can be completely expressed in terms of the function $S(Z)$ which, for a coulomb gas, can be calculated by the methods of Ch. III.

In this chapter it will be shown that the activity expansion for a coulomb gas involves all the cluster coefficients of an ordinary gas that interacts through the SSCP plus other terms that become small as the temperature is lowered such that the system is predominately composed of atoms and molecules. The high temperature convergence of the series depends on the parameter λ_z , the low temperature convergence depends on the magnitude of the cluster coefficients, and the intermediate temperature convergence depends upon both of these factors. An indication of the high temperature (plasma region) convergence of the multi-component quantum mechanical gas is obtained from a comparison of the

classical one-component perturbation expansion with BST. Finally, the grand partition function for an electron-proton system that is sufficient at moderate density, is given. Numerical results are presented and compared with a Saha calculation.

B. Ordered Classical Activity Expansion

It is instructive to write out a few terms resulting from the summation of the cluster integrals, as given by Eq. (IV.20), explicitly displaying the S_j components of S :

$$\frac{P}{kT} = z + S + \frac{z}{2} \left(\frac{\partial S}{\partial z} \right)^2 + \frac{z}{3!} \frac{\partial}{\partial z} z \left(\frac{\partial S}{\partial z} \right)^3 + \dots \quad (V.1)$$

where

$$S = S_{\text{Ring}} + S_2 + S_3 + \dots$$

so that

$$\begin{aligned} \frac{P}{kT} = & z + S_{\text{Ring}} + S_2 + S_3 + S_4 \dots \frac{z}{2!} \left[\left(\frac{\partial S_{\text{Ring}}}{\partial z} \right)^2 + \left(\frac{\partial S_2}{\partial z} \right)^2 \dots \right. \\ & + 2 \left(\frac{\partial S_{\text{Ring}}}{\partial z} \right) \left(\frac{\partial S_2}{\partial z} \right) + 2 \left(\frac{\partial S_{\text{Ring}}}{\partial z} \right) \left(\frac{\partial S_3}{\partial z} \right) + \dots \\ & \left. + \left(\frac{\partial S_2}{\partial z} \right) \left(\frac{\partial S_3}{\partial z} \right) + \dots \right] \\ & + \frac{z}{3!} \frac{\partial}{\partial z} z \left[\left(\frac{\partial S_{\text{Ring}}}{\partial z} \right)^3 + \left(\frac{\partial S_2}{\partial z} \right)^3 + \dots \right] + \dots \quad (V.2) \end{aligned}$$

Equation (V.2) contains all the cluster coefficients for the SSCP. From Eqs. (III.18) and (III.23) it follows that

$$S_2(z) = \frac{z^2 B_1}{2} + \frac{2\pi(\epsilon_1 \epsilon_4)^2 z^2 \lambda_D^2}{kT} - \frac{\pi}{2} \left(\frac{\epsilon_1 \epsilon_4}{kT} \right)^2 z^2 \lambda_D^2 \quad (V.3a)$$

$$\frac{\partial S_2(z)}{\partial z} = z\beta_1 + \frac{z^2}{2} \frac{\partial \beta_1}{\partial z} + \frac{2\pi(\xi_i \xi_j)}{kT} z\lambda_D^2 - \frac{9\pi}{8} \left(\frac{\xi_i \xi_j}{kT}\right) z\lambda_D \quad (V.3b)$$

$$S_3(z) = \frac{z^3 \beta_2}{3} + \text{other terms as given in Eq. (III.23)} \quad (V.3c)$$

$$\frac{\partial S_3}{\partial z} = z^2 \beta_2 + \frac{z^3}{3} \frac{\partial \beta_2}{\partial z} + \text{other terms} \quad (V.3d)$$

where for one component $\xi_i = \xi_j$

Substitution of Eqs. (V.3) into Eq. (V.2) shows that the second cluster coefficient for the SSCP is in S_2 . The third cluster coefficient is included in the terms

$$S_3 + \frac{z}{2} \left(\frac{\partial S_2}{\partial z}\right)^2 = z^3 \left(\frac{\beta_2}{3} + \frac{\beta_1^2}{2}\right) + \text{other terms.}$$

The fourth cluster coefficient is included in the terms

$$\begin{aligned} S_4 + z \left(\frac{\partial S_2}{\partial z}\right) \left(\frac{\partial S_3}{\partial z}\right) + \frac{z}{3!} \frac{\partial}{\partial z} z \left(\frac{\partial S_2}{\partial z}\right)^3 \\ = z^4 \left(\frac{\beta_3}{3} + \beta_1 \beta_2 + \frac{2}{3} \beta_1^3\right) + \text{other terms} \end{aligned}$$

Continuation of this process indicates that all the cluster coefficients of the SSCP are included in Eq. (V.2).

The generalization of Eq. (V.1) to two-components is straightforward but a large number of manipulations are required to completely work it out. It will involve the SSCP and contain the terms $b_{2,ee}$, $b_{2,ep}$, $b_{2,pp}$, $b_{3,ppp}$, $b_{3,epp}$, $b_{3,ppp}$, etc. The cluster coefficients $b_{2,ep}$, $b_{3,sep}$, $b_{3,pep}$, etc., for which bound states exist, are undefined. However, they can be replaced with their quantum mechanical equivalents, which are all finite. The quantum mechanical generalization of the terms in the expansion which do not correspond to cluster coefficients is not

immediate. Their importance, however, can be estimated by noting that wave mechanical effects are only important for $r \approx \lambda$, where λ is the thermal deBroglie wavelength. Because of this we can consider the potential to be cutoff for r_0 of order of λ , so that the classical integrals are finite. The value of r_0 can be estimated by requiring the appropriate classical cluster coefficient, with the integration ranging from r_0 to ∞ , to be equal to the numerically evaluated quantum cluster coefficient. The exactness of this procedure can only be determined by a more rigorous calculation. The ring terms do not appear as integrals and this cutoff procedure cannot be used. However, the quantum-mechanical generalization of the ^{next} two lowest such terms has been investigated and this work will be described in Section D.

In the temperature region at moderate to low density where the gas is predominately atoms and molecules $b_{2,ep}/(N a_0^3) \gg 1$, $\lambda_D/a_0 \gg 1$ and the cluster coefficients are the dominant terms (see Table V-3 and Table IV in Ref.41). Because of the large λ_D all the terms involving $S_{\text{Ring}} = 1/12\pi\lambda_D^3$ become small. Terms such as $\partial b_{2,ep}/\partial Z$, which appears in Eq. (V.3b) are small since the lowest bound states give the dominant contribution to the partition function and due to the large screening length, they are nearly independent of Z . A change in Z only effects high states appreciably, but, this produces only a small change in $b_{2,ep}$. Another way to see this is to note that the main contribution to the cutoff classical integrals comes from $r \approx r_0$ where $r_0 \ll \lambda_D$. Use of the cutoff in integrals such as the second term of Eq. (III.23) show that they are considerably

smaller, in the case of terms like $S_{3,app}$, $S_{3,eep}$ which involve the attractive SSCP, than the cluster integral that occurs in the same S_j .

This is because, in the case of $S_{3,app}$ and $S_{3,eep}$, the cluster integral involves two f -functions which are large near $r = r_0$, whereas this integral* only has one.

The fact that, at low temperatures, the grand partition function for a coulomb gas essentially involves only the cluster coefficients for the SSCP shows clearly how to obtain the many-body effect on the interaction of atoms and molecules, i.e., the coulomb potential is replaced with the SSCP in the usual perturbation procedure for calculating atomic and molecular interaction energies. When the screening length is large compared to the range of ordinary gas potentials, which is the case at moderate density, the many-body effect on them can be ignored. In the present study, therefore, the cluster coefficient can be factored into a power of $b_{2,ep}$, evaluated for the SSCP, multiplied by the appropriate second cluster coefficient of ordinary atomic and molecular gases.

