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Corrections to the Debye-Huckel Theory

Thomas James Murphy

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ames
Thomas J. Murphy
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E. G. D. Cohen
Professor, The Rockefeller University

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Abstract

The cluster expansion theory of Mayer is rearranged to obtain expressions for the potential of average force and the internal potential energy of the electron gas through order $n^{\frac{3}{2}}$ in the density n. The order n result for the potential of average force is applied to ionic solutions, and gives an expression for the activity coefficient through order n; the electron-gas result also enables us to extend the Fuoss-Onsager theory of the conductivity of ionic solutions to the case of asymmetric solutes. Some mathematical corrections are made to the Fuoss- Onsager theory, so that results for symmetric solutes are obtained which differ from those of Fuoss and Onsager.

Contents

I. Introduction

The theoretical determination of the physical properties of systems of particles, such as plasmas and electrolytes, which interact through the Coulomb potential involves difficulties which stem from the long range of the Coulomb force. In the case of particles interacting through a short-range potential, it is possible to obtain information about the macroscopic properties of the system by examining the behavior of a few particles taken in isolation; in the case of the Coulomb potential, however, it becomes necessary to examine the collective behavior of large numbers of particles.

The first successful approach to a treatment of the Coulomb system was that of Debye and Hückel [1]. Their picture of the collective behavior of the particles was that of "shielding": each particle, on the average, is surrounded with an excess number of particles of the opposite charge, so that the full effect of the potential due to the charge on a particle is not felt at large distances, due to the shielding effect of the surrounding particles.

In order to make a quantitative determination of the effect of this shielding phenomenon, Debye and Hückel made use of the "superposition approximation," in which it is assumed that the electrostatic potential at a point in the vicinity of several ions is just the sum of the shielded potential about each. In this approximation the pair distribution function $f_{ij}(r_{ij})$, that is, the average number density of pairs of particles of type i and j separated by a given distance r_{ij}, is given by the Boltzmann factor:

$$f_{ij}(r_{ij}) = n_i n_j \, e^{-\frac{e_i \psi_j(r_{ij})}{kT}} \tag{1.1}$$

Here n_i and n_j are the number densities of particles of type i and j, e_i is the charge on i, and $\psi_j(r)$ is the shielded electrostatic potential

about j ; k is Boltzmann's constant and T is the temperature. Use of (1.1) in the Poisson equation

(1.2) $$\Delta\psi_j = -\frac{4\pi}{D}\sum_i e_i \frac{f_{ij}}{n_j}$$ (D is the dielectric constant)

gives a differential equation for ψ_j ; expansion of the Boltzmann factor in a power series in which quadratic and higher order terms are neglected gives for electrically neutral systems

(1.3) $$\Delta\psi_j = \psi_j / R_D^2$$

where $R_D \equiv 1/\sqrt{4\pi(n_1e_1^2+n_2e_2^2)/DkT}$ is called the Debye length. The solution $\psi_j = \frac{e_j}{Dr}\exp(-\frac{r}{R_D})$ of (1.3), called the Debye-Hückel potential, gives together with (1.1):

(1.4) $$f_{ij}(r_{ij}) = n_i n_j \exp\left(-\frac{e_i e_j}{DkT}\frac{e^{-\frac{r}{R_D}}}{r}\right)$$

Using (1.4) for the pair distribution function, Debye and Hückel were able to determine the thermodynamic quantities of electrically neutral ionic solutions to lowest order in the density; moreover, together with Onsager [2], they were able to determine the conductivity and diffusion coefficient to the same order in the density. In the limit of low concentrations, they found that these macroscopic quantities varied as the square root of the particle density; the resulting "limiting laws" are in excellent agreement with the experimental results.

Attempts to extend the theory of Coulomb systems to higher order in the density encounter many difficulties; for example, the superposition approximation of Debye and Hückel is not sufficiently accurate. The pair distribution function in equilibrium may be obtained to the order required by the cluster method developed by Mayer [3]; a particularly simple formulation of the problem developed by Cohen and Ford [4] has made it possible for us to extend the theory to higher orders in the density than has previously been possible. In Chapter II we give a calculation of the pair distribution function and internal energy of the electron gas with a uniform positive background; this simple model exhibits the most

important characteristics of more complicated systems.

As we will show in Chapter II, together with Appendix B, the pair distribution function is of the form

(1.5) $$f_2(\xi_{12}) = n^2 e^{\Psi(\xi_{12})}$$

where $\xi_{12} = r_{12}/R_D$ and

(1.6) $$\Psi(\xi_{12}) = \varepsilon\Psi^{(1)}(\xi_{12}) + \varepsilon^2\Psi^{(2)}(\xi_{12}) + \varepsilon^3\ln\varepsilon\,\Psi^{(3')}(\xi_{12}) + \varepsilon^3\Psi^{(3)}(\xi_{12}) + \varepsilon^4\ln\varepsilon\,\Psi^{(4')}(\xi_{12}) + \cdots$$

where $\varepsilon \equiv e^2/kTR_D$ is proportional to $\sqrt{n}$ and

(1.7) $$\Psi^{(1)}(\xi) = -\frac{e^{-\xi}}{\xi}$$

$$\Psi^{(2)}(\xi) = \frac{\ln 3}{8}e^{-\xi} - \left(\frac{3}{8}\ln 3 + \frac{1}{6}\right)\frac{e^{-\xi}}{\xi} + \frac{1}{6}\frac{e^{-2\xi}}{\xi} + \frac{1}{8}\left[(\xi+3)\frac{e^{\xi}}{\xi}Ei(-3\xi) + (\xi-3)\frac{e^{-\xi}}{\xi}Ei(-\xi)\right]$$

$$\Psi^{(3')}(\xi) = \frac{e^{-\xi}}{12} - \frac{e^{-\xi}}{3\xi}$$

$\Psi^{(1)}$ is equivalent to the Debye-Hückel potential; $\Psi^{(3)}$ and $\Psi^{(4')}$ are somewhat lengthy and are given in Appendix B; $\Psi^{(3')}$, $\Psi^{(3)}$, and $\Psi^{(4')}$ represent new results, while $\Psi^{(2)}$ has been given previously by a number of authors [5]; some of the authors, however, leave $\Psi^{(2)}$ in the form of rather difficult integrals, while those who evaluate the integrals often differ as to the results.

We have also evaluated the internal energy $U(\varepsilon)$ of the electron gas; the result is:

(1.8) $$\frac{U(\varepsilon)}{NkT} = -\frac{\varepsilon}{2} - \frac{\varepsilon^2\ln\varepsilon}{4} - \left(\frac{\gamma_E}{2} + \frac{\ln 3}{4} - \frac{1}{3}\right)\varepsilon^2 - \frac{3}{8}\varepsilon^3\ln\varepsilon + (0.2528 \pm 0.0004)\varepsilon^3 + \cdots$$

where γ_E is Euler's constant. Up to order ϵ^2, this result has previously been given by Abe [6]. We have also resummed [7] the series (1.6) to deal with the fact that the $\Psi^{(n)}$ fall off more slowly at large ξ for higher n, so that for any fixed ϵ there is a ξ such that $\Psi^{(1)}$ is not the dominant term; the result of the resummation is of the form

(1.9) $$\Psi \xrightarrow[\xi\to\infty]{} -\epsilon C_1 \frac{e^{-C_2\xi}}{\xi}$$

with $$C_1 = 1 + \left(\frac{3}{8}\ln 3 + \frac{1}{6}\right)\epsilon + \cdots$$

$$C_2 = 1 + \frac{\ln 3}{8}\epsilon + \cdots$$

We have also examined the suggestion that Ψ is of the form $\sum_{m,n} \epsilon^n (\ln\epsilon)^m \Psi^{mn}$, and have found that some of the Ψ^{mn} are not finite.

The results (1.6) and (1.8) are compared with the Monte Carlo calculations of Brush, Sahlin, and Teller [8].

In Chapter III we apply some of the results of Chapter II to the case of ionic solutions, and obtain a simple formula for the logarithm of the activity coefficient γ, that is, for the excess Gibbs free energy per particle $g(\epsilon)-g(0)$:

(1.10) $$\ln\gamma(\epsilon) \equiv \frac{g(\epsilon)-g(0)}{kT} = \gamma_1\epsilon + \gamma_{2'}\epsilon^2\ln\epsilon + \gamma_2\epsilon^2 + \cdots$$

$$\gamma_1 = \frac{Z_1 Z_2}{2}$$

$$\gamma_{2'} = \frac{Z_1 Z_2}{6}(Z_1+Z_2)^2$$

$$\gamma_2 = -\frac{Z_1 Z_2}{6}\left[(Z_1+Z_2)^2\left(-\gamma_E + \ln\frac{b}{3} - \frac{1}{12}\right) + \frac{5}{2b} - \frac{1}{Z_1 Z_2 b^3}\right.$$
$$\left. + \sum_{n=3}^{\infty} \frac{(-b)^{n-2}\left(\frac{Z_1^n - Z_2^n}{Z_1 - Z_2}\right)(n+4)}{n!\,(n-2)(n+1)}\right]$$

where Z_i is the charge number of ionic species i and $b \equiv e^2/DkTa$.

(1.10) is based on a model in which the ions are represented by charged hard spheres of diameter a and the solvent is represented by an idealized medium characterized in the equilibrium case only by a dielectric constant D . γ_2 depends on the hard core diameter a ; fitting (1.10) to the experimental results tabulated by Shedlovsky [9] yields a value for a ; for NaCl at 25°C we find a = 5.2 Å and for $CaCl_2$ at 25°C we find 8.0 Å. Poirier [10] has made a similar calculation, and obtained somewhat different results; he, however, retained some of the terms of order higher than ϵ^2 in his calculations and fitted his expression to the experimental data at higher concentrations than we have used; moreover, in some parts of his calculation he departed from the model outlined above and used a more refined picture of the solvent. Haga and Friedman [11], working along similar lines, give results which include still more effects of order ϵ^3. In the present work, however, we wish to retain the simple model throughout, and retain only those terms which are of order ϵ^2, as these restrictions will be necessary in the non-equilibrium case and we wish to compare the non-equilibrium results with those of equilibrium.

In Chapter IV we use the non-equilibrium theory developed by Fuoss and Onsager [12], based on the same model as the equilibrium theory of Chapter III, to obtain an expression for the conductivity Λ per unit concentration of an ionic solution; the expression is of the form

$$\Lambda = \Lambda_0 + \Lambda_1 \epsilon' + \Lambda_{2'} \epsilon'^2 \ln \epsilon' + \Lambda_2 \epsilon'^2 + \cdots \tag{1.11}$$

where
$$\Lambda_1 = -\frac{q^2 \Lambda_0}{3(1+q)} + \frac{F^2}{N} \frac{(|z_1|+|z_2|)}{z_1 z_2} \frac{DkT}{6\pi\eta e^2}$$

$$\Lambda_{2'} = \frac{q^2 \Lambda_0}{6} + \frac{F^2}{N} \frac{(|z_1|+|z_2|)}{z_1 z_2} \frac{DkT}{6\pi\eta e^2} \left[\frac{q^2}{4} - \frac{(|z_1|-|z_2|)^2}{2 z_1 z_2} \right]$$

$$\epsilon' \equiv -z_1 z_2 \epsilon$$

F is Faraday's constant, N Avogadro's number, and η the viscosity.

$\Lambda = \Lambda_0 + \Lambda_1 \varepsilon'$ is the Onsager limiting law; Λ_2 is quite lengthy and is given in (4.49). (1.11) is not derived on such a firm basis as the results of Chapters II and III, which are based on equilibrium statistical mechanics. We repeat the derivation of the differential equation (4.13) for the pair distribution function given by Fuoss and Onsager, and modify this derivation only by using the results of Chapter II to extend the applicability of the equation to asymmetric electrolytes such as $CaCl_2$. We solve this differential equation, however, in a more straightforward manner than did Fuoss and Onsager, and obtain different results. Fitting our expression to the 1934 results of Shedlovsky et al.[13] gives a = 4.0 Å for NaCl at 25°C with $\Lambda_0 = 126.49$ cm^2 int. Ω^{-1} equiv^{-1}, and a = 6.2 Å for $CaCl_2$ at 25°C with $\Lambda_0 = 135.85$. These results are to be compared with the results a = 5.2 Å and a = 8.0 Å from Chapter III; the difference, which in this context should not be considered large, may be attributed to the fact that the deviations of the real solution from the idealized model do not necessarily affect the results in the same way in the equilibrium case as they do in the non-equilibrium case.

II. The Electron Gas

Introduction

The system we wish to consider consists of negatively charged classical point particles in thermal equilibrium, together with a uniform positive background for overall charge neutrality. We will compute the internal potential energy of this system by finding an expression for the pair distribution function, which will be given in terms of another quantity, the potential of average force. The potential of average force will be given for a general pair potential in section 1, in terms of a power series in the number density n . In section 2 it will be shown that in the case of the Coulomb potential the power series in n is not suitable, and the series is rearranged into a power series in the plasma parameter ε . In section 3 explicit expressions for the first two coefficients of the power series are obtained. In section 4 we compute the internal potential energy from the expression for the pair distribution function derived in the preceding sections, and in section 5 we compare our results with some numerical computations.

1. The Potential of Average Force

The equilibrium behavior of the system may be described in terms of the pair distribution function $f_2(\vec{r}_1,\vec{r}_2;n,T)$ which is the number of pairs of particles such that one is located in a unit volume element about $\vec{r}_1$ and the other in a unit volume element about $\vec{r}_2$; the overall number density is n and the absolute temperature is T . According to the cluster expansion theory of Mayer [14],

(2.1) $$f_2 = n^2 e^{\Phi/kT}$$

where k is Boltzmann's constant and where the potential of average force $\Phi(\vec{r}_1,\vec{r}_2;n,T)$ is given by

(2.2) $$\frac{\Phi}{kT} = -\frac{\phi_{12}}{kT} + \sum_{k=1}^{\infty} c_k n^k$$

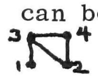
Here $\phi_{ij}(\vec{r}_{ij})$ is the potential energy of interaction of a pair of particles at $\vec{r}_i$ and $\vec{r}_j$, and $c_k(\vec{r}_1,\vec{r}_2;T)$ is given as a sum of products

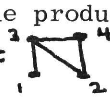
of "Mayer f-functions" f_{ij} :

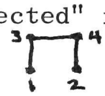
(2.3) $$c_k = \sum_{Q_k} \int \cdots \int d\vec{r}_3 \cdots d\vec{r}_{k+2} \frac{\prod_{Q_k} f_{ij}}{S_{Q_k}}$$

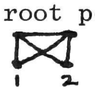
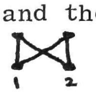
where

(2.4) $$f_{ij} = e^{-\frac{\phi_{ij}}{kT}} - 1 .$$

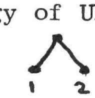
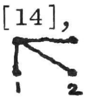
In order to explain the notation used in (2.3) we introduce some simple notions of graph theory. Each product of f_{ij} can be represented as a linear graph, called a "Mayer graph," such as  . Here the <u>points</u> represent the position vectors $\vec{r}_i$ of the particles; the points 1 and 2 will be called "root points" and the others "field points." Each term in the sum c_k corresponds to a graph which has k field points. The <u>lines</u> represent the f_{ij} that appear in the product, thus:

$$f_{13} f_{34} f_{42} f_{32} =$$ 

A graph is called "connected" if one can move over lines from any one point to any other; thus  is connected but  is not. The sum in (2.3) runs over all connected graphs with k field points satisfying the following criteria:

1) The graph is "simple"; that is, it would remain connected even if all lines terminating in the root points 1 and 2 were severed and the points 1 and 2 removed.  satisfies this criterion;  does not.

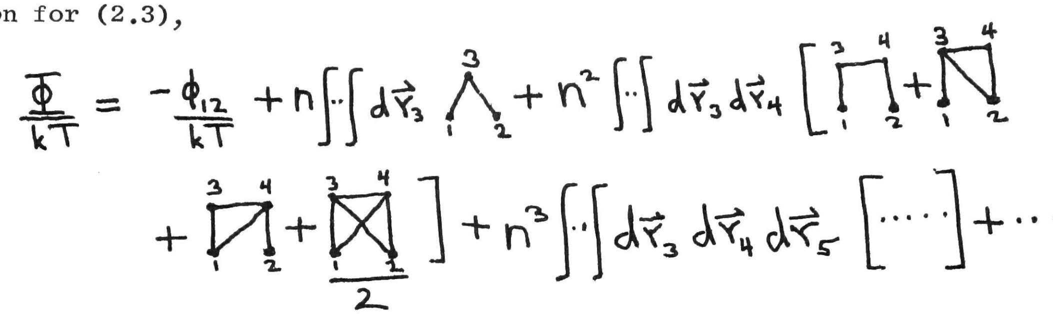
2) There is no line connecting 1 and 2.

3) If a line connecting 1 and 2 were added, the graph would be "irreducible," that is, it would remain connected even if all lines terminating in one particular point were severed and the point removed; in the terminology of Uhlenbeck and Ford [14], it would contain no "articulation points."  satisfies this;  does not.

S_{Q_k} is the symmetry number of the graph Q_k , that is, the number of different ways the labels on the field points may be rearranged without changing the connections; thus, if 2 is connected to 3 in one

arrangement, it must be so in the other.

Writing out the first few terms of (2.2), using the graphical notation for (2.3),

(2.5) 

$$= -\frac{\phi_{12}}{kT} + n\int\!\cdots\!\int d\vec{r}_3\, f_{13}f_{32} + n^2\int\!\cdots\!\int d\vec{r}_3\, d\vec{r}_4 \left[f_{13}f_{34}f_{42} + \cdots \right] + \cdots$$

2. The Case of Coulomb Forces

For the case of Coulomb forces where $\phi_{ij} = e^2/r_{ij}$, many of the integrals in (2.5) diverge for large distances. This is most easily seen in the case of $\int\!\cdots\!\int d\vec{r}_3 f_{13} f_{32}$, since for large distances $r_{13} \doteq r_{32}$ and $\int\!\cdots\!\int d\vec{r}_3 f_{13} f_{32} \doteq 4\pi \int_0^\infty dr\, r^2 (e^{-\frac{e^2}{r}} - 1)^2$, which diverges at large r. Therefore the Coulomb potential, due to its long-range nature, must be treated in a special manner. Since the coefficients of the powers of the density in (2.5) are not finite, we seek a rearrangement of the expansion in terms of some other parameter. The work of Debye and Hückel [1] suggests the use of the dimensionless parameter ε, called the "plasma parameter":

(2.6)
$$\varepsilon \equiv R_L / R_D$$
$$R_L \equiv e^2/kT$$
$$R_D \equiv 1/\sqrt{4\pi n R_L} = 1/\sqrt{4\pi n e^2/kT}$$

Here ε is the ratio of the two lengths which characterize the system: R_L, the "Landau length, is given by e^2/kT, the distance at which the

thermal kinetic energy of one particle approaching another equals the potential energy of the pair; and R_D, the "Debye Length," is given by $1/\sqrt{4\pi n R_L}$ and characterizes the collective behavior of the particles. Then, by substitution in (2.6), $\epsilon = \sqrt{4\pi n (e^2/kT)^3}$ so that an expansion in ϵ can be regarded as an expansion in the square root of the density.

We now proceed to express (2.2) explicitly as a power series in ϵ. To accomplish this, we express $\vec{r}$ in terms of the dimensionless variable $\vec{\xi} \equiv \vec{r}/R_D$, so that

(2.7) $$\frac{\phi_{ij}}{kT} = \frac{e^2}{kT} \cdot \frac{R_D}{R_D \cdot r_{ij}} = \frac{\epsilon}{\xi_{ij}} \qquad \text{and}$$

$$f_{ij} = e^{-\frac{\epsilon}{\xi_{ij}}} - 1 .$$

To obtain Φ/kT as a power series in ϵ we must:*

1) substitute (2.7) in (2.2);

2) use (2.6) to show that

(2.8) $$n \int \!\! \cdots \!\! \int d\vec{r}_i = n R_D^3 \int \!\! \cdots \!\! \int d\vec{\xi}_i = \frac{1}{4\pi\epsilon} \int \!\! \cdots \!\! \int d\vec{\xi}_i$$

3) expand all the $f_{ij} = e^{-\frac{\epsilon}{\xi_{ij}}} - 1$ in powers of ϵ:

$$f_{ij} = \sum_{m=1}^{\infty} \frac{\epsilon^m}{m!} \left(-\frac{1}{\xi_{ij}}\right)^m$$

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* For example,

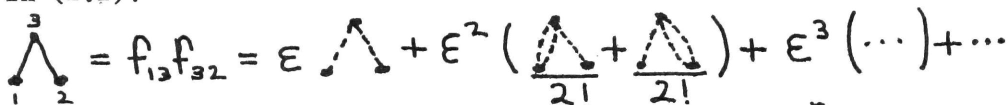
$$n \int \!\! \cdots \!\! \int d\vec{r}_3 \overset{3}{\underset{1 \quad 2}{\wedge}} = \frac{1}{4\pi\epsilon} \int \!\! \cdots \!\! \int d\vec{\xi}_3 \left(e^{-\frac{\epsilon}{\xi_{13}}} - 1\right)\left(e^{-\frac{\epsilon}{\xi_{32}}} - 1\right)$$

$$= \frac{1}{4\pi\epsilon} \int \!\! \cdots \!\! \int d\vec{\xi}_3 \left[\frac{\epsilon^2}{\xi_{13}\xi_{23}} - \frac{\epsilon^3}{2!}\left(\frac{1}{\xi_{13}^2 \xi_{32}} + \frac{1}{\xi_{13}\xi_{32}^2}\right) + \cdots\right]$$

This procedure gives immediately the formal result

(2.9)
$$\Psi(\xi_{12};\varepsilon) \equiv \frac{\Phi}{kT} = -\frac{\varepsilon}{\xi_{12}} + \sum_{n=1}^{\infty} C_n \varepsilon^n$$
$$C_n(\xi_{12}) \equiv \sum_{k=1}^{\infty} \frac{1}{(4\pi)^k} \sum_{P_k^{(n)}} \frac{1}{S_{P_k^{(n)}}} \int\!\!\cdots\!\!\int d\vec{\xi}_3 \cdots d\vec{\xi}_{k+2} \prod_{P_k^{(n)}} \frac{1}{m_{ij}!}\left(-\frac{1}{\xi_{ij}}\right)^{m_{ij}}$$

The graphs $P_k^{(n)}$, called "Coulomb graphs," satisfy the same rules as the graphs Q_k, except that they have not not just one but any number m_{ij} of lines joining the points i and j, and have exactly $n+k$ lines altogether. Each line in a Coulomb graph represents a function $-1/\xi_{ij}$ and is represented by a dotted line. For example, we have for the simplest Mayer graph in (2.2):



Here a given Coulomb graph appears in the coefficient of ε^n if it has n more lines than field points.*

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*In the case of electrically neutral mixtures of two different species of ions, only two minor changes need be made in the above derivation:

1) R_D is re-defined as $1/\sqrt{4\pi n(e^2/kT)(c_1 z_1^2 + c_2 z_2^2)}$ where c_i is defined as the number density of ions of charge $z_i e$, divided by the total number density. This change modifies the derivation only in that now

$$nR_D^3 = 1/4\pi\varepsilon(c_1 z_1^2 + c_2 z_2^2)$$

so that each graph with k field points must be multiplied by an additional factor $1/(c_1 z_1^2 + c_2 z_2^2)^k$.

