Correction to the Debye-Hückel Theory*

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The problem of a gas of particles all of the same charge, imbedded in a neutralizing medium of uniformly distributed charge of the opposite sign, is considered in terms of classical statistical mechanics. If a dimensionless parameter ϵ, roughly the inverse of the number of particles contained inside a Debye sphere, is small compared to unity the Debye-Hückel theory is a good first approximation. For this case the corrections in the next order in ϵ are derived for the potential of mean force and the interaction energy. It is shown how this correction has to be modified for very small particle separation; the expansion in powers of ϵ is not strictly a Taylor expansion and factors such as $\ln\epsilon$ appear in the higher terms. Methods are given for numerical calculation of some auxiliary functions even when the parameter ϵ is not small.

1. INTRODUCTION

In a recent paper[1] one of us has discussed cluster expansion methods for calculating the equation of state of a gas of particles interacting with a long-range potential. In this paper some numerical results will be presented for the case of charged particles. We consider N particles, each with charge q, in a box of volume V at a temperature T. The potential of mean force, $w(1,2)$, is defined by:

$$\exp[-w(1,2)]=Q_N^{-1}V^2\int\cdots\int d3\cdots dN \times\exp[-\sum_{1\le i<j\le N} u(i,j)],$$

where

$$Q_N=\int\cdots\int d1\cdots dN\exp[-\sum_{1\le i<j\le N} u(i,j)],$$

$u(i,j)\equiv U(\mathbf{r}_{ij})/kT$, $U(\mathbf{r}_{ij})$ being the interaction potential. $\int dj$ denotes integration of the vector position coordinate of particle j over the volume V. In reference 1 it was shown how $w(1,2)$ can be written as a cluster expansion in terms of a function $\Gamma(1,2)$ defined by the integral equation

$$\Gamma(1,2)=f(1,2)+\rho\int d3\, f(1,3)\Gamma(2,3), \qquad (1)$$

where $\rho=NV^{-1}$ is the particle density and

$$f(1,2)\equiv\exp[-u(1,2)]-1.$$

Γ is a scalar function of a single vector variable, the interparticle distance γ_{ij}. The potential of mean force can be written

$$w(1,2)=u(1,2)+f(1,2)-\Gamma(1,2)-X(1,2) \qquad (2)$$

where X consists of an infinite sum of multiple integrals. Each multiple integral corresponds to some "simple 12-irreducible, wiggly line" diagram. These diagrams are defined and discussed in reference 1 and some examples are given in Fig. 6 of that paper. The integrand of each multiple integral involves some combination of the functions Γ and f.

We consider only the special case of the Coulomb potential between particles of identical charge q (imbedded in a uniform neutralizing medium), so that $u(i,j)=q^2/r_{ij}kT$. It is convenient to introduce the Debye length λ_D as the unit of length and to define a dimensionless parameter ϵ,

$$\begin{aligned}&R\equiv r_{ij}/\lambda_D,\quad \lambda_D=(4\pi q^2\rho/kT)^{-\frac{1}{2}},\\ &\epsilon\equiv q^2/\lambda_D kT=(4\pi\rho\lambda_D{}^3)^{-1}=(4\pi)^{\frac{1}{2}}(q^2\rho^{\frac{1}{3}}/kT)^{\frac{3}{2}}.\end{aligned} \qquad (3)$$

The ratio of the Coulomb potential energy to the thermal energy is thus of the order of ϵ for separations of the order of the Debye length and is of order $\epsilon^{\frac{2}{3}}$ for separations of the order of the "interparticle distance" $\rho^{\frac{1}{3}}$. In this notation $u(1,2)=\epsilon/R$.

For a fixed value of R, the function f in Eq. (1) approaches $-u(1,2)=-\epsilon/R$ as ϵ approaches zero. In this limit $\Gamma(1,2)$ approaches the Debye-Hückel correlation function

$$\Gamma_0(1,2)=(-q^2/kTr_{1,2})\exp(-r_{12}/\lambda_D)=-(\epsilon/R)e^{-R}. \quad (4)$$

When ϵ is small the successive groups of cluster terms represent, at least in a certain sense, an expansion in powers of ϵ. The order of magnitude of a diagram containing l lines and k points is ϵ^{l-k}, since each line is of order ϵ and each integration gives a factor of order $\lambda_D{}^3\rho\sim\epsilon^{-1}$. We do not discuss the question of the rapidity of convergence of the higher terms in this expansion. However, we investigate another point which illustrates the fact that our expansion in powers of ϵ is not strictly a genuine Taylor expansion: for values of R in the range $\epsilon\ll R\ll 1$ we shall encounter no difficulty and are able to expand Γ in powers of ϵ, the first term being Γ_0; but for $R\lesssim\epsilon$, this expression fails and we have to modify the calculation.

In Sec. 2 we describe the evaluation of Γ up to second order in ϵ; including expressions valid for $R\ll\epsilon$.

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[1] E. E. Salpeter, Ann. Phys. 5, 183 (1958).

In this section we also describe numerical evaluations of $\Gamma(R)$ for any value of ϵ. In Sec. 3 we discuss the evaluation of the potential of mean force, $w(R)$, and of the correlation energy up to second order in ϵ. In Sec. 4 we discuss other auxiliary functions of R which contain partial summations of higher order cluster terms and can be evaluated numerically. Results are summarized in Sec. 5.