At moderate density only a few of the lowest terms of Eq. (V.2) should be sufficient at all temperatures to account for the electrostatic interaction of the free charges. For the one-component classical gas BST gives an essentially exact result against which to compare

* In the two-component case $S_{3,app}$, and $S_{3,eep}$ each would include two distinct integrals of the form $\int d\vec{x}_{12} d\vec{x}_{13} q(x_{12})q(x_{31})[\exp\{-q(x_{23})\}-1]$. One would involve a Mayer f -function for an attractive interaction and the other a f -function for a repulsive interaction.

the classical perturbation result. The convergence of the classical expansion should give an indication of where the two-component quantum-mechanical calculation has broken down, since the primary effect of quantum mechanics at moderate density and temperature is to place a lower limit on integrals that involve the attractive potential. Other terms remain nearly classical.

C. Comparison with BST

The S_2 and S_3 terms of the Abe density expansion are given by Eqs. (III.17) and (III.21). The S_2 correction to the gas has been calculated numerically.⁴² This term significantly improves the agreement with BST over the Debye-Huckel term. It is of interest to investigate how higher terms in the expansion effect the agreement with BST. The only numerical information on higher terms⁴³ in the Abe expansion is for $\Lambda \gg 1$ and $\Lambda \ll 1$. The evaluation of S_3 involves a six dimensional integration. However the convolution theorem produces the following two-dimensional integral.

$$S_3(n)/n = \frac{v^3}{3! \Lambda^2 \lambda_D^9 (4\pi)^2} \left[\int \frac{d^3 k}{(2\pi)^3} \{\tilde{w}_2(k)\}^3 + 3 \int \frac{d^3 k}{(2\pi)^3} \{\tilde{w}_2(k)\}^2 \tilde{w}_0(k) \right] \quad (V.4a)$$

where

$$\begin{aligned} \tilde{w}_2(k) &= \frac{1}{V} \int d\vec{r} \, w_2\left(\frac{\vec{r}}{\lambda_D}\right) e^{i\vec{k} \cdot \vec{r}} \\ &= \frac{4\pi}{\lambda_D^3 V} \int_0^\infty \sin(kx) x (\lambda_D e^{-\Lambda e^{-x}} / x - x - \Lambda e^{-x}) dx \end{aligned} \quad (V.4b)$$

$$\tilde{w}_0(k) = \frac{4\pi\Lambda}{(k^2 + 1)} \quad (V.4c)$$

Exact evaluations of S_4 and higher terms in the expansion present more difficult numerical problems and will not be calculated here. However, in the high density limit the S_j can be shown to be given, for $j > 2$ by³¹

$$S_{j,HD}/n = -\frac{\Lambda}{4j} \frac{(2j-5)}{(2j-4)} \frac{(2j-7)}{(2j-6)} \cdots \frac{1}{2} + \frac{1}{\pi(j-2)} \int_0^\infty x^2 dx \left\{ (1 - e^{-\Lambda e^x/x}) \int_0^\infty \frac{dk \cos kx}{(1+k^2)^{j-2}} \right\} \quad (V.5)$$

The sum of the leading terms of all the S_j exactly cancels the Debye-Huckel term in the high density limit. The second term in each $S_{j,HD}/n$ can be reduced to a one-dimensional integration by means of a contour integration to evaluate the integral over k . The results for S_3 and S_4 are

$$S_{3,HD}/n = -\frac{\Lambda}{8} + \frac{1}{2} \int_0^\infty dx x^2 e^{-x} (1 - e^{-\Lambda e^{-x}/x}) \quad (V.6a)$$

$$S_{4,HD}/n = -\frac{3\Lambda}{128} + \frac{1}{8} \int_0^\infty dx x^2 (1+x) e^{-x} (1 - e^{-\Lambda e^{-x}/x}) \quad (V.6b)$$

Numerical evaluation of S_2/n , S_3/n , $S_{3,HD}/n$, and $S_{4,HD}/n$ have been made for a wide range of Λ . These results are presented in Table V-1. A characteristic of the S_j is that they are all negative, corresponding to a net repulsion, whereas, the ring terms correspond to a net attraction. At low density ($\Lambda \ll 1$) the Abe series converges rapidly and is only a small correction to the Debye-Huckel gas. At high density the leading correction to the ideal gas comes from the second term of Eq. (V.2). The sum over these terms is very slowly convergent for $\Lambda \gg 1$. $S_{3,HD}$ is seen

to be a good approximation to S_3 for $\Lambda > 5$. This suggests that $S_{4,HD}$ is at least a fair approximation to S_4 for $\Lambda > 5$. The pressure obtained from these calculations of S_2 , S_3 , and $S_{4,HD}$ are compared with BST in Fig. V-1. The ring term correction to an ideal gas gives good agreement with BST for $\Lambda < 0.5$. Addition of S_2 results in good agreement out to $\Lambda = 2$. Addition of S_3 results in good agreement out to $\Lambda = 4$ and gives fairly good agreement out to $\Lambda = 10$. The addition of $S_{4,HD}$ results in good agreement out to $\Lambda = 7$ and fairly good agreement out to $\Lambda = 14$. So it is clear that the perturbation expansion is in excellent agreement with BST for values of Λ at least as large as 7. The way in which the Abe series converges to the Monte Carlo result indicates that the range of agreement between the two calculations is much larger than can be verified by the present limited results. The Monte Carlo result always lies above the Abe expansion, the effect of adding each S_j is to bend the pressure up toward BST.

It is of interest to see how the activity expansion agrees with BST. This is shown in Fig. V-2. The activity has been eliminated by numerically solving truncated forms of Eqs. (IV.20) and (IV.21). The approximation

$$\frac{P}{kT} = z(1 + \Lambda_z/3) \quad (V.7)$$

is the lowest order correction to an ideal gas given by Eq. (V.2) it is labeled A. It gives agreement with BST for $\Lambda < 0.5$. This is the same as that obtained with the Debye-Hückel term in the density expansion. The reason for this is that, as described in Ch. IV, the Debye-Hückel

Table V-1. Classical S_2/n and S_3/n for various values of Λ . Values of $S_{3,HD}/n$ and $S_{4,HD}/n$ obtained from the high density approximation are also given.

Λ	S_2/n	S_3/n	$S_{3,HD}/n$	$S_{4,HD}/n$
0.04	-3.9249-4	-2.5654-6	+7.7382-4	2.9220-4
0.08	-1.2575-3	-1.6426-5	1.4448-3	5.5840-4
0.12	-2.4198-3	-4.6693-5	2.0285-3	7.7317-4
0.16	-3.8309-3	-9.5923-5	2.5354-3	9.6959-4
0.24	-7.2209-3	-2.5601-4	3.3487-3	1.2868-3
0.36	-1.3378-2	-6.5517-4	4.1469-3	1.5986-3
0.48	-2.0494-2	-1.2419-3	4.5281-3	1.7447-3
0.64	-3.1094-2	-2.2988-3	4.5063-3	1.7202-3
0.80	-4.2676-2	-3.6445-3	3.9829-3	1.4826-3
1.0	-5.8222-2	-5.6928-3	+2.7464-4	9.3140-3
1.5	-1.0082-1	-1.2320-2	-2.5290-3	-1.436-3
2.0	-1.4709-1	-2.0682-2	-1.0111-2	-4.8959-3
2.5	-1.9585-1	-3.0399-2	-1.9371-2	-9.1845-3
3.0	-2.4642-1	-4.1206-2	-2.9917-2	-1.4132-2
4.0	-3.5149-1	-6.5370-2	-5.3895-2	-2.5563-2
5.0	-4.6021-1	-9.2120-2	-8.0699-2	-3.8558-2
6.0	-5.7148-1	-1.2081-1	-1.0956-1	-5.2736-2
7.0	-6.8463-1	-1.5101-1	-1.3998-1	-6.7847-2
8.0	-7.9924-1	-1.8241-1	-1.7164-1	-8.3716-2
10.0	-1.0317+0	-2.4803-1	-2.3779-1	-1.1723-1
20.0	-2.2274+0	-6.0705-1	-6.2223-1	-3.2532-1
100.0	-1.2120+1	-3.8161+0	-3.8209+0	-2.0694+0
500.0	-6.2057+1	-2.0401+1	-2.0409+1	-1.1682+1
1000.0	-1.2454+2	-4.1212+1	-4.1215+1	-2.3028+1
2000.0	-2.4954+2	-8.2862+1	-8.2865+1	-4.6438+1

Fig. V-1. Comparison of the Abe density expansion with BST.

