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EQUATION OF STATE OF
CLASSICAL SYSTEMS OF CHARGED PARTICLES

Livermore, California

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ABSTRACT

Recent developments in the classical theory of fully ionized gases and strong electrolyte solutions are reviewed, and are used to discuss the equation of state at high temperatures and low densities. The pressure is calculated using the ring-integral approximation, and quantitative estimates of higher correction terms are given. The effect of short range repulsive forces is shown by comparing the results with two kinds of potential functions: hard spheres of diameter a , and "soft" spheres for which the short range potential cancels the Coulomb potential at the origin, and decreases exponentially with distance. It is found that the use of either type of potential extends the range of validity of the ring-integral approximation to considerably higher densities and lower temperatures. Since there is little difference in the results for the hard spheres and the soft spheres in this range, the latter system is investigated more extensively since it is more easily handled by analytical methods. The expressions derived for the free energy of a system of charged particles can also be used in ionization equilibrium calculations, and the effect of electrostatic interactions on the equilibrium concentrations of various kinds of ions is indicated.

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I. INTRODUCTION

The first extensive study of the statistical mechanics of systems of particles interacting with long range Coulomb forces was made by S. R. Milner in 1912 (1). Milner attempted to calculate the virial of a mixture of ions, using the Maxwell-Boltzmann distribution for the probabilities of the various possible configurations of the ions. He naturally encountered the two difficulties inherent in this problem: (1) the divergence due to the long range character of the Coulomb force; (2) the divergence due to the short range character of the Coulomb force. The first divergence could be eliminated by summing first over the configurations of small groups of ions, using the fact that alternating (+-+-. . .) configurations are most probable, before extending the integrations to infinity; the second divergence was avoided by assuming the ions have a finite diameter. However, Milner's mathematical methods were not powerful enough to yield results which were either simple or exact, and about all that could be concluded was that the effect of interactions was to lower the total pressure (osmotic pressure in the case of electrolyte solutions). This was still a valuable result since it

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indicated that the hypothesis of complete dissociation of strong electrolytes in solution did not necessarily have to be rejected because the osmotic pressure of concentrated solutions was not proportional to concentration.

The famous theory of Debye and Hückel (to be referred to as DH) abandoned the strict statistical method in favor of more intuitive methods; the electrostatic potential was assumed to satisfy the so-called Poisson-Boltzmann equation, and the linearized version of this equation could be solved exactly to give simple limiting laws for the osmotic pressure, activity coefficients, conductivity, etc. (2). The DH theory was an immediate success with the chemists, and constituted a considerable advance in electrochemistry. Thus A. A. Noyes said in 1924,

"The treatment of Milner involved mathematical considerations so difficult as to make it scarcely available to chemists or physicists with ordinary mathematical training. The more recent derivation of Debye and Hückel, on the other hand, is based on a few fundamental physical principles whose application presents no serious mathematical difficulties." (3)

Milner had not continued his work on electrolytes after 1919 because of a serious illness, and "Debye taking up this work, went ahead so fast that Milner turned his attention to electromagnetic theory." (4) In 1926, Milner wrote,

"Since I have read Debye's calculation critically I think that his method of calculation of the effects of the interionic force is greatly superior to mine. All the laborious summations and approximations contained in my calculation of 1912 are done away with, without any sacrifice of accuracy, by what seems to me a stroke of genius - namely, his observation that the average potential of all the ions in a sphere containing a positive ion at the centre must satisfy Poisson's equation. Since the two calculations are based on the same assumptions and

mine contains admitted approximations, I am inclined to believe that the numerical differences between them are to a large extent attributable to these." (5).

While all subsequent work has confirmed the validity of the limiting laws for infinite dilution derived from the DH theory, the initial enthusiasm for the theory cooled somewhat after it was found that it could not be extended to more concentrated solutions in a satisfactory way. When the ionic diameter is introduced in the linearized Poisson-Boltzmann equation, results valid for somewhat higher concentrations can be obtained, but sometimes the diameter needed to fit the experimental results comes out negative. It is also possible to solve the non-linearized equation with rather more labor, but there are still objections; there is apparently a choice between two "charging processes" which lead to different values for the osmotic pressure; and the Poisson-Boltzmann equation itself implies neglect of fluctuations that probably become important at high concentrations. In addition, various effects such as dielectric saturation of the solvent may occur. It was eventually realized that reliable results could only be obtained by returning to a rigorous approach based on statistical mechanics.

The application of the DH theory to ionized gases, particularly in stars, was discussed by Rosseland (6) and Eddington (7). Eddington's principal conclusion was that the ionization produced at high temperatures would permit stellar matter to be compressed to an enormous degree, and yet still behave nearly like an ideal gas; it had earlier been supposed that it would condense to a liquid under such high pressures. In astrophysical problems the equation of state at high temperatures is determined primarily by the degree of ionization rather than directly by the electrostatic effects; when the density is so high or the temperature so low that the DH theory is invalid, other

effects such as pressure ionization and degeneracy must also be taken into account. However, we shall see that electrostatic effects have an important indirect effect on the pressure in certain regions since they influence the equilibrium concentrations of various kinds of ions, and an improved version of the DH theory is needed to describe this effect accurately.

During the last fifteen years, the problem of constructing a consistent generalization of the DH theory has been attacked along two lines, pursued more or less independently in the United States and Russia. In 1950, J. E. Mayer showed that the cluster expansion for the equation of state (apparently inapplicable to Coulomb forces because of the divergence of the second virial coefficient) could be rearranged by summing the most divergent integrals to give a finite result (8,9). The evaluation of the so-called ring integrals was found to yield just the DH result for Coulomb forces, and Mayer's formalism provided a systematic method for computing higher approximations. This theory was developed further by Haga (10), Meeron (11), Friedman (12) and Abé (13) so that we are now able to make a quantitative estimate of the contributions from more complicated cluster integrals and thus determine the region of validity of the DH theory itself.

An alternative to the cluster integral expansion is the method of integral equations for the distribution functions; both must of course give the same result if carried far enough, and it is merely a matter of convenience which one chooses for a particular problem. N. N. Bogolyubov had in 1946 developed the distribution function method in a form suitable for application to Coulomb forces, and showed that the DH theory was recovered in the lowest approximation, but he did not investigate the elimination of the short range divergence (14). This task was left for A. E. Glauber and I. R. Yukhnovskii (15,16,17) who worked with a "soft" potential function

$$U(r) = \pm(e^2/r)(1 - e^{-\gamma r}). \quad (\text{soft sphere}) \quad (1)$$

This form is appropriate for ions which contain bound electrons whose charge distribution has a mean radius of about γ^{-1} . With less justification one might use it for ions in a fully ionized gas, in which case, by analogy with the quantum mechanical theory, γ might be identified with the reciprocal of the thermal wavelength, i. e., with $(\hbar/\sqrt{2mkT})^{-1}$. When γ becomes temperature-dependent the relation between the free energy and the other thermodynamic functions will naturally be modified. In this paper we shall treat γ as constant.¹

Glauber and Yukhnovskii found that it was possible to obtain the distribution function explicitly to any desired degree of approximation by solving Bogolyubov's equation, and thus to calculate the free energy and other thermodynamic properties. Since their method employs the Fourier transform of the potential function, it is easier to have a continuous potential rather than the more usual "hard sphere,"

$$U(r) = \begin{cases} +\infty, & r \leq a, \\ \pm(e^2/r), & r > a. \end{cases} \quad (\text{hard sphere}) \quad (2)$$

It is possible to use the hard sphere potential in conjunction with a distribution function method, although the results are more complicated (19,20,21).

A third method, employing collective coordinates for the long range part of the potential, has been developed by Yukhnovskii (22,23); it gives the same results for the soft sphere system and can also be applied to other models. However, Siegert (24) [see also Moore (25)], who rederived the expansion by his method of Gaussian random functions, claims that Yukhnovskii's result for a general potential including short-range forces is incorrect. Kelbg (26) has obtained a similar expansion by a method of

¹Feix (18) has used this potential in the theory of transport properties of a plasma.

collective coordinates. These authors all agree on the form of the first correction to the DH term for soft spheres, though they may treat short-range repulsive forces differently. Finally we mention a recent paper by Theimer and Gentry (27) in which the DH result is derived by a method employing stochastic functions, though the correction terms are not obtained explicitly.

We shall show that the cluster integral method and the distribution function method both lead to the same expression for the free energy in the ring integral approximation when the soft sphere potential is used (proof of equivalence for all potentials is not given). It appears that the series derived by any of the above-mentioned methods could be rearranged so as to be identical. When one makes the identification $\gamma^{-1} \leftrightarrow \frac{3}{2} a$, the resulting ring-integral equation of state is very nearly the same for both hard and soft sphere systems over a wide range of temperatures and densities. (This is not surprising since the ring integral contribution is determined primarily by the long range part of the potential which is the same for both.) Moreover, the Glauber-Yukhnovskii theory indicates that under certain conditions the distribution function acquires a periodic character, a result which is not immediately apparent from theories based on the hard sphere model, though it has occasionally been noticed by previous writers (28,29).

Quantum effects are entirely ignored in this paper, except insofar as they can be considered to determine the value of γ . This should be a legitimate approximation over a large region of densities and temperatures of physical, chemical, and astrophysical interest; even where the more difficult quantum mechanical theory must be used, it is still useful to work out the classical theory to see how much difference quantum effects really make.

II. CLUSTER INTEGRAL THEORY²

We summarize in this section the results obtained by Mayer, Meeron, Friedman, and Abé, based on a modified cluster integral expansion.

Mayer's original cluster expansion for the equation of state of neutral atoms or molecules was based on writing the configuration integral in the form

$$\begin{aligned} \int e^{-\beta U} d\tau &= \int \exp \left[-\beta \sum_{i < j} U_{ij}(r_{ij}) \right] d\tau \\ &= \int \prod_{i < j}^N (1 + f_{ij}) d\tau \\ &= \int \left(1 + \sum_{i < j} f_{ij} + \sum_{ijk\ell} f_{ij} f_{k\ell} + \dots \right) d\tau \end{aligned} \quad (3)$$

where

$$f_{ij} = e^{-\beta U_{ij}(r_{ij})} - 1;$$

$$\beta = (kT)^{-1}.$$

If the force law is such that $U_{ij}(r_{ij})$ is effectively zero for $r_{ij} > a$, then f_{ij} will be zero unless the pair of molecules (i,j) is closer than a distance a , and a product of f 's in the expansion (3) will be non-zero only if the corresponding molecules form a "cluster" such that each f is non-zero. The number of clusters of various types is determined by combinatorial analysis, and the expansion is finally reduced to a sum over "irreducible" clusters. (A cluster of molecules is irreducible if the graph formed by drawing a line for each f function is doubly connected.)

When $U_{ij}(r_{ij}) = e^2/r_{ij}$, all the cluster integrals are divergent; this is not surprising, since when all the particles have the same charge one does

²For a more comprehensive treatment of cluster integral theory, we refer to the forthcoming monograph by Friedman (60).

not have any equilibrium state in the usual sense, and most of the particles are forced against the wall of the container. [A detailed description of this situation is given by Keller (30).] Only when the gas is electrically neutral can the much finer effect of the polarization of the medium due to Coulomb interactions be distinguished from the gross effect of unbalanced charge. One way of taking account of electrical neutrality is to assume a "one-component" system of electrons moving in a uniform background of positive charge. [Rayleigh (31) was probably the first to consider such a system, in another context.] However, if one wants to treat a more realistic two-component system, it is necessary to modify the Coulomb potential at short distances for ion-electron interactions to avoid a divergence.