It should be remembered that the problem investigated in this paper is somewhat of an academic question, since in any real problem with particles of positive charge, the negative neutralizing charge is of course also in the form of particles and not a uniform charge distribution. We could not investigate such a problem with the methods of the present paper which are based on classical statistical mechanics and "take seriously" the infinite potential at zero interparticle separation. For infinite attractive potentials any rigorous classical theory gives divergences which can only be eliminated by quantum mechanics. Apart from the academic interest of investigating a simple classical problem in detail, there are some practical problems in which particles of one sign contribute most to the correlation energy. For instance, in the ionized hydrogen gas in the interior of a very faint red dwarf star the electrons are fairly degenerate, with Fermi energy very much larger than the ionization potential of hydrogen. The electrons are then uniformly distributed to a fairly good approximation. The protons, on the other hand, are quite nondegenerate, so that classical statistical mechanics should be a fairly good approximation and our dimensionless parameter ϵ for the protons is slightly smaller than unity.

2. EVALUATION OF THE FUNCTION Γ

First we wish to show that the solution $\Gamma(R)$ of the integral equation (1) can be expressed in closed form in terms of a one-dimensional integral for any value of ϵ. We denote by $X(k)$ the three-dimensional Fourier transform of any spherically symmetric function $X(R)$.

$$X(k)=(4\pi/k)\int_0^\infty dr\, r\sin(kr)X(r),$$

$$X(R)=(2\pi^2R)^{-1}\int_0^\infty dk\, k\sin(kr)X(k).$$

The Fourier transform of Eq. (1) is then simply

$$\Gamma(k)=f(k)[1-\rho f(k)]^{-1}. \tag{5}$$

For large R the function $f(R)=e^{-u(R)}-1$ approaches $-u(R)$ and its Fourier transform is not well defined. We therefore use the usual procedure of replacing the Coulomb potential by a Yukawa potential, $u(R)=-(\epsilon/R)e^{-\alpha R}$, and let α tend to zero after evaluating the Fourier transform. This yields

$$f(k)=-(4\pi\epsilon/k^2)2ker_2\eta,\quad \eta\equiv(4\epsilon k)^{\frac{1}{2}}. \tag{6}$$

Substituting Eq. (6) into Eq. (5) we obtain from the inverse Fourier transform the desired result

$$\Gamma(R)=-\frac{2}{\pi}\frac{\epsilon}{R}\int_0^\infty dk\, k\frac{2ker_2\eta}{k^2+2ker_2\eta}\sin(kR). \tag{7}$$

Expression (7) for $\Gamma(R)$ can be evaluated numerically for any given values of ϵ and R, using tabulated[2] values of $ker_2\eta$. Such numerical evaluations were carried out for several values of ϵ and R. The results are plotted in Fig. 7 and discussed in Sec. 5.

For small k we can use the expansion of $ker_2\eta$ to get an expansion for $\Gamma(k)$ in positive powers of k and ϵ,

$$\begin{aligned}2ker_2\eta&=1-(\pi/16)\eta^2-(1/48)\eta^4\ln\eta+O(\eta^4),\\ \Gamma(k)&=-(4\pi\epsilon/k^2)[1-k^2-(\pi/4)\epsilon k^3-\tfrac{1}{6}\epsilon^2k^4\ln k\cdots].\end{aligned} \tag{8}$$

By carrying out the Fourier transform[3] of successive terms in this expansion, we obtain an asymptotic expansion for $\Gamma(R)$, the first few terms of which are

$$\Gamma(R)\approx 12\epsilon^2R^{-6}-20\epsilon^3R^{-7}+O(\epsilon^2R^{-8}\ln R). \tag{9}$$

This asymptotic expansion in inverse powers of R is a good approximation for any value of ϵ as long as $R\gg\epsilon$ as well as $R\gg 1$. Unlike the Debye-Hückel approximation $\Gamma_0(R)=-(\epsilon/R)e^{-R}$, the exact function $\Gamma(R)$ for finite values of ϵ does not fall off exponentially with R but only as R^{-6}. This falloff is still sufficiently fast for all integrals in the higher cluster terms to converge.

We now restrict ourselves to cases where $\epsilon\ll 1$ and attempt to express $\Gamma(R)$ in terms of an expansion in powers of ϵ. Let $f_0(R)=-u(R)=-\epsilon/R$ and

$$\Gamma_1(R)=\Gamma(R)-\Gamma_0(R);\qquad f_1(R)=f(R)-f_0(R)=e^{-\epsilon/R}-1+\epsilon/R, \tag{10}$$

where Γ_0 is the solution of the integral equation, Eq. (1), when f is replaced by f_0 and is given explicitly in Eq. (4). $\Gamma_1(k)$ and $\Gamma_0(k)$ are the three dimensional Fourier transform of $\Gamma_1(R)$ and $\Gamma_0(R)$, respectively, and

$$\Gamma_0(k)=f_0(k)[1-\rho f_0(k)]^{-1}.$$

From Eq. (5) we have $\Gamma_1(k)=\Gamma(k)-\Gamma_0(k)=f_1(k)\times[1-\rho f(k)]^{-1}[1-\rho f_0(k)]^{-1}$. Using the identity

$$[1-\rho f_0(k)][1+\rho\Gamma_0(k)]=1,$$

we find

$$\begin{aligned}\Gamma_1(k)&=f_1(k)[1+\rho\Gamma_0(k)]^2[1-Y(k)]^{-1},\\ Y(k)&\equiv\rho f_1(k)[1+\rho\Gamma_0(k)].\end{aligned} \tag{11}$$

Using Eq. (6) and the fact that $f_0(k)=-4\pi\epsilon k^{-2}$, one

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[2] For definition and tables of the ker_2 function, see H. B. Dwight, *Tables of Integrals* (The Macmillan Company, New York, 1949).