2) $i \cdots j = -z_i z_j/\xi_{ij}$ in the case of mixtures. This has as its consequence that each graph must be multiplied by the following factors:

1) $z_i^{M_1} z_j^{M_2}$, where i and j are the species of ions at the root points 1 and 2 ;

2) $c_1 z_1^{M_n} + c_2 z_2^{M_n}$ for each field point n. (c_i is the probability that a field point has charge $z_i e$.) Here M_n is the number of lines that terminate in the point n.

Thus the overall change in (2.9) in going from the case of the electron gas to the case of a binary mixture, taking into account the charge neutrality condition $c_1 z_1 = -c_2 z_2$, is to multiply each graph by $z_i^{M_1} z_j^{M_2}$, where i and j are the species of ions at the root points 1 and 2 , and by $\dfrac{z_1^{M_n-1} - z_2^{M_n-1}}{z_1 - z_2}$ for each field point n at which M_n lines terminate.

The factors $1/m_{ij}!$ in (2.9) can be considered as part of the symmetry number, if the definition of the symmetry number is extended to include permutations of the lines which connect two given points. If we call this more general symmetry number S', (2.9) becomes

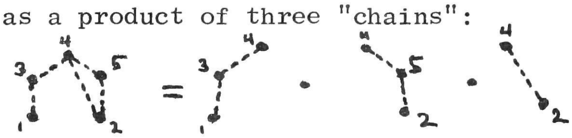
$$\Psi(\xi_{12};\varepsilon) = -\frac{\varepsilon}{\xi_{12}} + \sum_{n=1}^{\infty} C_n \varepsilon^n \tag{2.9'}$$

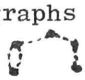
$$C_n(\xi_{12}) = \sum_{k=1}^{\infty} \frac{1}{(4\pi)^k} \sum_{P_k^{(n)}} \frac{1}{S'_{P_k^{(n)}}} \int\!\!\cdots\!\!\int d\vec{\xi}_3 \cdots d\vec{\xi}_{k+2} \prod_{P_k^{(n)}} \left(-\frac{1}{\xi_{ij}}\right)^{m_{ij}}$$

3. Summation Over "Chains"

Each coefficient C_n in (2.9) is represented by an infinite number of Coulomb graphs. In order to obtain a more tractable expression for the C_n, we will now perform a partial evaluation of the infinite sums involved.

We first remark that each Coulomb graph in (2.9) may be regarded as a product of "chains"; that is, a product of connected subgraphs whose "endpoints" are the points at which the subgraphs join to make up the original graph, and whose remaining field points, called "points of order two," have exactly two lines attached. Thus, for example, the graph  may be regarded as a product of three "chains":



We note that two graphs that differ only in the length of one of their "chains," such as  and , are of the same order in ε, as the difference between the number of lines and the number of field points in the two graphs is the same. We therefore proceed to sum over the chains of various lengths, thereby reducing the infinite set of Coulomb graphs in each coefficient C_n in (2.9) to a finite set of "Debye graphs," whose lines represent functions D_{ij} defined as follows:

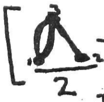
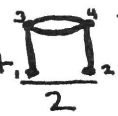
(2.10) $D_{ij}(\xi_{ij}) =$  $=$  $+ \frac{1}{4\pi}\int\!\!\cdots\!\!\int d\vec{\xi}_{3'}$  $+ \frac{1}{(4\pi)^2}\int\!\!\cdots\!\!\int d\vec{\xi}_{3'}\, d\vec{\xi}_{4'}$  $+ \cdots$

The function $D_{ij}(\xi_{ij})$ will be explicitly evaluated below. Substitution of (2.10) in (2.9') gives the following formal power series in ε :*

$$\Psi(\xi_{12};\varepsilon) = \sum_{n=1}^{\infty} C_n' \varepsilon^n \tag{2.11}$$

$$C_n'(\xi_{12}) \equiv \sum_{k=0}^{\infty} \frac{1}{(4\pi)^k} \sum_{O_k^{(n)}} \frac{1}{S_{O_k^{(n)}}} \int \cdots \int d\vec{\xi}_3 \cdots d\vec{\xi}_{k+2} \prod_{O_k^{(n)}} D_{ij}^{m_{ij}}$$

where the graphs $O_k^{(n)}$ satisfy the same rules as the $P_k^{(n)}$, except that  is allowed and the graphs may not contain points of order two. Writing out the first few terms,

(2.12) $\Psi(\xi_{12};\varepsilon) = \varepsilon$  $+\varepsilon^2\Big[$  $+$  $+$  $\Big] + \varepsilon^3 \cdots$

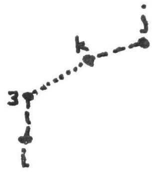
Here the heavy lines represent the functions D_{ij}, and the integration $\frac{1}{4\pi}\int\cdots\int d\vec{\xi}$ over each field point is understood. We now evaluate the sum of integrals in (2.10). Since each integral is of the convolution type, we use the Fourier transform of $1/\xi_{ij}$:

$$\frac{1}{\xi_{ij}} = \frac{1}{2\pi^2}\int\cdots\int d\vec{q}\ \frac{e^{i(\vec{q}\cdot\vec{\xi}_{ij})}}{q^2} \tag{2.13}$$

By the convolution theorem, the $(k-1)^{st}$ term in (2.10) is given by

---

*In performing the transition from (2.9') to (2.11), we must make certain that each Coulomb graph in (2.11), with D_{ij} given by (2.10), has the same numerical factor as in (2.9). To check this we divide each Coulomb graph into subgraphs, each of which consists of the m chains connecting the points i and j, where i and j are not points of order two; e.g.,  . If m_ℓ is the number of chains of length ℓ in such a subgraph, each graph in (2.9) containing that subgraph will appear in (2.11) $m!/\prod_\ell m_\ell!$ times, as the D_{ij} are expanded separately without regard to the fact that some Coulomb graphs are thus duplicated. On the other hand, the symmetry number of the Coulomb subgraph is $\prod_\ell m_\ell!$ while that of the Debye subgraph is $m!$, so that (2.11) is indeed correct.

(2.14) 

$$= \frac{1}{(4\pi)^{k-2}} \int \cdot\cdot \int d\vec{\xi}_3 \cdot\cdot d\vec{\xi}_k \; \frac{(-1)^{k-1}}{\xi_{13}\,\xi_{34}\cdot\cdot\,\xi_{(k-1)k}\,\xi_{kj}}$$

$$= \frac{(-1)^{k-1}}{2\pi^2} \int \cdot\cdot \int d\vec{q}\; \frac{e^{i(\vec{q}\cdot\vec{\xi}_{ij})}}{(q^2)^{k-1}}$$

Summing over all terms in (2.10),

$$D_{ij}(\xi_{ij}) = \frac{1}{2\pi^2} \int \cdot\cdot \int d\vec{q}\; e^{i(\vec{q}\cdot\vec{\xi}_{ij})} \sum_{k=2}^{\infty} \left(-\frac{1}{q^2}\right)^{k-1} \tag{2.15}$$

But $\displaystyle\sum_{k=2}^{\infty} \left(-\frac{1}{q^2}\right)^{k-1} = -\frac{1}{q^2} \sum_{k=0}^{\infty} \left(-\frac{1}{q^2}\right)^{k} = -\frac{1}{q^2\left(1+\frac{1}{q^2}\right)} = -\frac{1}{q^2+1}$

So

$$D_{ij}(\xi_{ij}) = -\frac{1}{2\pi^2} \int \cdot\cdot \int d\vec{q}\; \frac{e^{i(\vec{q}\cdot\xi_{ij})}}{q^2+1} = \frac{-e^{-\xi_{ij}}}{\xi_{ij}} \tag{2.16}$$ *

Thus we can write out explicitly the graphs in (2.12); for example

$$= -\frac{1}{4\pi} \int \cdot\cdot \int d\vec{\xi}_3 \left(\frac{e^{-\xi_{13}}}{\xi_{13}}\right)^2 \frac{e^{-\xi_{32}}}{\xi_{32}}$$

---

*The resummation procedure remains exactly the same in the case of mixtures discussed in the footnote on page 11, since at all the points over which we integrate $M_n = 2$, so

$$(z_1^{M_n-1} - z_2^{M_n-1})/(z_1 - z_2) = 1 .$$

It follows that the rules for the transition from the electron gas to mixtures are the same for Debye graphs in (2.17) as for the Coulomb graphs in (2.9).

and (2.11) becomes

$$\Psi(\xi_{12};\epsilon)=\sum_{n=1}^{\infty} C'_n\,\epsilon^n \tag{2.17}$$

$$C'_n(\xi_{12})=\sum_{k=0}^{\infty}\frac{1}{(4\pi)^k}\sum_{O_k^{(n)}}\frac{1}{S'_{O_k^{(n)}}}\int\!\!\cdots\!\!\int d\vec{\xi}_3\cdots d\vec{\xi}_{k+2}\prod_{O_k^{(n)}}\left(-\frac{e^{-\xi_{ij}}}{\xi_{ij}}\right)^{m_{ij}}$$

where the graphs

1) have m_{ij} lines connecting the points i and j ;

2) have no lines connecting 1 and 2, with the single exception of the graph ;

3) are simple, contain no points of order two, and would be irreducible if there were a line connecting 1 and 2.

The integrals  =  and  are evaluated in Appendix A; (2.12) becomes

$$\Psi(\xi;\epsilon) = -\epsilon\frac{e^{-\xi}}{\xi}+\epsilon^2\Bigg[\frac{\ln 3}{8}e^{-\xi}-\left(\frac{3}{8}\ln 3+\frac{1}{6}\right)\frac{e^{-\xi}}{\xi} \tag{2.18}$$

$$+\frac{1}{6}\frac{e^{-2\xi}}{\xi}+\frac{1}{8}\left\{(\xi+3)\frac{e^{\xi}}{\xi}Ei(-3\xi)+(\xi-3)\frac{e^{-\xi}}{\xi}Ei(-\xi)\right\}\Bigg]+\epsilon^3\cdots$$

where $Ei(-\lambda\xi)$ is the "exponential integral":

$$Ei(-\lambda\xi)\equiv-\int_{\xi}^{\infty}dx\,\frac{e^{-\lambda x}}{x}=\gamma_E+\ln(\lambda\xi)+\sum_{n=1}^{\infty}\frac{(-\lambda\xi)^n}{n!\,n}$$

The first term in (2.17) is just the Debye-Hückel potential $-\frac{e^2}{kT}\frac{e^{-r/R_D}}{r}$ (see 2.6). The higher order terms, representing deviations from the Debye-Hückel potential, include deviations from the "superposition principle" mentioned in Chapter I.

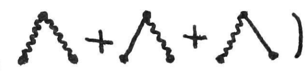
We would now like to evaluate the term C'_3 in (2.17). Unfortunately, C'_3 includes terms containing the subgraph , so that the integration over field points diverges logarithmically at $\xi_{ij}\to 0$. It is necessary, therefore, to perform a further resummation [7]. This we accomplish by summing all graphs identical except for the number m_{ij} of lines connecting i and j , where $m_{ij}\geq 2$:

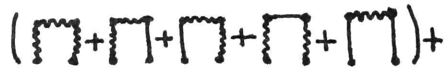
(2.19) ϵ^2  $/\,2!$ $+\,\epsilon^3$  $/\,3!$ $+\,\epsilon^4$  $/\,4!$ $+\cdots = e^{-\epsilon\frac{e^{-\xi_{ij}}}{\xi_{ij}}}-1+\epsilon\frac{e^{-\xi_{ij}}}{\xi_{ij}}\equiv f_{ij}$

(2.17) becomes

(2.20) $$\Psi(\xi_{12};\epsilon) = \sum_{k=0}^{\infty} \frac{1}{(4\pi\epsilon)^k} \sum_{R_k} \frac{1}{S_{R_k}} \int\!\cdots\!\int d\vec{\xi}_3 \cdots d\vec{\xi}_{k+2} \prod_{R_k} \left(-\epsilon \frac{e^{-\xi_{ij}}}{\xi_{ij}}\right) f_{mn}$$

where the graphs R_k with k field points have two types of lines; the first type is drawn as a solid line and represents a factor $-\epsilon \frac{e^{-\xi_{ij}}}{\xi_{ij}}$, and the other is drawn as a wavy line and represents a factor f_{mn}. The rules for constructing the graphs R_k are as follows: only one line may connect any two points, and there may be no points of order two such that two solid lines join at a point; the graphs must be simple, must become irreducible if a line is added between the root points 1 and 2, and must contain no line between 1 and 2, with the exception of the graph .
The first few terms are

(2.21) $\Psi(\xi_{12};\epsilon) =$  $+ \frac{1}{4\pi\epsilon} \int\!\cdots\!\int d\vec{\xi}_3$ 

$+ \frac{1}{(4\pi\epsilon)^2} \int\!\cdots\!\int d\vec{\xi}_3\, d\vec{\xi}_4$  $+ \cdots$

The expression (2.20) is not ordered in powers of ϵ ; we will, however, be able to extract the ϵ behavior of Ψ by finding the Fourier transform $F(q_{mn})$ of f_{mn} and using the convolution method to evaluate the integrals. The Fourier transform of f_{mn} was evaluated to the order required [17] by breaking up the integral into a long-distance and a short-distance part, expanding the exponential in the long-distance part, and using the substitution $U = 1/\xi_{mn}$ in the short-distance part. The result is

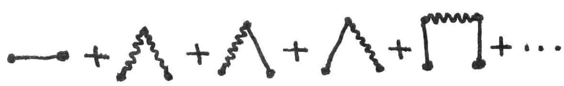
(2.22) $$F(q_{mn}) \equiv \frac{1}{4\pi} \int\!\cdots\!\int d\vec{\xi}\, e^{i(\vec{q}_{mn}\cdot\vec{\xi}_{mn})} f(\xi_{mn};\epsilon) = \frac{\epsilon^2}{2} \frac{\tan^{-1}\left(\frac{q_{mn}}{2}\right)}{q_{mn}} + \frac{\epsilon^3 \ln\epsilon}{6} + \frac{\epsilon^3}{6}\left[2\gamma_E + \ln 3 - \frac{17}{6} + 3\frac{\tan^{-1}\left(\frac{q_{mn}}{3}\right)}{q_{mn}} + \frac{1}{2}\ln\left(1 + \frac{q_{mn}^2}{9}\right)\right] + \frac{\epsilon^4 \ln\epsilon}{6} + \cdots$$

Use of (2.22) in (2.20) gives

$$\Psi(\xi;\epsilon) = \epsilon\,\Psi_1(\xi) + \epsilon^2\,\Psi_2(\xi) + \epsilon^3 \ln\epsilon\,\Psi_{3'}(\xi) + \epsilon^3\left[\Psi_{3X}(\xi) + \Psi_{3N}(\xi)\right] + \epsilon^4 \ln\epsilon\,\Psi_{4'}(\xi) + \cdots \tag{2.23}$$

where $\Psi_1(\xi)$ and $\Psi_2(\xi)$ agree with (2.18); the higher order terms are quite complex and are given in Appendix B. The coefficient of ϵ^3 is divided into two parts; the term $\Psi_{3X}(\xi)$ can be evaluated explicitly, while $\Psi_{3N}(\xi)$ must be found by numerical integration.

We will now make two remarks about (2.20). First: for fixed ϵ and increasing ξ, the $\epsilon^2 \frac{\ln 3}{8} e^{-\xi}$ term in (2.18) dominates the Debye-Hückel term $-\epsilon \frac{e^{-\xi}}{\xi}$; furthermore, the term  in the coefficient of ϵ^3 behaves as $\xi e^{-\xi}$ at large ξ, and it can be seen that the coefficient of ϵ^n behaves as $\xi^{n-2} e^{-\xi}$. To tame the long-distance behavior, therefore, we resum those terms in (2.20) which are chains of both types of lines [7]:

(2.24) $T(\xi;\epsilon) \equiv$ 

A graph with m solid lines and n wavy lines appears $(n+1)!/m!(n-m+1)!$ times in (2.24), provided $m \leq n+1$; the graph  is excluded. Using this fact, the binomial theorem, (2.22), (2.16), and the convolution theorem, we obtain

$$T(\xi;\epsilon) = -\frac{2\epsilon}{\pi\xi}\int_0^\infty dq\,\sin(q\xi)\,\frac{\epsilon q - q^3 F}{\epsilon(q^2+1) - q^2 F} - \left[e^{-\epsilon\frac{e^{-\xi}}{\xi}} - 1 + \epsilon\frac{e^{-\xi}}{\xi}\right] \tag{2.25}$$

We extract the long-distance behavior of T by a method described in Appendix B; the result is

$$T \underset{\xi\to\infty}{\longrightarrow} -\epsilon C_1 \frac{e^{-C_2\xi}}{\xi} \tag{2.26}$$

$$C_1 = 1 + \epsilon\left(\tfrac{3}{8}\ln 3 + \tfrac{1}{6}\right) + \cdots$$

$$C_2 = 1 + \epsilon\frac{\ln 3}{8} + \cdots$$

Here we have evaluated C_1 and C_2 only to order ϵ.

The second remark concerns the possibility of expressing (2.20) in terms of a double power series in ϵ and $\ln \epsilon$. (2.23) shows that this is the case up to order $\epsilon^4 \ln \epsilon$; however, examination of (2.20), (2.22), and (2.16) shows that the coefficient of $\epsilon^5 (\ln \epsilon)^2$ would consist of three finite terms plus a term proportional to $\int\!\!\cdot\!\!\int d\vec{q}\, e^{i\vec{q}\cdot\vec{\xi}}$; the coefficient of $\epsilon^5 \ln \epsilon$ contains a term proportional to $\int\!\!\cdot\!\!\int d\vec{q}\, e^{i\vec{q}\cdot\vec{\xi}} \ln(1+\frac{q^2}{q})$, and higher terms contain still more strongly divergent integrals. Thus, we have not yet removed all divergences and still further resummation is necessary. Whether this means that Ψ is not given by a series of the form $\sum_{m,n} \epsilon^m (\ln \epsilon)^n \Psi_{mn}$ is an open question.

4. The Internal Potential Energy

We now wish to calculate the internal potential energy of the electron gas. The potential energy associated with a single pair of particles, one at $\vec{r}_1$ and one at $\vec{r}_2$, is just e^2/r_{12}; moreover, we now know the pair distribution function f_2, so that we can compute the total potential energy

$$(2.27) \qquad U = \frac{e^2}{2} \int\!\!\cdot\!\!\cdot\!\!\int d\vec{r}_1\, d\vec{r}_2 \left[\frac{f_2}{r_{12}} - \frac{n^2}{r_{12}} \right]$$

Here the term $-\frac{e^2 n^2}{r_{12}} d\vec{r}_1\, d\vec{r}_2$ is the energy associated with the volume elements $d\vec{r}_1, d\vec{r}_2$ of the uniform positive background, and the factor $1/2$ is due to the redundancy in $\vec{r}_1$ and $\vec{r}_2$. Since from (2.1) and (2.9) $f_2(\xi_{12}; n, \epsilon) = n^2 \exp(\Psi(\xi_{12}; \epsilon))$ and $n = \frac{N}{V}$, we obtain

$$(2.28) \qquad \begin{aligned} U &= \frac{N}{2} n e^2 \int\!\!\cdot\!\!\cdot\!\!\int \frac{d\vec{r}_2}{r_{12}} \left(\exp\left(\frac{\Phi(r_{12})}{kT}\right) - 1 \right) \\ &= \frac{NkT}{2} \int_0^\infty d\xi\, \xi \left(\exp(\Psi(\xi)) - 1 \right) \end{aligned}$$

using (2.6).