Fig. V-1. Comparison of various approximations to $\ln \bar{Z}$ with BST. Curve A corresponds to Eq. (V-7), curve B corresponds to Eq. (V-8), and curve C corresponds to Eq. (V-9).

result for $\Lambda \leq 4$ is obtained from the activity expansion (Eq. (IV.20)) with the approximation $S = S_{\text{Ring}}$. However, starting with the term $z(\partial^2 S_{\text{Ring}} / \partial z^2)$ the activity expansion (Eq. (V.2)) has other terms of the same order. The small Λ_z expansion of $S_2(z)$ given by Eq. (III.19) indicates that the next higher order correction is given by

$$\frac{P}{kT} = z \left(1 + \frac{\Lambda_z}{3} + \frac{\Lambda_z^2}{8} \right) + S_2(z), \quad (\text{V.8})$$

This corresponds to the curve labeled B. There is close agreement with BST for $\Lambda < 2.2$, $\Lambda_z = 1.5$. This is about the same as keeping terms through S_2 in the density expansion. The agreement of Eq. (V.8) with BST is better than indicated by the size of the higher terms near $\Lambda_z = 1.5$. This is due to a cancellation in terms of the same size.

The density expansion only systematically includes terms of the same size to a certain point, e.g., in the case of the approximation $S = S_{\text{Ring}} + S_2$ this occurs when S_3 is the same size as terms which involve S_{Ring} and S_2 in Eq. (V.2). It appears, therefore, that keeping terms of the same size in Eq. (V.2) should result in better agreement with BST than can be obtained from the density expansion which includes the same set of the S_j . Because of the logarithms that appear in the expansion of the S_j no simple ordering of the terms beyond those in Eq. (V.8) is apparent. We thus collect terms according to their relative size, which can be obtained from Table V-1.

For $\Lambda_z < 2$, $S_3 < S_2/7$ so that S_3 is relatively unimportant, and terms in S_3 can be dropped from Eq. (V.2). The next approximation is found to be

$$\begin{aligned} \frac{P}{kT} = & z + S_{\text{Ring}} + S_2 + \frac{z}{2!} \left[\left(\frac{\partial S_{\text{Ring}}}{\partial z} \right)^2 + 2 \left(\frac{\partial S_{\text{Ring}}}{\partial z} \right) \left(\frac{\partial S_2}{\partial z} \right) \right] \\ & + \frac{z}{3!} \frac{\partial}{\partial z} z \left(\frac{\partial S_{\text{Ring}}}{\partial z} \right)^3 \end{aligned} \quad (\text{V.9})$$

It is noted that the last two terms of Eq. (V.9) are of opposite signs and give only a small correction to Eq. (V.8) near $\Lambda_z = 1.5$. This corresponds to the curve labeled C in Fig. IVa. The agreement with BST is good for $\Lambda < 3.5$, although, the agreement near $\Lambda = 1$ is slightly worse than for the approximation of Eq. (V.8). Equation (V.9) gives good agreement with BST about the same range of Λ as does the density expansion including terms through S_3 .

The convergence of Eqs. (V.7), (V.8), and (V.9) will be used as a criteria to determine when the two-component quantum-mechanical generalization of these equations has broken down due to the plasma interaction.

D. Quantum Mechanical Generalization of the Classical Expansion

Every term in Eq. (V.2) has a quantum-mechanical counterpart which reduces to the classical result in the limit $\hbar \rightarrow 0$. The quantum mechanical generalization of several of the lowest terms in Eq. (V.2) have been worked out. The quantum mechanical perturbation expansion for the ring terms has been given by Montroll and Ward⁴⁴ and by DeWitt.³³ The result is

$$\left(\frac{PV}{kT} \right)_{\text{Ring}} = \frac{V}{(2\pi)^3} \sum_{m=2}^{\infty} \frac{(-1)^m}{2^m} \int d^3k \sum_{t=-\infty}^{\infty} (u(k) \lambda_t(k))^m \quad (\text{V.10a})$$

where $u(k)$ is the Fourier transform of the pair potential,

$$\begin{aligned}\lambda_t(k) &= N \beta L(x^2, 2\pi i t) \\ &= \frac{N \beta}{F_{1/2}} \sum_{N=1}^{\infty} \frac{(-1)^{N+1}}{N^{1/2}} e^{N\alpha} \int_0^{\infty} du \exp(-Nx^2 u(1-u)) \\ &\quad + 2\pi i t N u),\end{aligned}\tag{V.10b}$$

$$x = \hbar k / \bar{p} = \hbar k / \sqrt{2mkT}, \text{ and} \tag{V.10c}$$

$$F_m(\alpha) = \frac{1}{\Gamma(m+1)} \int_0^{\infty} \frac{x^m dx}{e^{x-\alpha} + 1} \tag{V.10d}$$

are the Fermi integrals with $\alpha = \beta \mu$.

The result given by DeWitt^{33,35} for an electron-proton gas is

$$\frac{S_{\text{Ring}}}{Z} = \frac{\hbar}{3} P(\gamma_{ee}, \gamma_{ep}, \gamma_{pp}) = \frac{1}{12\pi z \lambda_D^3} P(\gamma_{ee}, \gamma_{ep}, \gamma_{pp}) \tag{V.11a}$$

where

$$\lambda_D = \left(\frac{4\pi}{kT} \sum_j z_j \epsilon_j^2 \theta_j \right)^{-1/2} \tag{V.11b}$$

is the generalized screening length that accounts for the fact that degenerate particles do not participate in the screening

$$\theta_j = F_{-1/2}(\alpha_j) / F_{1/2}(\alpha_j), \tag{V.11c}$$

$$\gamma_{ab} = \lambda_{ab} / \lambda_D = \hbar / \sqrt{2\mu_{ab} kT} / \lambda_D \tag{V.11d}$$

and

$$\begin{aligned}P(\gamma_{ee}, \gamma_{ep}, \gamma_{pp}) &= 1 - \frac{3\pi^{1/2}}{16} (\gamma_{ee} + 2\gamma_{ep} + \gamma_{pp}) \\ &\quad + \frac{1}{8} (\gamma_{ee}^2 + 2\gamma_{ep}^2 + \gamma_{pp}^2) \\ &\quad + \text{higher order unevaluated terms.}\end{aligned}\tag{V.11e}$$

The function P is the modification of the ring terms due to the uncertainty principle valid for the Maxwell-Boltzman distribution. Exact numerical evaluations of $P(\gamma)$ for a one-component plasma^{45,46} show that the Fermi corrections to $P(\gamma)$ are small in the region of weak to moderate degeneracy. Also the dynamic part of the many-body potential accounts for only a small percentage of $P(\gamma)$ for small γ (only 2% at $\gamma = 1$). For $\gamma > 50$ the dynamic part of the potential accounts for the major part of $P(\gamma)$. In the current work γ will never exceed three and a scaling of the exact one component results for the Maxwell distribution using only the static part of $P(\gamma)$ will be made. Furthermore the p-p term is always classical and can be ignored. A fit to the results of De Witt and Graboske valid for $\gamma < 3$, accurate to 0.07%, gives

$$\begin{aligned}
 P(\gamma_e) = 1 - 0.4655805 \gamma_e + 0.1931627 \gamma_e^2 \\
 - 0.0521885 \gamma_e^3 + 0.0060670 \gamma_e^4
 \end{aligned}
 \tag{V.12}$$

where $\gamma_e = \gamma_{ee} \sqrt{2}$. The static part of $P(\gamma)$ decreases slowly with γ and has the value 0.42 at $\gamma = 3$. Noting Eq. (V.11e) we observe that the two-component result is given approximately by the substitution in Eq. (V.12) of $x = (1 + \sqrt{2}) \sqrt{2} \gamma_{ee}$ for γ_e . In most of the present work $P(x)$ will be close to unity.