[3] For details of the evaluation, particularly the treatment of the term in $\ln k$, see M. J. Lighthill, *An Introduction to Fourier Analysis and Generalized Functions* (Cambridge University Press, New York, 1958), Chap. 4.

can show that

$$Y(k)=(1-2ker_2\eta)(1+k^2)^{-1}.$$

$Y(k)$ reduces to $\epsilon\pi k/4(1+k^2)$ when $\epsilon k\ll 1$ and $Y(k)$ is less than $(1+k^2)^{-1}$ for all ϵ and k. If $\epsilon\ll 1$, then the maximum value of Y is approximately $\frac{1}{8}\pi\epsilon$ and the Taylor expansion of Eq. (11),

$$\Gamma_1(k)=f_1(k)[1+\rho\Gamma_0(k)]^2\sum_{n=0}^{\infty}Y^n(k), \qquad (12)$$

converges rapidly. Substituting the form of $Y(k)$ given in Eq. (11) into Eq. (12) and taking the Fourier transform, we obtain the desired expression, an expansion for $\Gamma_1(R)\equiv\Gamma_1(1,2)$ in terms of an infiite series of multiple integrals,

$$\Gamma_1(1,2)=\sum_{n=0}^{\infty}\Gamma_1^{(n)}(1,2),$$

$$\begin{aligned}\Gamma_1^{(0)}(1,2)&-f_1(1,2)\\ &=2\rho\int d3\,\Gamma_0(1,3)f_1(3,2)\\ &\quad+\rho^2\int\int d3d4\,\Gamma_0(1,3)f_1(3,4)\Gamma_0(4,2),\end{aligned} \qquad (13)$$

$$\Gamma_1^{(1)}(1,2)=\rho\int d3\,f_1(1,3)f_1(2,3)+\cdots.$$

The remaining terms of $\Gamma_1^{(1)}$ and all terms of $\Gamma_1^{(2)}$, etc., involve integrals over two or more spatial variables. Any term in $\Gamma_1^{(n)}$ involves in its integral the product of $n+1$ factors f_1.

Keeping $\epsilon\ll 1$ we first consider the range $R\gg\epsilon$ (but not necessarily $R>1$). For this range we make the approximation of replacing f_1 wherever it occurs in Eq. (13) by the first term of its Taylor expansion in powers of ϵ, i.e., by

$$f_1(r)\approx\epsilon^2/2r^2. \qquad (14)$$

Carrying out the integrations in Eq. (13) after making this substitution gives

$$\begin{aligned}\Gamma_1^{(0)}(R)&-f_1(R)\\ &=(\epsilon^2/8R)[(R-3)e^{-R}E_i(R)-(R+3)e^RE_-(R)],\end{aligned} \qquad (15)$$

where

$$E_i(R)=\int_{-\infty}^{R}dx\,x^{-1}e^{-x},\quad E_-(R)=\int_R^{\infty}dx\,x^{-1}e^{-x}.$$

For $R\gg 1$, Eq. (15) becomes asymptotically $\Gamma_1^{(0)}(R)=12\epsilon^2R^{-6}$ which is simply the first term in our more general asymptotic expansion, Eq. (9). For $R\lesssim 1$, the right-hand side of Eq. (15) is of order $\epsilon^2(1+|\ln R|)$ and the error caused by the substitution of Eq. (14) is of relative order ϵ/R. In this range of $R\lesssim 1$, $\Gamma_1^{(1)}$ is of order $\epsilon^3(1+R^{-1})$ and $\Gamma_1^{(n)}$ is of order ϵ^{n+2} for $n\geq 2$. As long as $R\gg\epsilon$, we can replace Γ_1 by $\Gamma_1^{(0)}$ and use the expression (15) for $\Gamma_1^{(0)}$, the error being only of relative order ϵ for $R>1$, and order ϵ/R for $R<1$.

For all terms in the infinite series in Eq. (13) which involve integrations over two or more variables, the important range of each variable r_{ij} is of order unity, however small R is. The substitution of Eq. (14) in these integrals is then a good approximation for all values of R (always with $\epsilon\ll 1$).

However, there are just two terms in the series, each of which involves an integral over a single variable. For these two integrals one important range of integration is $r_{13}\sim r_{32}\sim r_{12}$, so that the approximation of Eq. (14) is inadmissable for $R\lesssim\epsilon$ and the exact expression $f_1(R)=e^{-\epsilon/R}-1+\epsilon/R$ must be used. In this range we have $R\ll 1$, since $\epsilon\ll 1$. Using this exact expression for f_1, but neglecting terms of order R^3 or higher, we find for the relevant integral in $\Gamma_1^{(0)}$

$$\begin{aligned}J(R)&\equiv 2\rho\int d3\,\Gamma_0(1,3)f_1(3,2)\\ &\approx\epsilon^2[(1+R^2/6)(\ln\epsilon+2C-\tfrac{3}{2})+\phi_1(R/\epsilon)\\ &\qquad+\tfrac{1}{6}R^2\phi_2(R/\epsilon)],\end{aligned} \qquad (16)$$

where $C\equiv-\psi(1)=0.57722$ and

$$\begin{aligned}\phi_1(x)&=x-\tfrac{1}{3}x^2+[1+\tfrac{1}{3}x^{-1}]E_-(x^{-1})\\ &\qquad+\tfrac{1}{3}(x^2-2x-1)\exp(-x^{-1}),\\ \phi_2(x)&=\tfrac{1}{2}x-\tfrac{1}{10}x^2+[1+x^{-1}+\tfrac{1}{4}x^{-2}+(60x^3)^{-1}]\\ &\quad\times E_-(x^{-1})+(1/60)\\ &\quad\times(60x^2-24x-47-14x^{-1}-x^{-2})\exp(-x^{-1}).\end{aligned} \qquad (17)$$

