

## Surface Tension of Ionic Solutions

FRANK P. BUFF AND FRANK H. STILLINGER, JR.

Chemistry Department, University of Rochester, Rochester, New York

(Received August 24, 1955)

As an illustration of the molecular theory of surface regions, the singlet and pair distribution functions are evaluated for very dilute ionic solutions. When they are substituted into the statistical mechanical formulas for surface tension, expressions are obtained for the increase in surface tension over that of the pure solvent. The results of the theory are in better agreement with experiment than the earlier calculation of Onsager and Samaras, which was based on integration of the Gibbs adsorption equation. Finally, the distribution function approach is simply related to Mayer's recent virial coefficient theory for strong electrolyte solutions.

## I.

THE initial evaluation of the surface tension of strong electrolyte solutions was carried out by Wagner<sup>1</sup> in the early days of the Debye-Hückel theory. He employed the Poisson-Boltzmann equation for the calculation of the superficial excess, which, in connection with a numerical integration of the Gibbs adsorption equation, yielded the increase in surface tension over that of the pure solvent. On the basis of minor simplifications, Onsager and Samaras<sup>2</sup> succeeded subsequently in effecting elegant analytical integrations of Wagner's theory, leading to results in substantial agreement with the earlier work. It is the purpose of this investigation to present the statistical mechanical formulation of the problem employing the conventional model for very dilute electrolyte solutions. For this purpose, the molecular distribution functions are calculated from a generalized form of Kirkwood's integral equation,<sup>3,4</sup> while the surface tension increase is directly computed from the molecular theory<sup>5,6</sup> for this thermodynamic parameter. Apart from its intrinsic interest to related problems in electrocapillarity, the present problem serves to clarify the difficulties encountered in the general program<sup>7</sup> of computing density variations in the interfacial region. Furthermore, we have succeeded in simply relating Mayer's<sup>8</sup> irreducible cluster expansion approach to both the integral equation method and the stress tensor integral for the surface tension increase. A comparison between theory and experiment is presented in Table I.

As a preliminary to the statistical mechanical theory, we recall that the general Kirkwood-Buff<sup>9</sup> or McMillan-Mayer<sup>10</sup> solution theories emphasize that under osmotic

conditions explicit solute-solute interactions occur exclusively in the general formulation. In view of this advantage, the molecular calculations will be carried out under these thermodynamic conditions. Next, we define the generic center-of-mass number density  $\rho_{n_1^{(n)} \dots n_\nu^{(n)}}(1, \dots, n)$  as the average density of sets containing  $n_1$  molecules of species 1,  $n_2$  molecules of species 2, etc., at the points  $\mathbf{R}_1, \dots, \mathbf{R}_N$  in an osmotic system of fixed volume  $V$ , where

$$n = \sum_{\alpha=1}^{\nu} n_{\alpha}$$

Designating the solvent by the subscript zero and the solute species by the subscript  $\alpha$ , we observe that in the interior of the bulk phase the singlet densities  $\rho^{(1)}$  of the several species are equal to their respective uniform volume concentrations  $c$ . Furthermore, it is frequently convenient to introduce correlation functions

$$g_{n_1 \dots n_\nu}^{(n)}(1, \dots, n)$$

which are defined by the following equation

$$\rho_{n_1 \dots n_\nu}^{(n)}(1, \dots, n) = \prod_{\alpha=1}^{\nu} \prod_{i_{\alpha}=1}^{n_{\alpha}} \rho_{\alpha}^{(1)}(\mathbf{R}_{i_{\alpha}}) \times g_{n_1 \dots n_\nu}^{(n)}(1, \dots, n). \quad (1)$$

These molecular distribution functions are related by grand ensemble theory to thermodynamic variables and potentials of molecular force. In the semiclassical limit

$$\rho^{(n)} = e^{\beta\Omega} \sum_{N_1=n_1 \dots N_{\nu}=n_{\nu}} \prod_{\alpha=1}^{\nu} \frac{\exp(\beta N_{\alpha} \bar{\mu}_{\alpha}')}{(N_{\alpha} - n_{\alpha})!} \times \int \dots \int \exp(-\beta W_{N_1 \dots N_{\nu}}^{(N)}) \prod_{k=n+1}^N dv_k,$$

$$\rho^{(0)} = 1; \quad \beta = 1/kT,$$

$$\bar{\mu}_{\alpha}' = \bar{\mu}_{\alpha} - \mu_{\alpha}^*; \quad \mu_{\alpha}^* = \lim_{\substack{c_0 \rightarrow 0 \\ \{c_{\alpha}\} \rightarrow 0}} (\bar{\mu}_{\alpha} - kT \ln c_{\alpha}), \quad (2)$$

$$\Omega = -\pi V + \Delta\gamma S,$$

$$W_{N_1 \dots N_{\nu}}^{(N)}(1, \dots, N) = \lim_{\{c_{\alpha}\} \rightarrow 0} W^{(N)}; \quad N = \sum_{\alpha=1}^{\nu} N_{\alpha}$$

<sup>1</sup> C. Wagner, *Physik. Z.* **25**, 474 (1924).

<sup>2</sup> L. Onsager and N. N. T. Samaras, *J. Chem. Phys.* **2**, 528 (1934).

<sup>3</sup> J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

<sup>4</sup> J. G. Kirkwood, *Chem. Revs.* **19**, 275 (1936).

<sup>5</sup> F. P. Buff, *Z. Elektrochem.* **56**, 311 (1952).

<sup>6</sup> F. P. Buff, *J. Chem. Phys.* **23**, 419 (1955).

<sup>7</sup> F. P. Buff, Conference on Nucleation and Interfacial Phenomena, August, 1951, Geophysical Research Directorate Report, A. F. Cambridge Research Center, Cambridge, Massachusetts.

<sup>8</sup> J. E. Mayer, *J. Chem. Phys.* **18**, 1426 (1950).

<sup>9</sup> J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.* **19**, 774 (1951).

In the special case of osmotic conditions this theory reduces to the results of reference 10.