A partial expansion of the exponential in (2.28), taking into

account the behavior of Ψ at $\xi \to 0$, gives to order ε^3

(2.29) $$\frac{2U}{NkT} = \int_0^\infty d\xi\,\xi\left[e^{\varepsilon\Psi_1} - 1\right] + \varepsilon^2\int_0^\infty d\xi\,\xi\,\Psi_2 + \varepsilon^3 \ln\varepsilon\int_0^\infty d\xi\,\xi\,\Psi_{3'}$$
$$+ \varepsilon^3\int_0^\infty d\xi\,\xi\left[\Psi_{3x} + \Psi_{3N}\right] + \varepsilon^3\int_0^\infty d\xi\,\xi\,\Psi_1\Psi_2 + \cdots$$

The first integral in (2.29) is evaluated by breaking it up into $\int_0^\alpha + \int_\alpha^\infty$; in evaluating $\int_0^\alpha$ we expand $e^{-\xi}$ and make the approximation $e^{-\varepsilon\frac{e^{-\xi}}{\xi}} \doteq e^{\varepsilon}e^{-\frac{\varepsilon}{\xi}}$ and the substitution $U \equiv 1/\xi$, and in evaluating $\int_\alpha^\infty$ we use the expansion $e^{\varepsilon\Psi_1} = 1 + \varepsilon\Psi_1 + \varepsilon^2\Psi_1^2/2! + \cdots$. All terms which diverge as $\alpha \to 0$ are seen to cancel, and α is set equal to zero; the result is

(2.30) $$\int_0^\infty d\xi\,\xi\left[e^{\varepsilon\Psi_1} - 1\right] = -\varepsilon - \frac{\varepsilon^2\ln\varepsilon}{2} - \varepsilon^2\left[\gamma_E + \frac{\ln 2}{2} - \frac{3}{4}\right]$$
$$- \frac{\varepsilon^3\ln\varepsilon}{2} - \varepsilon^3\left[\gamma_E + \frac{\ln 3}{2} - \frac{5}{4}\right] + \cdots$$

where the $\ln\varepsilon$ behavior stems from the non-analytic nature of $\exp\left(-\varepsilon\frac{e^{-\xi}}{\xi}\right)$ at $\xi = 0$.

Evaluation of $\int_0^\infty d\xi\,\xi\left[\varepsilon^2\Psi_2 + \varepsilon^3\Psi_{3x}\right]$ makes use of the formula

(2.31) $$\int_0^\infty d\tau\, e^{-s\tau}\tau^{\beta-1}E_i(-\tau) = \frac{\Gamma(\beta)}{\beta(1+s)^\beta}\,F\left(1,\beta;\beta+1;\frac{s}{s+1}\right)$$ [18]

where $\Gamma(\beta)$ is the usual gamma function and F the hypergeometric function; in this special case

(2.32) $$F(1, m+1; m+2; z) = -\frac{(m+1)!(-1)^m}{(m!)^2}\frac{d^m}{dz^m}\left[\frac{(1-z)^m\ln(1-z)}{z}\right]$$

We obtain the results

$$\varepsilon^2 \int_0^\infty d\xi\, \xi\, \Psi_2 = \varepsilon^2 \left[\frac{\ln \frac{2}{3}}{2} - \frac{1}{12} \right] \tag{2.33}$$

$$\varepsilon^3 \ln \varepsilon \int_0^\infty d\xi\, \xi\, \Psi_{3'} = -\frac{\varepsilon^3 \ln \varepsilon}{4}$$

$$\varepsilon^3 \int_0^\infty d\xi\, \xi\, \Psi_{3x} = \varepsilon^3 \left[-\frac{\gamma_E}{2} + \frac{\ln 3}{2} - \frac{3}{2} \ln 2 + \frac{5}{8} \right]$$

To evaluate $\int_0^\infty d\xi\, \xi\, \Psi_1 \Psi_2$ we must make use of the formula [19]

$$\frac{E_i(-x)}{x} = -\int_1^\infty d\tau\, e^{-\tau x} \ln \tau \tag{2.34}$$

We obtain

$$\varepsilon^3 \int_0^\infty d\xi\, \xi\, \Psi_1 \Psi_2 = \varepsilon^3 \left[\frac{1}{24} - \frac{3}{8} \ln 3 \frac{\ln \frac{4}{3}}{2} - \frac{1}{6} \ln \frac{2}{3} + \frac{3}{4} \int_1^\infty \frac{d\tau \ln \tau}{\tau(2+\tau)} \right] \tag{2.35}$$

where $\int_1^\infty \frac{d\tau \ln \tau}{\tau(2+\tau)}$ must be evaluated numerically.

Finally, we find by numerical integration that Ψ_{3N} gives a contribution $(-.0526 \pm .0008)\varepsilon^3$ to $\frac{2U}{NkT}$; our final result for the internal energy is then

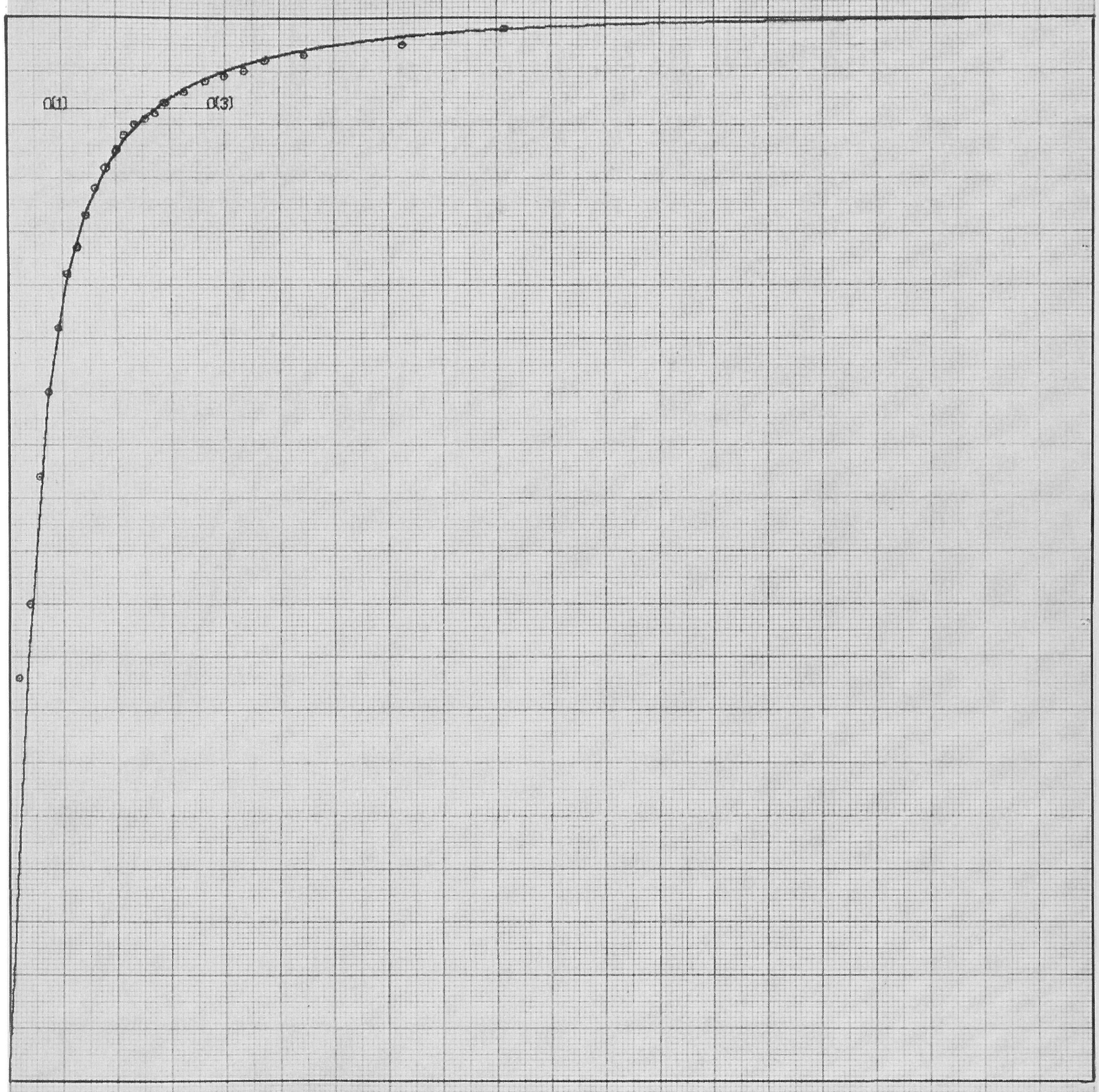
$$\frac{U}{NkT} = -\frac{\varepsilon}{2} - \frac{\varepsilon^2 \ln \varepsilon}{4} - \left[\frac{\gamma_E}{2} + \frac{\ln 3}{4} - \frac{1}{3} \right] \varepsilon^2 - \frac{3}{8} \varepsilon^3 \ln \varepsilon + (0.2528 \pm .0004)\varepsilon^3 + \ldots \tag{2.36}$$

5. Comparison with "Experiment"

Brush, Sahlin, and Teller [8] have made for the electron gas computations of the pair distribution function and the internal energy

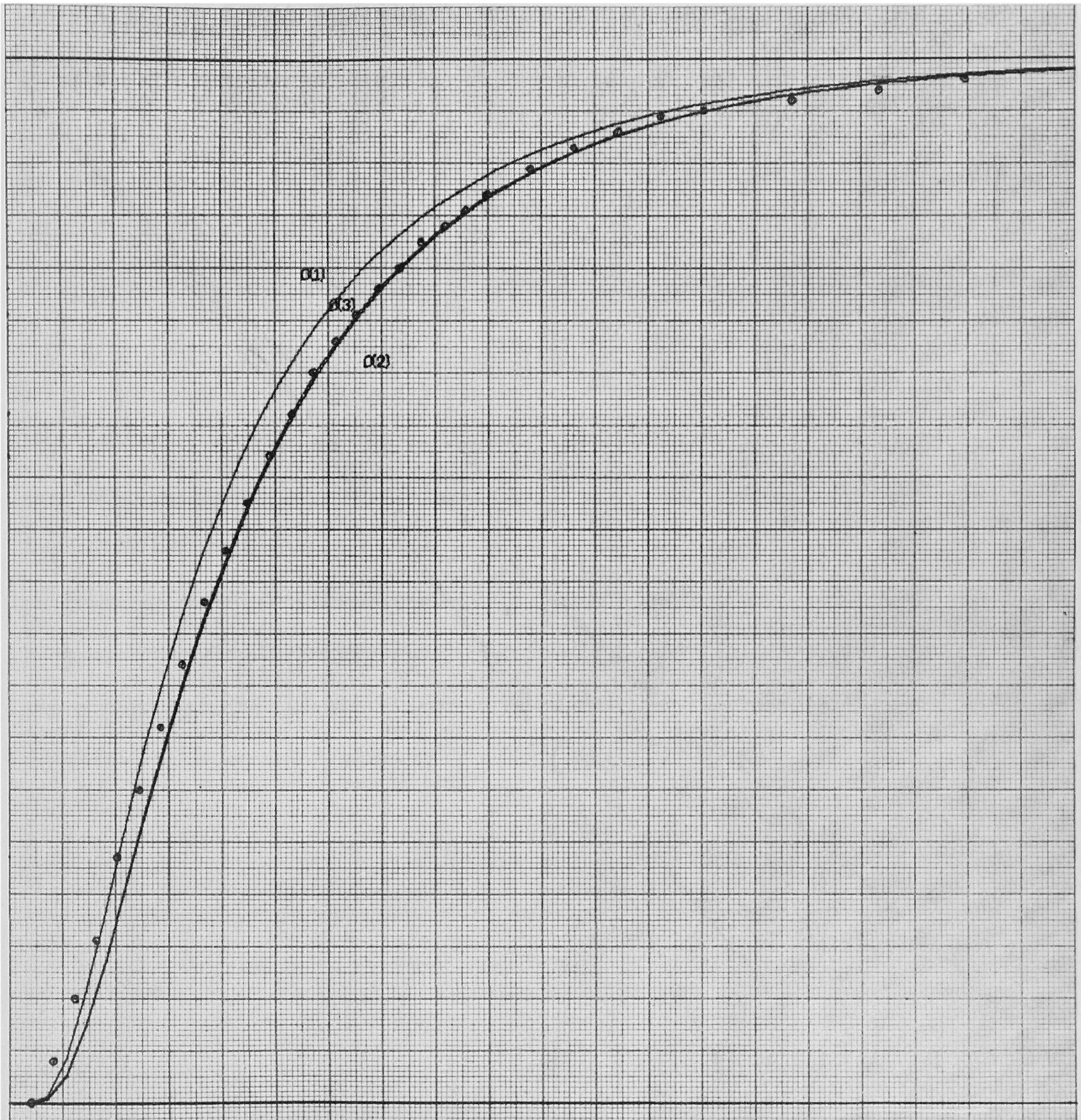
as a function of ε , using a Monte Carlo method.* Figs. 1 and 2 compare the pair distribution function calculated from (2.23) with the Monte Carlo results; 0 (1), 0 (2), and 0 (3) retain the terms in U/NkT of order ε, ε^2, and ε^3 respectively in the potential of average force. Fig. 3 compares the internal energy given by the Monte Carlo results with the internal energy calculated numerically from (2.28), with Ψ given by (2.23) through order ε^3 . Up to $\varepsilon = 0.7$ we have also plotted the function given by (2.36); the curves 0 (1), 0 (2), and 0 (3) retain only the terms in U/NkT through order $\varepsilon, \varepsilon^2$, and ε^3 respectively.

*The deviation of the Monte Carlo points from the expected results at small ε and small distances is probably due to inaccuracy in the Monte Carlo calculations.



RADIAL DISTRIBUTION FUNCTION VS REDUCED DISTANCE E= .0547

Fig. 1



RADIAL DISTRIBUTION FUNCTION VS REDUCED DISTANCE E= .6123

Fig. 2

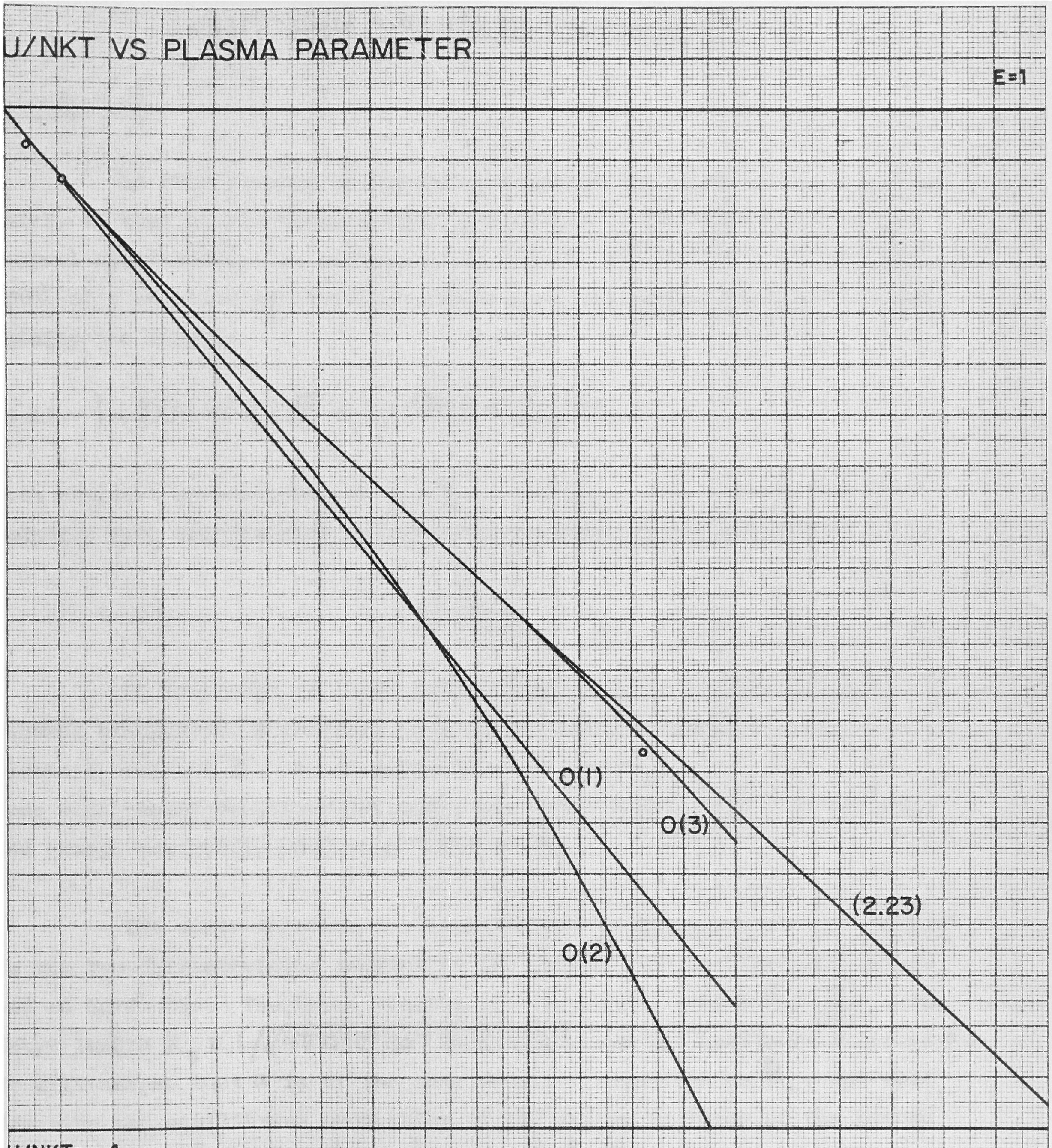


Fig. 3

III. Ionic Solutions In Equilibrium

Introduction

In this chapter we present a computation, based on a simplified model, of some of the thermodynamic properties of an ionic solution in thermal equilibrium. In particular we compute the activity coefficient $\gamma(n)$ of a solution of ions as a function of the number density n, obtaining the formula

$$\ln \gamma(n) = \gamma_1 \sqrt{n} + \gamma_{2'} n \ln n + \gamma_2 n + \cdots \tag{3.1}$$

with explicit expressions for γ_1, $\gamma_{2'}$, and γ_2. This formula will be compared with experimental measurements on some simple electrolytes.

1. The Model

We represent an ionic solution by a system of charged hard spheres of diameter a immersed in a medium characterized only by a dielectric constant D. We consider only the "binary" case of two types of ions with number densities $c_1 n$, $c_2 n$, and charges $z_1 e$, $z_2 e$, satisfying the charge neutrality condition $c_1 z_1 = -c_2 z_2$.

The ionic solution is characterized by three lengths, as opposed to the two characteristic lengths in the case of the electron gas, which has no hard core. The three lengths are the Landau length $R_L \equiv \frac{e^2}{DkT}$, the Debye length $R_D \equiv 1/\sqrt{4\pi n (e^2/DkT)(c_1 z_1^2 + c_2 z_2^2)}$, and the hard-core diameter a. We will assume that a is of the same order of magnitude as R_L, and will describe the equilibrium properties of the system in terms of the charge numbers z_1 and z_2, the plasma parameter $\epsilon \equiv R_L/R_D$, and the "Bjerrum parameter" $b \equiv R_L/a$, a number of order one. The assumption that the two species of ions have the same diameter can be justified by the fact that collisions between ions of opposite charge will occur more frequently than collisions between those of like charge, so that the effective

hard core diameter is the sum of the radii of two ions of different species.

2. Theory

As in the case of the electron gas, we will obtain the thermodynamic quantities by computing the pair distribution function. The most important thermodynamic quantity for the purpose of comparison with experiment is the activity coefficient, defined as

$$\gamma(n) \equiv \exp\left[\frac{g(n)-g(0)}{kT}\right] \tag{3.2}$$

where $g(n)$ is the Gibbs free energy per ion and $g(0)$ is the Gibbs free energy per ion in the limit of low density. ($g(0)$ is just the kinetic part of the Gibbs free energy, and is the same as the Gibbs free energy of an ideal gas.)

$g(n)-g(0)$ is computed in two parts [15]: One is the contribution to the Gibbs free energy of the hard-sphere potential, which is the same as in the case of the electrically neutral hard-sphere gas; and the other is the additional contribution due to the charge on the spheres, which will be found from the pair distribution function. Each part of $g(n)-g(0)$ will be computed to order n.

The contribution $[g(n)-g(0)]_a$ of the hard-sphere potential can be obtained from the density expansion (2.5); to first order in the density n it is given by $-2B_2 n$ where B_2 is the well-known second virial coefficient of the hard sphere gas:

$$\frac{[g(n)-g(0)]_a}{kT} = \frac{4\pi}{3} a^3 n \tag{3.3}$$

Using the charge neutrality condition and the definitions of ϵ, b, and R_D, we rewrite (3.3) as

$$\frac{[g(n)-g(0)]_a}{kT} = \frac{\epsilon^2}{3b^3(-z_1 z_2)} \tag{3.4}$$

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Equation (3.6) is not correct for our model due to the existence of the hard core potential. $p_c V$ can be calculated from the corresponding Helmholtz free energy $\frac{A_c}{NkT} = \frac{2}{3}\int_0 \frac{d\varepsilon'}{\varepsilon'}\left(\frac{U_c}{NkT}\right)$ by the formula: $\frac{p_c}{NkT} = -\frac{V}{NkT}\left(\frac{\partial A_c}{\partial V}\right)_T = \frac{\varepsilon}{2}\frac{\partial(A_c/NkT)}{\partial\varepsilon}$; as a consequence the final result (3.24) should be modified to read:

$$\gamma_2 = (-z_1 z_2)\Big[\frac{(z_1+z_2)^2}{6}\left(-\gamma_E + \ln\frac{b}{3} - \frac{1}{4}\right) + \frac{1}{2b} + \frac{1}{3(z_1 z_2)^2 b^3} + \sum_{n=3}^{\infty}\frac{(-b)^{n-2}}{(n+1)!\,(n-2)}\left(\frac{z_1^n - z_2^n}{z_1 - z_2}\right)^2\Big] \quad (3.24)$$

The quoted values of a change a few % only.