Although the other terms in $\Gamma_1^{(1)}$ are of order ϵ^3, the term shown in Eq. (13) is actually of order $\epsilon^3/(R+\epsilon)$ and must be included for very small values of R. We find

$$\begin{aligned}\rho\int d3\,f_1(1,3)f_1(2,3)&\equiv\epsilon^2F(R/\epsilon),\\ F(x)=\tfrac{1}{2}x^{-1}\int_0^{\infty}du\,uf_1(u)&\int_{|x-u|}^{x+u}dy\,yf_1(y).\end{aligned} \qquad (18)$$

We finally obtain for $R\ll 1$, neglecting terms of relative order R^3 and ϵ,

$$\begin{aligned}\Gamma_1(R)&-f_1(R)\\ &=\epsilon^2\{\ln\epsilon-0.0956+R^2[\tfrac{1}{12}\ln R+\tfrac{1}{6}\ln\epsilon-0.1206]\\ &\qquad+\phi_1(R/\epsilon)+F(R/\epsilon)+\tfrac{1}{6}R^2\phi_2(R/\epsilon)\}.\end{aligned} \qquad (19)$$

The functions ϕ_1, ϕ_2 and F are plotted in Fig. 1. For $x\ll 1$ one finds $\phi_1(x)\simeq x-\frac{1}{3}x^2$, $\phi_2(x)\simeq\frac{1}{2}x-\frac{1}{10}x^2$, $F(x)\simeq\frac{4}{3}\ln 2-\frac{1}{3}-\frac{1}{2}x+\frac{1}{4}x^2$ so that for $R\ll\epsilon$ Eq. (19) reduces to (neglecting R^2/ϵ^2 and higher terms)

$$\Gamma_1(R)-f_1(R)\simeq\epsilon^2(\ln\epsilon+0.4953+R/2\epsilon). \qquad (20)$$

For $\epsilon\ll R\ll 1$,

$$\phi_1(x)\simeq\ln x-0.0772+x^{-1}(\tfrac{1}{3}\ln x+0.7520),$$

$$\phi_2(x)\simeq\ln x-0.9106+x^{-1}(\ln x+0.9894),$$

$$F(x)\simeq\pi^2/16x,$$

so that in this range (neglecting ϵ^2/R^2, R^3 and higher terms)

$$\Gamma_1(R)-f_1(R)\simeq\epsilon^2\{\ln R-0.1728+(\epsilon/R)(\tfrac{1}{3}\ln(R/\epsilon)+1.3689)+R^2[\tfrac{1}{4}\ln R-0.2724]\}. \quad (21)$$

If the term in ϵ/R is neglected, then Eq. (21) reduces to the first few terms in the expansion in powers of R for the expression in Eq. (15).

3. SECOND ORDER APPROXIMATION TO w AND THE INTERACTION ENERGY

The two-body correlation function of greatest physical interest is usually $w(1,2)$, the "potential of mean force." It is mentioned in Sec. 1 and discussed in more detail in reference 1. $w(1,2)$ is related to the auxiliary function $\Gamma(1,2)$ by Eq. (2), where $X(1,2)\equiv\sum_{\nu=2}^{\infty}X_\nu(1,2)$ consists of an infinite sum of multiple integrals, each one related to some "simple 12, irreducible, wiggly line" cluster diagram. In the corresponding integral each single wiggly line stands for Γ and n wiggly lines in parallel stand for the expression

$$(n!)^{-1}\delta_1{}^n+[(n-1)!]^{-1}f\delta_1{}^{n-1},\qquad \delta_1(1,2)\equiv\Gamma(1,2)-f(1,2). \quad (22)$$

The order of magnitude of a diagram containing l wiggly lines and k points (other than the end points, which are not integrated over) is ϵ^{l-k}. We write $w(1,2)=\omega_0(1,2)+w_1(1,2)$, where $\omega_0(R)\equiv-\Gamma_0(R)=(\epsilon/R)e^{-R}$. We are interested in the correction w_1 only to its lowest order in ϵ, i.e., second order. To this order we have

$$\begin{aligned} w(1,2)&\approx f_1(1,2)-\Gamma(1,2)-X_2(1,2),\\ -w_1(1,2)&\approx[\Gamma_1(1,2)-f_1(1,2)]+X_2(1,2), \end{aligned} \quad (23)$$

where X_2 stands for all diagrams with $l-k=2$. The diagrams are shown in Fig. 2, and we have

$$X_2(1,2)=\rho\int d3\,\Gamma(1,3)[\Gamma^2(3,2)-f^2(3,2)]+\tfrac{1}{2}\rho^2\int d3\int d4\,\Gamma(1,3)\Gamma(4,2)[\Gamma^2(3,4)-f^2(3,4)].$$

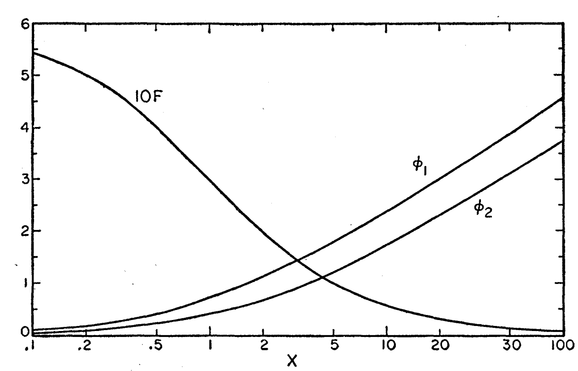

FIG. 1. The functions ϕ_1, ϕ_2, and F.