<sup>10</sup> W. G. McMillan and J. E. Mayer, *J. Chem. Phys.* **13**, 276 (1945).

where  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $\bar{\mu}_\alpha$  is the partial potential of solute  $\alpha$ ,  $\pi$  is the osmotic pressure,  $\Delta\gamma$  is the surface tension difference between the osmotic solution and the pure solvent,  $V$  is the volume of the system, and a piston of cross section  $s$  is located at the plane  $z=0$  of a Cartesian coordinate system. We shall now assume that  $W^{0(N)}$ , the potential of average force for sets  $\{N\}$  of solute species evaluated in the pure solvent, may be expressed in the form

$$W^{0(N)} = \sum_{\alpha=1}^{\nu} \sum_{i_\alpha=1}^{N_\alpha} V_\alpha^{(1)}(\mathbf{R}_{i_\alpha}) + \frac{1}{2} \sum_{\alpha,\beta=1}^{\nu} \sum_{i_\alpha=1}^{N_\alpha} \sum_{i_\beta=1}^{N_\beta} V_{\alpha\beta}(\mathbf{R}_{i_\alpha}, \mathbf{R}_{i_\beta}). \quad (3)$$

It will be shown in Sec. II that for our problem

$$V_\alpha^{(1)}(\mathbf{R}_i) = V_\alpha^{(1)}(z_i; c_0);$$

$$V_{\alpha\beta}^{(2)}(\mathbf{R}_i, \mathbf{R}_j) = V_{\alpha\beta}^{(2)}(R_{ij}, R_{ij}^{(im)}; c_0), \quad (4)$$

$$R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|; \quad R_{ij}^{(im)} = |\mathbf{R}_i - \mathbf{R}_j + 2z_j \mathbf{k}|,$$

where  $\mathbf{k}$  is the unit vector directed along the  $z$  axis. Kirkwood, in his pioneering investigation of homogeneous fluids, has shown that for the evaluation of distribution functions it is convenient to introduce a parameter  $\lambda_{1\alpha}$  which partially couples molecule 1 of type  $\alpha$  to the rest of the system. We similarly define  $W_{N_1 \dots N_\nu}^{0(N)}(1, \dots, N; \lambda_{1\alpha})$  by the relation

$$W_{N_1 \dots N_\nu}^{0(N)}(1, \dots, N; \lambda_{1\alpha}) = W_{N_1 \dots N_\nu}^{0(N-1)}(2, \dots, N) + \lambda_{1\alpha} w^0(1, \dots, N), \quad (5)$$

$$w^0(1, \dots, N) = V_\alpha^{(1)}(\mathbf{R}_1) + \sum_{\beta=1}^{\nu} \sum_{i_\beta=1}^{N_\beta} V_{\alpha\beta}^{(2)}(\mathbf{R}_1, \mathbf{R}_{i_\beta});$$

$$0 \leq \lambda_{1\alpha} \leq 1,$$

where  $W^{0(N)}(\lambda_{1\alpha}=1)$  corresponds to the actual potential of average force. The generalized distribution function

$\rho_{n_1 \dots n_\nu}^{(n)}(1, \dots, n; \lambda_{1\alpha})$  corresponding to the potential (5) may then be shown to be

$$\rho^{(n)}(\lambda_{1\alpha}) = \exp[\beta\Omega^\dagger(\lambda_{1\alpha})] \sum_{N_1=n_1 \dots N_\nu=n_\nu}^{\infty} \times \prod_{\alpha=1}^{\nu} \frac{\exp(\beta N_\alpha \bar{\mu}_\alpha')}{(N_\alpha - n_\alpha)!} \int^V \dots \int \exp[-\beta W^{0(N)}(\lambda_{1\alpha})] \prod_{k=n+1}^N dv_k, \quad (6)$$

where  $\rho^{(n)}(\lambda_{1\alpha}=1)$  again is equal to the actual number density  $\rho^{(n)}$ . When  $\lambda_\alpha$  is equated to zero in Eq. (6), an

elementary rearrangement yields the relation

$$\rho_{n_1 \dots n_\nu}^{(n)}(1, \dots, n; \lambda_{1\alpha}=0) = \exp\{\beta[\bar{\mu}_\alpha' + \Omega^\dagger(\lambda_{1\alpha}=0) - \Omega^\dagger(\lambda_{1\alpha}=1)]\} \times \rho_{n_1 \dots n_\nu}^{(n-1)}(2, \dots, n; \lambda_{1\alpha}=1) \quad (7)$$

implying that

$$\rho_{n_1 \dots n_\nu}^{(n)}(1, \dots, n; \lambda_{1\alpha}=0) = \rho_\alpha^{(1)}(1) \rho_{n_1 \dots n_\nu}^{(n-1)}(2, \dots, n). \quad (8)$$

Next, Eq. (6) is differentiated with respect to  $\lambda_{1\alpha}$

$$\left(\frac{\partial \rho^{(n)}}{\partial \lambda_{1\alpha}}\right)_{T, \{\beta \bar{\mu}_\alpha'\}, \nu} = -\beta \rho^{(n)}(\lambda_{1\alpha}) \left[ W^0(1, \dots, N) - \left(\frac{\partial \Omega^\dagger}{\partial \lambda_{1\alpha}}\right)_{T, \{\beta \bar{\mu}_\alpha'\}, \nu} \right] - \beta \sum_{\beta=1}^{\nu} \int V_{\alpha\beta}^{(2)}(\mathbf{R}_1, \mathbf{R}_{n+1}) \rho_{n_1 \dots n_\nu}^{(n+1)}(\lambda_{1\alpha}) dv_{n+1} \quad (9)$$

which, upon integration, leads to the desired expressions when Eqs. (7) and (8) are utilized

$$\beta \bar{\mu}_\alpha' = \ln \rho_\alpha^{(1)}(\mathbf{R}_1) + \beta V_\alpha^{(1)}(\mathbf{R}_1) + \beta \sum_{\beta=1}^{\nu} \int_0^1 d\lambda_{1\alpha} \int \rho_\beta^{(1)}(\mathbf{R}_2) V_{\alpha\beta}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) \times g_{\alpha\beta}^{(2)}(\mathbf{R}_1, \mathbf{R}_2; \lambda_{1\alpha}) dv_2, \quad (10)$$