The quantum mechanical generalization of the Λ_z^2 term of Eq. (V.8) has been formally worked out,⁴⁷ but so far the quantum corrections to the classical limit have not been evaluated. It will be assumed here that the classical expression for the grand partition function which

involves derivatives of S is sufficiently accurate, i.e., that in the near classical limit the non-factorizability of the quantum cluster coefficients is unimportant. For two components the $Z/2 (\partial^2 S / \partial Z^2)$ term of Eq. (V.1) becomes

$$Z_e \left(\frac{\partial S}{\partial Z_e} \right)^2 + Z_p \left(\frac{\partial S}{\partial Z_p} \right)^2 \quad (V.13)$$

Use of the ring approximation to S in this term gives

$$S_{\text{Ring},2} = \frac{\Lambda^2}{8} g(x) \quad (V.14a)$$

where

$$\begin{aligned} g(x) = & 1 - 1.086353x + 0.445516x^2 - 0.044630x^3 \\ & + 0.163204x^4 - 0.0478703x^5 + 0.0101348x^6 \\ & - 0.000686x^7 + 0.0000859x^8 \end{aligned} \quad (V.14b)$$

The multicomponent quantum mechanical generalization of the Abe S_2 has been formally derived.^{32,35} The result of DeWitt⁴⁶ in the contour representation of Glasgold, Heckrotte, and Watson⁴⁸ is

$$\begin{aligned} \frac{S_{2,ab}}{Z_a Z_b} = & -\frac{1}{2!} \int_c \frac{dE}{2\pi i} e^{-\beta E} \text{Tr} \left\{ \frac{1}{E - H_0 + \epsilon_b u_s} - \frac{1}{E - H_0} \right. \\ & + \frac{1}{E - H_0} \epsilon_b u_s \frac{1}{E - H_0} - \frac{1}{E - H_0} \epsilon_b u_s \frac{1}{E - H_0} \\ & \left. \epsilon_b u_s \frac{1}{E - H_0} \right\} \end{aligned} \quad (V.15)$$

where $H_0 = p^2/2\mu$ is the kinetic energy operator for the relative motion of two particles, E is the complex energy, u_s is the potential between two particles whose spatial Fourier transform for one component is given by

$$u_s(k_i, \beta_i - \beta'_i) = \sum_{v=-\infty}^{\infty} \frac{u(k_i) \exp\{2\pi i v (\beta_i - \beta'_i)/\beta\}}{1 + \beta u(k_i) \lambda_2(\lambda k_i, 2\pi i v)} \quad (V.16a)$$

where $u(k) = 4\pi e/k^2 v$, λ is the thermal de Broglie wavelength and

$$\lambda_2(\lambda k, 2\pi i v) = \int V d^3 p \exp(\alpha - \beta p^2/2m_i) \frac{1}{\beta} \int_0^\beta d\tau \exp\{2\pi i \tau/\beta - \tau[(\vec{p} + \hbar \vec{k})^2 - p^2]/2m_i\} \quad (V.16b)$$

The two component potential is similar to Eq. (V.16a) except the denominator is replaced with

$$\epsilon(k, 2\pi i v) = 1 + \beta u(k) [\xi_e^2 \lambda_2(\lambda_e k, 2\pi i v) + \xi_i^2 \lambda_2(\lambda_i k, 2\pi i v)] \quad (V.17)$$

In the limit $v \rightarrow 0$, $\lambda \rightarrow 0$ (V.16a) and (V.17) reduce to the classical static screened potential.

The third term of Eq. (V.15) is subtracted out to satisfy electroneutrality (this is unnecessary for a multicomponent plasma since the sum of all such terms is zero) the second term is subtracted out because it has been included in the ring sum. Since,⁴⁹

$$e^{-\beta H_{ab}} = \frac{1}{2\pi i} \int_C \frac{e^{-\beta E}}{H_{AB} - E} dE, \quad (V.18)$$

Equation (V.15) can be written as

$$\frac{S_{2,ab}}{Z_a Z_b} = b_{2,ab} + \text{---} \circ \text{---} + \text{---} \text{---} \text{---} \quad (V.19)$$

where $b_{2,ab} = -B_{2,ab}$ is the second cluster coefficient of the dynamic screened coulomb potential and the diagrams are representations of the first order and second order perturbation terms of Eq. (V.15). In the

present study it will be assumed that the SSCP is sufficiently accurate for the densities and temperatures of interest. Evidence of this is obtained from the ring terms for which the dynamic corrections are only a few percent for the region of interest. In this approximation the quantum mechanical perturbation result gives the same $b_{2,ab}$ as that obtained by replacing the classical expression with its quantum mechanical counterpart. The first order perturbation term is also the same as can be seen from the first Born approximation (see Ref. 4) Eq. (16). The second order term is the lowest order ring term. It is the $m = 2$ term of Eq. (V.10a) with $u(k)$ being the Fourier transform of the SSCP. It has the value⁵⁰

$$\text{Diagram: A rectangle with two horizontal lines. The top line has an arrow pointing right, and the bottom line has an arrow pointing left.} = -\frac{\pi}{2} \left(\frac{E_1 E_2}{kT} \right)^2 \lambda_D f(\epsilon_{ab}) \quad (\text{V.20a})$$

where

$$f(\epsilon_{ab}) = 1 + \epsilon_{ab}^2 \sum_{r=0}^{\infty} \frac{\epsilon_{ab}^{2r}}{(2r+1)!!} - \sqrt{\frac{\pi}{2}} \epsilon_{ab} e^{\epsilon_{ab}^2/2} \quad (\text{V.20b})$$

and

$$\epsilon_{ab} = \frac{\gamma_{ab}}{\sqrt{2}} \quad (\text{V.20c})$$

In the limit $\hbar \rightarrow 0$, $f(\epsilon_{ab}) \rightarrow 1$ and Eq. (V.20a) reduces to its classical counterpart.

The two-component quantum mechanical generalization of Eq. (V.8) can now be written down. It is

$$\begin{aligned} \frac{p}{kT} = & \frac{\ln Z_0(\alpha_e)}{v} + z_p + \frac{\Lambda_z}{3} P(x) + \frac{\Lambda_z^2}{8} g(x) \\ & + S_{2,ee} + 2S_{2,ep} + S_{2,pp} \end{aligned} \quad (\text{V.21a})$$

where,

$$\ln z_0(\alpha) = NF_{3/2}(\alpha)/F_{1/2}(\alpha_0), \quad (V.21b)$$

is the grand partition function of an ideal gas evaluated for the chemical potential μ of the interacting system.³³ This takes account of the degeneracy of electrons in the ideal gas term. The protons are essentially non-degenerate at moderate densities and temperatures due to their large mass compared to an electron. α_e is related to z_e according to Eq. (II.7b) and Λ_z , $P(x)$, $g(x)$, $S_{2,ee}$, $S_{2,ep}$, $S_{2,pp}$ are all functions of z_e and z_p .

Further progress at high temperature requires the quantum mechanical generalization of terms beyond those given in Eq. (V.8). The first of these are the last two terms of Eq. (V.9). At low temperatures higher cluster coefficients for the SSCP that allow the formation of molecules are required. In the present study only the low temperature calculation will be extended. At moderate density we know that the cluster coefficients factor into terms such as $(b_{2,ep})^2 b_{2,HH}$, evaluated for the SSCP, which result from the factorization of $b_{4,epp}$. Because of the large value of λ_p the term $b_{2,HH}$ is taken to be just the usual result for a hydrogen gas. For simplicity only the ground state electronic level will be included in this study. In this approximation

$$b_{2,HH} = 8 \left(\frac{\pi \hbar^2}{m_H k T} \right)^{3/2} \left(\frac{T}{2\theta_r} \right) \left(\frac{e^{-\theta_v/2T}}{1 - e^{-\theta_v/T}} \right) e^{-E_0/kT} \quad (V.22)$$

where θ_r is the characteristic temperature for rotation, θ_v is the characteristic temperature for vibration, and E_0 is the binding energy

relative to free atoms.

A similar expression can be used for $b_{2,HP}$, except the symmetry factor 2 in the rotational term does not appear. Experimental results for these constants are given in Table V-2.