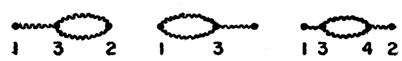

FIG. 2. All diagrams with $l-k=2$. These give the quantity X_2.

We need to evaluate X_2 only to lowest order in ϵ and therefore replace Γ by Γ_0 and f by f_0 in the integrals in Eq. (24). For these integrals (and any integrals for the higher terms X_ν) the range of integration $r_{ij}\sim\epsilon\ll 1$ is *not* of great importance even when $R\equiv r_{12}<\epsilon$. The integrals with or without these substitutions converge even when $R\to 0$ and the substitution of Γ by Γ_0 and f by f_0 causes no trouble for any value of R. With these substitutions the integrals in Eq. (24) can be carried out analytically and give

$$\begin{aligned} X_2(1,2)=(\epsilon^2/8R)\{&e^{-R}[\tfrac{4}{3}(e^{-R}-1)\\ &+(3-R)(E_-(R)+E_i(R)-\ln 3)]\\ &+e^R(3+R)[E_-(R)-E_-(3R)]\}. \end{aligned} \quad (24)$$

We now have to substitute this expression into Eq. (23), using for $\Gamma(1,2)$ the expression from Sec. 2 appropriate to the particular range of R, i.e., Eq. (15) if $R\gg\epsilon$, Eq. (19) if $R\ll 1$.

If Eq. (15) is appropriate it is interesting to note that our expression for $w_1(1,2)$ reduces to

$$w_1(R)=-(\epsilon^2/4\pi)\int d3\,\Gamma_0(1,3)\Gamma_0{}^2(3,2)+(\epsilon^2/2\pi^2)\int d3\int d4\,\Gamma_0(1,3)\Gamma_0{}^2(3,4)\Gamma_0(4,2),$$

which was first derived by Strel'tsova using an integral equation attack.[4]

We finally give the simplified forms our expressions for $w_1(R)$ take on when the various inequalities apply.

$$R\ll\epsilon:\quad w_1(R)=-\epsilon^2[\ln\epsilon+1.427+R/2\epsilon], \quad (25a)$$

$$\epsilon\ll R\ll 1:\quad w_1(R)=-\epsilon^2[\ln R+0.7592-R+R^2(\tfrac{1}{4}\ln R+0.3078)+(\epsilon/R)\times(\tfrac{1}{3}\ln(R/\epsilon)+1.3689)], \quad (25b)$$

$$\begin{aligned} R\gg 1:\quad w_1(R)=(\epsilon^2/8R)\{&e^{-R}[\tfrac{4}{3}(1-e^{-R})\\ &+(R-3)(E_-(R)-\ln 3)]\\ &+e^R(3+R)E_-(3R)\}\sim\epsilon^2e^{-R}\\ &\times[-0.1373+0.5786R^{-1}+O(\epsilon^{-R})], \end{aligned} \quad (25c)$$

The last expression shows that $w_1(R)$ falls off exponentially for large R, the R^{-6} term in $\Gamma-f$ having been cancelled by an equal and opposite term in X_2.

One of the quantities of interest one can compute from the potential of mean force is the correction energy due to the electrostatic interaction. It is defined as the sum of the mean of all the pairwise interaction

[4] E. A. Strel'tsova, Zhur. Eksp. i. teoret. Fiz. 26, 173 (1954).

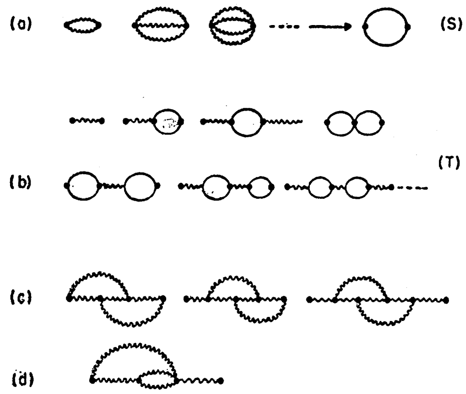

FIG. 3. (a) Diagrams forming the function S. (b) Diagrams forming the function T. (c) Lowest order diagrams not included in T, or T'. (Order ϵ^3.) (d) Lowest order diagrams in T' but not in T. (Order ϵ^3.)

energies per particle.

$$E_{\text{corr}}=(N/2V)\int d2\, U(1,2)[\exp(-w(1,2))-1]$$
$$=(kT/8\pi\epsilon)\int d\mathbf{R}\, u(R)[\exp(-w(R))-1], \quad (26)$$
$$E_{\text{corr}}/kT=\frac{1}{2}\int_0^\infty dR\, R[\exp(-w(R))-1].$$

The -1 in the integrand is from the interaction with the uniform background charge of opposite sign. To obtain the correlation energy through order ϵ^2 it is sufficient to compute

$$E_{\text{corr}}/kT=-\frac{1}{2}\int_0^\infty dR\, R\{w_0(R)+w_1(R)+[1-\exp(-w_0(R))-w_0(R)]\},$$

and use expression (25c) for w_1. The integrations can be carried out analytically. One obtains

$$E_{\text{corr}}/kT=-\tfrac{1}{2}\epsilon-\tfrac{1}{2}\epsilon^2[\tfrac{1}{2}\ln\epsilon+(C-\tfrac{2}{3}+\tfrac{1}{2}\ln 3)]. \quad (27)$$