$$\ln \left\{ \frac{\rho_{n_1 \dots n_\nu}^{(n)}(1, \dots, n; \lambda_{1\alpha})}{\rho_{n_1 \dots n_\nu}^{(n-1)}(2, \dots, n)} \right\} = -\beta \lambda_{1\alpha} \sum_{\beta=1}^{\nu} \sum_{i_\beta=1}^{n_\beta} V_{\alpha\beta}^{(2)}(\mathbf{R}_1, \mathbf{R}_{i_\beta}) - \beta \sum_{\beta=1}^{\nu} \int_0^{\lambda_{1\alpha}} d\lambda_{1\alpha} \times \int V_{\alpha\beta}^{(2)}(\mathbf{R}_1, \mathbf{R}_{n+1}) \rho_\beta^{(1)}(\mathbf{R}_{n+1}) \times \left[ \frac{g_{n_1 \dots n_\nu}^{(n+1)}(1, \dots, n+1; \lambda_{1\alpha})}{g_{n_1 \dots n_\nu}^{(n)}(1, \dots, n; \lambda_{1\alpha})} - g_{\alpha\beta}^{(2)}(1, n+1; \lambda_{1\alpha}) \right] dv_{n+1}. \quad (11)$$

Equations (10) and (11) were originally derived by Kirkwood<sup>3</sup> for the special case of homogeneous fluids on the basis of petit ensemble theory. In this case  $\rho_\alpha^{(1)}$  reduces to the uniform concentration  $c_\alpha$ , and Eqs. (11)

may be solved independently of Eq. (10), the latter relation providing a formula for the chemical potential  $\mu_\alpha$ . For inhomogeneous fluids Eqs. (10) and (11) must be solved simultaneously, subject to constancy of the partial potentials  $\{\bar{\mu}_\alpha\}$ . The physically realizable distribution functions  $\rho^{(n)}$  ( $\lambda=1$ ) are, of course, obtained by setting  $\lambda=1$  at the end of this procedure.

We conclude this section by presenting the relevant statistical mechanical expressions for  $\Delta\gamma$ . When the techniques of reference 5 are employed, the equivalent thermodynamic definitions

$$\Delta\gamma = \left( \frac{\partial\Omega}{\partial s} \right)_{T, \{\bar{\mu}_\alpha\}, V/S} + \frac{\pi V}{S} \quad (12)$$

and

$$\Delta\gamma = \left( \frac{\partial\Omega}{\partial s} \right)_{T, \{\bar{\mu}_\alpha\}, V} \quad (13)$$

imply that for  $W^{0(N)}$  given by Eqs. (3) and (4)

$$\begin{aligned} \Delta\gamma &= \int_0^\infty [\sigma_T(z) - \sigma_T(\infty)] dz, \\ \sigma_T(z_1) &= -kT \sum_{\alpha=1}^v \rho_\alpha^{(1)}(z_1) + \frac{1}{2} \sum_{\alpha, \beta=1}^v \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \\ &\times \left[ \frac{(x_1 - x_2)^2}{R_{12}} \frac{\partial V_{\alpha\beta}^{(2)}}{\partial R_{12}} + \frac{(x_1 - x_2)^2}{R_{12}^{(im)}} \frac{\partial V_{\alpha\beta}^{(2)}}{\partial R_{12}^{(im)}} \right] \\ &\times \rho_{\alpha\beta}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) dx_2 dy_2 dz_2 \quad (14) \end{aligned}$$

and\*

$$\begin{aligned} \Delta\gamma &= - \sum_{\alpha=1}^v \int_0^\infty z \frac{dV_\alpha^{(1)}}{dz} \rho_\alpha^{(1)}(z) dz + \int_0^\infty (\sigma_T - \sigma_N) dz, \\ \sigma_N(z_1) &= -kT \sum_{\alpha=1}^v \rho_\alpha^{(1)}(z_1) + \frac{1}{2} \sum_{\alpha, \beta=1}^v \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \\ &\times \left[ \frac{(z_1 - z_2)^2}{R_{12}} \frac{\partial V_{\alpha\beta}^{(2)}}{\partial R_{12}} + \frac{(z_1 + z_2)^2}{R_{12}^{(im)}} \frac{\partial V_{\alpha\beta}^{(2)}}{\partial R_{12}^{(im)}} \right] \\ &\times \rho_{\alpha\beta}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) dx_2 dy_2 dz_2. \quad (15) \end{aligned}$$

It is of interest to recall<sup>5</sup> that when rigorous distribution functions are utilized, Eq. (14) may be transformed into Eq. (15) and that these equations also lead to the Gibbs adsorption equation

$$d\gamma = - \sum_{\alpha=1}^v \Gamma_\alpha d\mu_\alpha; \quad \Gamma_\alpha = \int_0^\infty [\rho_\alpha^{(1)}(z) - c_\alpha] dz. \quad (16)$$

Consequently, an internal comparison provides a rough criterion for the failure of approximations required for the numerical implementation of the theory.

\* Equation (15) illustrates that surface tension is not always given by  $\int (\sigma_T - \sigma_N) dz$  since in our problem the first term, arising from the image potential, provides convergence. As in the theory of curved fluid interfaces Eq. (14) is of more general applicability.