Consider a system of N_e electrons in a volume V , the total charge $Q_e = -eN_e$ being balanced by N_i positive ions each of charge $+ze_i$. We are of course chiefly interested in the properties of the system in the limits

$$\lim_{N_e, V \rightarrow \infty} (N_e/V) = n_e; \quad \lim_{N_i, V \rightarrow \infty} (N_i/V) = n_i. \quad (4)$$

The Helmholtz free energy, including the second virial coefficient from ordinary cluster integral theory, is

$$\beta F = N_e F_{0e} + N_i F_{0i} + V (B_{2ee} n_e^2 + 2B_{2ei} n_e n_i + B_{2ii} n_i^2) \quad (5)$$

where

$$B_{2ee} = (2V)^{-1} \iint d\tau_1 d\tau_2 (e^{-\beta U_{ee}} - 1),$$

$$B_{2ei} = (2V)^{-1} \iint d\tau_1 d\tau_2 (e^{-\beta U_{ei}} - 1),$$

$$B_{2ii} = (2V)^{-1} \iint d\tau_1 d\tau_2 (e^{-\beta U_{ii}} - 1). \quad (6)$$

When

$$U_{ee} = e^2/r, \quad U_{ei} = -z_i e^2/r, \quad U_{ii} = z_i^2 e^2/r, \quad (7)$$

and the exponentials in Eq. (6) are expanded in Taylor series and the results substituted into Eq. (5), we obtain

$$\begin{aligned}
 \beta F &= N_e F_{0e} + N_i F_{0i} - (\beta/2V^2) \left(N_e^2 - 2N_e N_i z_i + N_i^2 z_i^2 \right) \int \int d\tau_1 d\tau_2 \left(e^2/r_{12} \right) + \\
 &+ \left(\frac{\beta^2}{2 \cdot 2! V^2} \right) \left(N_e^2 + 2N_e N_i z_i^2 + N_i^2 z_i^4 \right) \int \int d\tau_1 d\tau_2 \left(e^2/r_{12} \right)^2 + \\
 &- \left(\frac{\beta^2}{2 \cdot 3! V^2} \right) \left(N_e^2 - 2N_e N_i z_i^3 + N_i^2 z_i^6 \right) \int \int d\tau_1 d\tau_2 \left(e^2/r_{12} \right)^3 + \dots \\
 &= N_e F_{0e} + N_i F_{0i} - (\beta/2V^2) (N_e - z_i N_i)^2 \int d\tau (e^2/r) + \\
 &+ \left(\frac{\beta^2}{2 \cdot 2! V} \right) \left(N_e + z_i^2 N_i \right)^2 \int d\tau (e^2/r)^2 - \left(\frac{\beta^2}{2 \cdot 3! V} \right) \left(N_e - z_i^3 N_i \right)^2 \int d\tau (e^2/r)^3 + \dots
 \end{aligned} \tag{8}$$

For the particular case of an electron gas in a continuous positive charge background, all the linearly divergent terms in Eq. (8) are removed by the condition of electrical neutrality; the divergences of the other terms are eliminated by appropriate regrouping of the terms of the perturbation expansion: (1) The ideal-gas free energy of the positive charges, $N_i F_{0i}$, vanishes when they are converted into a fixed continuum. (2) The first integral drops out by electrical neutrality, $N_e = z_i N_i$. (3) Let $z_i \rightarrow 0$ and $N_i \rightarrow \infty$ and keep the product $z_i N_i$ constant. This eliminates all the integrals which are multiplied by $z_i^2 N_i$, $z_i^3 N_i$, etc. We are then left with

$$\beta F = N_e F_{0e} + N_e^2 \left(\frac{\beta^2}{2 \cdot 2! V} \right) \int d\tau (e^2/r)^2 + N_e^2 (2V)^{-1} \sum_{s=3}^{\infty} \frac{(-1)^s}{s!} \int d\tau (\beta e^2/r)^s. \tag{9}$$

There are two remaining divergences in Eq. (9). The first integral is linearly divergent since

$$\int_0^R r^2 dr (1/r^2) \sim R.$$

This term will be combined with other divergent parts of more complicated cluster integrals and summed to give a finite result (the "ring integral").

The other integral is not as bad as it looks, since

$$\sum_{s=3}^{\infty} \frac{(-1)^s}{s!} (\beta e^2/r)^s = e^{-(\beta e^2/r)} - 1 + (\beta e^2/r) - \frac{1}{2} (\beta e^2/r)^2 \quad (10)$$

is actually finite at the origin when multiplied by the factor r^2 from the volume element, and only the term $\int d\tau (\beta e^2/r)^3$ gives a logarithmic divergence at infinity. This term is similarly to be summed with contributions from other cluster integrals, leading to the so-called "watermelon" integral.

Detailed analysis of the cluster integrals, using a screened Coulomb potential³

$$U(r) = (e^2/r)e^{-\delta r} \quad (11)$$

shows that the most divergent integrals involving j particles are those of the type $\int f_{12} f_{23} \cdots f_{j-1,j} f_{j,1}$; each particle is joined to just two others, the whole cluster forming a ring. Furthermore, when the f functions are expanded in powers of the interaction $U(r)$, the first term is always the most divergent. It is then assumed that if one can sum the most divergent terms before integrating and thereby obtain a finite result, this result will give a larger contribution to the free energy than the other terms which were initially less divergent. (This assumption has apparently never been rigorously justified, although in this case the summation of the less divergent terms does turn out to give contributions of smaller order of magnitude.)

The virial coefficient B_j is thus approximated by the expression

$$B_j = (-1)^j \left(\frac{1}{2}\right) (j-1)! (\beta^j/j! V) \int \cdots \int d\tau_1 \cdots d\tau_j U(r_{12})U(r_{23}) \cdots U(r_{j,1}) \quad (12)$$

³ $e^{-\delta r}$ is used only as a convergence factor in the integrals and δ has no physical significance.

where the combinatorial factor $\frac{1}{2} (j - 1)!$ is the number of ways the j particles may be placed on the ring. This "convolution" integral may be evaluated for the potential (11) by introducing the Fourier representation

$$U(r) = (e^2/r)e^{-\delta r} = V(2\pi)^{-3} \int d\tilde{k} u(\tilde{k}) e^{i\tilde{k}\cdot\tilde{r}},$$

$$u(k) = V^{-1} \int d\tilde{r} U(r) e^{i\tilde{k}\cdot\tilde{r}} = \frac{4\pi e^2}{V(k^2 + \delta^2)}, \quad (13)$$

together with the Fourier representation of the delta function,

$$\delta(k) = (2\pi)^{-3} \int d\tilde{r} e^{i\tilde{k}\cdot\tilde{r}}.$$

The result is

$$B_j = \frac{(-1)^j (4\pi)(4\pi\beta e^2)^j V}{2^j (2\pi)^3} \int_0^\infty dk \frac{k^2}{(k^2 + \delta^2)^j} \quad (14)$$

For the pure Coulomb potential ($\delta = 0$) we see that B_j diverges as R^{2j-3} if the momentum integration is extended to a lower limit $k_{\min} = R^{-1}$. To eliminate this long range (small momentum) divergence, we sum over j before integrating over k , so that we obtain the ring contribution to the free energy

$$\beta F_{\text{ring}} = \sum_{j=2}^{\infty} B_j n^j = \frac{2\pi V}{(2\pi)^3} \int_0^\infty dk k^2 \sum_{j=2}^{\infty} \frac{1}{j!} \left(\frac{4\pi\beta e^2 n}{k^2 + \delta^2} \right)^j \quad (15)$$

Since

$$\ln(1+x) = - \sum_{j=1}^{\infty} \frac{1}{j} (-x)^j, \quad |x| \leq 1 \quad (16)$$

we can write Eq. (15) in closed form

$$\beta F_{\text{ring}} = \frac{2\pi V}{(2\pi)^3} \int dk k^2 \left\{ \frac{4\pi\beta e^2 n}{k^2 + \delta^2} - \ell n \left(1 + \frac{4\pi\beta e^2 n}{k^2 + \delta^2} \right) \right\} \quad (17)$$

$$= \frac{V}{(2\pi)^2 \lambda_D^3} \int dy y^2 \left\{ (y^2 + \eta^2)^{-1} - \ell n \left(1 + \frac{1}{y^2 + \eta^2} \right) \right\} \quad (18)$$

$$= - \frac{N}{(2\pi)^2 n \lambda_D^3} \cdot \frac{\pi}{3} \left[(1 + \eta^2)^{3/2} - \frac{3}{2} \eta - \eta^3 \right], \quad (19)$$

where we have introduced the new quantities

$$y = k\lambda_D,$$

$$\eta = \delta\lambda_D,$$

$$\lambda_D = (4\pi\beta e^2 n)^{-1/2} \quad (\text{Debye length}).$$

It will be observed that the quantity in brackets in Eq. (19) goes to unity as $\eta \rightarrow 0$ and one then recovers the same expression for the free energy as was found in the original DH theory. However, the passage from (15) to (17) is valid only when $\eta \geq 1$. It is customary to disregard the restriction $\eta \geq 1$ by asserting that Eq. (17) is really the correct form valid for all η , which one would have obtained directly from a better theory, and (15) merely an expansion of dubious validity. In other words, it is assumed that there exists an analytic continuation of the function obtained by summing the series for large k , into the region of small k . The use of this procedure leads here to a result which can be rigorously justified by other methods: it is shown in Appendix A that the DH result can be derived from Eq. (15) without using Eq. (17).

While Eq. (15) was first obtained by Mayer (8) and shown to be formally equivalent (in the sense described above) to the DH result, the closed form (17) was first given explicitly by Zubarev (9).

It is convenient to introduce a dimensionless parameter

$$\lambda = \beta e^2 / \lambda_D = 2\pi^{1/2} e^3 \beta^{3/2} n^{1/2}.$$

The classical DH result [$(\eta \rightarrow 0$ in Eq. (19)] is then

$$\beta F_{\text{ring}} = - N\lambda/3 \tag{20}$$

from which the pressure and internal energy are obtained as

$$\beta P = n \left(1 - \frac{1}{6}\lambda \right), \tag{21}$$

$$\beta E = N \left(\frac{3}{2} - \frac{1}{2}\lambda \right).$$

The above derivation of the DH result by summing ring integrals can be generalized to provide a complete diagram expansion for the free energy, in which each term is convergent for the Coulomb potential (11,12,13). We start from the Mayer expansion for the free energy based on Eq. (3),

$$S = \sum_{m=2}^{\infty} \frac{n^m}{m! V} \int \dots \int \sum_{m > i \geq j \geq 1} \prod f_{ij} d\tau_1 \dots d\tau_m \tag{22}$$

(sum over all products in which all particles are more than singly connected).