The numerical value of the coefficient in round brackets

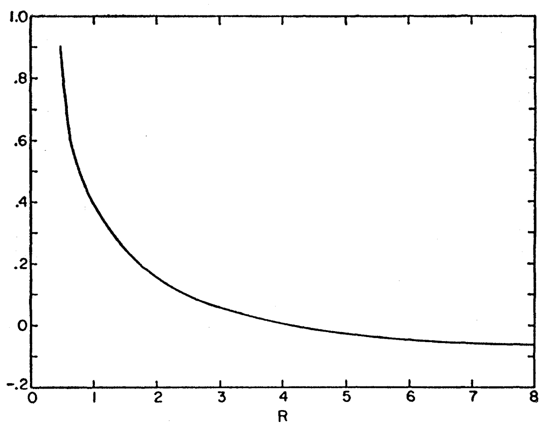

FIG. 4. The function $\epsilon^{-2}e^{R}w_1(R)$.

is 0.460. The first term of Eq. (27) is given by the Debye-Hückel theory.[5]

4. FURTHER SUMMATIONS

It is possible to sum explicitly certain sets of simple chain diagrams. Define $S(R)$ to be the contribution from the series of diagrams shown in Fig. 3(a).

$$S(R)=[1+f(R)]\{\exp[\Gamma(R)-f(R)]\}-1-\Gamma(R)$$
$$=\exp[\Gamma(R)-f_1(R)]-1-\Gamma(R). \quad (28)$$

Now we let $A(R)\equiv S(R)+f_1(R)$ and define $T(R)$ to be the contribution from the series of chains shown in Fig. 3(b). The Fourier transform of $T(R)$ is

$$T(k)=\Gamma(k)+\sum_{n=1}^{\infty}\rho^{n-1}S^n(k)[1+\rho\Gamma(k)]^{n+1}$$
$$=\Gamma(k)+S(k)[1+\rho\Gamma(k)]^2\{1-\rho S(k)[1+\rho\Gamma(k)]\}^{-1}.$$

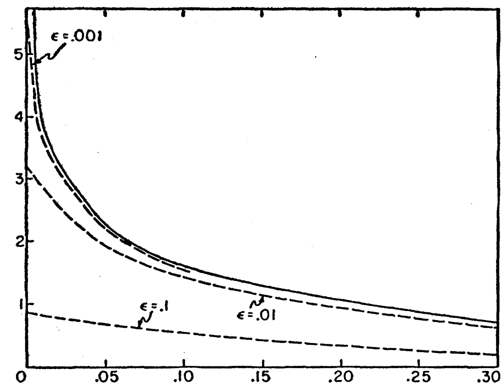

FIG. 5. The function $\epsilon^{-2}w_1(R)$ for small R using "small R approximation" for three values of ϵ (dashed curve). The "large R approximation," independent of ϵ (solid curve).

After some manipulation,

$$T(k)=\frac{S(k)+f(k)}{1-\rho[S(k)+f(k)]}=\frac{f_0(k)+A(k)}{1-\rho f_0(k)-\rho A(k)}. \quad (29)$$

Comparison with Eq. (5) shows that $T(k)$ is similar to $\Gamma(k)$. If in the formulas for $\Gamma(k)$ we replace $f_1(k)$ by $A(k)$ we obtain $T(k)$. Now $A(R)\sim f_1^2(R)\sim\epsilon^4R^{-4}$ for large R. Using this fact it can be shown that the leading nonexponential term in $T(R)$ varies asymptotically as ϵ^4R^{-10}.

One can write the diagrams now in terms of "T-lines" instead of "Γ-lines." A diagram with n "T-lines" in parallel will stand for

$$(n!)^{-1}[T-(S+\Gamma)]^n+[(n+1)!]^{-1}[S+\Gamma][T-(S+\Gamma)]^{n-1}$$

in exact analogy with the rule for "Γ-lines," Eq. (22).

[5] The expression of our Eq. (27) has also been obtained by R. Abe, Progr. Theoret. Phys. (Kyoto) **22**, 213 (1959) by a somewhat different method which does not involve the explicit evaluation of the correlation function $w(R)$. See also E. Meeron, J. Chem. Phys. **26**, 804 (1957).

Furthermore, corresponding to Eq. (2), we have

$$\begin{aligned} w(1,2) &= f_1(1,2) - [T(1,2) - S(1,2)] - X_T(1,2) \\ &= A(1,2) - T(1,2) - X_T(1,2), \end{aligned} \tag{30}$$

where X_T is the sum of "simple 12, irreducible T-line" diagrams. Note that $A-T$ contains all the terms of X_2 (Fig. 2) and that the leading terms of X_T are of order ϵ^3 (for $\epsilon \ll 1$). These arise from the diagrams shown in Fig. 3(c). It is possible to sum the "T-lines" exactly in the same way. Define $S'(R)$, $T'(R)$ to be the contribution from diagrams like those in Figs. 3(a), 3(b), respectively, with "T-lines" replacing the "Γ-lines." We find

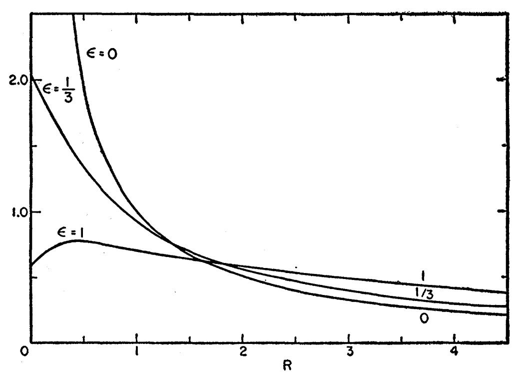

FIG. 6. The function $-\epsilon^{-1}e^R\Gamma(R)$ for $\epsilon=0$, $\frac{1}{3}$, 1.