## II.

In this section the detailed calculation of  $\Delta\gamma$  will be carried out on the basis of the conventional model for very dilute ionic solutions. We shall assume that our solution consists of a structureless solvent of everywhere uniform dielectric constant  $D$ , and of ionic species treated as point charges for the sake of simplicity. This permits calculation of the local free energy  $W^{0(N)}$  by electrostatics. Let  $\psi$  be the electrostatic potential in the solution and  $\psi_0$  be the electrostatic potential in the region separated from the ionic solution by the  $z=0$  plane.  $\psi(\mathbf{R})$  is then obtained by solving

$$\nabla^2 \psi = -\frac{4\pi}{D} \rho_e; \quad \rho_e = \sum_{i=1}^N \epsilon_i \delta(\mathbf{R} \cdot \mathbf{R}_i); \quad (17)$$

inside the ionic solution,

$\nabla^2 \psi_0 = 0$ , outside the ionic solution,

subject to

$$\begin{aligned} (\psi)_{z=0} &= (\psi_0)_{z=0}; \quad \mathbf{k} \times (\nabla \psi - \nabla \psi_0)_{z=0} = 0, \\ \mathbf{k} \cdot (D \nabla \psi - D_0 \nabla \psi_0)_{z=0} &= 0. \quad (18) \end{aligned}$$

Here  $\epsilon_i$  is the charge of ion  $i$ ,  $D_0$  is the dielectric constant of the external region and  $\delta(\mathbf{R} - \mathbf{R}')$  is the Dirac delta function. In the absence of mutual polarization of the ions, the solution of these equations is given by the expression

$$\psi(\mathbf{R}) = \sum_{i=1}^N \frac{\epsilon_i}{D |\mathbf{R} - \mathbf{R}_i|} + \frac{D - D_0}{D + D_0} \sum_{i=1}^N \frac{\epsilon_i}{D |\mathbf{R} - \mathbf{R}_i + 2\mathbf{k}z_i|} \quad (19)$$

so that  $W^{0(N)}$  follows directly

$$\begin{aligned} W^{0(N)} &= \frac{1}{2} \int \rho_e \psi dV \\ &= \sum_{i < j=1}^N \frac{\epsilon_i \epsilon_j}{DR_{ij}} + \frac{D - D_0}{D + D_0} \sum_{i=1}^N \frac{\epsilon_i^2}{4Dz_i} \\ &\quad + \frac{D - D_0}{D + D_0} \sum_{i < j=1}^N \frac{\epsilon_i \epsilon_j}{DR_{ij}^{(im)}}. \quad (20) \end{aligned}$$

Here the first sum is the usual Coulomb interaction, the second sum extends over the "external image potentials" and the last sum is over the "intermolecular image potentials." We note that for an aqueous medium  $(D - D_0)/(D + D_0)$  is effectively unity, and we shall henceforth ignore this factor.

For the estimation of the singlet and pair distribution functions we terminate the first member of Eqs. (11) by the superposition approximation<sup>2</sup>

$$\begin{aligned} g_{\alpha\beta\gamma}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3; \lambda_{1\alpha}) &= g_{\alpha\beta}^{(2)}(\mathbf{R}_1, \mathbf{R}_2; \lambda_{1\alpha}) \\ &\times g_{\alpha\gamma}^{(2)}(\mathbf{R}_1, \mathbf{R}_3; \lambda_{1\alpha}) g_{\beta\gamma}^{(2)}(\mathbf{R}_2, \mathbf{R}_3). \quad (21) \end{aligned}$$

We note that Kirkwood and Poirier<sup>11</sup> have recently shown the validity of this approximation for the Debye-Hückel limiting law, and we remark that the formulation of Sec. III constitutes an independent verification for inhomogeneous phases. Next the treatment is restricted to symmetrical ions and the pair correlation function is linearized

$$g_{\alpha\beta}^{(2)}(\mathbf{R}_1, \mathbf{R}_2; \lambda_{1\alpha}) = 1 - \frac{\beta\epsilon_\alpha\epsilon_\beta\lambda_{1\alpha}}{D}\chi(\mathbf{R}_1, \mathbf{R}_2), \quad (22)$$

again only valid in the limiting case.

Substitution of Eqs. (20), (21), and (22) into Eqs. (10) and (11) and utilization of the electroneutrality condition

$$\sum_{\alpha=1}^{\nu} \rho_\alpha^{(1)}\epsilon_\alpha = 0$$

finally yields

$$\beta\bar{\mu}_\alpha' = \ln\rho_\alpha^{(1)}(z_1) + \frac{\beta\epsilon_\alpha^2}{4Dz} - \frac{\beta\epsilon_\alpha^2}{8\pi D} \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \kappa^2(z_2) \times \left[ \frac{1}{R_{12}} + \frac{1}{R_{12}^{(im)}} \right] \chi(1,2) dx_2 dy_2 dz_2, \quad (23)$$

$$\kappa^2(z) = 4\pi\beta \sum_{\alpha=1}^2 \rho_\alpha^{(1)}(z)\epsilon_\alpha^2/D; \quad \epsilon_1^2 = \epsilon_2^2 = \epsilon^2; \quad \rho_1^{(1)} = \rho_2^{(1)} = \rho^{(1)}, \quad (24)$$

$$\chi(1,2) = \frac{1}{R_{12}} + \frac{1}{R_{12}^{(im)}} - \frac{1}{4\pi} \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \kappa^2(z_3) \times \left[ \frac{1}{R_{13}} + \frac{1}{R_{13}^{(im)}} \right] \chi(2,3) dx_3 dy_3 dz_3.$$

Although Eqs. (23) and (24) ideally constitute a coupled set of integral equations, we employ the approximation  $\kappa^2(z) = \kappa^2(\infty) = \kappa^2$  and note that when  $\chi(1,2)$  is defined to be an even function in  $z$ , both integrations may be extended over the whole space. In particular

$$\chi(1,2) = \frac{1}{R_{12}} + \frac{1}{R_{12}^{(im)}} - \frac{\kappa^2}{4\pi} \int_{\text{whole space}} \frac{\chi(2,3)}{R_{13}} dv_3. \quad (25)$$

This integral equation is now amenable to direct solution by the Fourier transform technique, with the result

$$\chi(1,2) = \frac{2}{\pi R_{12}} \int_0^\infty \frac{t \sin t R_{12}}{t^2 + \kappa^2} dt + \frac{2}{\pi R_{12}^{(im)}} \int_0^\infty \frac{t \sin t R_{12}^{(im)}}{t^2 + \kappa^2} dt$$

so that<sup>12</sup>

$$\chi(1,2) = \frac{\exp(-\kappa R_{12})}{R_{12}} + \frac{\exp(-\kappa R_{12}^{(im)})}{R_{12}^{(im)}}. \quad (26)$$