The Mayer f functions may now be expanded in powers of the potential to give a true perturbation expansion. The next step is to pick out the terms like those occurring in the second integral in Eq. (9); a term like $\int [U(r_{12})]^3$ is then combined with all the other terms in which one or more of the direct interactions $U(r_{12})$ is replaced by a chain of interactions of the type $U(r_{13})U(r_{34}) \dots U(r_{k,2})$. The points in a diagram representing particles 1 and 2, which are involved in more than two of the interactions, are called nodal points by Meeron (11) and junctions by Abé (13); these points serve as the ends of the chains of interactions in the diagrams we are considering. We can sum over all the chains which may connect two modal points, just as we

summed over all the rings in Eq. (15), using the Fourier representation of the potential function, the result being

$$\sum_{m=0} (-\beta)^{m+1} \frac{v}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} N^m [u(k)]^m,$$

which can be written in closed form as

$$\frac{v}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} \left(\frac{-\beta u(k)}{1 + \beta N u(k)} \right).$$

For the Coulomb potential ($\delta = 0$) we have

$$\beta N u(k) = \frac{4\pi\beta e^2 n}{k^2} = (\lambda_D k)^{-2}$$

and therefore we replace the real interaction $U(r)$ by a "shielded" interaction

$$U_s(r) = \frac{e^2}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} \left(k^2 + \lambda_D^{-2} \right)^{-1} = \frac{e^2}{r} e^{-r/\lambda_D},$$

$$r = |\mathbf{r}_1 - \mathbf{r}_2|. \quad (23)$$

When this shielded interaction is incorporated into the cluster expansion, one obtains a finite result for the sum of the divergent terms and ignores (in this approximation) the others; the general form of the modified virial series is now

$$\beta F = N_e F_{oe} + N F_{ring} + N \sum_{j=2}^{\infty} S_j(\lambda) \quad (24)$$

where [cf. Eq. (10)]

$$S_2 = \frac{1}{2} n \int_0^{\infty} 4\pi r^2 dr \left\{ e^{-\beta U_s(r)} - 1 + \beta U_s(r) - \frac{1}{2} [\beta U_s(r)]^2 \right\} \quad (25)$$

and S_3 , S_4 , etc. can also be written down if desired (11, 12). The integral (25) has been evaluated numerically by Trulio and Brush (32).

The general formula for the shielded potential $U_s(r)$ corresponding to a real potential $U(r)$ is

$$U_s(r) = F^{-1} \left\{ \frac{F U(r)}{1 + \beta N F U(r)} \right\} \quad (26)$$

where F denotes the Fourier transform operation. The shielded potential may also be identified with the "potential of average force," as will be more clear when we come to the distribution function approach in Section IV.

III. TWO-COMPONENT SYSTEM: SOFT SPHERES

The formulae of Section II can easily be generalized to the multi-component case, but the integrals now have a short range divergence when a pure Coulomb potential is used. Such divergences have often been eliminated by using a hard sphere potential, Eq. (2), but this type of potential is not very convenient when one is using a method based on Fourier transforms; neither is it particularly realistic for ionized gases. Kramers (33) employed the function

$$(e^2/r)(1 - \exp[-ar/2R])$$

where R is the position of the center of mass of the two atoms whose distance of separation is r . This particular form was chosen so that "the property of the energy to be a homogeneous function of the coordinates of the degree -1 is preserved"; the origin of coordinates was taken outside the container so that R was essentially constant. Glauber and Yukhnovskii (15,16) showed that the function

$$U(r) = (\pm e^2/r)(1 - e^{-\gamma r}) \quad (27)$$

is very convenient for analytical investigations based on the method of distribution functions, and it also turns out to be convenient for calculations using the formulae developed in Section II.

The Fourier transform of the function (27) is easily found to be

$$u(k) = \pm \frac{4\pi e^2}{V} \frac{\gamma^2}{k^2(k^2 + \gamma^2)} \quad (28)$$

The ring integral is

$$F_{\text{ring}} = \frac{\pi}{3} \frac{1}{4\pi^2 n \lambda_D^3} \left(\frac{1}{a} \right)^3 \left\{ \frac{3}{2} a - a^3 + \left[\frac{1}{2} a^2 - \frac{1}{2} (a^4 - 4a^2)^{1/2} \right]^{3/2} + \left[\frac{1}{2} a^2 + \frac{1}{2} (a^4 + 4a^2)^{1/2} \right]^{3/2} \right\} \quad (29)$$

where

$$a = \gamma \lambda_D.$$

The total pressure in the ring integral approximation is

$$\begin{aligned} \frac{P}{nkT} &= 1 - \frac{\lambda}{6} f_1(a), \\ f_1(a) &= a^3 \left(\frac{1}{4} w^3 - \frac{3}{2} w + 2 - \frac{3}{4w} \right), \\ w &= \left(1 + \frac{2}{a} \right)^{\frac{1}{2}}. \end{aligned} \quad (30)$$

The parameter λ is now defined for multi-component systems as

$$\lambda = \left(4\pi n \lambda_D^3 \right)^{-1} = (4\pi)^{\frac{1}{2}} \left(\sum_s e_s^2 n_s \right)^{3/2} \beta^{3/2} n^{-1/2} K^{-3/2}$$

where the mole fraction and charge of component s are denoted by n_s and e_s , respectively; K is the dielectric constant which can usually be set equal to one for ionized gases.

The function $f_1(a)$ may be expanded around the point $a^{-1} = 0$ [$w = 1$] giving

$$f_1(a) = 1 - (9/4a) + (9/2a^2) - (35/4a^3) + (135/8a^4) - \dots, \quad (31)$$

or around the point $a = 2$, giving

$$\begin{aligned} f_1(a) &= 16 - 11\sqrt{2} + \left(24 - \frac{135}{8}\sqrt{2} \right) y^2 + \left(30 - \frac{2709}{128}\sqrt{2} \right) y^4 + \dots, \\ y^2 &= 1 - (4/a^2). \end{aligned} \quad (32)$$

From Eq. (31) it is clear that one recovers the usual DH equation of state, Eq. (21), in the limit $\gamma \rightarrow \infty$.

It is interesting to compare the equation of state (30) for soft spheres with the well-known equation of state for the hard sphere potential⁴:

$$\frac{P}{nkT} = 1 - \frac{\lambda}{6} g_1(\delta), \quad (33)$$

$$g_1(\delta) = (3/\delta^3) \left[1 + \delta - \frac{1}{1+\delta} - 2 \ln(1+\delta) \right],$$

$$\delta = a/\lambda_D,$$

which can also be expanded in powers of δ ,

$$g_1(\delta) = 1 - (3\delta/2) + (9\delta^2/5) - (2\delta^3) + \dots \quad (34)$$

Thus, if the parameter γ in the soft sphere potential is equated to $(3/2a)$, we get

$$f_1(3\lambda_D/2a) = 1 - (3\delta/2) + 2\delta^2 - (70\delta^3/27) + \dots \quad (35)$$

or conversely putting $a = (3/2\gamma)$ we get

$$g_1(3/2\gamma\lambda_D) = 1 - (9/4a) + (81/20a^2) - (27/4a^3) + \dots \quad (36)$$

In Table I we give a few values of $f_1(a)$ together with corresponding values⁵ of $g_1(3/2\gamma\lambda_D)$. It is evident that hard spheres and soft spheres with appropriately chosen parameters have very nearly the same equation of state in the region where the ring integral approximation is valid.

To compute the next term, S_2 , in the modified cluster expansion (24), we need the shielded potential $U_s(r)$ which corresponds to the soft sphere potential. The result, using Eq. (26), is

$$\beta U_s(r) = \pm(\lambda/xy) \left[\exp \left\{ -x \left(\frac{2}{1+y} \right)^{\frac{1}{2}} \right\} - \left\{ \exp -x \left(\frac{2}{1-y} \right)^{\frac{1}{2}} \right\} \right]; \quad (37)$$

$$x = r/\lambda_D,$$

$$y = (1 - 4/a^2)^{\frac{1}{2}}$$

⁴The work of Hage (10) indicates that $g_1(\delta)$ as given here is accurate only to terms linear in δ in Eq. (34).

⁵Mostly computed by S. R. Brinkley, Jr., and R. F. Brinkley; see ref. (34), p. 176.

The expression on the right-hand side of Eq. (37) apparently becomes complex for $\alpha < 2$; however, it can still be written in real form (with $z = iy$),

$$\beta U_s(r) = \pm(2\lambda/xz) [\exp(-G_2 x)] \sin(G_1 x); \quad (38)$$

$$G_1 = \frac{\alpha}{2} \left(\frac{2}{\alpha} - 1 \right)^{\frac{1}{2}},$$

$$G_2 = \frac{\alpha}{2} \left(\frac{2}{\alpha} + 1 \right)^{\frac{1}{2}}.$$

We see that the shielded potential changes to a periodic form at $\alpha = 2$, though there is no discontinuity in the ring integral contribution to the pressure, $f_1(\alpha)$, at this point. As will be brought out more clearly in the next section, this implies a locally periodic spatial distribution of ions around any one ion. However, the existence of such a periodic structure in the system, if it really occurred, would seem to invalidate the use of any low-density expansion such as the one described here. We shall therefore regard $\alpha = 2$ as the limit of the region of applicability of the modified cluster integral theory, as far as the soft sphere model is concerned. In other words, we do not expect the theory to apply when the Debye screening length (λ_D) is less than twice the "mean radius" (γ^{-1}) of the ion. This is also a reasonable criterion for deciding when the soft sphere model itself ceases to provide a good description of real ions, since when the Debye length becomes so small that it is of the same order of magnitude as the ionic radius, one would expect the equation of state to depend strongly on the detailed structure of the ion itself.

Our final equation of state is thus

$$\frac{P}{nkT} = 1 - \frac{\lambda}{6} f_1(\alpha) + f_2(\lambda, \alpha) \quad (39)$$

where $f_2(\lambda, \alpha)$ is obtained by differentiating the appropriate form of S_2 with respect to the volume:

$$f_2(\lambda, \alpha) = \frac{S'_2}{n} - \frac{\partial S'_2}{\partial n},$$

$$S'_2 = 4\pi n \int_0^\infty \left[e^{-\beta U_s} + e^{\beta U_s} - (\beta U_s)^2 - 2 \right] r^2 dr. \quad (40)$$

(The generalization to an n-component system is not difficult; see Section IV.)

It is possible to derive a series expansion for $f_2(\lambda, \alpha)$ (see Appendix B); while S_2 (and presumably all the higher terms in the series) diverge in the limit $\alpha \rightarrow \infty$, an expansion similar to Eq. (32) is possible when α is somewhat larger than 2. If one works out the first term in the expansion he finds

$$f_2(\lambda, \alpha) = - \frac{17\sqrt{2}}{32768} \gamma^2 \lambda^3.$$

(For the case of symmetrical electrolytes, all the even powers of λ in Eq. (39) have vanishing coefficients.)

We have also evaluated $f_2(\lambda, \alpha)$ numerically; the results are given in Table II. Comparison with these shows that the above approximate formula works fairly well as long as both λ and γ are smaller than about 0.3, but it fails completely for large λ . Just as was found in the one-component case (32), the approximation based on the first term in an expansion of S_2 gives very misleading results in the region where the effect of S_2 begins to be important. Whereas, for small λ , S_2 gives a negative contribution to the pressure, for larger values of λ it gives a positive contribution which counteracts the effect of the ring integral $(-\frac{\lambda}{6} f_1(\alpha))$. This is fortunate inasmuch as the ring integral term by itself would lead to a negative total pressure at large values of λ and γ .

For numerical calculations we have used two values of γ to illustrate the dependence of the pressure on ionic size: (a) $\gamma = 0.29 \times 10^8 \text{ cm}^{-1}$, or $\gamma^{-1} = 3.45 \times 10^{-8} \text{ cm}$; (b) $\gamma = 0.58 \times 10^8 \text{ cm}^{-1}$, or $\gamma^{-1} = 1.725 \times 10^{-8} \text{ cm}$.