Due to the results of Chapter II, we already have the pair distribution function of the system at our disposal; therefore, the contribution $[g(n)-g(0)]_c$ of the Coulomb potential to the Gibbs free energy can readily be computed by first expressing it in terms of the internal potential energy U_c of the system, and then computing U_c from the pair distribution function. We begin with the thermodynamic relation

$$N\,[g(n)-g(0)]_c = U_c - TS_c + P_cV \tag{3.5}$$

where S_c and P_c are the contributions of the Coulomb potential to the entropy and pressure, and will be obtained in terms of U_c ; N is the total number of ions and V is the volume of the system.

P_cV is given in terms of U_c by the virial theorem, which, in the special case of the Coulomb potential, gives

$$P_cV = \frac{1}{3}U_c \tag{3.6}$$

The contribution S_c of the Coulomb potential to the entropy is found in terms of U_c by calculating the increase in entropy when the unit of charge e is increased from zero to its actual value at constant temperature and volume:

$$S_c(T,V,e) = \int_0^e de' \left[\frac{\partial S_c}{\partial e'}\right]_{T,V} \tag{3.7}$$

S_c depends on e only through the plasma parameter $\varepsilon = e^2/DkTR_D$, so

$$S_c = \int_0^\varepsilon d\varepsilon' \left[\frac{\partial S_c(T,\varepsilon')}{\partial \varepsilon'}\right]_V \tag{3.8}$$

where, although T is a function of ε, the derivative affects only the explicit ε dependence of S_c. At constant volume $\partial S_c = \partial U_c/T$, so

$$S_c = \int_0^\varepsilon d\varepsilon' \frac{1}{T}\left[\frac{\partial U_c}{\partial \varepsilon'}\right]_V \tag{3.9}$$

As in the case of the electron gas, we will be able to obtain an expression for U_c/T in terms of ε , so we use the substitution

$$\frac{\partial\left(\frac{U_c}{T}\right)}{\partial\varepsilon} = \frac{1}{T}\frac{\partial U_c}{\partial\varepsilon} + U_c\frac{\partial\left(\frac{1}{T}\right)}{\partial\varepsilon} \tag{3.10}$$

and calculate $\partial\left(\frac{1}{T}\right)/\partial\varepsilon$ from the definition of ε .

Making these substitutions in (3.9) gives

$$\begin{aligned} S_c &= \int_0^\varepsilon d\varepsilon'\,\frac{\partial\left(\frac{U_c}{T}\right)}{\partial\varepsilon'} - \frac{2}{3}\int_0^\varepsilon \frac{d\varepsilon'}{\varepsilon'}\left(\frac{U_c}{T}\right) \\ &= \frac{U_c}{T} - \frac{2}{3}\int_0^\varepsilon \frac{d\varepsilon'}{\varepsilon'}\left(\frac{U_c}{T}\right) \end{aligned} \tag{3.11}$$

(3.5), (3.6), and (3.11) together give

$$\frac{\left[g(n)-g(0)\right]_c}{kT} = \frac{1}{3}\frac{U_c}{NkT} + \frac{2}{3}\int_0^\varepsilon \frac{d\varepsilon'}{\varepsilon'}\left(\frac{U_c}{NkT}\right) \tag{3.12}$$

It now remains only to calculate $\frac{U_c}{NkT}$ in terms of ε . As in the case of the electron gas, U_c is given by the potential energy of interaction of a pair of particles and the pair distribution function; in the case of the ionic solution, however, the pair distribution function $f_{ij}(r_{12})$ depends on the species i and j of the ions at $\vec{r}_1$ and $\vec{r}_2$, so that

$$U_c = \frac{1}{2}\int\!\cdot\!\cdot\!\int d\vec{r}_1\,d\vec{r}_2 \sum_{i,j=1}^{2}\left(\frac{z_i z_j e^2}{D r_{12}}\right) f_{ij}(r_{12}) \tag{3.13}$$

Here $f_{ij}(r_{12})$ is given by

$$\begin{aligned} f_{ij} &= c_i c_j n^2 \exp\left(\Phi_{ij}(r_{12})/kT\right), \quad r_{12} > a \\ &= 0, \quad r_{12} < a \end{aligned} \tag{3.14}$$

where Φ_{ij} is the potential of average force, which is given for $r_{12} > a$ by (2.12) together with the modifications given in the footnote on page 11:*

---

*It can be shown that, to order ε^2, the hard core potential does not affect $\Phi_{ij}(r_{12})$ for $r_{12} > a$.

(3.15a) $$\frac{\Phi_{ij}}{kT} = \Psi_{ij} = \Psi_{ij}^{(1)}\epsilon + \Psi_{ij}^{(2)}\epsilon^2 + \cdots$$

(3.15b) $$\Psi_{ij}^{(1)}(\xi_{12}) = -z_i z_j \frac{e^{-\xi_{12}}}{\xi_{12}}$$

(3.15c) $\Psi_{ij}^{(2)}(\xi_{12}) = z_i z_j \Big[(z_i+z_j)(z_1+z_2)$  $/\,2! + (z_1+z_2)^2$  $/\,2! \Big]$

where  and  are given by (A.8) and (A.11).

Substituting (3.14) into (3.13) and using the charge neutrality condition and the definition of R_D, we obtain

(3.16) $$U_c = \frac{NkT}{2}\,\frac{(-z_1 z_2)}{(z_1 - z_2)^2}\int_{\epsilon/b}^{\infty} d\xi\,\xi\left[e^{\Psi_{11}} - 2e^{\Psi_{12}} + e^{\Psi_{22}}\right]$$

where $\frac{\epsilon}{b} = \frac{a}{R_D}$ and $\xi = \frac{r_{12}}{R_D}$.

We will now evaluate (3.16) to order ϵ^2. Taking into account the short-range behavior of Ψ_{ij}, we find that to order ϵ^2 we can write:

(3.17) $$e^{\Psi_{ij}} \doteq e^{\epsilon\Psi_{ij}^{(1)}} + \epsilon^2\Psi_{ij}^{(2)}$$

Moreover, we can rewrite $e^{\epsilon\Psi_{ij}^{(1)}}$ in (3.17) as

(3.18) $$e^{\epsilon\Psi_{ij}^{(1)}} = 1 + \epsilon\Psi_{ij}^{(1)} + \epsilon^2\frac{\Psi_{ij}^{(1)\,2}}{2!} + \sum_{n=3}^{\infty}\epsilon^n\frac{\Psi_{ij}^{(1)\,n}}{n!}$$

where we can use the approximation

(3.19) $$\Psi_{ij}^{(1)} \doteq \frac{-z_i z_j}{\xi}$$

in each term in the sum from 3 to infinity.*

Using (3.17), (3.18), (3.15b), and (3.19) in (3.16) gives

$$
\begin{aligned}
(3.20)\quad U_c \doteq \frac{NkT}{2}\,\frac{(-z_1 z_2)}{(z_1-z_2)^2}\Bigg[& -\varepsilon\left(z_1^2 - 2z_1z_2 + z_2^2\right)\int_{\frac{\varepsilon}{b}}^{\infty} d\xi\,\xi\,\frac{e^{-\xi}}{\xi} \\
& + \varepsilon^2\,\frac{\left((z_1^2)^2 - 2z_1^2z_2^2 + (z_2^2)^2\right)}{2!}\int_{\frac{\varepsilon}{b}}^{\infty} d\xi\,\xi\,\frac{e^{-2\xi}}{\xi^2} \\
& + \sum_{n=3}^{\infty}(-\varepsilon)^n\,\frac{\left((z_1^n)^2 - 2z_1^nz_2^n + (z_2^n)^2\right)}{n!}\int_{\frac{\varepsilon}{b}}^{\infty} d\xi\,\xi\,\frac{1}{\xi^n} \\
& + \varepsilon^2\int_{\frac{\varepsilon}{b}}^{\infty} d\xi\,\xi\left(\Psi_{11}^{(2)} - 2\Psi_{12}^{(2)} + \Psi_{22}^{(2)}\right)\Bigg]
\end{aligned}
$$

We rewrite the last term in (3.20), using (3.15c) and (2.33):

$$
(3.21)\quad \int_{\frac{\varepsilon}{b}}^{\infty} d\xi\,\xi\left(\Psi_{11}^{(2)} - 2\Psi_{12}^{(2)} + \Psi_{22}^{(2)}\right) = \int_{\frac{\varepsilon}{b}}^{\infty} d\xi\;\xi\Big[2\left(z_1^3 - z_1^2 z_2 - z_1 z_2^2 + z_2^3\right)(z_1+z_2)
$$

$$
\frac{}{2!} + (z_1-z_2)^2(z_1+z_2)^2
$$

$$
\frac{}{2!}
$$

$$
\doteq (z_1-z_2)^2(z_1+z_2)^2\,\frac{\left(\ln\frac{2}{3} - \frac{1}{6}\right)}{2}
$$

---

*It might be thought that the terms in the sum from 3 to infinity could be ignored due to the factor ε^n ; however, $\Psi_{ij} \sim e^{-n\xi}/\xi^n$ and the integration in (3.16) will give an additional factor $1/(\varepsilon/b)^{n-2}$, so that all terms contribute to order ε^2. If we write $\frac{e^{-n\xi}}{\xi^n} = \sum_{m=0}^{\infty}\frac{(-n)^m}{m!}\xi^{m-n}$ the factor coming from the integration becomes $1/(\varepsilon/b)^{n-m-2}$, so to order ε^2 we can set $m=0$ and obtain (3.19).

Since $z_1 + z_2 = 0$ for "symmetric" electrolytes such as NaCl, this term containing $\Psi_{ij}^{(2)}$ is needed only for "asymmetric" electrolytes such as $CaCl_2$.

Evaluating the integrals in (3.20) and expanding the results in powers of $\frac{\varepsilon}{b}$ gives, to order ε^2 (b is of order 1):

$$U_c \doteq \frac{NkT}{2}(-z_1 z_2)\Big[-\varepsilon\left(1-\frac{\varepsilon}{b}\right) - \frac{\varepsilon^2}{2}\left(\gamma_E + \ln\frac{2\varepsilon}{b}\right)(z_1+z_2)^2 + \varepsilon^2 \sum_{n=3}^{\infty} \frac{(-b)^{n-2}}{n!(n-2)}\left(\frac{z_1^n - z_2^n}{z_1 - z_2}\right)^2 + \varepsilon^2 (z_1+z_2)^2 \frac{\left(\ln\frac{2}{3} - \frac{1}{6}\right)}{2} \tag{3.22}$$

$$\doteq \frac{NkT}{2}(-z_1 z_2)\Big[-\varepsilon - \varepsilon^2 \ln\varepsilon \, \frac{(z_1+z_2)^2}{2} + \varepsilon^2\Big\{\frac{(z_1+z_2)^2}{2}\left(-\gamma_E + \ln\frac{b}{3} - \frac{1}{6}\right) + \sum_{n=3}^{\infty}\frac{(-b)^{n-2}}{n!(n-2)}\left(\frac{z_1^n - z_2^n}{z_1 - z_2}\right)^2\Big\}\Big]^{*}$$

---

*The infinite sum can also be written

$$\sum_{n=3}^{\infty}\frac{(-b)^{n-2}}{n!(n-2)}\left(\frac{z_1^n - z_2^n}{z_1 - z_2}\right)^2 = \frac{1}{(z_1-z_2)^2}\Big[\frac{z_1^2}{2}\Big\{Ei(-z_1^2 b) - e^{-z_1^2 b}\left(\frac{1}{z_1^4 b^2} - \frac{1}{z_1^2 b}\right)\Big\} + \frac{z_2^2}{2}\Big\{Ei(-z_2^2 b) - e^{-z_2^2 b}\left(\frac{1}{z_2^4 b^2} - \frac{1}{z_2^2 b}\right)\Big\} - 2 z_1 z_2 \Big\{Ei(-z_1 z_2 b) - e^{-z_1 z_2 b}\left(\frac{1}{z_1^2 z_2^2 b^2} - \frac{1}{z_1 z_2 b}\right)\Big\} + (z_1 - z_2)^2\Big\{\frac{3}{4} - \frac{\gamma_E}{2} - \frac{1}{2 z_1 z_2 b} - \frac{\ln b}{2}\Big\} + \frac{1}{2}\Big\{z_1^2 \ln z_1^2 + z_2^2 \ln z_2^2 - 2 z_1 z_2 \ln(-z_1 z_2)\Big\}\Big]$$

A similar, though somewhat more involved, expression for the infinite sum in (3.24) can in principle be obtained from (3.12).

We now substitute (3.22) in (3.12), and (3.12) and (3.4) in (3.2) to get the final expression for $\ln \gamma(n)$. In evaluating the integral in (3.12), which is basically an integral over the unit of charge e, we must express b in terms of ϵ as follows:

$$b = \epsilon^{\frac{2}{3}} \left[4\pi a^3 n (c_1 z_1^2 + c_2 z_2^2) \right]^{-\frac{1}{3}} \tag{3.23}$$

Then (3.2) becomes

$$\ln \gamma(\epsilon) = \gamma_1 \epsilon + \gamma_{2'} \epsilon^2 \ln \epsilon + \gamma_2 \epsilon^2 + \cdots \tag{3.24}$$

$$\gamma_1 = \frac{z_1 z_2}{2}$$

$$\gamma_{2'} = \frac{z_1 z_2}{6} (z_1 + z_2)^2$$

$$\gamma_2 = -\frac{z_1 z_2}{6} \left[(z_1 + z_2)^2 \left(-\gamma_E + \ln \frac{b}{3} - \frac{1}{12} \right) + \frac{5}{2} b - \frac{1}{z_1 z_2 b^3} + \sum_{n=3}^{\infty} \frac{(-b)^{n-2} (n+4)}{n!\,(n-2)(n+1)} \left(\frac{z_1^n - z_2^n}{z_1 - z_2} \right)^2 \right.$$

We would now like to make the following remarks about (3.24):

1) Since $\epsilon \sim \sqrt{n}$, (3.24) is essentially the same as (3.1).

2) (3.24) includes all deviations from the superposition principle mentioned in Chapter I to order ϵ^2.

3) (3.24) is based on a model that treats the solvent as an idealized medium, and ignores many effects which, if treated more realistically, would give a different value for γ_2. The medium used in the model has no free energy of its own; hence, in comparison with experiment the free energy calculated above is to be compared with the free energy of the solution minus that of the pure solvent.

4) γ_2 is a function of b, while γ_1 and $\gamma_{2'}$ are not; in comparisons with experiment the parameter b is so chosen as to make

(3.24) agree with the experimental results as closely as possible.

3. Comparison with Experiment

In Fig. 4 we plot the theoretical curve for $\ln \gamma(\varepsilon)$ from $\varepsilon = 0$ to $\varepsilon = 0.2$ with $b = 1.38$ for the top curve and $b = 1.6$ for the bottom curve. The experimental points are taken from measurements on NaCl in water at 25°C [9]. In this case the maximum value of $\varepsilon = 0.2$ corresponds to a concentration of about .007 moles/liter and $b = 1.38$ corresponds to a hard sphere diameter of about 5.2 Å.

In the asymmetric case of $CaCl_2$ in water at 25°C the theory matches the experimental results for $b = .89$ ($a = 8.0$ Å). The term $\Psi_{ij}^{(2)}$ in this case accounts for about 30% of the deviation from the $\sqrt{n}$ law.

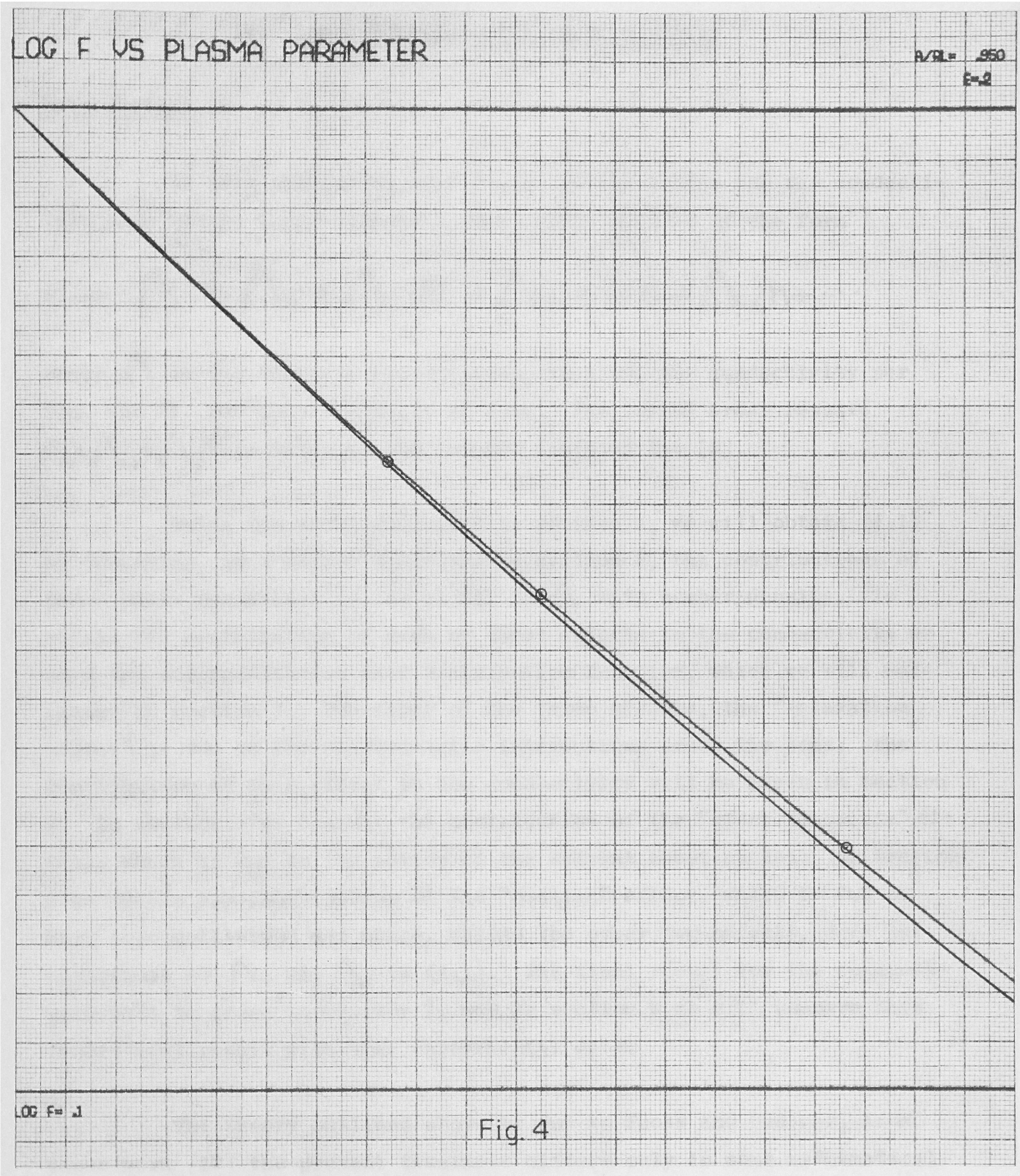

Fig. 4

IV. Ionic Solutions Not in Equilibrium

Introduction

In this chapter we will obtain an expression for the conductivity of a binary ionic solution. The result will be of the form

$$\Lambda = \Lambda_0 + \Lambda_1 \sqrt{n} + \Lambda_{2'} n \ln n + \Lambda_2 n + \cdots \tag{4.1}$$

where Λ is the specific conductivity, that is, the conductivity per ion, and n the number density of ions. The lowest order result: $\Lambda = \Lambda_0 + \Lambda_1 \sqrt{n}$ is known as the Onsager limiting law [2].

Using the model described in section 1, we will obtain (4.1) by combining, in a manner described in section 2, the contributions of three basic mechanisms to the change in Λ with number density. To obtain the contribution of each of these effects to the conductivity we need the non-equilibrium pair distribution function, which we will calculate in section 3. The first of the three effects, the "relaxation effect", is due to the electrostatic interactions among the ions; the contribution of this effect to the conductivity will be given in section 4. In section 5 we compute the contribution of the "electrophoresis" effect, which is due to the motion of the solvent about an ion; in section 6 we obtain the contribution of the "osmotic" effect, which is due to hard core collisions and which, unlike the other two effects, does not contribute to Λ_1 and $\Lambda_{2'}$ in (4.1). The final result for the conductivity will be given in section 7, and in section 8 we will compare this theoretical result with some experimental data.

The theory outlined above is due to Fuoss and Onsager, from whose work [12] the present treatment differs only in some mathematical aspects; the theory is based on a number of plausible assumptions and is not rigorously deduced from the basic foundations of statistical mechanics, as was the equilibrium theory presented in Chapter III.

1. The Model

In the non-equilibrium case it is necessary to define the model of the ionic solution more sharply than in the case of equilibrium. The medium is regarded as an incompressible fluid characterized by its viscosity η as well as by its dielectric constant D. The medium determines the migration velocity of the ions through friction and through the diffusion process:

$$\vec{v}_{i,j}(\vec{r}_{12}) = \omega_i \left(\vec{K}_{i,j} - kT \frac{\nabla f_{ij}}{f_{ij}} \right) * \tag{4.2}$$

where $\vec{v}_{i,j}(\vec{r}_{12})$ is the velocity of an ion of species i at $\vec{r}_1$ relative to the surrounding solvent, if there is an ion of species j at $\vec{r}_2$; ω_i is the mobility (velocity per unit force) of an ion i in the solvent, $\vec{K}_{i,j}$ the force on the ion i in the presence of ion j , and f_{ij} the pair distribution function for the species i and j . $1/\omega_i$ is the familiar friction coefficient and $\omega_i kT \frac{\nabla f_{ij}}{f_{ij}}$ is the Einstein expression for the diffusion velocity.