When  $\chi(1,2)$  is substituted into Eq. (23) and the resulting expression is evaluated with use of dipolar coordinates, the well-known Debye-Hückel limiting law is obtained

$$\beta\bar{\mu}_\alpha' = \ln c_\alpha - \frac{\beta\epsilon_\alpha^2\kappa}{2D} \quad (27)$$

as well as the relation

$$\ln \frac{\rho_\alpha^{(1)}}{c_\alpha} = -\frac{\beta\epsilon_\alpha^2}{4Dz} + \frac{\beta\epsilon_\alpha^2\kappa^2}{8\pi D} \int_{\text{whole space}} \frac{e^{-\kappa R_{12}}}{R_{12}R_{12}^{(im)}} dv_2 \quad (28)$$

$$= -\frac{\beta\epsilon_\alpha^2}{4Dz} + \frac{\beta\epsilon_\alpha^2\kappa^2}{8Dz} \int_0^\infty e^{-\kappa R_{12}} dR_{12} \int_{|R_{12}-2z|}^{R_{12}+2z} dR_{12}^{(im)},$$

i.e.,

$$\rho^{(1)} = c \exp\{-\beta\epsilon^2 e^{-2\kappa z}/4Dz\}.$$

Equation (28), previously obtained by different techniques,<sup>1,2</sup> clearly shows the screening effect on the image potential.

Our next task is the evaluation of the stresses  $\sigma_T$  and  $\sigma_N$  given by Eqs. (14) and (15), and the last two members of Eq. (20). We again linearize  $g_{\alpha\beta}^{(2)}$ , utilize the electroneutrality condition and Eq. (26), and take  $\kappa^2$  constant

$$\sigma_T(z_1) = -2\rho^{(1)} \left[ kT + \frac{\epsilon^2\kappa^2}{8\pi D} \int \left[ \frac{(x_1 - x_2)^2}{R_{12}^3} + \frac{(x_1 - x_2)^2 e^{-\kappa R_{12}}}{R_{12}^{(im)3}} \right] dv_2 \right], \quad (29)$$

$$\sigma_N(z_1) = -2\rho^{(1)} \left[ kT + \frac{\epsilon^2\kappa^2}{8\pi D} \int \left[ \frac{(z_1 - z_2)^2}{R_{12}^3} + \frac{(z_1 + z_2)^2 e^{-\kappa R_{12}}}{R_{12}^{(im)3}} \right] dv_2 \right]. \quad (30)$$

These integrals can be evaluated with use of dipolar coordinates, with the result

$$\sigma_T(z) = 2\rho^{(1)}(z) \left\{ -kT + \frac{\epsilon^2\kappa}{D} \left[ \frac{1}{6} + \frac{1}{u^3} - \frac{e^{-u}}{2u} - \frac{e^{-u}}{u^2} - \frac{e^{-u}}{u^3} \right] \right\}, \quad (31)$$

$$u = 2\kappa z,$$

$$\sigma_N = 2\rho^{(1)}(z) \left\{ -kT + \frac{\epsilon^2\kappa}{D} \left[ \frac{1}{6} + \frac{1}{2u} - \frac{2}{u^3} + \frac{e^{-u}}{2u} + \frac{2e^{-u}}{u^2} + \frac{2e^{-u}}{u^3} \right] \right\}. \quad (32)$$

Upon designating the surface tension increase corresponding to Eq. (14) by  $\Delta\gamma^I$  and the increase according to Eq. (15) by  $\Delta\gamma^{II}$ , these quantities may be exhibited

<sup>11</sup> J. G. Kirkwood and J. C. Poirier, J. Phys. Chem. **58**, 591 (1954).

<sup>12</sup> A. Erdélyi, *Tables of Integral Transforms* (McGraw-Hill Book Company, Inc., New York, 1954), Vol. I, p. 65.

as follows:

$$\Delta\gamma^I = \frac{c\epsilon^2}{D} \left\{ \left( \frac{1}{6} - \frac{1}{2y} \right) \int_0^\infty [\exp(-ye^{-u}/u) - 1] du \right. \\ \left. + \int_0^\infty \exp(-ye^{-u}/u) \left[ \frac{1}{u^3} - \frac{1}{u^2y} - \frac{e^{-u}}{2u} \right] du \right\}; \quad (33)$$

$$y = \epsilon^2 \kappa / 2DkT,$$

$$\Delta\gamma^{II} = \frac{c\epsilon^2}{D} \int_0^\infty \exp\left(-\frac{ye^{-u}}{u}\right) \left[ \frac{3}{u^3} - \frac{3}{u^2y} - \frac{e^{-u}}{u} \right] du. \quad (34)$$

The analytical evaluation of prototype integrals is presented in the appendix and leads to

$$\Delta\gamma^{(\alpha)} = \frac{c\epsilon^2}{D} F^{(\alpha)}(y), \quad \alpha = I, II$$

$$F^{(\alpha)}(y) = L(y) + \sum_{n=1}^{\infty} \frac{y^n}{n!(n+2)!} [A_n^{(\alpha)} \ln y + B_n^{(\alpha)}], \quad (35)$$

where

$$L(y) = -\frac{1}{2} \ln y - \gamma + \frac{3}{4},$$

$$A_n^I = (n+1)^n \frac{(n^2-2)}{2} - \frac{n^n}{6} (5n^2-3n-2);$$

$$B_n^I = \frac{(n+1)^n}{2} \{ (n^2-2)(\ln(n+1)+1) \\ - n(n+1)\psi(n+1) - (n-1)(n+2)\psi(n+2) \\ + 2(n+1)\psi(n+3) \} - \frac{n^n}{6} \{ (5n^2-3n-2) \ln n \\ + (5n^2+3n-2) + 2(n+1)(n+2)\psi(n+1) \\ - 6n^2[\psi(n)+\psi(n+3)] \};$$