Since $\lambda_D = 6.9 (T/n)^{\frac{1}{2}}$ cm when T is in $^{\circ}\text{K}$ and n is in ions/cm³, we have in case (a), $a = 2 \times 10^8 (T/n)^{\frac{1}{2}}$, and in case (b), $a = 4 \times 10^8 (T/n)^{\frac{1}{2}}$. In Table III we give the magnitude of the various contributions to the right-hand side of Eq. (39). The Debye contribution for point charges, $\frac{\lambda}{6}$, is given in column (1), the ring integral $\frac{\lambda}{6} f_1(a)$ in column (2), the contribution from S_2 , viz. $f_2(\lambda, a)$, in column (3), and the total values of P/nkT in column (4). No real gas would be completely ionized at the lowest temperatures given in the table, but the numbers are still useful in indicating the electrostatic contributions to the equation of state in those regions where the variation of the degree of ionization can be ignored.

It will be observed that, except at low temperatures, the condition $a > 2$ is a more stringent restriction on the region of validity of the theory than the condition that λ be small. The former condition corresponds to a straight line in the temperature-density plane: by doubling the temperature, one doubles the maximum permissible density. On the other hand, since $f_2(a)$ varies as $(1 - 4/a^2)$ when the latter quantity is small, we see that halving the ionic radius at a given temperature permits one to go up to densities four times as high. However, this can only be done provided that λ does not thereby become too large. When the temperature is high enough to produce complete ionization, the ions will be just nuclei and electrons, and one could then make the ionic radius much smaller (but not zero) and thus extend the region of validity to much higher densities. One would still have to worry about how well the soft sphere model describes the actual short-range interactions in this case, however.

It has not been conclusively established that the periodic form, Eq. (38), is meaningless; it may be that the cluster integral theory still provides an adequate description of the system in the region where $\gamma\lambda_D < 2$. In fact,

Villars (35) has used the corresponding pair distribution function as a starting point for a numerical calculation of the equation of state of a dense plasma, based on a theory of H. S. Green (36). We merely wish to emphasize the need for further justification of the validity of the theory in this case.

For a discussion of the magnitude of the S_2 contribution for a hard sphere potential, we refer to the article by Meeron (37).

IV. THE DISTRIBUTION FUNCTION METHOD

The distribution function approach was applied to electrolyte solutions by Kirkwood (38) in 1935; Kirkwood derived an integral equation for the potential of mean force [cf. Onsager (39)], defined as proportional to the logarithm of the pair distribution function, and showed that for Coulomb forces the potential of mean force is simply the Debye shielded potential. However, Kirkwood's later work employed the superposition approximation, and it remained for Bogolyubov (14) and later Glauber and Yukhnovskii (15,16,17) to develop an exact series expansion for the distribution function. Bogolyubov did not go beyond the DH term because he found that higher approximations to the distribution function became successively more divergent at the origin. Glauber and Yukhnovskii avoided this difficulty by using a soft sphere potential, Eq. (1); they obtained a first approximation for the equation of state which corresponds to the ring integral approximation in cluster integral theory, and a distribution function which is very similar in form to the shielded potential given in Eqs. (37,38). In fact, there is a close relation between their solution of the integral equation for the distribution function and the chain summation in the cluster integral theory. The similarity between the distribution function theory and the cluster integral theory has not been generally recognized, though it is well known that both

must give the same result when carried to a sufficiently high degree of approximation. Aside from the fact that Glauber and Yuknovskii's work has previously been available only in Russian, there has been some confusion because they made an error in obtaining their final formula for the free energy. The correct expression for the free energy has been given by Kessler and Gorbanev (40), and it turns out to be exactly equivalent to Eq. (29).

Let D_N represent the probability distribution function for the positions of all N molecules, given by

$$D_N = D_N(r_1, \dots, r_N) = Q_N^{-1} e^{-\beta U} \quad (41)$$

where Q_N is the same configuration integral introduced in Eq. (3),

$$Q_N = \int \dots \int e^{-\beta U} dr_1 \dots dr_N,$$

$$U = \sum U_{ij}(r_{ij}).$$

The distribution functions $F_s(r_1, \dots, r_s)$ with $s = 1, 2, 3, \dots$, are defined in such a way that

$$V^{-s} F_s(r_1, \dots, r_s) dr_1 dr_2 \dots dr_s$$

represents the probability that the positions of a given set of s molecules lie in the volume element $(r_1, r_1 + dr_1) \dots (r_s, r_s + dr_s)$. In particular, F_s is related to D_N by the identity

$$F_s(r_1, \dots, r_s) = V^{-s} \int \dots \int D_N(r_1, \dots, r_N) dr_{s+1} \dots dr_N \quad (42)$$

By differentiating F_s with respect to the α -component of the position vector of molecule 1, and using Eqs. (41) and (42), one can derive the equation

$$\left(\frac{\partial F_s}{\partial r_1^\alpha}\right) + \beta \left(\frac{\partial U_s}{\partial r_1^\alpha}\right) F_s + n\beta \left(1 - \frac{s}{N}\right) \int \left(\frac{\partial U(r_{ij})}{\partial r_1^\alpha}\right) F_{s+1} dr_{s+1} = 0 \quad (43)$$

where

$$U_s = \sum_{1 \leq i < j \leq s} U(r_{ij}).$$

Since we shall be interested only in the lower-order distribution functions (e. g., only F_2 is needed to calculate the equation of state) we can assume $s \ll N$ and achieve a slight simplification in Eq. (43):

$$\left(\frac{\partial F_s}{\partial r_1^a}\right) + \beta \left(\frac{\partial U_s}{\partial r_1^a}\right) F_s + n\beta \int \left(\frac{\partial U(r_{ij})}{\partial r_1^a}\right) F_{s+1} dr_{s+1} = 0. \quad (44)$$

Equation (44) is to be solved for F_s with the conditions

$$F_s(r_1, \dots, r_s) - \prod_{1 \leq i \leq s} F_1(r_i) \rightarrow 0 \quad (45)$$

when all the $r_{ij} \rightarrow \infty$;

$$\lim_{V \rightarrow \infty} V^{-1} \int F_1(r) dr = 1, \quad (46)$$

$$\lim_{V \rightarrow \infty} V^{-1} \int F_{s+1}(r_1, \dots, r_{s+1}) dr_{s+1} = F_s(r_1, \dots, r_s). \quad (47)$$

In the case of short range forces, Bogolyubov shows how one can solve Eq. (44) by expanding the distribution functions in powers of the density, thereby obtaining the Ursell-Mayer cluster expansion. In the case of long range Coulomb forces, the appropriate dimensionless parameter is $\lambda = (4\pi n \lambda_D^3)^{-1}$; the factor of 4π is of course optional and is omitted by Bogolyubov and by Glauber and Yukhnovskii, who also absorb the factor λ_D^{-3} into the definition of the higher approximations to F . Thus, they write the pair distribution function

$$F_{ab} = 1 + n^{-1} F_{ab}^0 + n^{-2} F_{ab}^1 + n^{-3} F_{ab}^2 + \dots \quad (48)$$

F_{ab}^2 denotes the second approximation term in the pair distribution function for particles of kinds a and b.

In the case when the superposition approximation

$$F_{abc} = F_{ab} F_{ac} F_{bc} \quad (49)$$

is used, one can derive a system of equations for the successive terms in Eq. (48),

$$F_{ab}^0 + n_c \int V_{ac} F_{bc}^0 dr'' = -V_{ab}, \quad (50)$$

$$F_{ab}^1 + n_c \int V_{ac} F_{bc}^1 dr'' = \frac{1}{2} (F_{ab}^0)^2 - n_c \int F_{bc}^0 \int_{\infty}^{|r-r''|} (dV_{ac}/dt) F_{ac}^0 dt dr'', \quad (51)$$

where

$$V_{ab} = n\beta U_{ab},$$

$$n_c = N_c/N$$

(N_c is the number of particles of kind c). The system (50,51, etc.) is solved by Fourier transforms; each of these equations has the form

$$F_{ab} + n_c \int V_{ac} F_{bc} dr'' = L_{ab}, \quad (52)$$

and the various functions occurring in Eq. (52) have the Fourier representations

$$F_{ab} = \int K_{ab}(k, r) e^{ik \cdot \tilde{r}} d\tilde{k},$$

$$V_{ac} = (4\pi)^{-1} \int Y_{ac}(|\tilde{k}|) e^{ik \cdot (\tilde{r} - \tilde{r}'')} d\tilde{k},$$

$$L_{ab} = \int M_{ab}(|\tilde{k}|) e^{ik \cdot (\tilde{r} - \tilde{r}')} d\tilde{k}.$$

The general solution for K_{ab} is

$$K_{ab} = M_{ab} - \frac{2\pi^2 \sum_c Y_{ac} n_c M_{cb}}{1 + 2\pi^2 \sum_c Y_{cc} n_c} \quad (53)$$

In the special case of the soft sphere potential, whose Fourier transform is given by Eq. (28), it is found that the Fourier transform of the zeroth approximation to the pair distribution function is

$$K_{ab}^0 = - (2\pi)^{-2} \frac{e_a e_b}{4\pi \sum_c e_c^2 n_c} \frac{\gamma^2}{\lambda_D^2 k^2 (\gamma^2 + k^2) + \gamma^2} \quad (54)$$

(in this case L_{ab} is just $-V_{ab}$). Inverting the Fourier transform, one thus gets

$$F_{ab}^0 = - \frac{2}{\pi} \frac{e_a e_b}{4\pi \sum_c e_c^2 n_c} \frac{\gamma^2}{r} \int \frac{k \sin(kr) dk}{\lambda_D^2 k^2 (\gamma^2 + k^2) + \gamma^2} \quad (55)$$

$$= - \frac{e_a e_b}{4\pi \sum_c e_c^2 n_c} \frac{p^2 q^2}{p^2 - q^2} \frac{e^{-qr} - e^{-pr}}{r}, \quad (56)$$

where

$$p = \frac{\gamma}{2} \left[\left(1 + 2/a\right)^{\frac{1}{2}} + \left(1 - 2/a\right)^{\frac{1}{2}} \right],$$

$$q = \frac{\gamma}{2} \left[\left(1 + 2/a\right)^{\frac{1}{2}} - \left(1 - 2/a\right)^{\frac{1}{2}} \right],$$

$$p^2 + q^2 = \gamma^2; \quad p^2 q^2 = \gamma^2 / \lambda_D^2.$$

When $a < 2$, p and q become complex but F_{ab}^0 can then be written in the real form

$$F_{ab}^0 = \frac{2}{\lambda_D^2} \frac{e_a e_b}{4\pi \sum_c e_c^2 n_c} \frac{\exp\left[-\frac{1}{2} \gamma r \left(\frac{2}{a} + 1\right)^{\frac{1}{2}}\right]}{(4/a^2 - 1)^{\frac{1}{2}}} \frac{\sin\left[\frac{1}{2} \gamma r \left(\frac{2}{a} - 1\right)^{\frac{1}{2}}\right]}{r} \quad (57)$$