In the determination of the conductivity, the solution is subject to a homogeneous external electric field $X\hat{i}$, where $\hat{i}$ is the unit vector in the $+X$ direction. This field is considered to be sufficiently weak so that effects of order X^2 can be ignored.

---

*This is a more refined version of the familiar equation for the migration velocity of a particle i at position $\vec{r}$:

$$\vec{v}_i(\vec{r}) = \omega_i \left(\vec{K}_i(\vec{r}) - kT \frac{\nabla n_i(\vec{r})}{n_i(\vec{r})} \right)$$

where $\vec{K}_i(\vec{r})$ is the force on the ion i and $n_i(\vec{r})$ is the number density of particles i at $\vec{r}$. The form (4.2) implies that the particles i and j lie outside each other's hydrodynamical wake; this will be the case if the Stokes radius (distance of closest approach of the solvent to the center of the ion) is sufficiently small compared to R_D .

2. The Conductivity Equation

The specific conductivity Λ is the sum of the specific conductivities λ_i due to each species of each ion. λ_i is given by $F U_i \frac{|z_i|}{z_i}$, where F is Faraday's constant and U_i is the velocity of an ion of species i in the field direction per unit local field. U_i is the sum of the velocity of the ion relative to the surrounding solvent and the velocity of the solvent itself; the velocity relative to the solvent per unit local field is given by $z_i e \omega_i$ and the velocity in the field direction of the surrounding solvent per unit local field we call U_i^s, so that $U_i = z_i e \omega_i + U_i^s$. Writing ΔX for the difference between the local field and the applied field and using $e = F/N$, where N is Avogadro's number, we obtain

$$\lambda_i = \frac{F^2}{N}\left[|z_i|\omega_i + |z_i|\frac{U_i^s}{z_i e}\right]\left[1 + \frac{\Delta X}{X}\right] \tag{4.3}$$

The change in field ΔX, that is, the change in the force on an ion per unit charge, is composed of two parts: $\Delta X = \Delta_R X + \Delta_o X$, where $\Delta_R X$ is the change in the local electrostatic field due to the relaxation effect, and $\Delta_o X$ is the average force on an ion per unit charge due to the osmotic effect.

Then for binary electrolytes,

$$\Lambda = \left[\Lambda_o + \frac{F^2}{N}\left\{|z_1|\frac{U_1^s}{z_1 e} + |z_2|\frac{U_2^s}{z_2 e}\right\}\right]\left[1 + \frac{\Delta X}{X}\right] \tag{4.4}$$

where Λ_o, the specific conductivity for vanishing ion density, depends only on the behavior of the isolated ions and not on their interactions:

$$\Lambda_o = \frac{F^2}{N}\left[|z_1|\omega_1 + |z_2|\omega_2\right] \tag{4.5}$$

3. The Pair Distribution Function

We will obtain the pair distribution function from the two-particle continuity equation, which expresses the conservation of particle pairs. We first derive the continuity equation from the second B-B-G-K-Y hierarchy equation [16]:

$$\frac{\partial F_{ij}}{\partial \tau} + \mathcal{H}_2 F_{ij} = n \sum_{k=1}^{2} \int \cdots \int d\vec{r}_3 d\vec{p}_3 \left(\Theta_{ik} + \Theta_{kj}\right) F_{ijk} \tag{4.6}$$

$$\mathcal{H}_2 \equiv \frac{\vec{p}_1}{m_1} \cdot \frac{\partial}{\partial \vec{r}_1} + \frac{\vec{p}_2}{m_2} \cdot \frac{\partial}{\partial \vec{r}_2} - \Theta_{ij}$$

$$\Theta_{ij}(\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2) \equiv \frac{\partial \phi_{ij}(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1} \cdot \frac{\partial}{\partial \vec{p}_1} + \frac{\partial \phi_{ij}(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_2} \cdot \frac{\partial}{\partial \vec{p}_2}$$

Here $F_{ij}(\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2; \tau)$ is the pair distribution function and $F_{ijk}(\vec{r}_1, \vec{p}_1, \cdots \vec{r}_3, \vec{p}_3; \tau)$ is the three-particle distribution function; i, j, and k are the species of the particles at $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}_3$ respectively. We integrate (4.6) over $\vec{p}_1$ and $\vec{p}_2$; then the Θ terms vanish since the distribution functions vanish as $\vec{p}_1, \vec{p}_2$, and $\vec{p}_3 \to \infty$. The integration gives us the continuity equation for particle pairs:

$$\frac{\partial}{\partial \tau}\left[\int \cdots \int d\vec{p}_1 d\vec{p}_2 F_{ij}\right] = -\frac{\partial}{\partial \vec{r}_1}\left[\int \cdots \int d\vec{p}_1 d\vec{p}_2 F_{ij} \frac{\vec{p}_1}{m_1}\right] - \frac{\partial}{\partial \vec{r}_2}\left[\int \cdots \int d\vec{p}_1 d\vec{p}_2 F_{ij} \frac{\vec{p}_2}{m_2}\right] \tag{4.7}$$

or

$$\frac{\partial f_{ij}}{\partial \tau} = -\frac{\partial}{\partial \vec{r}_1}\left[f_{ij} \vec{V}_{i,j}\right] - \frac{\partial}{\partial \vec{r}_2}\left[f_{ij} \vec{V}_{j,i}\right]$$

where

$$f_{ij} \equiv \int \cdots \int d\vec{p}_1 d\vec{p}_2 F_{ij}$$

and

$$f_{ij} \vec{V}_{i,j} \equiv \int \cdots \int d\vec{p}_1 d\vec{p}_2 F_{ij} \frac{\vec{p}_i}{m_i}$$

$f_{ij}(\vec{r}_1, \vec{r}_2; \tau)$ is the pair distribution function for i and j in configuration space and $\vec{V}_{i,j}$ is the average velocity of an ion of species i at $\vec{r}_1$ given that there is an ion of species j at $\vec{r}_2$. If $\vec{V}_{i,j}$ and f_{ij} are

functions only of $\vec{r}_1 - \vec{r}_2$ (homogeneous outside forces), we have $\frac{\partial}{\partial \vec{r}_1} = -\frac{\partial}{\partial \vec{r}_2}$; it follows that if i and j are the same species $\partial f_{ii}/\partial t = 0$ and $f_{ii} = f_{ii}^{(0)}$, where $f_{ii}^{(0)}$ is the equilibrium pair distribution function for ions of species i . This can be seen by considering what would happen if the applied field were slowly reduced to zero: since $\partial f_{ii}/\partial t = 0$, there would be no change in f_{ii} ; the system would then be in equilibrium and we would have $f_{ii} = f_{ii}^{(0)}$; hence $f_{ii} = f_{ii}^{(0)}$ for any field.

We wish to consider only a binary electrolyte in the steady state; (4.7) becomes

$$\frac{\partial}{\partial \vec{r}_1} (f_{12} \vec{V}_{1,2}) - \frac{\partial}{\partial \vec{r}_2} (f_{12} V_{2,1}) = 0 \tag{4.8}$$

where $\vec{V}_{1,2}$ is found from (4.2):

$$\vec{V}_{1,2} = \vec{V}_1^s + \omega_1 \left[\vec{K}_{1,2} - kT \frac{\frac{\partial f_{12}}{\partial \vec{r}_1}}{f_{12}} \right] \tag{4.9}$$

Here $\vec{V}_1^s$ is the velocity of the solvent surrounding $\vec{r}_1$.

We will proceed by first finding an expression for $\vec{K}_{1,2}$ in terms of the electrostatic potential, and then using an iteration procedure to find the expressions for f_{12} and the electrostatic potential that satisfy (4.8) and the Poisson equation; to complete this procedure we will also calculate an expression for $\vec{V}_1^s$.

The ion 1 in the presence of 2 experiences an electrostatic force

$$\vec{K}_{1,2} = X z_1 e \hat{i} - z_1 e \frac{\partial \psi_{1,2}}{\partial \vec{r}_1} \tag{4.10}$$

where $\psi_{1,2}$ is the electrostatic potential at $\vec{r}_1$, given a particle of species 2 at $\vec{r}_2$. This equation can be simplified by using the superposition approximation discussed in Chapter I; we will now indicate why this approximation is of sufficient accuracy to give the correct value of the conductivity to order n .

The potential felt by the ion can be thought of as consisting of three parts: the potential $\overline{\psi}_1$ due to the atmosphere of 1,* the potential due to the ion 2 and its atmosphere, and the change in potential due to the distortion of the atmosphere of each ion due to the presence of the other:

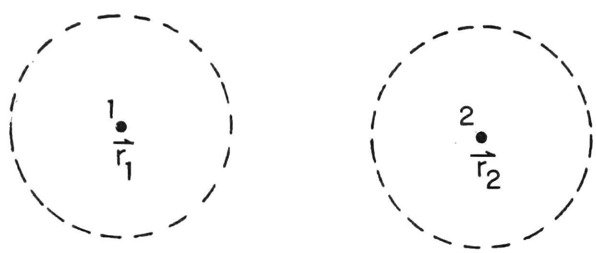

Fig. 5

(4.11) $$\psi_{1,2}(\vec{r}_{12}) = \overline{\psi}_1(0) + \psi_2(-\vec{r}_{12}) + \psi''(r_{12})$$

The effect ψ'' of the distortion of the ionic atmospheres (which is neglected in the superposition approximation) will be considered to be of higher order in $\varepsilon = R_L/R_D$ than $\overline{\psi}_1$ and ψ_2 . since the

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The line: "Now it will be shown later ... be ignored" should be deleted.

The potential felt by the ion can be thought of as consisting of three parts: the potential $\overline{\psi}_1$ due to the atmosphere of 1,* the potential due to the ion 2 and its atmosphere, and the change in potential due to the distortion of the atmosphere of each ion due to the presence of the other:

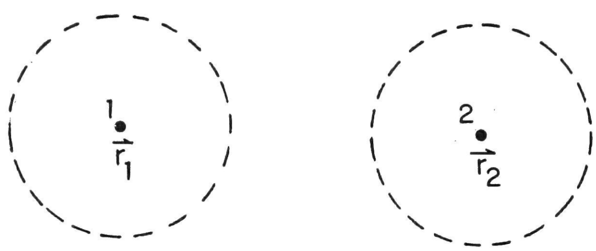

Fig. 5

$$(4.11) \qquad \psi_{1,2}(\vec{r}_{12}) = \overline{\psi}_1(0) + \psi_2(-\vec{r}_{12}) + \psi''(r_{12})$$

The effect ψ'' of the distortion of the ionic atmospheres (which is neglected in the superposition approximation) will be considered to be of higher order in $\varepsilon = R_L/R_D$ than $\overline{\psi}_1$ and ψ_2 , since the interaction producing the distortion has a characteristic length R_L and the ionic atmospheres have characteristic length R_D . Now it will be shown later that all terms in (4.8) containing $\psi_{1,2}(\vec{r}_{12})$ contribute only to order $\varepsilon^2 \sim n$ in the conductivity, so $\psi''(\vec{r}_{12})$ would contribute only to order ε^3 and can for our purposes be ignored. Thus (4.10) becomes

$$(4.12) \qquad \vec{K}_{1,2}(\vec{r}_{12}) \doteq X z_1 e \hat{i} - z_1 e \frac{\partial \overline{\psi}_1(0)}{\partial \vec{r}_1} - z_1 e \frac{\partial \psi_2(-\vec{r}_{12})}{\partial \vec{r}_1}$$

---

*To be precise, $\overline{\psi}_1(r) = \psi_1(r) - \frac{z_1 e}{r}$.

where $\overline{\Psi}_1(0)$ is the potential due to the atmosphere about ion 1 and ψ_2 is the potential due to ion 2 and its atmosphere.

Substituting (4.12) in (4.9) and (4.9) in (4.8) gives

$$(4.13)\quad \Delta f_{12}' - \kappa^2 q^2 e^{\Psi_{12}} f_{12}' = \frac{D}{4\pi}\frac{c_2 n}{z_1 e}\kappa^2 q^2 e^{\Psi_{12}}\frac{\partial \Psi_{12}}{\partial x} X$$

$$-\frac{D}{4\pi}\frac{c_2 n}{z_1 e}\kappa^2 q^2 e^{\Psi_{12}}\frac{\partial \Psi_{12}}{\partial r}\left[\frac{\partial \frac{\psi'}{\cos\theta}}{\partial x} - \left(\frac{\partial \frac{\psi'}{\cos\theta}}{\partial x}\right)_a\right] + \kappa^2 \Psi_{12} f_{12}'$$

$$+\frac{\partial \Psi_{12}}{\partial r}\frac{\partial \frac{f_{12}'}{\cos\theta}}{\partial x} - \frac{(V_{1r}^s - V_{2r}^s)}{(\omega_1+\omega_2)}\frac{c_1 c_2 n^2}{kT} e^{\Psi_{12}}\frac{\partial \Psi_{12}}{\partial r}$$

Here we have written

$$(4.13')\quad \begin{aligned} f_{12} &= f_{12}^{(0)} + f_{12}' \\ \psi_1 &= \psi_1^{(0)} - \psi_1' \\ \psi_2 &= \psi_2^{(0)} + \psi_2' \end{aligned}$$

where $f_{12}^{(0)}$, $\psi_1^{(0)}$, and $\psi_2^{(0)}$ are the equilibrium values of f_{12}, ψ_1, and ψ_2, and f_{12}', ψ_1', and ψ_2' represent the departures from the equilibrium values proportional to X; since $f_{12} = f_{12}^{(0)} = 0$ for $r_{12} < a$ we must have $f_{12}' = 0$ for $r_{12} < a$. We give below in (4.14) the identities we have used in obtaining (4.13) from (4.8); from (a), (b), and (d) in (4.14) we see that $\psi_1' = \psi_2'$ and we write $\psi' \equiv \psi_1' = \psi_2'$.

$$(4.14)\quad \left.\begin{aligned} &\text{(a)} \quad \Delta\psi_1' = \frac{4\pi f_{12}' z_2 e}{D c_1 n} \\ &\text{(b)} \quad \Delta\psi_2' = -\frac{4\pi f_{12}' z_1 e}{D c_2 n} \\ &\text{(c)} \quad \Delta\psi' = \frac{4\pi f_{12}' z_2 e}{D c_1 n} \end{aligned}\right\} \quad \text{(Poisson)}$$

$$\text{(d)} \quad c_1 z_1 = -c_2 z_2 \qquad \text{(charge neutrality)}$$

(e) $f_{12}^{(0)} = c_1 c_2 n^2 e^{\Psi_{12}}, \; r>a$
$\phantom{f_{12}^{(0)}} = 0, \; r<a$

(f) $\frac{z_2 e}{kT}\psi_1^{(0)} = \frac{z_1 e}{kT}\psi_2^{(0)} = \Psi_{12}, \; r>a$

(g) $\Delta \psi_i^{(0)} = \kappa^2 \psi_i^{(0)}$

(to lowest order in ϵ; $\psi_i^{(0)}$ is just the Debye-Hückel potential.)

(h) $\nabla \cdot \vec{V}_i^s = 0$ (incompressibility)

(i) $\hat{i} \cdot \hat{r} = x$

(j) $x/r = \cos\theta$

(k) $\hat{i} = \frac{\partial}{\partial \vec{r}}(r\cos\theta)$

(l) $\hat{i} \cdot \frac{\partial f(r)}{\partial \vec{r}} = \frac{\partial f(r)}{\partial x} = \cos\theta \frac{\partial f(r)}{\partial r}$

(m) $\frac{\partial f_{12}^{(0)}}{\partial \vec{r}} \cdot \frac{\partial \psi'}{\partial \vec{r}} = \frac{\partial f_{12}^{(0)}}{\partial r} \frac{\partial \frac{\psi'}{\cos\theta}}{\partial x}$

(n) $\vec{r} \cdot \frac{\partial f_{12}'}{\partial \vec{r}} = x \frac{\partial (f_{12}'/\cos\theta)}{\partial r}$

(o) $\vec{r} \cdot \frac{\partial \psi_i^{(0)}}{\partial r} = r \frac{\partial \psi_i^{(0)}}{\partial r}$

(p) $(\vec{V}_i^s \cdot \vec{r})/x = V_{i_r}^s/\cos\theta$

(q) $\vec{V}_i^s \cdot \frac{\partial f_{12}^{(0)}}{\partial \vec{r}} = V_{i_r}^s \frac{\partial f_{12}^{(0)}}{\partial r}$

$V_{i_r}^s$ is the radial component of $\vec{V}_i^s$; $\left(\frac{\partial}{\partial x}\right)_a$ is the value of the x-derivative at $r=a$; q is defined by

$$q^2 \equiv \frac{4\pi n e^2}{\kappa^2 DkT} \, \frac{c_1 z_1^2 \omega_1 + c_2 z_2^2 \omega_2}{\omega_1 + \omega_2} \tag{4.15}$$

and Ψ_{12} is given by (3.15). In this chapter we use the notation $\kappa \equiv 1/R_D$ and write κr instead of ξ, in order to be consistent with the notation

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The equation: $K_{1,2} = X z_1 e \hat{t}$ should be replaced by:

$$K_{1,2} = X z_1 e \hat{t} - z_1 e \frac{\partial \psi_2}{\partial r_1} .$$

of Fuoss and Onsager [12].

We obtain the <u>lowest order solution</u> $f_{12}'^{(1)}$ to (4.13) from the equation

$$\Delta f_{12}'^{(1)} - \kappa^2 q^2 f_{12}'^{(1)} = \frac{D}{4\pi}\frac{c_2 n}{z_1 e}\kappa^2 q^2 \frac{\partial \Psi_{12}^{(1)}}{\partial x} X \tag{4.16}$$

where we assume that the terms in (4.13) that are omitted in (4.16) contribute to the conductivity only to order ε^2. The basis for this assumption is as follows: (4.16) is the continuity equation that would be obtained if in (4.9) we had set $\vec{V}_i^s = 0$ and $\vec{K}_{12} = X z_1 e \hat{i}$, and used the lowest order approximation for $f_{12}^{(0)}$. When we substitute the solution $f_{12}'^{(1)}$ from (4.16), together with the corresponding solution $\psi'^{(1)}$ to the Poisson equation, into the terms in (4.13) omitted in (4.16), we will see that these terms indeed contribute only to order ε^2 in the conductivity, which is consistent with the assumption we made above.

Using (3.15) for $\Psi_{12}^{(1)}$ and the condition $f_{12}' \xrightarrow[r\to\infty]{} 0$, we have for the solution to (4.16):

$$f_{12}'^{(1)} = -\frac{c_1 z_1 n e X q^2}{4\pi k T (1-q^2)} \cos\theta\, \mathcal{F}_1(r), \quad r > a \tag{4.17}$$

The solution to the Poisson equation (4.14c), using $f_{12}'^{(1)}$ from (4.17) for f_{12}', is

$$\psi'^{(1)} = -\frac{z_1 z_2 e^2 X}{DkT}\frac{q^2}{(1-q^2)} \cos\theta\, \mathcal{F}_2(r) \tag{4.18}$$

We have used the notation

$$\mathcal{F}_1(r) \equiv \frac{e^{-\kappa r}(1+\kappa r) - e^{-q\kappa r}(1+q\kappa r)}{r^2}$$

$$\mathcal{F}_2(r) \equiv \frac{q^2[e^{-\kappa r}(1+\kappa r)-1] - [e^{-q\kappa r}(1+q\kappa r)-1]}{q^2\kappa^2 r^2} \tag{4.19}$$

(4.17) and (4.18) are sufficiently accurate to give the Onsager limiting law. However, in order to continue the iteration procedure so as to obtain an accurate enough expression for f_{12}' to give the conductivity correct to order ϵ^2, we must solve the complete equation (4.13). To accomplish this, we must first obtain an expression for $V_{i_r}^s$ in (4.13), that is, for the radial component of the velocity of the solvent at an ion. This we will find from the Navier-Stokes equation for an incompressible fluid

$$\nabla \times (\nabla \times \eta \vec{V}_i^s) = \vec{F} - \nabla p \tag{4.20}$$

where $\vec{F}$ is the volume force on the fluid and p is the pressure.

Following Fuoss and Onsager [12] we define the vector $\vec{U}$ as follows:

$$\eta \vec{V}_i^s \equiv \nabla(\nabla \cdot \vec{U}) - \Delta \vec{U} \tag{4.21}$$

and (4.20) becomes:

$$\Delta \Delta \vec{U} - \nabla(\nabla \cdot \vec{U}) = \vec{F} - \nabla p \tag{4.22}$$

where we have used the identity $\nabla \times \nabla \vec{A} = \Delta \vec{A} + \nabla(\nabla \cdot \vec{A})$. To find $\vec{U}$ we equate the vector terms of (4.22):

$$\vec{F} = \Delta \Delta \vec{U} \tag{4.23}$$

But $\vec{F}$ follows from the Poisson equation,

$$\vec{F} = z_i e X \hat{i} \frac{f_{12}}{n_j} = \frac{-D}{4\pi} \Delta \psi_i X \hat{i} \tag{4.24}$$

Solving (4.23), using (4.24), gives:

$$\Delta \vec{U} = -\frac{D X \hat{i}}{4\pi} \psi_i + \Delta \vec{W} \tag{4.25}$$

where $\vec{W}$ is any function such that $\Delta\Delta\vec{W} = 0$.