$$A_n^{II} = (n+1)^{n+1}(n-1) - 3n^{n+2};$$

$$B_n^{II} = (n+1)^{n+1} \{ (n-1)[\ln(n+1)+1-\psi(n+1)] \\ - (n+2)\psi(n+2) + 3\psi(n+3) \} \\ - 3n^{n+2} \left\{ \ln n + \frac{n+1}{n} \psi(n) - \psi(n+3) \right\};$$

$$\psi(n) = -\gamma + \sum_{m=1}^{n-1} \frac{1}{m};$$

$$\gamma = \text{Euler's constant} = 0.5772157 \dots$$

It will be noted that the same limiting law is obtained for cases I and II, which for a uni-univalent electrolyte takes the form

$$\Delta\gamma = \frac{80.00}{D} c \log_{10} \frac{1.130 \times 10^{-13} (DT)^3}{c} \frac{c(\text{moles/liter})}{\gamma(\text{dynes/cm})} \quad (36)$$

when recent<sup>13</sup> values are employed for the physical constants. The limiting law obtained is also identical with that found by Onsager and Samaras on the basis of their integration of the Gibbs adsorption equation (16), subject to relations (27) and (28). This result is to be expected owing to the validity of the approximations in this region. In more concentrated solutions, the basic model begins to break down and, furthermore, the use of approximate distribution functions in rigorous formulas for thermodynamic variables leads to internal discrepancies. For example, the difference between  $\Delta\gamma^I$  and  $\Delta\gamma^{II}$  arises from the failure of the hydrostatic condition, since it can be shown that although the approximated Born and Green equations imply Eqs. (26) and (28), the first moment of the singlet Born and Green equation is already in error at higher concentrations. Despite the fact that the Gibbs adsorption equation satisfies an important thermodynamic consistency relation, its use similarly produces some discrepancies when charge expansions to different orders are employed for  $\Gamma$  and  $\mu$ .

In order to illustrate these numerical differences and to indicate the applicability of the theory in the experimental region, we express  $\Delta\gamma$  in the form

$$\Delta\gamma/y^2 (\text{dynes/cm}) = 7.868 \times 10^{-12} D^2 T^3 F(y), \\ y^2 = 1.766 \times 10^{13} (DT)^{-3} c (\text{moles/liter}).$$

Table I summarizes the results for our cases I and II, the corresponding Onsager-Samaras  $A\Delta\alpha/2$  values (O.S.), and the experimental values obtained by passing a curve through Schwenker's<sup>14</sup> rather scattered data (Exp.). The agreement between (O.S.) and I is quite close, although II is in better agreement with the difficult experimental measurements. In closing, we remark that within the framework of the model, slightly better agreement could be achieved by taking into account the finite size of the ions as well as the explicit variation of  $\kappa(z)$ .

TABLE I.

$y^2$	$F^{O.S.}(y)$	$F^I(y)$	$F^{II}(y)$	$F_{Exp.}(y)$	$c(\text{moles/liter})$ at 18°C <sup>a</sup>
0.0063	1.486	1.492	1.549		0.0046
0.0126	1.325	1.333	1.405		0.0091
0.0189	1.233	1.242	1.323		0.0137
0.0315	1.117	1.130	1.223	1.25	0.0228
0.0378	1.077	1.090	1.189	1.22	0.0273
0.0630	0.966	0.981	1.095	1.18	0.0456
0.0944	0.880	0.899	1.023	1.14	0.0683
0.1259	0.819	0.839	0.974	1.12	0.0911
0.1574	0.772	0.794	0.937	1.06	0.1138
0.1889	0.735	0.758	0.908	1.03	0.1366
0.2014	0.722	0.745	0.897	1.02	0.1457
0.2266	0.697	0.722	0.879	1.00	0.1639

<sup>a</sup> The dielectric constant of water has been calculated from the Akerlof-Oshry equation, *J. Am. Chem. Soc.* **72**, 2844 (1950),  
 $D = (5321/T) + 233.76 - 0.9297T + 0.001417T^2 - 0.08292T^3$ ,  
 $T = 273.1 + t$ .

<sup>13</sup> J. W. M. DuMond and R. E. Cohen, *Revs. Modern Phys.* **25**, 691 (1953).

<sup>14</sup> G. Schwenker, *Ann. Physik* **11**, 525 (1931).

III.

It is the purpose of this section to relate our particular application of the general distribution function approach to Mayer's recent electrolyte theory<sup>8</sup> which he based on the osmotic virial expansion<sup>10</sup> for homogeneous fluids. It will be recalled that for verification of the Debye-Hückel limiting law Mayer first evaluated, with use of a convergence factor, the individual linearized cyclic irreducible cluster integrals and then summed their contribution to the thermodynamic variables. On the other hand, we have found that, particularly for the inhomogeneous case, it is advantageous to reverse this order of evaluation. Upon directly summing the cyclic cluster integrals in a formal manner, the relevant sums can be shown to obey our earlier integral Eq. (24). Consequently, a simple technique is provided for the calculation of the cluster sums and, by comparison with the distribution function theory, an additional justification becomes available for the validity of superposition in the limiting concentration range. In summary, the following analysis again leads to the earlier singlet density and to an expression for  $\Delta\gamma$  identical with the previous  $\Delta\gamma^I$ .