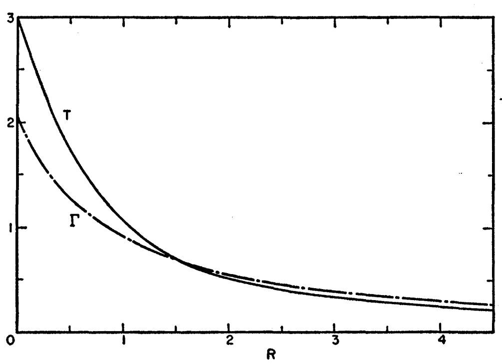

FIG. 7. The functions $\Gamma(R)$ and $T(R)$, each multiplied by $\epsilon^{-1}e^R$ for $\epsilon=\frac{1}{3}$.

$$\begin{aligned} S'(R) &= [1+S(R)+\Gamma(R)] \\ &\quad \times \exp[T(R)-S(R)-\Gamma(R)] - 1 - T(R) \\ &= \exp[T(R)-A(R)] - 1 - T(R), \end{aligned} \tag{31}$$

$$T'(k) = \frac{f_0(k)+A'(k)}{1-\rho f_0(k)-\rho A'(k)}, \tag{32}$$

where

$$\begin{aligned} A_1'(1,2) &= S'(1,2) + A(1,2); \\ w(1,2) &= A'(1,2) - T'(1,2) - X_{T'}, \end{aligned} \tag{33}$$

with $X_{T'}$ being the sum of "simple 12, irreducible T'-line" diagrams. T' contains T and the leading terms in T' that are not in T (for $\epsilon \ll 1$) arise from the diagrams shown in Fig. 3(c). These are of order ϵ^3. The leading terms in $X_{T'}$, like those in X_T, are those from the diagrams in Fig. 3(c).

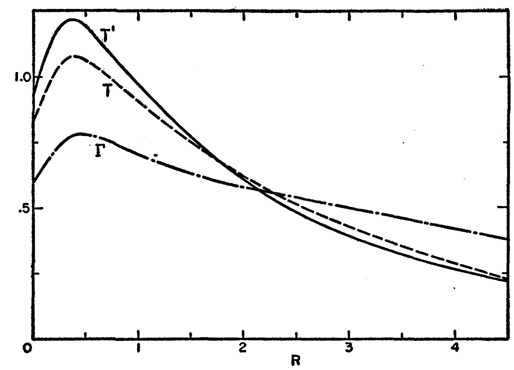

FIG. 8. The functions $\Gamma(R)$, $T(R)$, and $T'(R)$, each multiplied by $\epsilon^{-1}e^R$ for $\epsilon=1$.

This process can be carried on *ad infinitum*. Hopefully the sequence T, T', $\cdots$ will converge, and the limit function, T^∞, can be used in the evaluation of diagrams of higher connectivity, like those in Fig. 3(c). These equations are equivalent to those derived by Meeron and Rodemich.[6]

We have calculated $T(R)$, $A(R)$ and $T'(R)$, $A'(R)$ numerically for the coulomb case for $\epsilon=\frac{1}{10}$, $\frac{1}{3}$, 1. $\Gamma(R)$ was found by performing numerically the integral indicated in Eq. (7), using tabulated values of the ker_2 function. $A(R)$ is then given by Eq. (28) and from it $A(k)$ computed. Equation (29) is used to obtain $T(k)$ and one more numerical transform gives $T(R)$. Similarly, $T(R)$ and $A(R)$ into Eq. (31) give $A'(R)$; its transform into Eq. (32) gives $T'(k)$ and a final integration provides $T'(R)$, The results are shown in Figs. 7, 8, and 9 and will be discussed in the next section.

5. DISCUSSION OF RESULTS

We discuss first our results for the potential of mean force $w(R)$, where R is the distance between two charges

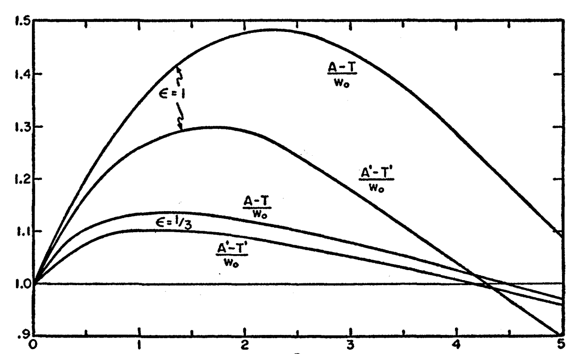

FIG. 9. The functions $(A-T)/w_0$ and $(A'-T')/w_0$, plotted against R for $\epsilon=\frac{1}{3}$ and for $\epsilon=1$.

[6] E. Meeron and R. R. Rodemich, Phys. Fluids **1**, 246 (1958). E. Meeron, J. Math. Phys. (in press) has demonstrated the convergence except at isolated singularity points.