We wish to find $\vec{U}$ for $r > a$; to do so we insert the value for ψ_i for $r > a$ and integrate (4.25); then to find the constant of integration we will also determine $\vec{U}$ for $r < a$. To lowest order in both ϵ and X , $\psi_i = \frac{e_i}{D}\frac{e^{-\kappa r}}{r}$ for $r > a$; integration of (4.25) gives a constant of integration $\vec{C}$ such that $\Delta\vec{C} = 0$, so that $\Delta\vec{W}$ can be absorbed in $\vec{C}$. Thus we have:

$$U_x = -\frac{X z_i e}{4\pi\kappa^2}\frac{e^{-\kappa r}}{r} + C_x \,, \quad U_y = C_y \,, \quad U_z = C_z \tag{4.26}$$

Replacing $\vec{U}$ in (4.21) by (4.26), using (4.14i), (4.14j), and (4.141), we obtain for the radial component of $\vec{V}_i^s$:

$$\eta V_{i\,r}^s = -\frac{X z_i e}{2\pi\kappa^2}\cos\theta\,\frac{e^{-\kappa r}(1+\kappa r)}{r^3} + \left[\nabla(\nabla\cdot\vec{C})\right]_r \tag{4.27}$$

where $[\nabla(\nabla\cdot\vec{C})]_r$ is the radial component of $\nabla(\nabla\cdot\vec{C})$.

We obtain $[\nabla(\nabla\cdot\vec{C})]_r$ from the boundary condition $V_{i\,r}^s = 0$ at the Stokes radius $R < a$; in this region $r < a$ there are no charges, so $\psi_i^{(0)} = \frac{z_i e}{D r}$ + const. and we take $[\nabla(\nabla\cdot\vec{C}')]_r = \frac{X z_i e}{2\pi\kappa^2}\frac{\cos\theta}{r^3}$. To the order required in ϵ , we can set $\vec{C}' = \vec{C}$ so that we finally get

$$\eta V_{i\,r}^s = \frac{X z_i e}{2\pi\kappa^2}\,\frac{1 - e^{-\kappa r}(1+\kappa r)}{r^3}\cos\theta \tag{4.28}$$

Substituting (4.17), (4.18), and (4.28) into the higher order terms of (4.13) gives an equation for $f_{12}'^{(2)}(\vec{r}_{12})$, the second approximation of $f_{12}'(\vec{r}_{12})$:

$$\Delta f_{12}'^{(2)} - \kappa^2 q^2 f_{12}'^{(2)} = \cos\theta \sum_{n=1}^{6} g_n(r) \tag{4.29}$$

$$g_1(r) \equiv \frac{D}{4\pi} X \frac{c_2 n}{z_1 e} \kappa^2 q^2 e^{\Psi_{12}} \frac{\partial \Psi_{12}}{\partial r}$$

$$g_2(r) \equiv -\frac{c_1 n z_1 e}{4\pi kT} X \frac{q^2}{1-q^2} x^2 \mathcal{F}_1(r)\left[q^2(e^{\Psi_{12}}-1)+\Psi_{12}\right]$$

$$g_3(r) \equiv -\frac{c_1 n z_1 e}{4\pi kT} X \frac{q^2}{1-q^2} \frac{\partial \Psi_{12}}{\partial r} \frac{\partial \mathcal{F}_1(r)}{\partial r}$$

$$g_4(r) \equiv -\frac{c_1 n z_1 e}{4\pi kT} X \frac{q^2}{1-q^2} e^{\Psi_{12}} \frac{\partial \Psi_{12}}{\partial r} x^2 q^2 \frac{\partial \mathcal{F}_2(r)}{\partial r}$$

$$g_5(r) \equiv \frac{c_1 n z_1 e}{4\pi kT} X \frac{q^2}{1-q^2} e^{\Psi_{12}} \frac{\partial \Psi_{12}}{\partial r} x^2 q^2 \left[\frac{\partial \mathcal{F}_2(r)}{\partial r}\right]_{r=a}$$

$$g_6(r) \equiv \frac{(z_2 - z_1) e}{\omega_1 + \omega_2} X \frac{c_1 c_2 n^2}{2\pi \eta kT} e^{\Psi_{12}} \frac{\partial \Psi_{12}}{\partial r} \frac{1-e^{-xr}(1+xr)}{x^2 r^3}$$

We proceed to find the solution to (4.29). We already have $f_{12}' = 0$ for $r < a$; for $r > a$ the solution to (4.29) is given by the Green's function method:

$$(4.30) \quad f_{12}'^{(2)}(\vec{r}) = \frac{1}{4\pi} \int\!\!\cdots\!\!\int d\vec{r}\,' \sum_{n=1}^{6} g_n(r') \cos\theta' \frac{e^{-qx|\vec{r}-\vec{r}\,'|}}{|\vec{r}-\vec{r}\,'|}$$

These integrals are evaluated partially in Appendix C; the result is

$$(4.31) \quad f_{12}'^{(2)}(\vec{r}) = \frac{\cos\theta}{2q^3 x^3 r^2} \Big[e^{-qxr}(1+qxr) \int_a^r dr' \sum_{n=1}^{6} g_n(r') \cdot \\ \cdot \left\{ e^{qxr'}(1-qxr') - e^{-qxr'}(1+qxr') \right\} + \left\{ e^{qxr}(1-qxr) \right. \\ \left. - e^{-qxr}(1+qxr) \right\} \int_r^\infty dr' \sum_{n=1}^{6} g_n(r')\, e^{-qxr'}(1+qxr') \Big]$$

The integrals in (4.31) cannot be evaluated further; nevertheless, we will be able to extract the conductivity to order ε^2 from (4.31) in the following sections. As we have seen above, only $g_1(r)$ contributes to Λ_1 in (4.1); as we will see below, both $g_1(r)$ and the term $g_6(r)$ that stems from the motion of the solvent will give contributions to $\Lambda_{2'}$. All 6 terms contribute to Λ_2.

4. The Relaxation Effect

The difference between the magnitude of the local electrostatic field felt by an ion and the external applied field, due to the relaxation effect, that is, to the net effect of the other ions, is given by

$$\Delta_R X = -\left[\frac{\partial \psi'}{\partial x}\right]_a \tag{4.32}$$

where the x-derivative is evaluated at $r=a$ *; ψ' is given by (4.14c). Now (4.14c) is solved for ψ' by using (4.31) for f_{12}' , and then applying the Green's function method in a similar manner as in the case of the continuity equation (4.29); the resulting ψ' is then used in eq.(4.32). Details are given in Appendix C; the result is

$$\Delta_R X \doteq \frac{4\pi z_2 e}{3Dc_1 n q^2\kappa^2}\int_a^\infty dr \sum_{n=1}^{6} g_n(r)\left[e^{-q\kappa r}(1+q\kappa r)-1\right] + \frac{2\pi z_2 e}{9Dc_1 n}\, a^2 \int_a^\infty dr \sum_{n=1}^{6} g_n(r) \tag{4.33}$$

---

*If the charge is evenly distributed on the surface of the ion at $r=a$, the force on the ion will be the same as if the charge were concentrated at the center. We choose to regard the charge to be at $r=a$ for mathematical convenience (see Appendix C).

The equilibrium part of Ψ_1 is centrally symmetric, and therefore does not contribute to $\Delta_R X$.

The evaluation of these integrals is also outlined in Appendix C; the result to order ε^2 * is

$$
\begin{aligned}
(4.34)\quad \frac{\Delta_R X}{X} \doteq -\frac{q^2}{3}\Bigg[& \frac{\varepsilon'}{1+q} - \frac{\varepsilon'^2 \ln \varepsilon'}{2} + \frac{\varepsilon'^2}{2}\Bigg\{ -2\gamma_E - \left(1 + \frac{q^2(1+q^2)}{2(1-q^2)}\right)\ln(2+q) - \frac{1-2q^2}{1-q^2}\ln(1+2q) \\
& - \frac{(1-q^2)^2}{2q^2}\ln(1+q) + \frac{3}{2} + \frac{(2q-3q^2+4q^3-5q^4+2q^5)}{4q^2(1-q^2)} \\
& + \frac{2q^2}{3(1+q)^2} + Ei(b') - e^{b'}\left(\frac{1}{3b'^2} + \frac{1}{b'}\right) + \frac{1}{3b'^2} \\
& - \frac{(z_1+z_2)^2}{2z_1 z_2 (1-q^2)}\left(\frac{1}{3} - \frac{2q^2}{1-q^2}\ln\frac{3}{2+q}\right)\Bigg\}\Bigg] \\
& + \varepsilon' \frac{\chi}{6\pi\eta}\,\frac{1}{4(\omega_1+\omega_2)}\Bigg[\frac{1-q^2+\frac{5}{2}q}{2q} - \\
& - \frac{(1-q^2)^2}{2q^2}\ln(1+q) + \frac{(q^2-4)}{2}\ln(2+q) + Ei(b') \\
& - 2\gamma_E - \ln\varepsilon' - \frac{e^{b'}(b'-1)+1}{3b'^2}\Bigg]
\end{aligned}
$$

*We assume $\dfrac{\chi}{\eta(\omega_1+\omega_2)}$ is order ε .

where for convenience we have written $\varepsilon' \equiv -z_1 z_2 \varepsilon$ and $b' \equiv -z_1 z_2 b$. The lowest order term $\varepsilon'/(1+q)$ appears in the Onsager limiting law; the term

$$-\frac{(z_1+z_2)^2}{2z_1 z_2(1-q^2)}\left(\frac{1}{3}-\frac{2q^2}{1-q^2}\ln\frac{3}{2+q}\right)$$

stems from the term $\Psi_{12}^{(2)}$ in the potential of average force, and is zero for symmetrical electrolytes. The terms in the final set of square brackets stem from the solvent velocity $V_{i_Y}^{S}$.

5. Electrophoresis

We now wish to calculate the terms U_i^S in (4.4), that is, the velocity of the solvent in the field direction at the location $\vec{Y}$ of an ion of species i , per unit local field. The contribution $dV_{i_x}^{S}(\vec{Y})$ to the velocity of the solvent in the field direction at $\vec{Y}$ due to a force dF_i acting on a volume element dV at the origin (see Fig. 6) can be derived from

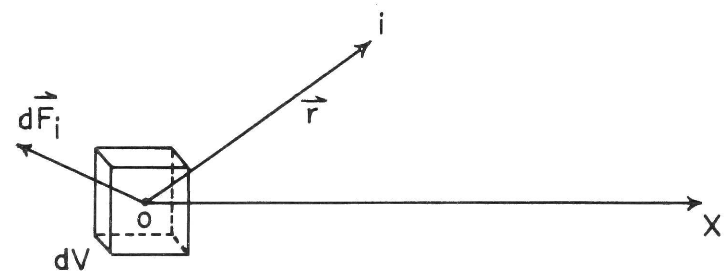

Fig. 6

the Navier-Stokes equations for an incompressible fluid:

$$dV_{i_x}^{s} = \left[\hat{i}\cdot d\vec{F_i} + (\hat{Y}\cdot dF_i)\cos\theta\right] / 8\pi\eta r \tag{4.35}$$

From now on we will set $i=1$ for clarity. It will be shown below that $d\vec{F}_1$ is of the form

(4.36) $$\frac{d\vec{F}_1(\vec{r})}{dV} = \sum_n f_1^{(n)}(r)\frac{\partial}{\partial\vec{r}}\left[g_1^{(n)}(r)\cos\Theta\right]$$

so using

(4.37) $$\frac{\partial}{\partial\vec{r}}\left[R(r)\cos\Theta\right] = \hat{i}\left[R/r\right] + \hat{r}\left[\frac{\partial R}{\partial r} - \frac{R}{r}\right]\cos\Theta$$

we obtain

(4.38) $$dV_{1x}^s = dV\left[\sum_n f_1^{(n)}(r)\left\{g_1^{(n)}(r)\frac{(1-\cos^2\Theta)}{r} + 2\frac{dg_1^{(n)}(r)}{dr}\cos^2\Theta\right\}\right]/8\pi\eta r$$

Integrating over all space, we obtain the total velocity of the solvent in the field direction:

(4.39) $$V_{1x}^s = \frac{1}{3\eta}\int_a^\infty dr\sum_n f_1^{(n)}(r)\frac{d\left[r g_1^{(n)}\right]}{dr}$$

We now find expressions for $f_1^{(n)}$ and $g_1^{(n)}$ in (4.36) so that we may explicitly evaluate (4.39). Now the force on a volume element of solvent at the origin is, in the steady state, just the force on the ions in the volume element, including the so-called diffusion force:

(4.40) $$\frac{d\vec{F}_1}{dV} = \frac{f_{11}}{c_1 n}\vec{K}_{1,1} + \frac{f_{12}}{c_2 n}\left[\vec{K}_{2,1} - kT\frac{\nabla f_{12}}{f_{12}}\right]$$

To evaluate (4.40) we use (4.12), (4.13'), (4.18), and (4.14k) for $\vec{K}_{1,2}$ and similar expressions for $\vec{K}_{1,1}$ and $\vec{K}_{2,2}$; we use (4.13') and (4.17) for f_{12} and ignore terms that will disappear upon integration due to the central symmetry of $f_{ij}^{(0)}$ and $\psi_i^{(0)}$. To the accuracy required to obtain the conductivity to order ε^2, we have then:

(4.41) $$\frac{d\vec{F}_1}{dV} = c_1 n e^{\Psi_{11}} \Big[z_1 e X \frac{\partial}{\partial \vec{r}} (r \cos\Theta) + \frac{z_1^2 z_2 e^3 q^2}{DkT(1-q^2)} X \Big\{ \frac{\partial}{\partial \vec{r}} (\mathcal{F}_2(r) \cos\Theta) + \Big(\frac{\partial}{\partial \vec{r}} (\mathcal{F}_2(r)\cos\Theta) \Big)_{r=a} \Big\} \Big]$$
$$+ c_2 n e^{\Psi_{12}} \Big[z_2 e X \frac{\partial}{\partial \vec{r}} (r\cos\Theta) + \frac{z_2^2 z_1 e^3 q^2}{DkT(1-q^2)} X \Big\{ \frac{\partial}{\partial \vec{r}} (\mathcal{F}_2(r)\cos\Theta)$$
$$+ \Big(\frac{\partial}{\partial \vec{r}} (\mathcal{F}_2(r)\cos\Theta) \Big)_{r=a} \Big\} - \frac{kT}{c_1 n} e^{-\Psi_{12}} \frac{z_2 e q^2 X}{4\pi kT(1-q^2)} \frac{\partial}{\partial \vec{r}} (\mathcal{F}_1(r)\cos\Theta) \Big]$$

(4.41) is of the form (4.36); $\left(\frac{\partial}{\partial \vec{r}}\right)_{r=a}$ is the value of the gradient at $r=a$, and $\mathcal{F}_1$ and $\mathcal{F}_2$ are given by (4.19).

To the accuracy required, (4.19) gives

(4.42) $$\left(\frac{\partial}{\partial \vec{r}} (\mathcal{F}_2 \cos\Theta) \right)_{r=a} = (1-q)\frac{X}{3}\,\hat{i}$$

Using (4.41), (4.42) and (4.36) in (4.39), we obtain

(4.43) $$V_{1_x}^{S} \doteq \frac{2X}{3\eta} \left[1 + \frac{z_1 z_2 e^2}{DkT} \frac{q^2}{1+q} \frac{\chi}{3} \right] ne \int_a^\infty dr\, r \left[c_1 z_1 e^{z_1^2 \zeta} + c_2 z_2 e^{z_1 z_2 \zeta} \right] - \frac{X}{3\eta} \frac{q^2}{1-q^2} \frac{z_1 z_2 e^2}{DkT} ne \int_a^\infty dr \left[c_1 z_1 e^{z_1^2 \zeta} \right.$$
$$\left. + c_2 z_2 e^{z_1 z_2 \zeta} \right] \frac{d[r\mathcal{F}_2(r)]}{dr} + \frac{c_2}{c_1} \frac{z_2 e}{3\eta} \frac{X}{4\pi} \frac{q^2}{1-q^2} \int_a^\infty dr \frac{d[r\mathcal{F}_1(r)]}{dr}$$

with $$\zeta(r) \equiv -\frac{e^2}{DkT} \frac{e^{-\chi r}}{r}.$$

The last two integrals are straightforward; to the required accuracy we get

(4.44) $$V^s_{1_x} \doteq \frac{z_1 e \kappa X}{6\pi\eta}\left[\frac{1}{z_1(z_1-z_2)\varepsilon}\int_{\frac{\varepsilon}{b}}^{\infty} d\xi\,\xi\left\{\exp\left(-z_1^2\varepsilon\frac{e^{-\xi}}{\xi}\right) - \exp\left(-z_1 z_2 \varepsilon\frac{e^{-\xi}}{\xi}\right)\right\} + \frac{\varepsilon'}{4}\left\{\frac{q}{1+q} + \frac{2q^2\ln 2}{1-q^2} - \frac{(1+q^2)\ln(1+q)}{1-q^2}\right\} - \frac{\varepsilon' q^2}{4b'}\right]$$

so that in (4.4)

(4.45) $$\frac{|z_1|U_1^s}{z_1 e} + \frac{|z_2|U_2^s}{z_2 e} = \frac{\kappa}{6\pi\eta}\left[\frac{1}{(|z_1|+|z_2|)\varepsilon}\int_{\frac{\varepsilon}{b}}^{\infty} d\xi\,\xi\left\{\exp\left(-z_1^2\varepsilon\frac{e^{-\xi}}{\xi}\right) - 2\exp\left(-z_1 z_2\varepsilon\frac{e^{-\xi}}{\xi}\right) + \exp\left(-z_2^2\varepsilon\frac{e^{-\xi}}{\xi}\right)\right\} + (|z_1|+|z_2|)\frac{\varepsilon'}{4}\left\{\frac{q}{1+q} + \frac{2q^2\ln 2}{1-q^2} - \frac{(1+q^2)\ln(1+q)}{1-q^2} - \frac{q^2}{b'}\right\}\right]$$

Here we have retained the ε and b notation in the remaining integral in (4.45), since the same integral has been evaluated in Chapter III (c. f. (3.20)); our final result for the electrophoresis effect in (4.4) is:

(4.46) $$\frac{|z_1|U_1^s}{z_1 e} + \frac{|z_2|U_2^s}{z_2 e} = \frac{-\kappa}{6\pi\eta}\left[(|z_1|+|z_2|)\left\{1 - \varepsilon'\left\{\frac{1}{b'} + \frac{1}{4}\left(\frac{q}{1+q} + \frac{2q^2\ln 2}{1-q^2} - \frac{(1+q^2)\ln(1+q)}{1-q^2} - \frac{q^2}{b'}\right) + \frac{(|z_1|-|z_2|)^2}{2z_1 z_2}\left(\gamma_E + \ln\frac{2\varepsilon'}{b'}\right) - \frac{1}{z_1 z_2}\sum_{n=3}^{\infty}\frac{\left(\frac{b'}{z_1 z_2}\right)^{n-2}\left(\frac{z_1^n - z_2^n}{z_1 - z_2}\right)^2}{n!\,(n-2)}\right\}\right\}\right]$$

6. The Osmotic Effect

The pressure on the "surface" of an ion of species i due to collisions with ions of the opposite species is $\frac{f_{12}(a)}{c_i n}kT$; since $f_{ii} = f_{ii}^{(0)}$ is centrally symmetric, there is no net force due to collisions with ions of the same species. The net force k_x on the ion of species i in the field direction $\hat{i}$ is obtained by integrating the pressure times the x-component of the normal to the surface over the entire surface of the ion:

$$k_x = kTa^2\int_0^{\pi} d\theta \sin\theta\left[\frac{f_{12}'(a)}{nc_i}\cos\theta\right]\int_0^{2\pi} d\phi \tag{4.47}$$

$$= \frac{4\pi kT}{3c_i n}a^2\left[\frac{f_{12}'(a)}{\cos\theta}\right] \doteq \frac{z_i e X}{6qx}\left[e^{-qxa}(1+qxa)-e^{qxa}(1-qxa)\right]\int_a^{\infty}\frac{dr}{r^2}e^{-\frac{z_1 z_2 e^2}{DkTr}}$$

where we have used (4.31); to the order in which we are interested there is a contribution only from $g_1(r)$. We express k_x as a force per unit charge so that it may be added to $\Delta_R X/X$:

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Further investigation has shown that equation (4.17), Fuoss and Onsager's result for $f'^{(1)}_{12}$, while of sufficient accuracy to give the Onsager limiting law, is not of sufficient accuracy, when substituted in the higher order terms, to give all $\mathcal{O}(\varepsilon^2)$, contributions to the conductivity. The result (4.49) and the values of a given in §8 must be modified accordingly.