For comparison with Eqs. (37) and (38) we note the identities

$$p = \gamma \left(\frac{1+y}{2}\right)^{\frac{1}{2}} = \lambda_D^{-1} \left(\frac{2}{1-y}\right)^{\frac{1}{2}},$$

$$q = \gamma \left(\frac{1-y}{2}\right)^{\frac{1}{2}} = \lambda_D^{-1} \left(\frac{2}{1+y}\right)^{\frac{1}{2}},$$

where

$$y = (1 - 4/a^2)^{\frac{1}{2}}.$$

We see that the shielded potential $U_s(r)$ calculated by summing chains contains the same function as the zeroth approximation to the pair distribution function which Glauber and Yukhnovskii obtained by solving a set of integral equations,

$$\beta U_s(r) = n^{-1} F_{ab}^0(r). \quad (58)$$

The energy of the system may now be calculated from the formula

$$U_N = (4\pi/V) \sum_{a,b} \frac{1}{2} N_a N_b \int U(r_{ij}) F_{ab}(r_{ij}) r_{ij}^2 dr_{ij} \quad (59)$$

which gives, using the soft sphere potential and the expression (56) for the distribution function,

$$U_N = - (1/2K) \sum_a N_a e_a^2 \frac{p^2 q^2}{p^2 - q^2} \left[\frac{p-q}{pq} - \frac{p-q}{pq + a(p+q) + a^2} \right]. \quad (60)$$

The free energy is determined by the relation

$$F = - T \int (U/T^2) dT. \quad (61)$$

Glauber and Yukhnovskii (16) obtained the result

$$F = (\gamma^3/4\pi\beta) \left[\frac{1}{5} (X - 1)^5 - \frac{2}{3} (X - 1)^3 + (X - 1) + \frac{1}{20} (X - 2)^5 + \frac{1}{4} (X - 2)^4 X \right],$$

$$X = (1 + 2/a)^{\frac{1}{2}} - 1,$$

which is incorrect; the correct result,

$$F = (\gamma^3/16\pi\beta) \left[(X - 1)^2 - 2(X - 1) + \frac{2}{3}(X - 1)^3 - \frac{1}{2}(X - 1)^4 + \frac{5}{6} \right], \quad (62)$$

was first given by Kessler and Gorbanev (40). Equation (62) is equivalent to Eq. (29) and thus it turns out that the equation of state based on the first approximation to the pair distribution function, Eq. (56), is identical to that calculated from the ring integral sum in the modified cluster expansion.

To obtain higher approximations from the distribution function method, it is necessary to eliminate the superposition approximation. This has been done by Glauber and Yukhnovskii in another paper (41); they express the distribution functions $F_s(r_1, \dots, r_s)$ in terms of certain auxiliary functions introduced by Bogolyubov (14),

$$\begin{aligned} F_a(r) &= g_a(r), \\ F_{ab}(r, r') &= g_a(r)g_b(r') + n^{-1} g_{ab}(r, r'), \\ F_{abc}(r, r', r'') &= g_a(r)g_b(r')g_c(r'') + n^{-1} \left[g_{ab}(r, r')g_c(r'') + g_{ac}(r, r'')g_b(r') \right. \\ &\quad \left. + g_{bc}(r', r'')g_a(r) \right] + n^{-2} g_{abc}(r, r', r''), \end{aligned} \quad (63)$$

The g functions satisfy similar integral equations, which can be solved by expanding in powers of n^{-1} (the corresponding dimensionless parameter is λ)

$$\begin{aligned} g_{a_1, \dots, a_s}(r_1, \dots, r_s) &= g_{a_1, \dots, a_s}^0(r_1, \dots, r_s) \\ &\quad + n^{-1} g_{a_1, \dots, a_s}^1(r_1, \dots, r_s) + \dots \end{aligned} \quad (64)$$

We shall refer to the g 's as correlation functions. The problem of finding an approximation of a given order to a correlation function for a

specified number of molecules can be reduced to the determination of the approximation of next lower order to the correlation function for a group containing one more molecule. Thus, to determine g_{ab}^1 one needs to find g_{abc}^0 , etc. According to Glauber and Yukhnovskii (41) the solution has the form

$$g_{abc}^0 = g_{ab}^0 g_{ac}^0 + g_{bc}^0 g_{ac}^0 + \sum_c n_c \int g_{da}^0 g_{db}^0 g_{dc}^0 dr_d, \quad (65)$$

$$g_{ab}^1 = \frac{1}{2!} (g_{ab}^0)^2 + \frac{1}{2!} \sum_c n_c \int (g_{ac}^0)^2 g_{cb}^0 dr_c + \frac{1}{2!} \sum_c n_c \int g_{ac}^0 (g_{cb}^0)^2 dr_c \\ + \frac{1}{2!} \sum_{c,d} n_c n_d \int g_{ad}^0 (g_{dc}^0)^2 g_{cb}^0 dr_c dr_d. \quad (66)$$

The first term in Eq. (66) represents the corresponding term in the expansion of $\exp [n^{-1} g_{ab}^0]$ in powers of $n^{-1} g_{ab}^0$; the remaining three terms are correlation integrals describing the influence of an arbitrary third molecule on the probability of a given configuration of two selected molecules a and b; the last integral also includes the effect of a fourth molecule.

The difference between g_{ab}^1 , the first approximation to the pair distribution function calculated from the exact expansion, and F_{ab}^1 , the corresponding approximation calculated with the superposition approximation, is found to be

$$\Delta = g_{ab}^1 - F_{ab}^1 = \sum_c n_c \int g_{bc}^0 \left\{ \int_{\infty}^r \frac{d}{dr} (g_{ac}^0 - v_{ac}) g_{ac}^0 dr \right\} dr_c \\ + \sum_{c,d} n_c n_d \int g_{ad}^0 g_{cb}^0 \left\{ \int_{\infty}^r \frac{d}{dr} (g_{dc}^0 - v_{dc}) g_{dc}^0 dr \right\} dr_c dr_d. \quad (67)$$

In the case of the soft sphere potential, Glauber and Yukhnovskii estimate that the superposition approximation is applicable only for concentrations less than about 0.01 mole/liter.

Yukhnovskii (17) has given a more detailed analysis of the series expansion of the pair distribution function. He finds that, just as g_{ab}^1 contains according to Eq. (66) a term $\frac{1}{2!} (g_{ab}^0)^2$ plus several "correlation" terms, g_{ab}^2 contains a term $\frac{1}{3!} (g_{ab}^0)^3$ together with more complicated correlation terms, and similarly for g_{ab}^3 , etc. If the correlation terms were absent, the pair distribution function could be written as $\exp [n^{-1} g_{ab}^0]$, in which case $g_{ab}^0/n\beta$ or $U_s(r)$ could be interpreted very simply as the potential of average force. Actually the correlation terms do not vanish, and may become rather important at higher densities.

The general expression for the pair distribution function given by Yukhnovskii is:

$$\begin{aligned}
 F_{ab} = & 1 + n^{-1} g_{ab}^0 + n^{-2} \left[\frac{1}{2} (g_{ab}^0)^2 + \frac{1}{2} n_c \int \left\{ (g_{ac}^0)^2 g_{cb}^0 + g_{ac}^0 (g_{ab}^0)^2 \right\} dr_c \right. \\
 & \left. + \frac{1}{2} n_c n_d \int g_{ac}^0 (g_{cd}^0)^2 g_{db}^0 dr_c dr_d \right] + \dots \\
 & + n^{-k-1} \left[\frac{(g_{ab}^0)^{k+1}}{(k+1)!} + \sum n_c \int \left\{ \frac{(g_{ac}^0)^{k+1}}{(k+1)!} g_{cb}^0 + \dots \right\} dr_c + \dots \right. \\
 & \left. + \sum \dots \sum n_1 \dots n_{2k} \int \dots \int g_{a,2k}^0 \dots \frac{(g_{k+1,k}^0)^2}{2} dr_1 \dots dr_{2k} \right] \\
 & + \dots \quad (68)
 \end{aligned}$$

There is of course a prescription for constructing each term in the series, and it would not be difficult to show by a suitable rearrangement of these terms that the free energy is identical to the modified virial series, Eq. (24), derived by Meeron, Friedman, and Abé.

Nevertheless, Yukhnovskii was not satisfied with the above method, and in a later paper he says (42):

"Until recently the determination of the thermodynamic characteristics of ionic systems has been carried out by the use of partial distribution functions — single-particle and binary functions. The calculations involved cumbersome computations and the solution of complicated systems of integro-differential equations. In these calculations for systems of charged particles short-range forces could be taken into account only with special forms of force law. . . "

He then adopted the method of collective variables, developed by Bohm and Pines, Zubarev (9), Bazarov (23), and others, and attempted to derive a general expression for the free energy which could be used with any kind of short range force law. We shall not describe the details of the method since a translation of this paper has already been published (42); the result is

$$\begin{aligned}
 F = - NkT \ln V + N^{-1} \sum_k [\alpha(k) - \ln(\alpha(k) + 1)] + \frac{1}{2} n \sum_{a,b} n_a n_b \int \left(e^{-h_{ab}} - 1 \right. \\
 \left. + h_{ab} - \frac{1}{2} h_{ab}^2 \right) dr_1 + (n^2/3!) \sum_{a,b,c} n_a n_b n_c \left[\int \left(e^{-h_{ac}} - 1 + h_{ac} \right) \right. \\
 \times \left(e^{-h_{cb}} - 1 + h_{cb} \right) (3h_{ab}) dr_1 dr_2 + \int \left(e^{-h_{ab}} - 1 + h_{ab} \right) \\
 \left. \times \left(e^{-h_{ac}} - 1 + h_{ac} \right) \left(e^{-h_{cb}} - 1 + h_{cb} \right) dr_1 dr_2 \right] + \dots \quad (69)
 \end{aligned}$$

where

$$\alpha(k) = u(k) \sum_c (e_c^2 n_c n\beta),$$

$u(k)$ is the Fourier transform of the potential, and h_{ab} is just the screened potential βU_g defined by Eq. (26). Equation (69) is applicable for the soft sphere potential, and is identical to the modified virial expansion, Eq. (24), the terms S_2 and S_3 being given explicitly by Yukhnovskii. There is another formula, slightly more complicated than Eq. (69), which is valid when more singular short range forces are included (22), but which, according to Siegert (24), requires some modification.

V. HIGH-DENSITY LIMIT OF THE LOW-DENSITY EXPANSION

It has now been shown that a modified virial expansion can be constructed for the equation of state of a system of particles interacting with long range Coulomb forces; this expansion can be carried out in three equivalent ways, and short range forces can also be included (12,22). While it is very important to know that the expansion can be arranged in such a way that each term is finite, it is probably not worthwhile to calculate terms beyond S_2 . The practical usefulness of the theory will probably be limited to the region of validity of the ring integral approximation, and by computing S_2 one can obtain a fairly good idea of the boundary of this region.