TABLE V-2

	θ_r deg.	θ_r deg.	E_0 eV
H_2	87.5	6322	4.722
H_2^+	42.9	3304	2.771

The one other bound state that is usually considered in a hydrogen gas is H^- . The binding energy of the electron relative to the atom is 0.92 eV. The phase shifts of several of the lowest states of the H-e interaction have been calculated⁵¹ but will not be included since similar parts of H_2^+ are not available. Therefore

$$b_{2,eH} = 8 \left(\frac{\pi \hbar^2}{2\mu_{eH}} \right)^{3/2} e^{-0.92/kT} \quad (V.23)$$

Addition of the higher cluster coefficients to Eq. (V.21)

gives

$$\begin{aligned} \frac{P}{kT} = & \frac{2N}{V} \frac{Z_0(\alpha_e)}{V} + Z_p + \frac{\Lambda}{3} Z_p P(x) + \frac{\Lambda^2}{8} g(x) \\ & + S_{2,ee} + 2S_{2,ep} + S_{2,pp} + Z_e^2 Z_p b_{2,ep} b_{2,eH} + Z_e Z_p^2 b_{2,ep} b_{2,pH} \\ & + Z_e^2 Z_p^2 (b_{2,ep})^2 b_{2,HH} \end{aligned} \quad (V.24)$$

the activity is eliminated through the equations

$$n_e = N_0/V = Z_e \frac{\partial}{\partial Z_e} \left(\frac{P}{kT} \right) \quad (V.25a)$$

$$n_p = N_0/V = Z_p \frac{\partial}{\partial Z_p} \left(\frac{P}{kT} \right) \quad (V.25b)$$

E. Results and Comparison with the Saha Equation

The solution of Eqs. (V.24), V.25a), and (V.25b) is quite complex and numerical methods are applied. The Newton-Rahpson method is used to solve for z_e and z_p . The procedure is to start with an initial guess of the activities (z_e^0, z_p^0) for one mole of hydrogen atoms at a fixed T and V and then refine the guess, using a Taylor series expansion about (z_e^0, z_p^0), according to

$$z_e^1 = z_e^0 + (gf_y - fg_y)/(f_x g_y - g_x f_y) \quad (V.26a)$$

$$z_p^1 = z_p^0 + (fg_x - gf_x)/(f_x g_y - g_x f_y) \quad (V.26b)$$

where

$$f = n_e - z_e \frac{\partial}{\partial z_e} \left(\frac{P}{KT} \right) \quad (V.26c)$$

$$g = n_p - z_p \frac{\partial}{\partial z_p} \left(\frac{P}{KT} \right) \quad (V.26d)$$

and f_x, f_y, g_x , and g_y denote partial derivatives. This process is repeated, using the current estimate of (z_e, z_p), until

$$\begin{aligned} |f/n_e - 1| < 10^{-5}, |z_e^{n+1}/z_e^n - 1| < 10^{-5} \\ |g/n_p - 1| < 10^{-5}, |z_p^{n+1}/z_p^n - 1| < 10^{-5} \end{aligned} \quad (V.27)$$

At the highest temperature the initial guess is $z_a = n_a$. At lower temperature, along an isochore, the initial guess is taken to be the solution for the previous temperature plus a small decrement (since z always decreases with T).

Each evaluation of f and g requires that $b_{2,ee}$, $b_{2,ep}$, and $b_{2,pp}$ and other terms that depend on λ_D be calculated. The cluster coefficients are obtained from a sum over the eigenvalues and phase shifts of the SSCP for the current value of λ_D . This requires extensive numerical calculation, as described in Refs. 41 and 52 necessitating the use of fitting formula and tabular interpolation.

The eigenvalues of 45 states of the SSCP, as a function of λ_D , are given in Tables I and II of Ref. 52. Each $E_{nl}(\lambda_D)$ was accurately fit to a least square polynomial of the form

$$E_{nl}(\lambda_D) = C_1 x + C_2 x^2 + C_3 x^3 + C_4 x^4 + C_5 x^5 \quad (V.28a)$$

where

$$x = \frac{\lambda_D - \lambda_{D,nl}^c}{\lambda_D - C_0 \lambda_{D,nl}^0}, \quad (V.28b)$$

$\lambda_{D,nl}^0$ is the value of the screening length for which the state nl has zero energy. The constant C_0 in x is the value that minimizes the mean square error in the five coefficient least squares polynomial in x . The value of C_0 was found to be approximately 0.3 in all cases.

A partial list of the calculated values of the weighed phase shift sum over angular momentum states, G , for various values of q , see Eq. (3), in Ref. 4], and λ_D is given in Tables I and II of Ref. 41. Values of the phase shift sum outside the table are obtained from the asymptotic fit

$$G = \pm \frac{2\lambda_D^2 q}{\pi} + \frac{\lambda_D}{2\pi q} + \frac{-2\pi(\lambda_D q^2/4.61)}{3\pi q^2} \quad (V.29)$$

where the top sign is for the attractive SSCP and the bottom sign is for the repulsive SSCP. The first term in Eq. (V.29) can be derived

analytically from the first Born approximation. The remaining terms were obtained from a study of the numerical results. The asymptotic fit gives very good results for high q , as verified by Tables I and II in Ref. 41.

The bound state part of $b_{2,ab}$ is obtained by evaluating the fits to $E_{n\ell}(\lambda_D)$. The continuum state part is obtained by integrating the momentum integral (see Eqs. (11), (13), and (14) in Ref. 41) using the values of G given in Tables I and II in Ref. 41 and Eq. (V.29), for four values of λ_D^{Tab} in the vicinity of λ_D . The value of the integral at λ_D is obtained by LaGrange interpolation.

Some representative values of the second virial coefficients are given in Tables III and IV in Ref. 41. The total second virial coefficient for Fermi particles is given by $B_{\text{exch}} + B_{\text{int},F}$ where B_{exch} is the exchange contribution from the ideal gas and $B_{\text{int},F}$ is the result of twobody interactions. When B_{exch} is added to $B_{\text{int},F}$ (see Eq. (14) in Ref. 41) the result is very close in value to the second virial coefficient for Boltzmann particles, $B_{\text{int},B}$, except at very low temperature and/or short screening lengths. The primary effect of Fermi statistics in the interaction part of the virial coefficient is to cancel out B_{exch} so that statistics play little part in the EOS of a gas at moderate temperature and density. This cancellation of the exchange has been discussed previously.⁵³ A comparison of the values of $S_{2,ab}$, which result from subtraction of the appropriate terms from $B_{\text{int},B}$, with several analytical evaluations of the high temperature asymptotic limit are given in Appendix D.

After the solution of Eqs. (V.24), (V.25a), and (V.25b) has been obtained all other thermodynamic functions can be evaluated. The ones which will be tabulated are the energy and the Helmholtz free energy which were obtained from the relations

$$E = - \left(\frac{\partial \ln \bar{Z}}{\partial \beta} \right)_{\alpha_i, \alpha_p} \quad (\text{V.30a})$$

$$F = N_e \mu_e + N_p \mu_p - PV \quad (\text{V.30b})$$

To check the consistency some values were also calculated from thermodynamic relations.

Results are given in Tables V-3 for eight isochores which range from 10^4 cc/mole-H to 20 cc/mole-H and for a series of temperatures in the range 0.25 eV - 4 Ryd, λ_D and Λ_Z are also tabulated.

As the temperature is reduced from 4 Ryd the screening length initially decreases with decreasing temperature. The rate of decrease is a decreasing function of the temperature due to the formation of hydrogen atoms. At temperatures below 1 eV, where nearly all the particles in the system are in atomic and molecular states, λ_D increases very rapidly with decreasing temperature. Λ_Z attains a maximum value at temperatures slightly below those for which λ_D is a minimum. At small volumes, where Λ_Z exceeds 1.5 and the one-component calculation indicates that higher terms are essential, this decrease in Λ_Z at low temperatures suggests that the calculation becomes valid again at some lower temperature where Λ_Z again falls below 1.5. However, the importance of the interactions H-e, H-p, and H-H, etc., is not included in this criteria.