Although in the presence of external fields the usual virial development must be extended,<sup>15</sup> this generalization is straightforward for the cyclic diagrams due to their symmetry. Restricting this treatment to the contribution from cyclic clusters and employing a  $W^{(N)}$  given by Eq. (20), it is found that the desired formulas may be expressed in the form

$$\beta\bar{\mu}_\alpha' = \ln\rho_\alpha^{(1)}(1) + \beta V_\alpha^{(1)}(1) + \sigma_\alpha(1; \xi = 1), \quad (37)$$

$$\Delta\gamma = \int_0^\infty [\pi(\infty) - \pi(z)] dz, \quad (38)$$

$$\beta\pi(z) = \sum_\alpha \rho_\alpha^{(1)}(1) + \sum_\alpha \rho_\alpha^{(1)}(1) \left\{ \sigma_\alpha(1; \xi = 1) - \int_0^1 \sigma_\alpha(1; \xi) \xi^2 d\xi \right\}, \quad (39)$$

where

$$\begin{aligned} \sigma_\alpha(1; \xi) = & \sum_\beta \int \rho_\beta^{(1)}(2) f_{\alpha\beta}(1,2) dv_2 \\ & - \frac{1}{2} \sum_{\beta,\gamma} \xi^2 \int \int \rho_\beta^{(1)}(2) \rho_\gamma^{(1)}(3) f_{\alpha\beta}(1,2) \\ & \times f_{\beta\gamma}(2,3) f_{\gamma\alpha}(3,1) dv_2 dv_3 \\ & - \frac{1}{2} \sum_{\beta,\gamma,\delta} \xi^4 \int \int \int \rho_\beta^{(1)}(2) \rho_\gamma^{(1)}(3) \rho_\delta^{(1)}(4) \\ & \times f_{\alpha\beta}(1,2) f_{\beta\gamma}(2,3) f_{\gamma\delta}(3,4) f_{\delta\alpha}(4,1) \\ & \times dv_2 dv_3 dv_4 \dots; \quad 0 \leq \xi \leq 1 \end{aligned} \quad (40)$$

and

$$f_{\alpha\beta}(i,j) = \exp[-\beta V_{\alpha\beta}^{(2)}(i,j)] - 1.$$

<sup>15</sup> J. Yvon, *Actualités scientifiques et industrielles* (Hermann and Cie, Paris, 1935), No. 203.

For the evaluation of the auxiliary function  $\sigma_\alpha(1; \xi)$  we first expand

$$f_{\alpha\beta}(1,2) = -\frac{\beta\epsilon_\alpha\epsilon_\beta}{D} k(1,2) + \frac{1}{2} \frac{\beta^2\epsilon_\alpha^2\epsilon_\beta^2}{D^2} k^2(1,2) - \dots, \quad (41)$$

$$k(1,2) = \frac{1}{R_{12}} + \frac{1}{R_{12}^{(im)}}$$

so that to terms of the same order, with use of the electroneutrality condition,

$$\sigma_\alpha(1; \xi) = -\frac{\beta\epsilon_\alpha^2}{2D} \int \frac{\kappa^2(2)k(1,2)}{4\pi} K(1,2; \xi) dv_2,$$

where

$$\begin{aligned} K(1,2; \xi) = & k(1,2) - \frac{\xi^2}{4\pi} \int \kappa^2(3)k(2,3)k(3,1) dv_3 \\ & + \left(\frac{\xi^2}{4\pi}\right)^2 \int \int \kappa^2(3)\kappa^2(4)k(2,3) \\ & \times k(3,4)k(4,1) dv_3 dv_4. \end{aligned} \quad (42)$$

From the theory of integral equations,<sup>16</sup> the coefficients in Eq. (42) are recognized as iterated kernels so that this equation is the Neumann series for the reciprocal kernel,<sup>17</sup> which itself satisfies the integral equation

$$K(1,2; \xi) = k(1,2) - \frac{\xi^2}{4\pi} \int \kappa^2(3)k(1,3)K(3,1; \xi) dv_3. \quad (43)$$

This equation has already been encountered and its solution is

$$K(1,2; \xi) = \frac{\exp[-\xi\kappa R_{12}]}{R_{12}} + \frac{\exp[-\xi\kappa R_{12}^{(im)}]}{R_{12}^{(im)}}; \quad \text{for } \kappa^2 \text{ constant} \quad (44)$$

so that again using earlier results

$$\sigma_\alpha(1; \xi) = -\frac{\beta\epsilon_\alpha^2\kappa}{2D\xi} - \frac{\beta\epsilon_\alpha^2}{4D\xi^2} (1 - e^{-2\xi\kappa}); \quad \text{for } \kappa^2 \text{ constant.} \quad (45)$$

Substituting of  $\sigma_\alpha(1; \xi)$  into Eqs. (37) and (39) then leads to

$$\rho^{(1)} = c \exp(-ye^{-u}/u); \quad y = \epsilon^2\kappa/2DkT; \quad u = 2\kappa z, \quad (46)$$

and

$$\pi(z) = 2\rho^{(1)}(z) \left\{ kT - \frac{\epsilon^2\kappa}{D} \left[ \frac{1}{6} + \frac{1}{u^3} - \frac{e^{-u}}{2u} - \frac{e^{-u}}{u^2} - \frac{e^{-u}}{u^3} \right] \right\}. \quad (47)$$

By comparison with Eq. (32) it is seen that  $\pi(z) = -\sigma_T(z)$  and that Eq. (47) in conjunction with Eq. (38) implies our earlier expression for  $\Delta\gamma^I$ , Eq. (33).

<sup>16</sup> R. Courant and D. Hilbert, *Methoden der Mathematischen Physik* (Verlag Julius Springer, Berlin, 1931), p. 116.

<sup>17</sup> Reference 16, p. 119.

Consequently, the  $\Delta\gamma^1$  column of the table serves as a numerical summary for the results of both Secs. II and III.