It would of course be helpful to know something about the convergence of the series $\sum S_j(\lambda)$. Since the series is extremely complicated and is not just a power series in λ , this convergence is rather difficult to establish. However, it is possible to obtain some information about the high-density limit ($\lambda \gg 1$) of each of the $S_j(\lambda)$. For this purpose we consider again the case of a one-component electron gas in a uniform positively charged background. Following Abé (13), it is convenient to introduce various types of bonds connecting nodal points:

$$W_0 = -q,$$

$$W_1 = \sum_{n=1}^{\infty} \frac{(-q)^n}{n!} = e^{-q} - 1, \quad (70)$$

$$W_2 = \sum_{n=2}^{\infty} \frac{(-q)^n}{n!} = e^{-q} - 1 + q,$$

.....

where $q = q(x) = q(r/\lambda_D)$ is the screened Debye interaction,

$$q = \beta U_s = \frac{\lambda e^{-x}}{x} \quad (71)$$

Using the notation of Eqs. (70) and (71), we can write $S_2(\lambda)$ in the form

$$\begin{aligned} S_2 &= (1/2\lambda) \int_0^\infty x^2 W_3 dx \\ &= -(\lambda/8) + \frac{1}{2} + (1/2\lambda) \int_0^\infty x^2 W_1 dx. \end{aligned} \quad (72)$$

The term in the free energy arising from the " $\frac{1}{2}$ " in Eq. (72) can be shown to vanish by electrical neutrality by the same arguments used in deriving Eq. (9). The third term can be estimated by replacing W_1 by -1 for $x < x_0$ and by zero for $x > x_0$, where x_0 is the solution of the transcendental equation

$$\frac{\lambda e^{-x_0}}{x_0} = 1, \quad (73)$$

viz.

$$x_0 = \ln \lambda - \ln \ln \lambda + \dots \quad (74)$$

Thus, the high-density limit of S_2 is found to be

$$S_2 = -(\lambda/8) - \frac{(\ln \lambda)^3}{6\lambda} + \dots \quad (75)$$

This result can be verified by numerical evaluation of the integral (32).

The high-density form of S_3 may be found in the same way. Its explicit form is [cf. Eq. (69)]

$$S_3 = (1/3! \lambda^2) \int \int [3W_0(x_{12})W_2(x_{23})W_2(x_{13}) + W_2(x_{12})W_2(x_{23})W_2(x_{13})]. \quad (76)$$

Note that $W_2 = W_0 + W_1$ and that the largest term in λ comes from products of W_0 . In diagram notation S_3 can be written

$$\begin{aligned}
 S_3 &= (1/3! \lambda^2) \left\{ \triangle + 3 \triangle \right. \\
 &= (1/3! \lambda^2) \left\{ \left[- \triangle + 3 \triangle - 3 \triangle + \triangle \right] + 3 \left[\triangle - 2 \triangle + \triangle \right] \right\} \\
 &= (1/3! \lambda^2) \left\{ 2 \triangle - 3 \triangle + \triangle \right\} \tag{77}
 \end{aligned}$$

where the dashed line indicates a W_0 bond, a single line indicates W_1 , and a double line W_2 . The $W_0(x_{12})W_0(x_{23})W_0(x_{31})$ term, indicated by \triangle , can be evaluated by the usual convolution method in Fourier space and the result is

$$\triangle = (-\lambda)^3 \frac{2}{\pi} \int_0^\infty \frac{k^2 dk}{(k^2 + 1)^3} = -\frac{\lambda^3}{8} \tag{78}$$

The other terms in Eq. (77) give contributions of order λ^2 or smaller, so we find

$$S_3(\lambda) = -(\lambda/24) + \frac{1}{2} - \frac{O(x_0^9)}{6\lambda^2} \tag{79}$$

The high-density limits of the $S_j(\lambda)$ for $j > 3$ may be studied in the same way, by multiplying the products of W_2 functions to obtain integrals involving products of W_0 and W_1 . The algebra involved in rearranging the diagrams representing S_j increases tremendously with increasing j . However, certain regular features appear, and it seems possible that useful high-density results may be obtainable from this diagrammatic analysis. Beginning with $j = 4$, complications appear. There are always rings of $W_0(x)$ functions which are proportional to λ^j , and hence give a contribution to S_j proportional to λ . Also there are rings of $W_0(x)$ with one replaced by $W_1(x)$, and hence one power of λ smaller than the ring of W_0 's. The complications appear in many terms with multiplicative factors of λ ranging from λ^j up to $\lambda^{2(j-1)}$, but with integrals of the type $\int e^{-q} dx$ connecting vertices. Since e^{-q} becomes a step function,

$$e^{-q} \rightarrow \eta(x) = \begin{cases} 0, & x < x_0, \\ 1, & x > x_0. \end{cases}$$

in the limit $\lambda \rightarrow \infty$, it is difficult to see how large these terms are. Finally, there is a group of terms which represent precisely the j th virial coefficient B_j of a gas of hard spheres of radius $x_0 \approx \ell n \lambda$. This contribution to S_j is of order $(\ell n \lambda)^{3j} / \lambda^{j-1}$ and hence negligible.

By counting, the following result has been established:

$$S_j(\lambda) = (1/j! \lambda^{j-1}) \left\{ \frac{(j-1)!}{2} \left[(-1)^{j+1} (j-1) \text{[hexagon]} + (-1)^j j \text{[hexagon]} \right] \right\} \quad (80)$$

(smaller terms multiplied by λ^j to $\lambda^{2(j-1)}$)

The hexagon of dashed lines symbolizes a polygon of j q-bonds, and the second hexagon has one q replaced by W_1 . Using only the first of these and applying the convolution theorem, we find that

$$\text{[hexagon]} = (-1)^j \lambda^j (2/\pi) \int_0^\infty \frac{k^2 dk}{(k^2 + 1)^j} \quad (81)$$

and thus the high-density limit of $S_j(\lambda)$ is

$$S_j(\lambda) \sim -\lambda \frac{(j-1)}{2j} \frac{2}{\pi} \int_0^\infty \frac{k^2 dk}{(k^2 + 1)^j} = -\lambda \frac{(j-1)(2j-5)!!}{2^{j+1} j(j!)} \quad (82)$$

If we now sum the S_j from 2 to ∞ , we obtain

$$\begin{aligned} \sum_{j=2}^{\infty} S_j(\lambda) &= -\frac{\lambda}{\pi} \int_0^\infty k^2 dk \sum_{j=2}^{\infty} \frac{(j-1)}{j} (k^2 + 1)^{-j} \\ &= -\frac{\lambda}{\pi} \int_0^\infty k^2 dk \left\{ \frac{(k^2 + 1)^{-1}}{1 - (k^2 + 1)^{-1}} + \ell n (1 - (k^2 + 1)^{-1}) \right\} \\ &= -\frac{\lambda}{3} \end{aligned} \quad (83)$$

which exactly cancels the DH term, Eq. (20). [N. B. This is true only for the classical system.]

This result might have been expected, since the DH equation of state, $(P/nkT) = 1 - \lambda/6$, predicts a negative pressure for $\lambda > 6$, which means that the electron gas would collapse. We see that this eventuality has at least

been avoided, though the difficult problem of finding the high-density limit of the classical electron-gas equation of state still remains.

One possibility is that at sufficiently high densities the electrons are forced into a lattice. The free energy would then have the form (28)

$$(\beta F/N) = + C \lambda^{2/3} \quad (84)$$

so that the internal energy would be the Madelung energy of a lattice

$$(\beta E/N) = \frac{3}{2} C \lambda^{2/3} = C_M (e^2/\ell), \quad \ell = n^{-1/3}. \quad (85)$$

Presumably the "other terms" in Eq. (80) will sum to a quantity of order $\lambda^{2/3}$, but this has not yet been demonstrated.

It can readily be shown that the ring terms in Eq. (80) with one W_1 bond do not give anything like the lattice energy. Summing the polygons with one solid line gives

$$\sum \text{[Diagram]} = \frac{1}{2} (2/\pi) \int_0^\infty \frac{k^2 dk}{(k^2 + 1)^{j-1}} \phi(k) \quad (86)$$

where

$$\phi(k) = \int dx e^{-k \cdot x} W_1(x) \approx \int k^2 \frac{\sin kx}{kx} W_1(x) dx.$$

The result is

$$\sum \text{[Diagram]} \approx \frac{1}{2} \int_0^{x_0} x(1 - e^{-x}) dx. \quad (87)$$

The contribution to $(\beta P/n)$ from Eq. (87) is approximately $-\frac{1}{4} \ln \lambda$, which is quite small compared to the supposed $\lambda^{2/3}$ contribution from the Madelung energy.

VI. EFFECT OF INTERACTIONS ON IONIZATION EQUILIBRIUM

If one wishes to apply the theory developed in the preceding sections to real ionized gases, he has to introduce some new features which cannot be

satisfactorily treated in a completely classical model. In deriving the equation of state from the free energy, we have up to now implicitly assumed that the numbers of ions of various types remained constant when density and temperature change. This is hardly ever true, of course, in real gases; instead one must consider an equilibrium mixture of molecules, atoms, ions, and free electrons, each of which may have internal degrees of freedom. By the time the mixture has reached such a high temperature that only bare nuclei and electrons remain, one has to start worrying about relativistic effects, radiation pressure, and electron-positron pair production.

In practice one simply puts into the free energy formula (or its equivalent, the Saha equation for ionization equilibrium) a set of empirically determined ionization potentials and electronic energy levels appropriate to the particular substance, and a computer does the rest of the work. However, there still remain some interesting theoretical problems, for these ionization potentials and energy levels are not unaffected by the presence of the surrounding ionized gas. In fact, one knows that at sufficiently high densities all bound electronic levels disappear and the ionization potentials go to zero ("pressure ionization").

Several approximate theories have been proposed to take account of the effect of the variation of energy levels with density and temperature. It has been recognized that an electron can become essentially free as a result of the perturbing action of nearby ions, though there is no agreement on the best way to calculate quantitatively the effects of such perturbations. One can also take the viewpoint that the plasma as a whole changes the effective law of force between charged particles from Coulomb's law to something like the Debye-Hückel potential, Eq. (23). Thus one could use as energy levels the eigenvalues of the Schrödinger equation in which the Coulomb potential is

replaced by the Debye-Hückel potential; one would then have only a finite number of bound states, and the usual difficulty of the divergence of the partition function would be avoided. Such an approach finds theoretical justification in the modified cluster expansion described in Section II; the summation over chains of intermediate particles used in deriving Eq. (23) can be interpreted as an inclusion of the effects of polarization of the medium. Approximate solutions of the Schrödinger equation for a Debye potential have been given by Ecker and Weizel (43) and more recently by Harris (44). The same mathematical problem has also been studied by nuclear physicists interested in bound states of particles in a Yukawa potential (45, 46, 47).

It should be noted that the relation between energy levels and the thermodynamic functions becomes more complicated when the former are considered to be temperature-dependent; for a general discussion of this point we refer to Landsberg's recent book (48).

Without getting involved in quantum-mechanical considerations, we can point out one way in which Coulomb interactions can shift the ionization equilibrium. This is a type of pressure ionization which acts independently of any change in the energy levels, and was apparently first discussed by Timan (49) though it is at least implicit in many earlier treatments. Timan found that when electrostatic effects are included in the free energy formula along with the ionization potentials, using the DH approximation for point charges, there is a minimum in the degree of ionization as a function of pressure. At very low pressures, an increase of pressure suppresses ionization, as predicted by the mass action law and the Saha equation, but at sufficiently high pressures the degree of ionization increases with pressure. Thus the electrostatic terms have the same effect as a temperature- and density-dependent variation of the ionization potential.

Timan's result was not entirely convincing since the DH approximation may not be accurate enough at the pressure at which this minimum is alleged to occur. In order to decide whether electrostatic effects on the free energy would, by themselves, produce pressure ionization, it is necessary to use the generalizations of the Debye-Hückel theory which we have discussed earlier in this paper. We found, by calculating the next correction term (S_2), that over a fairly wide range of temperatures and densities the effect of ionic size is appreciable while higher-order correction terms such as S_2 are still negligible (Table II). Hence, we shall use the ring integral approximation with the soft sphere potential using the estimated magnitudes of higher terms to indicate in what region this approximation is reliable.