Table V-3. Equation of State of a Hydrogen Gas.

$V = 10,000$ cc/mole H

T	$PV/N_0 kT$	$P_S V/N_0 kT$	E	F	λ_D	Λ_Z
eV			$\frac{\text{Mbar-cc}}{\text{Mole H}}$	$\frac{\text{Mbar-cc}}{\text{Mole H}}$	a_0	
54.38	1.998	2.000	1.57+2	-1.81+3	94.5	0.005
27.19	1.995	2.000	7.82+1	-8.51+2	67.0	0.015
20.393	1.992	2.000	5.85+1	-6.21+2	58.1	0.023
13.595	1.987	2.000	3.87+1	-3.98+2	47.7	0.042
10.0	1.979	1.999	2.93+1	-2.84+2	41.1	0.066
7.5	1.966	1.996	2.09+1	-2.07+2	36.0	0.101
6.0	1.951	1.989	1.64+1	-1.62+2	32.5	0.139
5.0	1.933	1.976	1.33+1	-1.32+2	30.1	0.181
4.0	1.897	1.935	9.99+0	-1.04+2	27.6	0.246
3.0	1.801	1.778	5.64+0	-7.58+1	25.7	0.352
2.5	1.686	1.589	2.14+0	-6.25+1	25.9	0.420
2.0	1.480	1.325	-3.28+0	-5.01+1	29.2	0.465
1.5	1.223	1.098	-9.36+0	-3.93+1	44.8	0.404
1.0	1.050	1.007	-1.20+1	-2.99+1	135.8	0.200
0.5	0.889	0.904	-1.29+1	-2.12+1	4.20+3	0.013
0.25	0.509	0.509	-1.49+1	-1.77+1	8.82+6	1.0-6

Table V-3 (cont.)

V = 3000 cc/mole H

T	$PV/N_O kT$	$P_S V/N_O kT$	E	F	λ_D	Λ_Z
eV			$\frac{\text{Mbar-cc}}{\text{Mole H}}$	$\frac{\text{Mbar-cc}}{\text{Mole H}}$	a_o	
54.38	1.997	2.000	1.54+2	-1.68+3	51.8	0.010
27.19	1.991	2.000	7.79+2	-7.88+2	36.8	0.027
20.393	1.987	2.000	5.82+1	-5.74+2	32.0	0.042
13.595	1.976	1.99	3.83+1	-3.67+2	26.3	0.076
10.0	1.962	1.996	2.77+1	-2.61+2	22.8	0.119
7.5	1.941	1.986	2.03+1	-1.90+2	20.1	0.180
6.0	1.916	1.966	1.57+1	-1.48+2	18.3	0.247
5.0	1.886	1.929	1.24+1	-1.21+2	17.1	0.317
4.0	1.832	1.830	8.76+0	-9.50+1	16.0	0.424
3.0	1.712	1.585	3.79+0	-6.97+1	15.5	0.585
2.5	1.597	1.392	-5.11-2	-5.78+1	16.2	0.673
2.0	1.428	1.195	-5.36+0	-4.68+1	19.1	0.709
1.5	1.229	1.055	-1.04+1	-3.72+1	31.0	0.585
1.0	1.069	1.001	-1.23+1	-2.87+1	9.83+1	0.276
0.5	0.791	0.818	-1.34+1	-2.07+1	3.33+3	0.016
0.25	0.505	0.505	-1.49+1	-1.76+1	7.58+6	1.0-6

Table V-3 (cont.)

 $V = 1000 \text{ cc/mole H}$

T	$PV/N_0 kT$	$P_S V/N_0 kT$	E	F	λ_D	Λ_Z
eV			$\frac{\text{Mbar-cc}}{\text{Mole H}}$	$\frac{\text{Mbar-cc}}{\text{Mole H}}$	a_0	
54.38	1.995	2.000	1.56+2	-1.57+3	30.0	0.017
27.19	1.985	2.000	7.74+1	-7.30+2	21.3	0.047
20.393	1.978	1.999	5.76+1	-5.31+2	18.6	0.072
13.595	1.961	1.996	3.77+1	-3.39+2	15.4	0.130
10.0	1.939	1.987	2.70+1	-2.41+2	13.4	0.202
7.5	1.908	1.961	1.94+1	-1.75+2	11.9	0.303
6.0	1.874	1.910	1.46+1	-1.36+2	11.0	0.412
5.0	1.836	1.830	1.13+1	-1.16+2	10.4	0.522
4.0	1.774	1.670	7.40+0	-8.74+1	9.9	0.685
3.0	1.663	1.405	2.19+0	-6.43+1	9.9	0.916
2.5	1.577	1.252	-1.67+0	-5.36+1	10.5	1.033
2.0	1.457	1.118	-6.79+0	-4.37+1	12.8	1.059
1.5	1.278	1.032	-1.14+1	-3.52+1	21.7	0.835
1.0	1.077	0.996	-1.26+1	-2.75+1	73.1	0.372
0.5	0.702	0.733	-1.37+1	-2.03+1	2.78+3	0.020
0.25	0.503	0.503	-1.49+1	-1.74+1	6.61+6	2.0-6

Table V-3 (cont.)

V = 500 cc/mole H

T	PV/N ₀ kT	P _S V/N ₀ kT	E	F	λ_D	Λ_Z
eV			$\frac{\text{Mbar-cc}}{\text{Mole H}}$	$\frac{\text{Mbar-cc}}{\text{Mole H}}$	a_0	
54.38	1.993	2.000	1.56+2	-1.50+3	21.2	0.024
27.19	1.980	2.000	7.70+1	-6.94+2	15.2	0.066
20.393	1.970	1.999	5.71+1	-5.04+2	13.2	0.101
13.595	1.948	1.993	3.71+1	-3.21+2	11.0	0.182
10.0	1.921	1.976	2.63+1	-2.28+2	9.7	0.281
7.5	1.884	1.928	1.87+1	-1.65+2	8.7	0.419
6.0	1.846	1.845	1.42+1	-1.29+2	8.0	0.563
5.0	1.807	1.734	1.05+1	-1.05+2	7.7	0.711
4.0	1.749	1.554	6.57+0	-8.26+1	7.4	0.923
3.0	1.661	1.310	1.41+0	-6.10+1	7.4	1.220
2.5	1.607	1.187	-2.38+0	-5.09+1	7.9	1.369
2.0	1.526	1.086	-7.48+0	-4.17+1	9.7	1.396
1.5	1.337	1.022	-1.20+1	-3.39+1	17.1	1.062
1.0	1.074	0.991	-1.29+1	-2.68+1	60.7	0.448
0.5	0.655	0.686	-1.40+1	-2.01+1	2.50+3	0.022
0.25	0.502	0.502	-1.49+1	-1.73+1	6.06+6	2.0×10^{-6}

Table V-3 (cont.)

V = 200 cc/mole H

T	$PV/N_0 kT$	$P_s V/N_0 kT$	E	F	λ_D	Λ_z
eV			$\frac{\text{Mbar-cc}}{\text{Mole H}}$	$\frac{\text{Mbar-cc}}{\text{Mole H}}$	a_0	
54.38	1.989	2.000	1.55+2	-1.40+3	13.5	0.037
27.19	1.970	1.999	7.62+1	-6.47+2	9.7	0.103
20.393	1.957	1.996	5.62+1	-4.69+2	8.5	0.157
13.595	1.927	1.982	3.61+1	-2.97+2	7.1	0.282
10.0	1.895	1.943	2.53+1	-2.11+2	6.3	0.432
7.5	1.856	1.851	1.77+1	-1.53+2	5.7	0.638
6.0	1.818	1.722	1.29+1	-1.19+2	5.3	0.851
5.0	1.781	1.586	9.45+0	-9.75+1	5.1	1.063
4.0	1.725	1.408	5.64+0	-7.65+1	5.0	1.364

V = 100 cc/mole H

54.38	1.985	2.000	1.55+2	-1.33+3	9.6	0.052
27.19	1.962	1.998	7.54+1	-6.11+2	6.9	0.145
20.393	1.945	1.993	5.54+1	-4.42+2	6.1	0.220
13.595	1.913	1.966	3.53+1	-2.8+2	5.1	0.391
10.0	1.880	1.772	2.46+1	-1.98+2	4.6	0.596
7.5	1.834	1.660	1.68+1	-1.44+2	4.2	0.872
6.0	1.781	1.528	1.19+1	-1.12+2	3.9	1.150
5.0	1.716	1.415	8.42+0	-9.16+1	3.8	1.415

Table V-3 (cont.)