APPENDIX

Equations (33) and (34) lead to integrals of the type

$$I_{\alpha\epsilon}(y) = (-1)^\alpha \int_0^\infty \exp(-ye^{-u}/u) \cdot \frac{e^{-\epsilon u}}{u^\alpha} du \quad \alpha, \epsilon \text{ integers} \quad (A1)$$

$$= \int_{-\infty}^0 \exp(ye^z/z) \cdot \frac{e^{\epsilon z}}{z^\alpha} dz \quad \begin{matrix} \alpha \geq \epsilon \geq 1; \\ \alpha \geq 2 \text{ when } \epsilon = 0 \end{matrix}$$

$$\int_0^\infty [\exp(-ye^{-u}/u) - 1] du = \int_0^y I_{11}(y) dy. \quad (A2)$$

These integrals may be evaluated by expansion in terms of modified Bessel functions of the third kind or, more directly, by a straightforward extension of the contour integral technique developed by Onsager and Samaras<sup>2</sup> in their calculation of the left-hand side of Eq. (A2). Let

$$\phi = \frac{1}{2\pi i} \int_{-\infty}^{(0+)} \exp(ye^z/z) \cdot \frac{e^{\epsilon z} \left(\frac{e^z}{z}\right)^\beta}{z^\alpha} dz \quad | \beta | < 1; \quad | \arg z | \leq \pi, \quad (A3)$$

where the contour is taken from  $-\infty$  counterclockwise around the origin and back to  $-\infty$ . In analogy with Hankel's treatment of the gamma function,<sup>18</sup>  $\Gamma(z)$ , Eq. (A3) may be transformed

$$\begin{aligned} \phi &= \frac{\sin \pi \beta}{\pi} \int_{-\infty}^{-0} \exp(ye^z/z) \cdot \frac{e^{\epsilon z}}{z^\alpha} (-z)^{-\beta} dz \\ &+ \frac{1}{2\pi i} \int_{-\infty}^{(0+)} \exp(ye^z/z) \cdot \frac{e^{\epsilon z} \left(\frac{e^z}{z}\right)^\beta}{z^\alpha} dz \quad (A4) \\ &= \phi_1 + \phi_2. \end{aligned}$$

Then it follows that

$$I_{\alpha\epsilon} = \lim_{\beta \rightarrow 0} \frac{\partial \phi_1}{\partial \beta} = \left[ \frac{\partial \phi - \phi_2}{\partial \beta} \right]_{\beta=0}. \quad (A5)$$

For the evaluation of  $\phi$ ,  $\exp\{ye^z/z\}$  is expanded, and in the resulting series, Hankel's formula for the gamma function is utilized

$$\begin{aligned} \phi &= \sum_{n=0}^\infty \frac{y^n}{n!} \frac{1}{2\pi i} \int_{-\infty}^{(0+)} \frac{e^{(n+\epsilon+\beta)z}}{z^{(n+\alpha+\beta)}} dz \\ &= \sum_{n=0}^\infty \frac{y^n}{n!} \frac{(n+\epsilon+\beta)^{n+\alpha+\beta-1}}{\Gamma(n+\alpha+\beta)}. \end{aligned} \quad (A6)$$

<sup>18</sup> E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, New York, 1943), p. 244.

$\phi_2$  is evaluated by setting  $t = ze^{-z}$ , and then employing the extended form of Lagrange's theorem<sup>19</sup>

$$e^{(\epsilon-\alpha)z} dz = \sum_{n=0}^\infty \frac{t^n (\epsilon-\alpha+n+1)^n dt}{n!} \quad |t| \leq e^{-1}. \quad (A7)$$

Therefore,

$$\phi_2 = \sum_{n=0}^\infty \frac{(\epsilon-\alpha+n+1)^n}{n!} \frac{1}{2\pi i} \int_{-0}^{(0+)} e^{y/t} t^{n-\alpha-\beta} dt \quad (A8)$$

so that the substitution  $v = t^{-1}$  finally yields

$$\begin{aligned} \phi_2 &= \sum_{n=0}^\infty \frac{(\epsilon-\alpha+n+1)^n}{n!} \frac{1}{2\pi i} \int_{-\infty}^{(0+)} e^{yv} v^{\beta+\alpha-n-2} dv \\ &= \sum_{n=0}^\infty \frac{(\epsilon-\alpha+n+1)^n}{n!} \frac{y^{n-\alpha-\beta+1}}{\Gamma(n-\alpha-\beta+2)}. \end{aligned} \quad (A9)$$

Then,  $I_{\alpha\epsilon}$  is directly evaluated

$$\begin{aligned} I_{\alpha\epsilon} &= \left\{ \frac{\partial}{\partial \beta} \sum_{n=0}^\infty \frac{1}{n!} \left[ \frac{(n+\epsilon+\beta)^{n+\alpha+\beta-1}}{\Gamma(n+\alpha+\beta)} y^n \right. \right. \\ &\quad \left. \left. - \frac{(\epsilon-\alpha+n+1)^n}{\Gamma(n-\alpha-\beta+2)} y^{n-\alpha-\beta+1} \right] \right\}_{\beta=0}, \\ I_{\alpha\epsilon} &= \sum_{n=0}^\infty \frac{y^n (n+\epsilon)^{n+\alpha-1}}{n! (n+\alpha-1)!} \left[ \ln(n+\epsilon) y + 1 + \frac{\alpha-\epsilon-1}{n+\epsilon} \right. \\ &\quad \left. - \psi(n+1) - \psi(n+\alpha) \right] + (-1)^\alpha \sum_{n=0}^{\alpha-2} \\ &\quad \times \frac{(\alpha-\epsilon-n-1)^n}{n!} (\alpha-n-2)! y^{n-\alpha+1}; \quad \epsilon \geq 1 \quad (A10) \end{aligned}$$

where

$$\psi(z) = \Gamma'(z)/\Gamma(z),$$

$$\begin{aligned} I_{\alpha\epsilon} &= \delta_{\alpha 2} + \sum_{n=1}^\infty \frac{y^n n^{n+\alpha-1}}{n! (n+\alpha-1)!} \left[ \ln n y + 1 + \frac{\alpha-1}{n} \right. \\ &\quad \left. - \psi(n+1) - \psi(n+\alpha) \right] + (-1)^\alpha \sum_{n=0}^{\alpha-2} \\ &\quad \times \frac{(\alpha-n-1)^n}{n!} (\alpha-2-n)! y^{n-\alpha+1}; \quad \epsilon = 0 \quad (A11) \end{aligned}$$

when it is recognized<sup>20</sup> that for negative integers  $-m$

$$\lim_{z \rightarrow -m} \frac{\psi(z)}{\Gamma(z)} = (-1)^{m-1} m!. \quad (A12)$$

<sup>19</sup> Reference 18, p. 132.  
<sup>20</sup> A. Erdélyi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York 1953), Vol. I, pp. 46-47.