6. The Osmotic Effect

The pressure on the "surface" of an ion of species i due to collisions with ions of the opposite species is $\frac{f_{12}(a)}{c_i n} kT$; since $f_{ii} = f_{ii}^{(0)}$ is centrally symmetric, there is no net force due to collisions with ions of the same species. The net force k_x on the ion of species i in the field direction $\hat{i}$ is obtained by integrating the pressure times the x-component of the normal to the surface over the entire surface of the ion:

$$(4.47) \qquad k_x = kT a^2 \int_0^{\pi} d\theta \sin\theta \left[\frac{f_{12}'(a)}{n c_i} \cos\theta \right] \int_0^{2\pi} d\phi$$

$$= \frac{4\pi kT}{3 c_i n} a^2 \left[\frac{f_{12}'(a)}{\cos\theta} \right] \doteq \frac{z_i e X}{6 q \kappa} \left[e^{-q\kappa a}(1+q\kappa a) - e^{q\kappa a}(1-q\kappa a) \right] \int_a^{\infty} \frac{dr}{r^2} e^{-\frac{z_1 z_2 e^2}{DkTr}}$$

where we have used (4.31); to the order in which we are interested there is a contribution only from $g_1(r)$. We express k_x as a force per unit charge so that it may be added to $\Delta_R X/X$:

$$(4.48) \qquad \frac{\Delta_0 X}{X} \equiv \frac{k_x}{z_i e X} \doteq \frac{q^2}{q} \frac{\varepsilon'^2}{b'^3} \left(e^{b'} - 1 \right)$$

7. Final Form of the Conductivity Equation

We add (4.48) to (4.34) and substitute the result, and also (4.46), into (4.4); then retaining only terms of order ε'^2 we obtain

$$(4.49) \qquad \Lambda = \Lambda_0 + \Lambda_1 \varepsilon' + \Lambda_{2'} \varepsilon'^2 \ln \varepsilon' + \Lambda_2 \varepsilon'^2 + \cdots$$

$$\Lambda_1 = -\frac{q^2}{3(1+q)} \Lambda_0 + \frac{F^2}{N} \frac{(|z_1|+|z_2|)}{z_1 z_2} \frac{DkT}{6\pi\eta e^2}$$

$$\Lambda_{2'} = \frac{q^2}{6} \Lambda_0 + \frac{F^2}{N} \frac{(|z_1|+|z_2|)}{z_1 z_2} \frac{DkT}{6\pi\eta e^2} \left[\frac{q^2}{4} - \frac{(|z_1|-|z_2|)^2}{2 z_1 z_2} \right]$$

$$\Lambda_2 = -\frac{q^2}{6}\Lambda_0\Bigg[-2\gamma_E - \left\{1+\frac{q^2(1+q^2)}{2(1-q^2)}\right\}\ln(2+q) - \frac{(1-2q^2)}{1-q^2}\ln(1+2q)$$

$$-\frac{(1-q^2)^2}{2q^2}\ln(1+q) + \frac{3}{2} + \frac{2q-3q^2+4q^3-5q^4+2q^5}{4q^2(1-q^2)} + \frac{2q^2}{3(1+q)^2}$$

$$+\mathrm{Ei}(b') - e^{b'}\left\{\frac{2}{3b'^3}+\frac{1}{3b'^2}+\frac{1}{b'}\right\} + \frac{2}{3b'^3}+\frac{1}{3b'^2}$$

$$-\frac{(z_1+z_2)^2}{2z_1z_2(1-q^2)}\left\{\frac{1}{3}-\frac{2q^2}{1-q^2}\ln\frac{3}{2+q}\right\}\Bigg] - \frac{F^2}{N}\,\frac{(|z_1|+|z_2|)}{z_1z_2}\,\cdot$$

$$\cdot\frac{DkT}{6\pi\eta e^2}\Bigg[\frac{1}{b'} + \frac{1}{3}\frac{q^2}{1+q} + \frac{1}{4}\Bigg\{\frac{q}{1+q} + \frac{2q^2\ln 2}{1-q^2}$$

$$-\frac{(1+q^2)\ln(1+q)}{1-q^2} - \frac{q^2}{b'}\Bigg\} + \frac{(|z_1|-|z_2|)^2}{2z_1z_2}\left(\gamma_E+\ln\frac{2}{b'}\right)$$

$$-\frac{1}{z_1z_2}\sum_{n=3}^{\infty}\frac{\left(\frac{b'}{z_1z_2}\right)^{n-2}\left(\frac{z_1^n-z_2^n}{z_1-z_2}\right)^2}{n!\,(n-2)} + \frac{q^2}{3(1+q)} + \frac{q^2}{4}\Bigg\{\frac{(1-q^2+\frac{5}{2}q)}{2q}$$

$$-\frac{(1-q^2)^2\ln(1+q)}{2q^2} + \frac{q^2-4}{2}\ln(2+q) + \mathrm{Ei}(b') - 2\gamma_E$$

$$-\frac{e^{b'}(b'-1)+1}{3b'^2}\Bigg\}\Bigg]$$

where to obtain the expression in the final set of square brackets in (4.49) from the final set of square brackets in (4.34) we have used

(4.50) $$q^2 = \frac{|z_1|\,\omega_1 + |z_2|\,\omega_2}{(|z_1|+|z_2|)(\omega_1+\omega_2)}$$

which follows from the definitions of q and κ and the neutrality condition; (4.50) and (4.5) give

$$\frac{\Lambda_0}{\omega_1+\omega_2} = \frac{F^2}{N} q^2(|z_1|+|z_2|). \tag{4.51}$$

The equation (4.49) includes, to order ϵ^2, all deviations from the superposition approximation mentioned in Chapter I. $\Lambda_{2'}$ agrees with the results of Fuoss and Onsager [12], but Λ_2 does not, as they did not evaluate the solution of (4.13) with sufficient accuracy.

8. Comparison with Experiment

In Fig. 7 we have plotted the theoretical curve for $\Lambda_{2'}\epsilon^2\ln\epsilon + \Lambda_2\epsilon^2$, that is, for the deviation of Λ from the Onsager limiting law. The curves are plotted from $\epsilon'=0$ to $\epsilon'=0.2$ with $\Lambda_0 = 126.49$ cm^2 int. Ω^{-1} equiv^{-1}; the center curve corresponds to b' = 1.78, the top curve to b' = 1.55, and the bottom curve to b' = 2.00; the top and bottom curves are drawn to show the sensitivity of Λ to changes in b'. The experimental points were taken from measurements by Shedlovsky [13] on NaCl in water at 25°C; in this case $b' \equiv -z_1z_2 b = b$ and the b = 1.78 curve, corresponding to a hard core diameter of 4.0 Å, should be compared with the result b = 1.38 (a = 5.2 Å) in the equilibrium case described in Chapter III. (The difference between the two values of b can be attributed to deviations of the actual solvent from the idealized model of the solvent, which do not necessarily have the same effect in the non-equilibrium case as in the equilibrium case.) In the case of the asymmetric solute $CaCl_2$ in water at 25°C [13], the theoretical curve matches the experimental results with $\Lambda_0 = 135.85$ and b = 1.125 (a = 6.4 Å), which is to be compared with b = .89 (a = 8.0 Å) in the equilibrium case. As in the equilibrium case, an error of about 30% in the deviation from the $\sqrt{n}$ law appears, if the equilibrium potential of average force $\Psi_{ij} \doteq \epsilon\Psi_{ij}^{(1)} + \epsilon^2\Psi_{ij}^{(2)}$ is approximated by the Debye-Hückel potential $\epsilon\Psi_{ij}^{(1)}$.

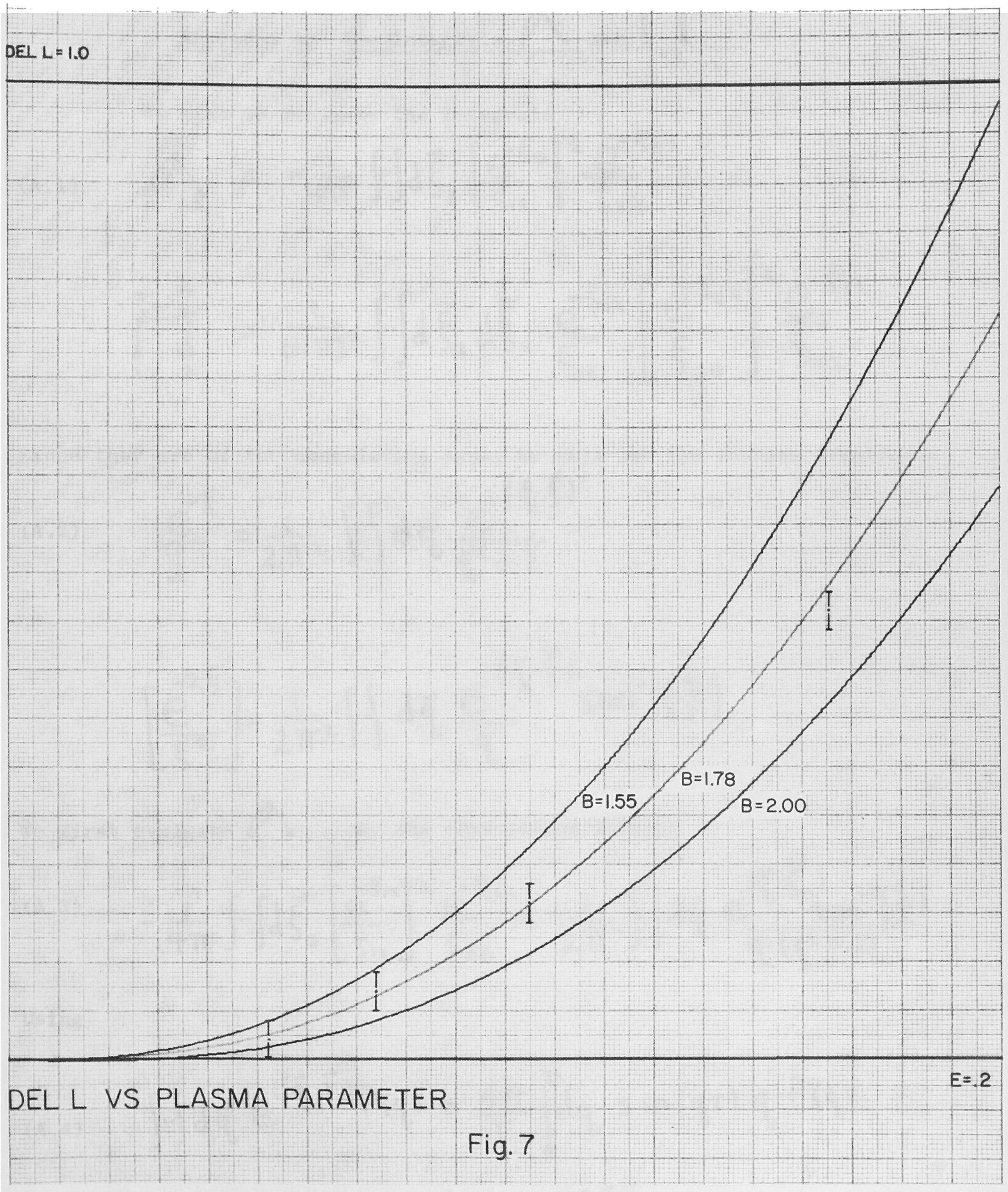
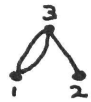


Fig. 7

Appendix A: The Integrals  and 

We wish to evaluate the integrals

(A.1)  $$= -\frac{1}{4\pi}\int\!\cdots\!\int d\vec{\xi}_3 \left[\frac{e^{-\xi_{13}}}{\xi_{13}}\right]^2 \frac{e^{-\xi_{32}}}{\xi_{32}}$$

 $$= \frac{1}{(4\pi)^2}\int\!\cdots\!\int d\vec{\xi}_3\, d\vec{\xi}_4\, \frac{e^{-\xi_{13}}}{\xi_{13}} \left[\frac{e^{-\xi_{34}}}{\xi_{34}}\right]^2 \frac{e^{-\xi_{42}}}{\xi_{42}}$$

Since they are of the convolution type, we will use the Fourier transforms

(A.2) $$\frac{e^{-\xi}}{\xi} = \frac{1}{2\pi^2}\int\!\cdots\!\int d\vec{q}\, \frac{e^{i(\vec{q}\cdot\vec{\xi})}}{q^2+1}$$

$$\left[\frac{e^{-2\xi}}{\xi^2}\right] = \frac{1}{2\pi^2}\int\!\cdots\!\int d\vec{q}\, \frac{e^{i(\vec{q}\cdot\vec{\xi})}}{q}\tan^{-1}\left(\frac{q}{2}\right)$$

We first evaluate  . By the convolution theorem

(A.3) $$-\frac{1}{4\pi}\int\!\cdots\!\int d\vec{\xi}_3 \left[\frac{e^{-\xi_{13}}}{\xi_{13}}\right]^2 \frac{e^{-\xi_{32}}}{\xi_{32}} = -\frac{1}{2\pi^2}\int\!\cdots\!\int d\vec{q}\, \frac{e^{i(\vec{q}\cdot\vec{\xi}_{12})}\tan^{-1}\left(\frac{q}{2}\right)}{q(q^2+1)}$$

Using

(A.4) $$\int\!\cdots\!\int d\vec{q}\, e^{i(\vec{q}\cdot\vec{r})} f(q) = \frac{4\pi}{r}\int_0^\infty dq\, \sin(qr)\, q\, f(q)$$

and $$\sin(qr) = \frac{1}{2i}\left[e^{iqr} - e^{-iqr}\right]$$

we obtain, since $\sin \cdot \tan^{-1}$ is an even function,

$$\Lambda = -\frac{1}{2\pi i\xi}\left[\int_{-\infty}^{\infty} dq\, \frac{e^{iq\xi}\tan^{-1}\left(\frac{q}{2}\right)}{q^2+1} - \int_{-\infty}^{\infty} dq\, \frac{e^{-iq\xi}\tan^{-1}\left(\frac{q}{2}\right)}{q^2+1}\right] \tag{A.5}$$

Replacing q by $-q$ in the second integral and noting that, by analytical continuation in the complex plane,

$$\tan^{-1}\left(\frac{q}{2}\right) = \frac{1}{2i}\ln\frac{2+iq}{2-iq}$$

we have the contour integral

$$\Lambda = \frac{1}{2\pi\xi}\int_{-\infty}^{\infty} dq\, \frac{e^{iq\xi}}{(q+i)(q-i)}\ln\frac{2+iq}{2-iq} \tag{A.6}$$

We evaluate this integral by choosing a contour in the upper half plane which excludes the branch cut from $2i$ to $i\infty$:

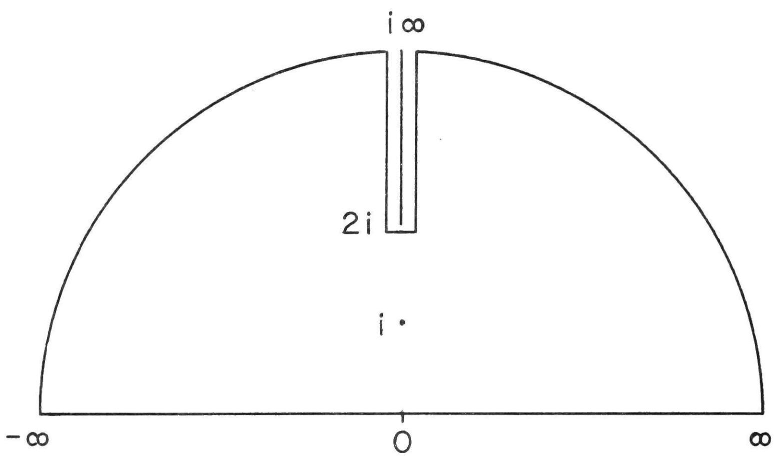


Fig. 8

The integral has a simple pole at $q=i$ and the integrand $\rightarrow \frac{1}{|q|^2}$ as $|q| \rightarrow \infty$; we obtain

(A.7) $$\Lambda = \frac{1}{2\pi\xi}\left[2\pi i\cdot\frac{e^{-\xi}}{2i}\ln\frac{1}{3} - \int_{2i-\varepsilon}^{i\infty-\varepsilon} dq\,\frac{e^{iq\xi}}{q^2+1}\ln\frac{2+iq}{2-iq}\right.$$

$$\left. + \int_{2i+\varepsilon}^{i\infty+\varepsilon} dq\,\frac{e^{iq\xi}}{q^2+1}\ln\frac{2+iq}{2-iq}\right]$$

We evaluate (A.7) by substituting $q \to \varepsilon + iQ$ in the first integral and $q = -\varepsilon + iQ$ in the second integral, and then letting $\varepsilon \to 0$. Remembering that the value of the logarithm on the right side of the branch cut exceeds that on the left side by $2\pi i$, we obtain

(A.8) $$\Lambda = -\frac{\ln 3}{2}\,\frac{e^{-\xi}}{\xi} - \frac{1}{2\xi}\left[\int_2^\infty dQ\,\frac{e^{-Q\xi}}{Q+1} - \int_2^\infty dQ\,\frac{e^{-Q\xi}}{Q-1}\right]$$

$$= -\frac{\ln 3}{2}\,\frac{e^{-\xi}}{\xi} - \frac{1}{2\xi}\left[-e^{\xi}\,Ei(-3\xi) + e^{-\xi}\,Ei(-\xi)\right]$$

where $Ei(-x) \equiv -\int_x^\infty dy\,\frac{e^{-y}}{y}$.

We evaluate Π in the same fashion. By the convolution theorem

(A.9) $$\Pi = \frac{1}{2\pi^2}\int\cdots\int d\vec{q}\,\frac{e^{i(\vec{q}\cdot\vec{\xi})}\tan^{-1}\left(\frac{q}{2}\right)}{q\,(q^2+1)^2}$$

As before, in the complex plane,

(A.10)  $$= -\frac{1}{2\pi\xi}\int_{-\infty}^{\infty} dq\, \frac{e^{iq\xi}}{(q+i)^2(q-i)^2}\ln\frac{2+iq}{2-iq}$$

Integrating around the same contour as for , but remembering that the pole is now of order 2, we obtain

(A.11)  $$= -\frac{1}{2\pi\xi}\Bigg[2\pi i \lim_{q\to i}\frac{d}{dq}\left\{\frac{e^{iq\xi}}{(q+i)^2}\ln\frac{2+iq}{2-iq}\right\}$$

$$- 2\pi\int_2^{\infty} dQ\, e^{-Q\xi}\cdot\frac{1}{4}\left\{\left[\frac{1}{(Q+1)^2}+\frac{1}{(Q-1)^2}+\frac{1}{Q+1}-\frac{1}{Q-1}\right]\right\}\Bigg]$$

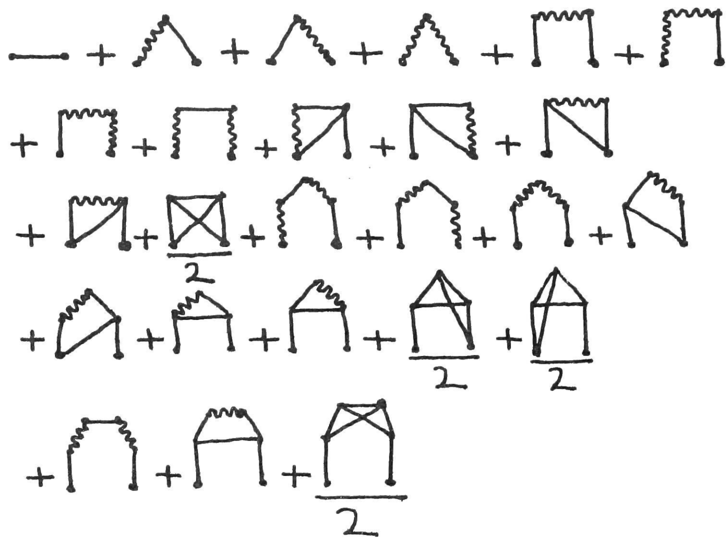
$$= \frac{\ln 3}{4}e^{-\xi} + \left[\frac{\ln 3}{4}-\frac{1}{3}\right]\frac{e^{-\xi}}{\xi} + \frac{1}{3}\frac{e^{-2\xi}}{\xi}$$

$$+ \frac{1}{4}\left[(\xi-1)\frac{e^{\xi}}{\xi}Ei(-3\xi) + (\xi+1)\frac{e^{-\xi}}{\xi}Ei(-\xi)\right]$$

Appendix B: Higher Order Terms in the Potential of Average Force of the Electron Gas

Examination of equations (2.20) and (2.22) shows that, to order $\varepsilon^4 \ln \varepsilon$,

(B.1) $$\Psi(\xi;\varepsilon) \doteq$$



where the integration over all field points is understood. Evaluation of these integrals is by the convolution method, and is similar to the evaluation of the integrals in Appendix A; the Fourier transform of the factors f_{mn} (wavy lines) is given by (2.22). The result is

(B.2) $$\Psi(\xi;\varepsilon) = \varepsilon\,\Psi_1(\xi) + \varepsilon^2\,\Psi_2(\xi) + \varepsilon^3 \ln\varepsilon\,\Psi_{3'}(\xi) + \varepsilon^3\left[\Psi_{3X}(\xi) + \Psi_{3N}(\xi)\right] + \varepsilon^4 \ln\varepsilon\,\Psi_{4'}(\xi) + \cdots$$

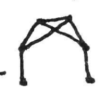
$$\Psi_1(\xi) = -\frac{e^{-\xi}}{\xi}$$

$$\Psi_2(\xi) = \frac{\ln 3}{8} e^{-\xi} - \left[\frac{3}{8}\ln 3 + \frac{1}{6}\right]\frac{e^{-\xi}}{\xi} + \frac{1}{6}\frac{e^{-2\xi}}{\xi}$$
$$+ \frac{1}{8}\left[(\xi+3)\frac{e^{\xi}}{\xi}\,\mathrm{Ei}(-3\xi) + (\xi-3)\frac{e^{-\xi}}{\xi}\,\mathrm{Ei}(-\xi)\right]$$

$$\Psi_{3'}(\xi) = \frac{e^{-\xi}}{12} - \frac{e^{-\xi}}{3\xi}$$

$$\Psi_{3x}(\xi) = \left(2\gamma_E + 3\ln 2 - \frac{17}{6}\right)\frac{e^{-\xi}}{12} - \left(2\gamma_E + \frac{21}{8}\ln 2 - \frac{31}{12}\right)\frac{e^{-\xi}}{3\xi}$$
$$+ \frac{1}{12}\frac{e^{-3\xi}}{\xi} + \frac{1}{6}\left[\xi + \frac{13}{4}\right]\frac{e^{\xi}}{\xi}\,\mathrm{Ei}(-4\xi) + \frac{1}{12}\left[\xi - \frac{5}{2}\right]\frac{e^{-\xi}}{\xi}\,\mathrm{Ei}(-2\xi)$$

$\Psi_{3N}(\xi) =$  $/\,4$ $+\,3$  $/\,4$ $+\,2$  $+$  $/\,2$ $+\,3$  $/\,4$

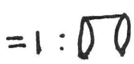
$+$  $+$  $+$  $+$  $/\,4$ $+$  $/\,2$ $+$  $/\,2$

$$\Psi_{4'}(\xi) = \frac{1}{4!}\left[-\left\{\frac{37}{3} + \frac{39}{4}\ln 3\right\}\frac{e^{-\xi}}{\xi} + \left\{\frac{7}{3} + \frac{17}{4}\ln 3\right\}e^{-\xi} - \frac{\ln 3}{4}\,\xi e^{-\xi}\right.$$
$$+ 4\frac{e^{-2\xi}}{\xi^2} + \frac{13}{3}\frac{e^{-2\xi}}{\xi} - \frac{e^{-2\xi}}{6} - \frac{1}{4}\left\{\left(-\xi - 17 - \frac{39}{\xi}\right)e^{\xi}\,\mathrm{Ei}(-3\xi)\right.$$
$$\left.\left. + \left(\xi - 17 + \frac{39}{\xi}\right)e^{-\xi}\,\mathrm{Ei}(-\xi)\right\}\right]$$

In (B.2) we have divided the coefficient of ε^3 into two parts, an explicitly evaluated part $\Psi_{3x}(\xi)$ and a part $\Psi_{3N}(\xi)$ which can be obtained only by numerical integration. We have written double solid lines in the expression for $\Psi_{3N}(\xi)$ in place of the wavy lines representing factors f_{mn}, since to order ε^3 only the first term $\frac{\varepsilon^2}{2}\frac{\tan^{-1}(\frac{q_{mn}}{2})}{q_{mn}}$ in (2.22) is needed and this term is just the Fourier transform of $\frac{1}{2}(-\varepsilon\frac{e^{-\xi}}{\xi})^2$. The values of the graphs in $\Psi_{3N}(\xi)$ are listed in (B.3):

(B.3)
$$\frac{2(-1)^n}{\pi\xi}\int_0^\infty dq\,\frac{\sin(q\xi)\left[\tan^{-1}(\frac{q}{2})\right]^2}{q(q^2+1)^n}$$

$n=0:$  $n=2:$ 

$n=1:$  $n=3:$ 

$$-\frac{(-1)^{n+m}}{\pi^2\xi}\int_0^\infty dq\,\frac{\sin(q\xi)}{(q^2+1)^n}\int_0^\infty dq'\,\frac{\tan^{-1}(\frac{q'}{2})}{(q'^2+1)^m}\ln\frac{(q+q')^2+1}{(q-q')^2+1}$$

$n=1, m=1:$  $n=1, m=2:$ 

$n=2, m=1:$  $n=2, m=2:$ 

$$-\frac{2(-1)^n}{\pi^3\xi}\int_0^\infty dq_1\,\frac{\sin(q_1\xi)}{q_1(q_1^2+1)^n}\sum_{b=0}^\infty(2b+1)\int_0^\infty dq_2\,\frac{Q_b(x_{12})}{q_2^2+1}\int_{q_2}^\infty dq_3\,\frac{Q_b(x_{23})Q_b(x_{13})}{q_3^2+1}$$

$n=0:$ 

$n=1:$ 

$n=2:$ 

Here $x_{ij}\equiv(q_i^2+q_j^2+1)/2q_iq_j$, and $Q_b(x_{ij})$ is the b^{TH} Legendre

Polynomial of the second kind.