V = 50 cc/mole H

T	$PV/N_0 kT$	$P_s V/N_0 kT$	E	F	λ_D	Λ_z
eV			$\frac{\text{Mbar-cc}}{\text{Mole H}}$	$\frac{\text{Mbar-cc}}{\text{Mole H}}$	a_0	
54.38	1.980	2.000	1.54+2	-1.26+3	6.8	0.074
27.19	1.953	1.996	7.44+1	-5.75+2	4.9	0.203
20.393	1.933		5.44+1	-4.16+2	4.3	0.307
13.595	1.890	1.938	3.44+1	-2.63+2	3.7	0.542
10.0	1.859	1.497	2.36+1	-1.86+2	3.3	0.819
7.5	1.775	1.415	1.54+1	-1.34+2	3.1	1.174
6.0	1.654	1.321	1.01+1	-1.05+2	3.0	1.500

V = 20 cc/mole H

54.38	1.972	2.000	1.52+2	-1.16+3	4.3	0.116
27.19	1.941	1.992	7.30+1	-5.28+2	3.2	0.316
20.393	1.922		5.31+1	-3.81+2	2.8	0.474
13.595	1.866	1.877	3.26+1	-2.40+2	2.5	0.824
10.0	1.730		2.02+1	-1.70+2	2.3	1.196
7.5	1.503		1.09+1	-1.23+2	2.3	1.596

For this reason the EOS in this region will be subject to uncertainty until a more refined calculation is performed. For volumes greater than 200 cc/mole-H Λ_z does not exceed 1.5. At $V = 200$ cc/mole-H, Λ_z attains the value 1.5 at $T \approx 3.5$ eV. At a temperature of 2500°K the gas is essentially all molecules and the second virial coefficient as given in Hirshfeld, Curtiss, and Bird gives a 3.5% correction to the ideal gas pressure. This indicates that a more detailed treatment of the interactions is desirable for all temperatures in the range 0.25 eV to 3.5 eV. It is felt that for volumes of 500 cc/mole H and greater that the present procedure is adequate for all temperatures greater than a few hundred degrees kelvin (at very high temperature it will be necessary to add the contribution of the photon gas). As the volume is decreased the temperature at which Λ_z exceeds 1.5 increases slowly. At a volume of 20 cc/mole-H this occurs at $T \approx 8$ eV.

Figures IV-3 to IV-7 show $PV/N_0 kT$ vs T for the current method of calculating the EOS (solid line) and for the Saha equation (dashed line). The procedure suggested by Larkin which subtracts the terms $-1 - \beta E_{ne}$ from each exponential term in the partition function has been used to obtain the Saha result. Calculations were also made for the more usual ideal gas procedure of using just the ground state energy for all species. Over the range of the table the two methods give very similar results. The only differences are at high temperature where the Larkin procedure effectively is cutting off even the ground state. The pressure differences never exceed 2%. Some other procedures that have been applied

Fig. V-3. Results of this study for $V = 10000$ cc/mole-H compared with a Saha calculation.

Fig. V-4. Results of this study for $V = 3000$ cc/mole-H compared with a Saha calculation.

Fig. V-5. Results of this study for $V = 1000$ cc/mole-H compared with a Saha calculation.

Fig. V-6. Results of this study for $V = 500$ cc/mole-H compared with a Saha calculation.

Fig. V-7. Results of this study for $V = 200$ cc/mole-H compared to a Saha calculation.

to ideal gas calculations would result in larger differences. At a volume of 10^4 cc/mole-H the present method, which includes the effect of interactions in a consistent way, is less than the Saha result at high temperature and greater than the Saha result for $0.7 \text{ eV} \lesssim T \lesssim 3 \text{ eV}$. At high temperature the pressure is lower than that of an ideal gas because of the electrostatic interaction in the ionized gas. At intermediate temperature it is higher than that of an ideal gas because there are substantial numbers of hydrogen atoms present whose energy levels are weakened due to the effect of the free charge in the system. There are, thus, two compensating effects taking place due to interactions. At high temperature the electrostatic effect dominates and at intermediate temperature the perturbation of bound states dominates. At $T = 3 \text{ eV}$ the two effects essentially balance one another. For $T < 0.7 \text{ eV}$ the present procedure agrees very closely with the Saha result.

At volumes less than 10^4 cc/mole-H the same type of behavior occurs, except the differences become more pronounced. At $V = 500$ cc/mole-H the present procedure gives pressures that are 40% greater than the Saha result at $T = 2 \text{ eV}$. The depression of the pressure due to the electrostatic interaction becomes increasingly pronounced at high temperature as the density is increased at $V = 200$ cc/mole-H $PV/N_0 kT$ goes through a minimum at $T = 3 \text{ eV}$ and then increases to a maximum at $T = 2 \text{ eV}$. However, Λ_2 exceeds 1.5 at $T = 3.5 \text{ eV}$ and this behavior of $PV/N_0 kT$ in the 1-3 eV range should not be taken to be an accurate description of the real gas.

F. Some Possible Extensions

The present work has given a fairly precise calculation of the equation of state of an electron-proton gas at moderate densities. The generalization to many component systems is formally straightforward, but, the numerical evaluation of the result would require considerable effort. For instance, for an electron, proton, alpha particle system the cluster coefficient for the $H_e^+ - e$ interaction, taking proper account of the many-body screening, would need to be calculated.* The extension to higher density, at relatively high temperature, could be obtained by working out the quantum-mechanical theory for higher terms of the expansion such as given by Eq. (V.9). At lower temperature an extension to higher density can be made by including the contribution of higher bound states and the phase shifts of atoms and molecules. At sufficiently low temperature it appears that the gaseous EOS can be calculated solely from the cluster coefficients of the SSCP (provided dynamic effects are unimportant).

A practical, and also fairly accurate, procedure for obtaining the eigenvalues and phase shift for complicated atoms and their ions would be to use the Thomas-Fermi potential in the Schroedinger equation solutions.⁵⁴⁻⁵⁷ This would require solving the Thomas-Fermi problem appropriate to the SSCP. Fairly accurate solutions to the Schroedinger equation can be obtained from the 1st and 2nd WKB approximations. This

* The $H_e^{++} - e$ cluster coefficient can be obtained from the results given in this study. The $H_e^+ - e$ calculation requires about the same amount of effort.

is described for the phase shift problem in Ref. 41. The eigenvalue problem is discussed by Krieger.⁵⁸ Considerable numerical effort would be saved if the Wigner-Kirkwood expansion⁵⁹ could be adapted to these calculations since it does not require individual solutions to the Schroedinger equation.

Another avenue of exploration that may prove fruitful, once sufficient work has been done to check it out, is the use of the quantum mechanical forms of S_{Ring} , S_2 , etc., in the classical activity generating expression (Eq. IV.2c) and the use of short distance cutoffs in the classical integrals. A refinement to the cutoff procedure would be to find a universal pseudo-potential which replaces the SSCP near the origin. Several⁶⁰⁻⁶² potentials have been suggested in the case of the pure coulomb potential. The simplest of these, suggested by Glauber and Yukhnovskii, modifies the coulomb potential by the factor $(1 - e^{-r/r_0})$. Similar expressions should also apply to the SSCP since the screening has little effect for $r < r_0$.

The SSCP as used in this study was obtained in the limit $\hbar \rightarrow 0$. The static potential in quantum-mechanical regions may differ somewhat from the SSCP. An interesting extension would be to obtain the exact static potential and see how it differs from the SSCP. This can be done by inverting Eq. (V.16a) in the limit $v \rightarrow 0$. The r dependence of the potential is the same as the SSCP; the differences all appear as corrections to λ_D . A calculation with the dynamic screened potential appears far too complicated to be worthy carrying out at present; especially in view of the very small effect it has on S_{Ring} .