We consider a gas of a single element, at a temperature such that there is an ionization equilibrium between atoms ionized to the n th and $(n-1)$ th degrees (other ions having negligible concentrations). The thermodynamic condition for this equilibrium is

$$\mu_n + \mu_e = \mu_{n-1} \quad (88)$$

where μ_{n-1} , μ_n , and μ_e are the chemical potentials of $(n-1)$ - and n -fold ionized atoms, and electrons, respectively. The chemical potentials are to be calculated from the free energy using the formula

$$\mu_n = (\partial F / \partial N_n)_{V, T} \quad (89)$$

where N_n is the number of n -fold ionized atoms, etc.

The free energy may be written as the sum of an ideal gas and the electrostatic correction,

$$F = F_{id} + F_e \quad (90)$$

where F_e is given by Eq. (29) or (62). The chemical potential for an ideal gas of N_n ions in unit volume is

$$\mu_{id} = kT \ln N_n - kT \ln Z_n,$$

$$Z_n = (2\pi m_n kT/h^2)^{3/2} Q_n, \quad (91)$$

$$Q_n = \sum g_i e^{-\beta E_i}.$$

Carrying out the indicated operations, we obtain the equilibrium condition:

$$\frac{N_n N_e}{N_{n-1}} = \frac{Z_n Z_e}{Z_{n-1}} \exp \left\{ \frac{(z_n^2 - z_{n-1}^2 + 1)}{2kT} \left[\gamma e^2 (1 - w^{-1}) \right] \right\} \quad (92)$$

where $z_n e$ is the charge of an n -fold ionized atom and $w = (1 + 2/a)^{1/2}$ is the same quantity used in Eq. (30). In the limit $\gamma \rightarrow \infty$ or alternatively $\lambda_D \rightarrow \infty$ this reduces to Timan's result

$$\frac{N_n N_e}{N_{n-1}} = \frac{Z_n Z_e}{Z_{n-1}} \exp \left\{ \frac{(z_n^2 - z_{n-1}^2 + 1)}{(kT)^{3/2}} e^3 \pi^{1/2} n^{1/2} \right\}. \quad (93)$$

To put this in more familiar form, we make some minor approximations:

(1) $m_n \approx m_{n-1}$; (2) the gas is very nearly ideal, i. e., the electrostatic interactions influence the pressure only indirectly through their effect on the number of ions. We then replace the densities N_n by the partial pressures or concentrations,

$$p_n = N_n kT = c_n p$$

and introduce the "equilibrium constant"

$$K^{(n)} = \frac{\beta Z_{n-1}}{Z_n Z_e}.$$

Equation (92) then becomes

$$\frac{c_{n-1}}{c_n c_e} = p K^{(n)} \exp \left\{ - \left(z_n^2 - z_{n-1}^2 + 1 \right) \left[\beta \gamma e^2 (1 - w^{-1}) / 2 \right] \right\}. \quad (94)$$

To investigate the effect of the exponential factor on the ionization equilibrium, we consider the case studied by Timan: assume the temperature is such that nearly all atoms are singly ionized, and consider the equilibrium between singly and doubly ionized electrons. Defining the degree of double ionization as $\alpha_2 = N_2/N$, where N is the total number of atoms before ionization, one finds (50) that α_2 is a minimum when the pressure satisfies the equation

$$p = \left[1 + \frac{4e(\pi p)^{\frac{1}{2}}}{\gamma kT} \right]^3 (kT)^4 / 4\pi e^6. \quad (95)$$

In deriving Eq. (95) it has been assumed that $K^{(2)}$ is independent of pressure, but this restriction could easily be eliminated if one wanted to put in an explicit pressure dependence of the equilibrium constant.

For oxygen at 20,000°K, Timan claims that there is a minimum in the degree of double ionization at about 380 atm pressure, using Eq. (95) with $\gamma^{-1} = 0$. However, when we put in a reasonable finite value of γ^{-1} , say $\gamma^{-1} = 10^{-8}$ cm, we find that the pressure of minimum ionization calculated from Eq. (95) increases to about 1050 atm. The corresponding density, which can be estimated from the ideal gas law, is about $3.7 \times 10^{20}/\text{cm}^2$, which is too high for the ring integral approximation to be valid (see Table III).

From the form of Eq. (95) it can be seen that the predicted pressure for minimum ionization would increase rapidly with increasing temperature because of the T^4 factor, and would also increase if one took a smaller value of γ . On the other hand, the corrections to the ring integral approximation also become larger for larger values of γ and lower temperatures.

Fortunately there still remains an intermediate region in which the DH theory, corrected for ionic size, is still valid, and in which the ionization goes through a minimum at not too large a pressure. For example, with

$T = 15,625^\circ\text{K}$ and $\gamma^{-1} = 1.725 \times 10^{-8}$ cm, the minimum occurs at a pressure of about 750 atm. (Since $f_2(\lambda_0)$ is small here we assume the DH equation of state is still valid even though λ is about 2.3.)

At higher temperatures it is difficult to determine whether this type of pressure ionization can occur, since much higher densities and pressures are involved and the cluster expansion results are no longer reliable.

The electrostatic effects have been included in several recent ionization equilibrium calculations, using the Debye-Hückel approximation for point charges (51-55). In some cases it has been claimed that there is a significant effect on the equilibrium composition and on the equation of state; however, such assertions should be examined critically in the light of the above remarks.

References to many other works on this subject may be found in a bibliography issued by this laboratory (56).

VII. CONCLUDING REMARKS

The classical theory of ionized systems still holds considerable interest since the quantum-mechanical theory, which can be formulated in general terms, still encounters many mathematical difficulties. Whereas the classical virial expansion for a system of charged particles can now be derived in several different ways, and the ring integral and the next correction term can be calculated without too much difficulty, the quantum-mechanical ring integral is so complicated that the only results available so far are valid only in very small regions. Thus, for practical calculations of the equation of state, the best one can do at present is to use the classical theory together with certain intuitively chosen modifications which may approximately account for quantum effects; and one usually has to hope that the quantum effects are fairly small in the region of interest.

It is to be expected that a complete quantum-mechanical theory will eventually be worked out so that the equation of state can then be calculated fairly accurately at all temperatures and densities. Even then, the classical theory would not be forgotten, since one still needs to know the predictions of classical theory in order to understand to what extent a given physical phenomenon requires quantum mechanics for its explanation.

While we have mostly used only one potential function, the soft sphere model, in presenting the theory, in order to avoid inessential mathematical complications, it will of course be understood that the results are valid for a fairly large class of other potentials. For detailed discussion of this point, and for the derivation of several results given here without proof, we must refer the reader to the original papers cited.

APPENDIX A

DERIVATION OF THE DEBYE-HÜCKEL RESULT FROM
THE RING INTEGRAL SUM

In this appendix we will derive the DH expression for the free energy [Eq. (20)] in the limit of pure Coulomb forces from the ring integral sum [Eq. (15)] for the screened Coulomb potential. We wish to avoid the use of the closed logarithmic form [Eq. (17)] to which the sum converges for $(x^2 + \eta^2) < 1$, since the closed form assumes the validity of an analytic continuation for values of x such that $(x^2 + \eta^2) \geq 1$. For this purpose we employ a Mellin transform to write the sum as an integral in the complex plane, and then perform the x integration first. This method and its usefulness in statistical mechanics problems were discussed recently by Iwata (57).

We write the ring integral sum, Eq. (15), as

$$\beta F_{\text{ring}} = - (N\lambda/2\pi) G(\eta),$$

$$G(\eta) = \sum_{n=2}^{\infty} \frac{(-1)^n}{n} \int_0^{\infty} dx \frac{x^2}{(x^2 + \eta^2)^n} \quad (\text{A1})$$

Using the Mellin transform of the summation, the function $G(\eta)$ becomes

$$G(\eta) = (2\pi i)^{-1} \int_{-i\infty}^{+i\infty} ds \frac{\pi}{s \sin(\pi s)} \int_0^{\infty} dx \frac{x^2}{(x^2 + \eta^2)^s}, \quad 1 < \Re(s) < 2. \quad (\text{A2})$$

With the change of variable $x = \eta \tan \theta$, the x integration in (A2) becomes:

$$\eta^{3-2s} \int_0^{\frac{1}{2}\pi} d\theta \sin^2 \theta \cos^{2s-4} \theta = \frac{1}{2} \eta^{3-2s} \frac{\Gamma(3/2) \Gamma(s - 3/2)}{\Gamma(s)}$$

so that we have

$$G(\eta) = \frac{\Gamma(3/2)}{4\pi i} \int_C ds \frac{\pi \eta^{3-2s}}{s \sin(\pi s)} \frac{\Gamma(s - 3/2)}{\Gamma(s)} \quad (\text{A3})$$

In order to generate a series in powers of η appropriate to small η the contour defined in Eq. (A2) is closed to the left. Thus, the contour C encloses the entire real axis to the left of and including the point $s = 3/2$. Similarly, to generate a series in $1/\eta$ appropriate for large η , the contour is to the right.

The integrand of Eq. (A3) has simple poles at $s = 3/2, 1/2, \dots, -m + 3/2, \dots$ from $\Gamma(s - 3/2)$ and two additional simple poles at $s = 1$ and 0 from $(\sin \pi s)^{-1}$. The residues of the poles enclosed in the contour closed to the left give the result for $G(\eta)$ as:

$$G(\eta) = \frac{\pi}{3} + \frac{\pi}{2} \eta^2 + \sum_{n=2}^{\infty} \frac{(-1)^n (2n-5)! \eta^{2n}}{2^n n!} - \frac{\pi}{2} \eta - \frac{\pi}{3} \eta^3. \quad (\text{A4})$$

The summation in powers of η^2 is recognized to be the binomial expansion of $(1 + \eta^2)^{3/2}$. Hence we find

$$G(\eta) = \frac{\pi}{3} \left\{ (1 + \eta^2)^{3/2} - \frac{3}{2} \eta - \eta^3 \right\}, \quad (\text{A5})$$

in agreement with Eq. (19). In the limit of $\eta = 0$, Eq. (A5) becomes $G(0) = \frac{\pi}{3}$ so that $\beta F_{\text{ring}} = -N\lambda/3$, the Debye-Hückel result.

It should be pointed out that the screened potential,

$$u(r) = (e^2/r) \exp(-r/r_0),$$

has been used only to give definition to the Fourier transform of the pure Coulomb potential, e^2/r . Other screening functions are equally acceptable, and the Mellin transform may be used in the same way. For example, one may use $\exp(-r^2/r_0^2)$ as the screening function and obtain a function of η analogous to Eq. (A5) which again reduces to $\frac{\pi}{3}$ in the limit $r_0 \rightarrow \infty$, i. e., $\eta \rightarrow 0$.