Finally, we wish to indicate how we determine the long-range behavior of $T(\xi;\varepsilon)$ in (2.25). The integral is evaluated as in Appendix A, using the contour of Fig. 8. The branch cut extends from $i\infty$ down to $2i$, so we surmise that the integral around the branch cut behaves as $e^{-2\xi}$ for large ξ (the exponential behavior, as in the case of Λ and Π, stems from the factor $e^{iq\xi}$ in the integrand). The dominant behavior of (2.25) at large distances, therefore, should be given by the simple pole which we find at about $q = i\left(1+\varepsilon\frac{\ln 3}{8}+\cdots\right)$; the contribution from this pole gives (2.26).

Appendix C: Some Integrals in Chapter IV

1. Derivation of Equation (4.31)

Equation (4.30) is equivalent to

$$f_{12}'(\vec{r}) = \frac{1}{4\pi}\int_a^\infty dr'\, r'^2 \sum_{n=1}^{6} g_n(r') \int_0^\pi d\theta'' \, \frac{\exp\left(-q_\kappa \sqrt{r^2+r'^2-2rr'\cos\theta''}\right)}{\sqrt{r^2+r'^2-2rr'\cos\theta''}} \cdot \sin\theta'' \int_0^{2\pi} d\phi \cos\theta' \tag{C.1}$$

where the angles are as indicated in Fig. 9:

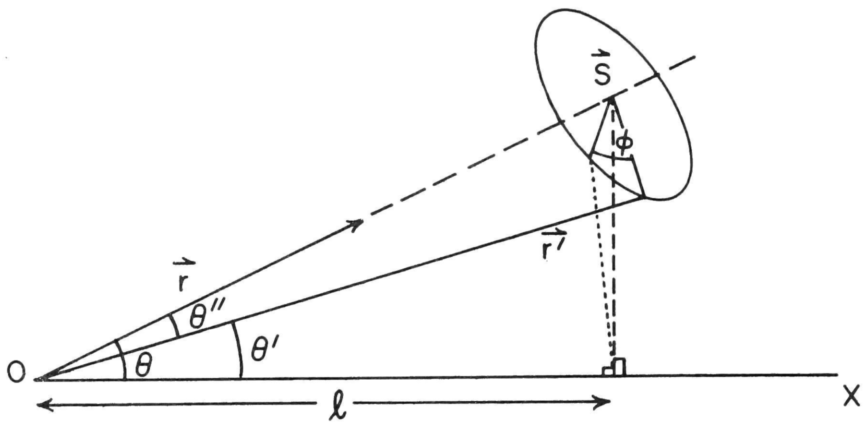


Fig. 9

The integration is carried out in spherical coordinates about the $\vec{r}$-axis. We define the point $\vec{S}$ as the intersection of the ray along which $\vec{r}$ lies with that plane perpendicular to $\vec{r}$ in which the point $\vec{r}'$ lies, and choose the scale of length such that $|\vec{S}|=1$. We choose $\phi = 0$ so that a perpendicular dropped from $\vec{r}'$ to the x-axis intersects the x-axis at the same point as a perpendicular dropped from $\vec{S}$; this point is $\ell = \cos\theta$ from the origin. Then we have

$$r'\cos\theta' = \cos\theta + \cos\theta\, \sin\theta''\, \sin\phi \tag{C.2}$$

but $r = 1/\cos\theta''$, so that

(C.3) $$\int_0^{2\pi} d\phi \cos\theta' = 2\pi \cos\theta \cos\theta''$$

and (C.1) becomes

(C.4) $$f'_{12}(\vec{r}) = -\frac{\cos\theta}{2q\kappa r}\int_a^\infty dr'\,r' \sum_{n=1}^{6} g_n(r')\Bigg[\left\{1 - \frac{q\kappa|r-r'|+1}{q^2\kappa^2 r r'}\right\} e^{-q\kappa|r-r'|} + \left\{1 + \frac{q\kappa(r+r')+1}{q^2\kappa^2 r r'}\right\} e^{-q\kappa(r+r')}\Bigg]$$

where we have used

(C.5) $$\int_{-1}^{1} dx\, \frac{x\, e^{-\sqrt{a+bx}}}{\sqrt{a+bx}} = -\frac{2}{b^2}\Big[(b+2\sqrt{a+b}+2)\,e^{-\sqrt{a+b}} + (b-2\sqrt{a-b}-2)\,e^{-\sqrt{a-b}}\Big]$$

with

(C.6) $$a \equiv q^2\kappa^2(r^2+r'^2)$$

$$b \equiv -2q^2\kappa^2 r r'$$

In order to write (C.4) in the more convenient form (4.31), we eliminate the absolute value $|r-r'|$ by splitting up $\int_a^\infty$ into $\int_a^r + \int_r^\infty$;

(4.31) then follows by a simple rearrangement of terms.

2. Derivation of Equation (4.33)

Combining (4.14c) and (4.31), we get

$$\Delta\psi' = -\frac{2\pi z_1 e\cos\theta}{Dc_2 n q^3 x^3 r^2}\left[e^{-qxr}(1+qxr)\int_a^r dr'\,k(r') + \left\{e^{-qxr}(1+qxr) - e^{qxr}(1-qxr)\right\}\int_r^\infty dr'\,\ell(r')\right] \tag{C.7}$$

$$k(r') \equiv \left\{e^{-qxr'}(1+qxr') - e^{qxr'}(1-qxr')\right\}\sum_{n=1}^{6} g_n(r')$$

$$\ell(r') \equiv e^{-qxr'}(1+qxr')\sum_{n=1}^{6} g_n(r')$$

(C.7) is solved in exactly the same way as (4.29), except that the Green's function is now $1/|\vec{r}-\vec{r}'|$; the solution is

$$\psi' = -\frac{\pi z_1 e\cos\theta}{Dc_2 n q^3 x^3}\int_a^\infty dr'\,m(r')\int_0^\pi d\theta''\frac{\sin\theta''\cos\theta''}{\sqrt{r^2+r'^2-2rr'\cos\theta''}} \tag{C.8}$$

$$= -\frac{2}{3}\,\frac{\pi z_1 e\cos\theta}{Dc_2 n q^3 x^3}\left[\frac{1}{r^2}\int_a^r dr'\,r'm(r') + r\int_r^\infty dr'\,\frac{m(r')}{r'^2}\right]$$

where $m(r')$ is the quantity in brackets in (C.7).

We now wish to use (C.8) in (4.32) to obtain the change in field $\Delta_R X$ .Since (C.8) is of the form $h(r)\cos\theta$, (4.32) becomes

(C.9) $$\Delta_R X = - \left[\frac{\partial}{\partial x}\{h(r)\cos\theta\}\right]_a = -\cos^2\theta\left[\frac{\partial h}{\partial r}\right]_a - \frac{h(a)}{a}\left[1-\cos^2\theta\right]$$

but examination of (C.8) shows that the $\cos^2\theta$ terms in (C.9) cancel, and that

(C.10) $$h(a) = -\frac{2}{3}\frac{\pi Z_1 e a}{D c_2 n q^3 \kappa^3}\int_a^\infty dr'\,\frac{m(r')}{r'^2}$$

so that (C.9) becomes

(C.11) $$\Delta_R X = -\frac{h(a)}{a} = \frac{2}{3}\frac{\pi Z_1 e}{D c_2 n q^3 \kappa^3}\int_a^\infty \frac{dr'}{r'^2}\Big[e^{-q\kappa r'}(1+q\kappa r')\int_a^{r'} dr''\,k(r'') + \left\{e^{-q\kappa r'}(1+q\kappa r') - e^{q\kappa r'}(1-q\kappa r')\right\}\int_{r'}^\infty dr''\,\ell(r'')\Big]$$

(C.11) is evaluated by changing the order of integration:

(C.12) $$\int_a^\infty dr'\int_a^{r'} dr'' = \int_a^\infty dr''\int_{r''}^\infty dr' \qquad \int_a^\infty dr'\int_{r'}^\infty dr'' = \int_a^\infty dr''\int_a^{r''} dr'$$

We obtain

$$\text{(C.13)}\qquad \Delta_R X = \frac{2}{3}\,\frac{\pi z_1 e}{D c_2 n q^3 \kappa^3}\int_a^\infty dr \left[k(r)\int_a^\infty \left\{ -\frac{\partial}{\partial r'}\frac{e^{-q\kappa r'}}{r'} \right\} dr' + l(r)\int_a^r \left\{ \frac{\partial}{\partial r'}\frac{e^{q\kappa r'}}{r'} - \frac{\partial}{\partial r'}\frac{e^{-q\kappa r'}}{r'} \right\} dr' \right]$$

$$= \frac{2}{3}\,\frac{\pi z_1 e}{D c_2 n q^3 \kappa^3}\int_a^\infty dr \sum_{n=1}^{6} g_n(r)\left[2q\kappa + \left[\frac{e^{-q\kappa a}}{a} - \frac{e^{q\kappa a}}{a} \right] e^{-q\kappa r}(1+q\kappa r) \right]$$

We expand $e^{-q\kappa a} - e^{q\kappa a}$ in (C.13); examination of (C.13) and of the $g_n(r)$ in (4.29) shows that to order ε^2, $\kappa^5 a^5$ and higher terms in the expansion of $e^{-q\kappa a} - e^{q\kappa a}$ may be ignored, and that in the $\kappa^3 a^3$ term, $e^{-q\kappa r}(1+q\kappa r)$ may be set equal to one; we thus obtain (4.33).

3. Derivation of Equation (4.34)

We discuss (4.33) term by term; the evaluation of the integrals proceeds mainly by tedious algebra based on the formula

$$\text{(C.14)}\qquad \int_a^\infty dr\,\frac{e^{-\lambda r}}{r^n} = \frac{e^{-\lambda a}}{(n-1)!\,a^{n-1}}\sum_{m=0}^{n-2}(-\lambda a)^m (n-2-m)! + \frac{(-\lambda)^{n-1}}{(n-1)!}\,Ei(-\lambda a)$$

Wherever possible, exponential functions in (4.33) are expanded in power series in ε, and terms of higher order than ε^2 are ignored; in

determining the order in ϵ to which a term contributes, it is necessary to examine its short-distance behavior, since a factor $1/\kappa r$ in the integrand of (4.33) may lead to a factor $1/\kappa a = b'/\epsilon'$ in $\Delta_R X$.

$\underline{g_1(r)}$: $\frac{\partial \Psi_{12}}{\partial x}$ may be approximated by $\frac{\partial \Psi_{12}^{(1)}}{\partial x}\epsilon + \frac{\partial \Psi_{12}^{(2)}}{\partial x}\epsilon^2$ *; we will first evaluate the terms containing $\frac{\partial \Psi_{12}^{(1)}}{\partial x}$. We call the contribution to $\Delta_R X$ from these terms $\Delta_R X_{g_1^{(1)}}$, and find to order ϵ^2

$$\Delta_R X_{g_1^{(1)}} \doteq \frac{-z_1 z_2 e^2 X}{3DkT} \int_a^\infty dr\, e^{\Psi_{12}^{(1)}\epsilon} \frac{e^{-\kappa r}(1+\kappa r)}{r^2} \cdot \left\{e^{-q\kappa r}(1+q\kappa r)-1\right\} - \frac{z_1 z_2 e^2 X q^2 \kappa^2 a^2}{18DkT} \int_a^\infty \frac{dr}{r^2}\, e^{\Psi_{12}^{(1)}\epsilon} \tag{C.15}$$

$$\doteq -\frac{z_1 z_2 R_L X}{3}\Bigg[\int_a^\infty \frac{dr}{r^2}\, e^{-\kappa r}(1+\kappa r)\left\{e^{-q\kappa r}(1+q\kappa r)-1\right\}$$

$$-\underline{z_1 z_2 R_L} \int_a^\infty \frac{dr}{r^3}\, e^{-2\kappa r}(1+\kappa r)\left\{e^{-q\kappa r}(1+q\kappa r)-1\right\}$$

$$-z_1 z_2 R_L \frac{q^2\kappa^2}{2}\int_0^{b'} \frac{du}{u^2}\left(e^u-1-u\right)\Bigg]$$

$$+\frac{q^2\kappa^2 a^2}{18} X \int_0^{b'} du\, e^u$$

$$-\frac{\Delta_R X_{g_1^{(1)}}}{X} \doteq \frac{\epsilon'}{3} q^2\left[\frac{1}{1+q} - \frac{\epsilon' \ln \epsilon'}{2} + \frac{\epsilon'}{2}\left\{Ei(b') - 2\gamma_E - \ln(2+q) - \frac{e^{b'}}{b'} + \frac{3}{2} - \frac{e^{b'}-1}{3b'^2}\right\}\right]$$

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*In all other cases Ψ_{12} may be approximated by $\epsilon \Psi_{12}^{(1)}$.

where we have made the substitution $U = \frac{-Z_1 Z_2 R_L}{r}$; in the integrals in which this substitution was made, we were able to ignore terms in the integrand of higher order in κr than those which were retained.

$\Delta_R X_{g_1^{(1)}}$ contains the only term in ΔX of order ε, that is, the term $-\frac{\varepsilon' q^2}{3(1+q)}$.

We call $\Delta_R X_{g_1^{(2)}}$ the contribution to $\Delta_R X$ of the terms in $g_1(r)$ containing $\partial \Psi_{12}^{(2)}/\partial x$; here we may approximate $e^{\Psi_{12}}$ by 1. We use (3.15c) and the formulas

$$\int_a^\infty dr\, e^{-\lambda r}\, Ei(-\lambda' r) = \frac{e^{-\lambda a}}{\lambda}\, Ei(-\lambda' a) + \frac{1}{\lambda}\int_a^\infty dr\, \frac{e^{-(\lambda+\lambda')r}}{r} \tag{C.16}$$

$$\doteq \frac{\ln \lambda' - \ln(\lambda+\lambda')}{\lambda}$$

$$\int_a^\infty dr\, r\, e^{-\lambda r}\, Ei(-\lambda' r) = \left[\frac{a e^{-\lambda a}}{\lambda} + \frac{e^{-\lambda a}}{\lambda^2}\right] Ei(-\lambda' a) + \frac{1}{\lambda}\int_a^\infty dr\, \frac{e^{-(\lambda+\lambda')r}}{r}\left(\frac{1}{\lambda}+r\right)$$

$$\doteq \frac{1}{\lambda(\lambda+\lambda')} + \frac{\ln\lambda' - \ln(\lambda+\lambda')}{\lambda'^2}$$

and find

$$\frac{\Delta_R X_{g_1^{(2)}}}{X} \doteq \frac{\varepsilon'^2}{12}\, \frac{(z_1+z_2)^2}{z_1 z_2}\, \frac{q^2}{1-q^2}\left[\frac{1}{3} - \frac{2q^2}{1-q^2}\ln\left(\frac{3}{2+q}\right)\right] \tag{C.17}$$

<u>$g_2(r), g_3(r), g_4(r)$</u> : We call the contributions to $\Delta_R X$ from these terms $\Delta_R X_{g_{2,3,4}}$; we can set $e^{\Psi_{12}} \doteq 1$ and need only make exhaustive use of (C.14) to find

(C.18) $$\frac{\Delta_R X_{g_{2,3,4}}}{X} \doteq \frac{\epsilon'^2}{3(1-q^2)}\left[-\frac{2q-3q^2+4q^3-5q^4+2q^5}{8}\right.$$

$$\left.+\frac{q^4(1+q^2)}{4}\ln(2+q)+q^2\left(\tfrac{1}{2}-q^2\right)\ln(1+2q)+\frac{(1-q^2)^3}{4}\ln(1+q)\right]$$

$g_5(r)$: By inspection, $g_5(r)=\frac{g_1(r)}{X}\left[\frac{\partial\psi'}{\partial x}\right]_a$, but $-\left[\frac{\partial\psi'}{\partial x}\right]_a=\Delta_R X$ and we have seen in the discussion of the $g_1(r)$ term that to lowest order in ϵ, $\frac{\Delta_R X}{X} \doteq \frac{-\epsilon' q^2}{3(1+q)}$, so it follows that

(C.19) $$\frac{\Delta_R X_{g_5}}{X} = \frac{-\epsilon'^2 q^4}{9(1+q)^2}$$

$g_6(r)$:

(C.20) $$\frac{\Delta_R X_{g_6}}{X} \doteq \frac{-Z_1Z_2R_L}{6\pi\eta(\omega_1+\omega_2)}\left[\frac{1}{\chi^2q^2}\int_a^\infty \frac{dr}{r^5}\, e^{\epsilon\Psi_{12}^{(1)}}\, e^{-\chi r}(1+\chi r)\cdot\right.$$

$$\left.\cdot\left\{e^{-\chi r}(1+\chi r)-1\right\}\left\{e^{-q\chi r}(1+q\chi r)-1\right\}+\frac{a^2}{6}\int_a^\infty\frac{dr}{r^3}\, e^{\epsilon\Psi_{12}^{(1)}}\left(-\frac{\chi^2}{2}\right)\right]$$

$$\doteq \frac{-Z_1Z_2R_L}{6\pi\eta(\omega_1+\omega_2)}\left[\frac{1}{\chi^2q^2}\int_a^\infty\frac{dr}{r^5}\, e^{-\chi r}(1+\chi r)\left\{e^{-\chi r}(1+\chi r)-\right.\right.$$

$$\left.\left.-1\right\}\left\{e^{-q\chi r}(1+q\chi r)-1\right\}+\frac{1}{\chi^2q^2}\int_0^{b'}\frac{du}{u}(e^{u}-1)\left(-\frac{q^2\chi^2}{2}\right)\left(-\frac{\chi^2}{2}\right)-\frac{\chi^2}{12b'^2}\int_0^{b'} du\,u e^{u}\right]$$

$$\doteq \frac{\epsilon'}{4}\;\frac{\chi}{6\pi\eta(\omega_1+\omega_2)}\left[\frac{1-q^2+\frac{5}{2}q}{2q}-\frac{(1-q^2)^2}{2q^2}\ln(1+q)\right.$$

$$\left.+\frac{q^2-4}{2}\ln(2+q)+Ei(b')-2\gamma_E-\ln\epsilon'-\frac{e^{b'}(b'-1)+1}{3b'^2}\right]$$

Here we have used the same substitution $U \equiv -\frac{Z_1 Z_2 R_L}{r}$ as in the evaluation of $\Delta_R X g_1^{(1)}$.

Finally, we add $\Delta_R X g_1^{(1)} + \Delta_R X g_1^{(2)} + \Delta_R X g_{2,3,4} + \Delta_R X g_5 + \Delta_R X g_6$ and obtain (4.34).

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