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Appendix A. Derivations of Eq. II.12 from the Canonical Partition Function

Consider a two-component system composed of N_H atoms that are not interacting with any other particle and N_{H_2} pairs of atoms which are interacting with each other but with no other particles. The canonical partition function for this situation is

$$Z = \left(\frac{Z_H}{N_H!} \right)^{N_H} \left(\frac{Z_{H_2}}{N_{H_2}!} \right)^{N_{H_2}} \quad A-1$$

where Z_{H_2} includes the translational states of the interacting pair as well as the internal states. The free energy is, therefore,

$$F = -kT \ln Z = -N_H kT \ln \left(\frac{e v}{N_H} (2\pi m_H kT)^{3/2} \right) - N_{H_2} kT \ln \left(\frac{e v}{N_{H_2}} (2\pi m_{H_2} kT) Z_{int} \right) \quad A-2$$

where Z_{int} is given by Eq. (II.5). Minimization of the free energy, using the constraint $N = N_H + 2N_{H_2}$, gives

$$\frac{\partial F}{\partial N_H} = \ln \left(\frac{v}{N_H} (2\pi m_H kT)^{3/2} \right) - \frac{1}{2} \ln \left(\frac{v}{N - N_H} (2\pi m_{H_2} kT) Z_{int} \right) = 0 \quad A-3$$

Since

$$b_2 = \left(\frac{2\pi k^2}{\mu kT} \right) Z_{int} \quad A-4$$

Equation A-3 gives the result

$$\frac{N - N_H}{N_H} \left(\frac{v}{2b_2} \right) = 1 \quad A-5$$

Appendix B. Comparison with Other Calculations of S_2

The high temperature asymptotic form of the quantum mechanical S_2 has been given by DeWitt,¹ Kraeft and Kremp,² Hoffman and Ebeling,³ and Kopyshv.⁴ These authors use somewhat different approaches to the problem and all agree, for an electron-proton gas, on the form

$$S_{2,ab}/n_a n_b = - \left(\frac{\epsilon_a \epsilon_b}{\epsilon_a^2} \right) \frac{\Lambda^2}{12} \left[\log \left(\frac{\lambda_{ab}}{\lambda_D} \right) + D_q \right] \quad (B-1)$$

where

$$\lambda_{ab} = \hbar / \sqrt{2\mu_{ab} kT} \quad \text{and } D_q \text{ is a constant}$$

The calculation of DeWitt is the most closely related to the present work as he replaces the dynamic screened potential which results from the perturbation expansion of the grand partition function with the SSCP. He gives D_q in the form of a complicated unevaluated integral. The other authors all agree that $D_q = \ln 3 + C/2 - 1/2$ where C is the Euler constant.

Tables B-1 and B-2 give the result of the present approach together with the value given by the asymptotic formula using $D_q = \ln 3 + D/2 - 1/2$. The tables are in atomic units, so that, for an electron-proton interaction T_0 corresponds to the temperature in Rydbergs and a_μ is in Bohr radii. For an electron-electron interaction T_0 corresponds to the temperature in Rydbergs $\times 1/2$ and a_μ is in units $2a_0$. Table B-1 is for the repulsive SSCP. It shows that at low temperature the difference between the two results is quite large and the asymptotic formula is clearly

Table B-1. S_2 for a repulsive SSCP and comparison with the quantum mechanical perturbation expansion (S_2^A).

$T/\lambda_D a_\mu$	4		10		24		40	
	S_2	S_2^A	S_2	S_2^A	S_2	S_2^A	S_2	S_2^A
0.1	4.58+2	-5.46+3	2.24+3	2.22+3	4.98+3	9.56+3	7.15+3	1.38+4
0.2	1.53+2	-3.19+2	4.72+2	6.41+2	9.30+2	1.56+3	1.27+3	2.09+3
0.4	3.72+1	5.49+0	9.13+1	1.25+2	1.63+2	2.40+3	2.12+2	3.07+2
0.6	1.51+1	9.49+0	3.37+1	4.50+1	5.71+1	7.90+1	7.26+1	9.88+1
0.8	7.80+0	6.36+0	1.64+1	2.13+1	2.68+1	3.57+1	3.36+1	4.40+1
1.0	4.61+0	4.19+0	9.30+0	1.19+1	1.49+1	1.92+1	1.84+1	2.35+1
2.0	8.50-1	8.87-1	1.54+0	1.85+0	2.30+0	2.76+0	2.75+0	3.30+0
4.0	1.46-1	1.56-1	2.41-1	2.76-1	3.42-1	3.91-1	3.90-1	4.58-1
6.0	5.07-2	5.41-2	7.96-2	8.97-2	1.10-1	1.24-1	1.22-1	1.43-1

Table B-2. S_2 for an attractive SSCP and comparison with the quantum mechanical perturbation expansion (S_2^A).

$T/\gamma_D a_\mu$	4		10		24		40	
	S_2	S_2^A	S_2	S_2^A	S_2	S_2^A	S_2	S_2^A
0.1	-2.36+5	5.45+3	-2.44+6	-2.22+3	-6.95+6	-9.55+3	-9.52+6	-1.38+4
0.2	-4.24+3	3.19+2	-1.46+4	-6.41+2	-2.55+4	-1.56+3	-3.03+4	-2.09+3
0.4	-2.63+2	-5.49+0	-5.81+2	-1.25+2	-8.64+2	-2.40+2	-9.98+2	-3.07+2
0.6	-5.66+1	-9.49+0	-1.30+2	-4.50+1	-1.87+2	-7.90+1	-2.16+2	-9.88+1
0.8	-2.66+1	-6.36+0	-4.90+1	-2.13+1	-6.96+1	-3.57+1	-8.04+1	-4.40+1
1.0	-1.34+1	-4.19+0	-2.37+1	-1.19+1	-3.34+1	-1.92+1	-3.86+1	-2.35+1
2.0	-1.70+0	-8.87-1	-2.77+0	-1.85+0	-3.81+0	-2.76+0	-4.39+0	-3.30+0
4.0	-2.29-1	-1.56-1	-3.52-1	-2.76-1	-4.74-1	-3.90-1	-5.40-1	-4.58-1
6.0	-7.19-2	-5.41-2	-1.07-1	-8.97-2	-1.42-1	-1.24-1	-1.61-1	-1.43-1

inadequate. At high temperatures the differences are of order 10-15% and depend somewhat on the screening length. At high temperature where the asymptotic formula is valid, S_2 is only a small part of the b_2 which results from the sum over eigenvalues and phase shifts of the SSCP. For $\gamma_D = 40, T_0 = 6$ the ratio of S_2/b_2 is only 4×10^{-5} . Since the relative error in b_2 is about 3×10^{-6} the numerical uncertainty in S_2 is 8%. The percentage error increases rapidly with temperature and a comparison at higher temperatures than those listed in the table becomes meaningless. At the highest temperature and screening length listed in the table the correction to the classical counterpart of Eq. 8-1 due to higher terms is a few percent and it increases with decreasing temperature and screening length. Therefore, all that can be said at this point is that the current work and the asymptotic formula are compatible.

Table B-2 gives the comparison of the current work with the asymptotic formula for the attractive SSCP. Here the differences between the current result for S_2 and the asymptotic formula are substantially larger at the lower temperatures than they were for the repulsive case. At high temperature the differences are similar to those for the repulsive potential.

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Solving for N_H we have

$$N_H = \frac{V}{4b_2} [-1 + \sqrt{1 + 8nb_2}] \quad A-6$$

The pressure is given by

$$P = -\frac{\partial F}{\partial V} = \frac{kT}{2V} [N + N_H] \quad A-7$$

$$= \frac{kT}{2} \left[n + \frac{1}{4b_2} \{ \sqrt{1 + 8nb_2} - 1 \} \right] \quad A-8$$

This is exactly Eq. II.12. This approach shows clearly that all the two-body effects have been included in b_2 , i.e., b_3 , b_4 , etc. only involve three or more bodies interacting at a time.