APPENDIX B

EVALUATION OF S_2 FOR SOFT SPHERES

We discuss here the evaluation of the integral (25) for the case when U_s is given by Eq. (37). The linear and quadratic terms in the integrand can be taken care of immediately and we then have

$$S_2 = (1/2\lambda)I_1(\lambda, y) + I_2 \quad (B1)$$

where

$$I_1 = \int_0^{\infty} x^2 dx [e^{-q(x)} - 1], \quad (B2)$$

$$I_2 = \frac{1}{2} + (\lambda/8\sqrt{2}y^3) \left[1 - (1-y^2)^{\frac{1}{2}} \right] \left[(1-y^2)^{\frac{1}{2}} - (1+y)^{\frac{1}{2}} \right], \quad (B3)$$

$$q(x) = (\lambda/xy) \left[\exp \left\{ -x \left(\frac{2}{1+y} \right)^{\frac{1}{2}} \right\} - \exp \left\{ -x \left(\frac{2}{1-y} \right)^{\frac{1}{2}} \right\} \right].$$

The integral (B2) has been evaluated numerically and the results are given in a report available from this Laboratory (58).

For small values of λ and y the following expansion is useful:

$$I_1 = \sum_{n=1}^{\infty} \frac{(-\lambda)^n}{n!} J_n \quad (B4)$$

where

$$J_n = (T/n)^3 R^n \sum_{j=0}^{\infty} \delta_{n,2j} (Q/n)^{2j},$$

$$T = \sqrt{2} (1-y^2)^{\frac{1}{2}} / \left[(1+y)^{\frac{1}{2}} + (1-y)^{\frac{1}{2}} \right],$$

$$R = 2\sqrt{2} / \left\{ (1-y^2)^{\frac{1}{2}} \left[(1+y)^{\frac{1}{2}} + (1-y)^{\frac{1}{2}} \right] \right\},$$

$$Q = 2y / \left[1 + (1-y^2)^{\frac{1}{2}} \right],$$

$$\delta_{n,2j} = \frac{(2j+1)(2j+2)}{2^{2j}} \sum_{k=0}^{2j} (-1)^{2j-k} \binom{2j}{k} n^{2j-k} 2^k B_k^{(-n)},$$

and $B_k^{(-n)}$ is the Bernoulli number of order $(-n)$ and degree k [see (59), p. 134]. The following special cases should be noted:

$$\delta_{n,0} = 2,$$

$$\delta_{n,2} = n,$$

$$\delta_{n,4} = (n/8)(5n - 2),$$

$$\delta_{n,6} = (n/72)(35n^2 - 42n + 16).$$

The first few terms in the expansion lead to the expression

$$\begin{aligned} I_1 = & -\lambda + (\lambda^2/8\sqrt{2})(1 + \frac{3}{8}y^2 + \frac{11}{128}y^4 + \dots) \\ & - (\lambda^3/81)(1 + \frac{11}{12}y^2 + \frac{2408}{3456}y^4 + \dots) \\ & + (\lambda^4\sqrt{2}/768)(1 + \frac{3}{2}y^2 + \frac{909}{512}y^4 + \dots) \\ & - (\lambda^5/3750)(1 + \frac{21}{10}y^2 + \dots) \\ & + \dots \end{aligned} \tag{B5}$$

It is necessary to work out this many terms because most of them cancel out when one calculates the pressure for symmetrical electrolytes, combining $I_1(\lambda)$ and $I_1(-\lambda)$.

The contribution to the pressure for small λ and y may be determined using the general relation (36)

$$\beta P = \beta P_{DH} + A'(\underline{n}) - \sum_{i=1}^s n_i \frac{\partial}{\partial n_i} A'(\underline{n}) \tag{B6}$$

which is valid for an s -component system; \underline{n} is the set of concentrations, $n_1 \dots n_s$, and P_{DH} is the Debye-Hückel (ring-integral) contribution given in Eq. (30).

For a two-component system of soft spheres, we have $n_1 = n_2$, and

$$\begin{aligned} A'(n) = nS_2' &= 4\pi n^2 \int_0^\infty \left[\exp(-\beta U_s) + \exp(\beta U_s) - (\beta U_s)^2 - 2 \right] r^2 dr \\ &= 4\pi n^2 \lambda_D^3 \left[I_1(\lambda, y) + I_1(-\lambda, y) + (2\lambda)(2I_2 - 1) \right]. \end{aligned} \quad (B7)$$

The contribution to the pressure from S_2' , defined as

$$\beta P - \beta P_{DH} = (1/2\lambda) \int_0^\infty x^2 dx \left[q' e^q - q' e^{-q} - 2qq' \right], \quad (B8)$$

$$q' = n(dq/dn),$$

has been computed numerically for a large range of values of λ and y ; the results are given in Table II.

For small λ and y we may use the expansion (B5) for I_1 ; retaining only the first nonvanishing term, we find

$$\beta P = \beta P_{DH} - n\lambda^3 y^2 (17\sqrt{2}/32768). \quad (B9)$$

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TABLE I
Ring Integral Contributions to the Pressure

a	$f_1(a)$	$g_1(3/2a)$	(A)*	(B)*
∞	1.0000	1.0000	1.0000	
80	0.9726	0.9726	0.9726	
40	0.9465	0.9462	0.9465	
20	0.8978	0.8968	0.8978	
10	0.8127	0.8097	0.8129	
5	0.6795	0.6712	0.6870	0.6062
3	0.5528	0.5377	0.6343	0.5402
2.5	0.5041	0.4860		0.5013
2.0	0.4437	0.4220		0.4437
1.5	0.3671	0.3411		0.4105
1.0	0.2679	0.2377		0.6637
0.5	0.1382	0.1086		
0	0.0000	0.0000		

* (A) and (B) were calculated from the first few terms of the series expansions valid near $a^{-1} = 0$ and $a = 2$, respectively:

$$(A) f_1(a) = 1 - (9/4a) + (9/2a^2) - (35/4a^3) + (135/8a^4),$$

$$(B) f_1(a) = 0.443651 + 0.1351464y^2 + 0.069496y^4$$

where $y^2 = 1 - (4/a^2)$.

TABLE II

Values of $f_2(\lambda, a)$

Note: Instead of a , the variable $y = (1 - 4/a^2)^{\frac{1}{2}}$ has been used. The numbers in parentheses indicate the power of 10 by which the other number is to be multiplied.

$\lambda \backslash y$	0.05	0.1	0.2	0.4	0.6	0.8	0.9	0.99	0.995
0.1	-0.14(-8)	-0.73(-8)	-0.32(-7)	-0.17(-6)	-0.63(-6)	-0.31(-5)	-0.11(-4)	-0.30(-3)	-0.0020
0.2	-0.75(-8)	-0.54(-7)	-0.25(-6)	-0.13(-5)	-0.50(-5)	-0.25(-4)	-0.88(-4)	-0.0038	-0.0155
0.4	0.95(-7)	-0.30(-6)	-0.19(-5)	-0.104(-4)	-0.40(-4)	-0.12(-3)	-0.0012	-0.0239	-0.124
0.6	.27(-3)	0.79(-4)	0.27(-4)	0.25(-4)	0.38(-3)	-0.80(-3)	-0.0062	-0.0927	-0.751
0.8	.0724	.0196	.0063	.0031	.0017	-0.0037	-0.0133	-0.354	
1.0	0.356	.0912	.0250	.0076	.0019	-0.0077	-0.0223	-1.510	-47.3
1.5	1.415	.347	.0843	.0177	0.00032	-0.0200	-0.0606	-106.8	0.641(5)
2.0	2.60	0.631	.148	.0278	-0.00120	-0.0374	-0.142	-0.104(5)	-0.992(8)
3.0	4.90	1.188	0.278	0.0536	0.00125	-0.0838	-0.453	0.135(10)	0.80(16)

TABLE III

Equation of state of a system of positive and negative charges with soft sphere interaction. Contributions to P/nkT as given by Eq. (39).

T = Temperature in °K

n = Total number of charged particles, in units of 10^{20}

Column (1): $\lambda/6$, Debye-Hückel contribution for point charges ($\gamma^{-1} = 0$)

Column (2): $(\lambda/6)f_1(a)$, ring integral contribution for soft spheres

Row (a) computed with $\gamma^{-1} = 3.45 \times 10^{-8}$ cm

Row (b) computed with $\gamma^{-1} = 1.725 \times 10^{-8}$ cm

Column (3): $f_2(\lambda, a)$, contribution from S_2 , rows (a) and (b) as above.

Column (4): $(P/nkT) = 1 - (\lambda/6)f_1(a) + f_2(\lambda, a)$

T	n	(1)	(2)	(3)	(4)
15,625	0.0625	0.05165	(a) 0.0420	(a) -0.0067	(a) 0.9513
			(b) 0.0464	(b) -0.0544	(b) 0.8992
	0.25	0.1033	(a) 0.0702	(a) -0.0088	(a) 0.9210
			(b) 0.0840	(b) -0.0410	(b) 0.8750
	1.0	0.2066	(a) 0.1041	(a) 0.0013	(a) 0.8972
			(b) 0.1404	(b) -0.0477	(b) 0.8119
1.5586	0.2579	(a) 0.1145	(a) 1.53	(a) 2.42	
		(b) 0.1617	(b) -0.0415	(b) 0.7968	
4.0	0.4132	(b) 0.2083	(b) -0.0016	(b) 0.7901	
		6.2344	0.5158	(b) 0.2290	(b) 5.109
62,500	0.25			0.0129	(a) 0.0105
		(b) 0.0116			
	1.0	0.0258	(a) 0.0175	(a) -0.00005	(a) 0.98245
(b) 0.0210			(b) -0.0006	(b) 0.9784	
4.0	0.05165	(a) 0.0260	(a) -0.00002	(a) 0.9740	
		(b) 0.0351	(b) -0.0005	(b) 0.9644	

TABLE III (Continued)

T	n	(1)	(2)	(3) ^a	(4)
62,500	6.2344	0.0645	(a) 0.0286 (b) 0.0404	(a) 0 (b) -0.0003	(a) 0.9714 (b) 0.9593
	16.0	0.1033	(b) 0.0521	(b) 0.0004	(b) 0.9483
	24.94	0.1290	(b) 0.0573	(b) 0.0487	(b) 0.9914
250,000	1.0	0.00323	(a) 0.0026 (b) 0.0029	(a) 0 (b)	(a) 0.9974 (b)
	4.0	0.00645	(a) 0.0044 (b) 0.0052	(a) 0 (b) 0	(a) 0.9956 (b) 0.9948
	16.0	0.0129	(a) 0.0065 (b) 0.0088	(a) 0 (b) 0	(a) 0.9935 (b) 0.9912
	24.94	0.0161	(a) 0.0072 (b) 0.0101	(a) 0 (b) 0	(a) 0.9928 (b) 0.9899
	64.0	0.0258	(b) 0.0130	(b) 0	(b) 0.9870
	99.75	0.0322	(b) 0.0143	(c) 0	(b) 0.9857
1,000,000	4.0	0.0008	(a) 0.0007 (b) 0.0007	(a) 0 (b) 0	(a) 0.9993 (b) 0.9993
	16.0	0.0016	(a) 0.0011 (b) 0.0013	(a) 0 (b) 0	(a) 0.9989 (b) 0.9987
	64.0	0.0032	(a) 0.0016 (b) 0.0022	(a) 0 (b) 0	(a) 0.9984 (b) 0.9978
	99.75	0.0040	(a) 0.0018 (b) 0.0025	(a) 0 (b) 0	(a) 0.9982 (b) 0.9975
	256	0.00645	(b) 0.00325	(b) 0	(b) 0.99675
399	0.0081	(b) 0.0036	(b) 0	(b) 0.9964	

^a Values reported as 0 if less than 0.00005.

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