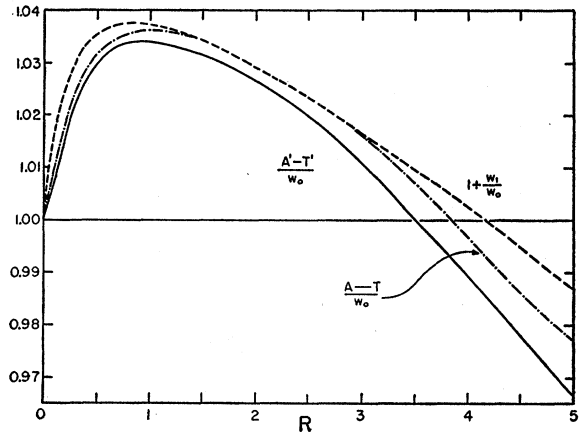

FIG. 10. The functions $(A-T)/w_0$, $(A'-T')/w_0$, and $1+w_1/w_0$, plotted against R for $\epsilon=0.1$.

expressed in Debye radii, up to and including second order in the small parameter ϵ. To first order we have simply the Debye-Hückel expression $w_0=(\epsilon/R)e^{-R}$. The second order correction w_1 is given by Eq. (24). For $\epsilon \ll R$, Γ_1 is given by Eq. (15) and the resulting expression for $\epsilon^{-2}w_1(R)$ is then independent of ϵ. This expression is plotted against R in Fig. 4. It should be noted that the "nearest neighbor distance" $\rho^{-\frac{1}{3}}$ corresponds in our units to $R\sim\epsilon^{\frac{1}{3}}$, so that for small ϵ values of $R\sim\epsilon$ correspond to particle separations much less than $\rho^{-\frac{1}{3}}$.

For values of R which are not necessarily large compared with ϵ, but for $R\ll 1$, w_1 is given by Eq. (23) with Γ_1 taken from Eq. (19). The functions $\phi_1(x)$, $\phi_2(x)$ and $F(x)$ in this expression are plotted in Fig. 1. $\epsilon^{-2}w_1$ taken from this expression is plotted against R for a few different values of ϵ in Fig. 5. For comparison the "large R approximation" to w_1, using Eq. (14) is also given which would be appropriate for all R only if $\epsilon\to 0$. For a finite but small value of ϵ, both approximations Eq. (14) and Eq. (19) are quite good in the range $\epsilon\ll R\ll 1$ and the leading terms in both expressions are identical. The relative errors in Eq. (19) are of order R^3, those in Eq. (14) of order ϵ/R; so that Eq. (19) is more reliable if $R<\epsilon^{\frac{1}{4}}$, Eq. (14) if $R>\epsilon^{\frac{1}{4}}$.

For the auxiliary function $\Gamma(R)$ we have found, besides the approximations Eq. (14) and (19), which are valid only if $\epsilon\ll 1$, a method of numerical evaluation for any value of ϵ. The results of such evaluations for $-\epsilon^{-1}e^{R}\Gamma(R)$ are plotted in Fig. 6 for $\epsilon=\frac{1}{3}$ and 1. Also shown is this expression for $\epsilon=0$ which is simply the function R^{-1}. As the graph shows $\epsilon^{-1}\Gamma(R)$ does not deviate very strongly from e^{-R}/R for moderate values of R, and ϵ smaller than one. Note however that $\epsilon^{-1}\Gamma(R)$ is finite at the origin (unlike R^{-1}) and of order ϵ^{-1} and that for very large R the function $\Gamma(R)$ does not decrease exponentially but only with the sixth power of R.

We have computed numerically the additional auxiliary functions $T(R)$ and $T'(R)$ which include in them further infinite subsets of diagrams. As shown in Figs. 7 and 8, $T(R)$ is of the same order of magnitude as $\Gamma(R)$ for moderate R, and the smaller ϵ, the nearer $T(R)$ is to $\Gamma(R)$. Similarly $T'(R)$ approaches $T(R)$ even more closely. For $\epsilon=\frac{1}{3}$, $T'(R)$ is everywhere within 2% of $T(R)$. For $\epsilon=1$, they differ at most by 10%. Evidently even for $\epsilon=1$ the sequence T, T', $\cdots$ seems to converge rapidly.

We see from Eqs. (30) and (32) that the functions $A(R)-T(R)$ and $A'(R)-T'(R)$ are approximations to $w(R)$, although we must remember in both cases we are omitting terms of the order ϵ^3. These functions are shown in Fig. 9, taken as ratios to the first order approximation $w_0(R)$. The ratio does not vary far from unity. Notice that for $\epsilon=\frac{1}{3}$, the maximum deviation of $A-T$ from w_0 is about 10% which is approximately ϵ^2 and $A'-T'$ differs from $A-T$ by at most 3% which is about ϵ^3 (see Fig. 10). This is just what one would expect. We are led to suspect that $w(R)$ stays rather near $w_0(R)$ even for moderately large values of ϵ but we can say nothing rigorous, for although we have included several infinite series of diagrams in T', many more remain.

TABLE I. Results of successive approximations to $u(0)-w(0)$ for different values of ϵ.

ϵ	From w_0	From small R 2nd order approx.	From $T-A$	From $T'-A'$
0.1	0.100	0.091	0.085	0.086
0.33	0.33	0.37	0.24	0.25
1	1.00	2.43	0.56	0.60

TALBE II. Various approximations for the quantity $-2E_{\rm corr}/kT$ for three values of ϵ.

ϵ	1st order approx.	2nd order approx.	w_0	Numerical $A-T$	$A'-T'$
0.1	0.1000	0.0931	0.0889	0.0905	0.0904
0.33	0.333	0.323	0.258	0.279	0.274
1	1.000	1.460	0.625	0.792	0.778

A quantity of some interest is $w(0)-u(0)$, the potential at a particle due to the average polarized charge cloud about it. This quantity has been computed using our four approximations to $w(R)$ and the results are shown in Table I. Again $T-A$ and $T'-A'$ give very similar results, even for $\epsilon=1$.

Another quantity of interest is the energy $E_{\rm corr}$, defined in Eq. (26). In Table II values are given for this quantity as obtained from the first and second order approximations in Eq. (27) which involved also expansions of the exponential in the integrand of Eq. (26). Values are also given (the last three columns) as obtained by numerical integration of Eq. (26) using w_0, $A-T$ and $A'-T'$, respectively, as approximations for w.