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General Restriction on the Distribution of Ions in Electrolytes

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The rigorous second-moment condition previously derived for "primitive-model" electrolyte ion atmospheres in equilibrium is generalized to arbitrary mixtures of electrolytes of unrestricted charge species. No special assumptions regarding the nature of solvent dielectric behavior are required, and the condition remains valid even in the presence of specific chemical interactions that lead to complex ion formation.

I. INTRODUCTION

In an earlier paper¹ devoted to the statistical thermodynamics of the so-called "primitive-model" electrolyte, we pointed out the existence of a rigorous second-spatial-moment condition on the ionic pair correlation functions for that model. Since it was demonstrated also that this condition has important implications for the distribution of ions at high concentration, it is important to see if a similar second-moment condition can be established for less restrictive models. This article provides the desired generalization.

The "primitive-model" electrolyte consists of rigid-sphere ions, all of equal diameter a , suspended in a structureless linear dielectric solvent. The model furthermore is charge symmetric, i.e., there are equal numbers of anions (charge $-Ze$) and cations (charge $+Ze$). In addition it is presumed that the spherical ions are cut out of a material with precisely the same dielectric constant ϵ_0 as the structureless solvent; thus with spherical charge symmetry in each ion, the electrostatic interaction between any pair of ions i and j is precisely

$$\pm Z^2 e^2 / \epsilon_0 r_{ij}, \quad (1)$$

for all $r_{ij} > a$.

The class of electrolytes of interest in the following represents full relaxation of the "primitive-model"

conditions, and to that extent the final result actually applies to real electrolytes in the laboratory. We shall assume at the outset that the electrolytic solution comprises an arbitrary number of charge species, so in fact our final generalized second-moment condition [Eq. (23) below] accommodates any mixture of electrolytes as well as the single-component solutions.

Several ways in which the general second-moment condition may be useful in electrochemical studies are discussed in the final section.

II. GENERAL SECOND-MOMENT-CONDITION DERIVATION

It will eventually be convenient to suppose that our electrolyte is contained within a macroscopic rectangular box V to which periodic boundary conditions apply. Since our objective consists partly in observing the electrolyte's linear response to static external electrostatic fields, the underlying system periodicity makes it natural to consider separately exciting fields of different wavelengths.

Let \mathbf{k} denote a vector from the reciprocal lattice generated by the periodicity cell chosen. When V is initially empty, an externally applied charge density

$$q_{\text{ap}}(\mathbf{r}) = (\psi_0 k^2 / 4\pi) \sin(\mathbf{k} \cdot \mathbf{r}) \quad (2)$$

(ψ_0 is a small real constant) will produce an applied potential $\psi_{\text{ap}}(\mathbf{r})$ that must satisfy Poisson's equation, which in Gaussian units is

$$\nabla^2 \psi_{\text{ap}}(\mathbf{r}) = -4\pi q_{\text{ap}}(\mathbf{r}). \quad (3)$$

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¹ F. H. Stillinger, Jr., and R. Lovett, *J. Chem. Phys.* **48**, 3858 (1968); also see the paper following it: R. Lovett and F. H. Stillinger, Jr., *J. Chem. Phys.* **48**, 3869 (1968).

The requisite solution (for which we may specify the homogeneous equation solution to vanish) is also a pure sinusoid,

$$\psi_{\text{ap}}(\mathbf{r}) = \psi_0 \sin(\mathbf{k} \cdot \mathbf{r}). \quad (4)$$

Were V to have initially been filled with a classical linear dielectric continuum (as the "primitive model" uses for a solvent), the Poisson equation [(3)] would merely have been modified by inclusion of a k -independent dielectric constant ϵ_0 ,

$$\nabla^2 \psi(\mathbf{r}) = -(4\pi/\epsilon_0) q_{\text{ap}}(\mathbf{r}). \quad (5)$$

Likewise Eq. (4) would exhibit a corresponding change, with the potential ψ in this case simply given by

$$\psi(\mathbf{r}) = (\epsilon_0)^{-1} \psi_{\text{ap}}(\mathbf{r}) = (\psi_0/\epsilon_0) \sin(\mathbf{k} \cdot \mathbf{r}), \quad (6)$$

so that the corresponding amplitude is diminished or "shielded" by factor ϵ_0^{-1} .

Real fluid dielectrics of course are molecular, not structureless continua. According to Kirkwood's general dielectric theory,² the dielectric constant (for spatially homogeneous electric fields) results in part from orientational correlation between neighboring molecules. For \mathbf{k} sufficiently large that $\sin(\mathbf{k} \cdot \mathbf{r})$ changes significantly over the neighbor distance, one cannot expect the full macroscopic value of the dielectric constant to obtain. Instead, a different (probably smaller) value is relevant. This indicates the necessity of spatial dispersion in real dielectric fluids; when $q_{\text{ap}}(\mathbf{r})$ is applied to a real molecular dielectric in V we must expect to find a resultant mean electrostatic potential

$$\bar{\psi}(\mathbf{r}) = [\psi_0/\epsilon_0(k)] \sin(\mathbf{k} \cdot \mathbf{r}), \quad (7)$$

where the usual dielectric constant quoted for the substance (to which Kirkwood's theory applies) is simply $\epsilon_0(0)$.

We finally consider the case in which V contains an electrolytic solution, comprising ionic species $1 \cdots \nu$ present in concentrations $C_1 \cdots C_\nu$, and bearing charges $Z_1 e \cdots Z_\nu e$. The result of perturbing the system now with the same applied charge density (2) may phenomenologically be still described in terms of a k -dependent dielectric function, $\epsilon(k)$. The mean potential $\bar{\psi}(\mathbf{r})$ now may be written in a form entirely analogous to (7),

$$\bar{\psi}(\mathbf{r}) = [\psi_0/\epsilon(k)] \sin(\mathbf{k} \cdot \mathbf{r}), \quad (8)$$

thereby defining $\epsilon(k)$. Unlike the previous cases, however, we are now dealing with a conducting fluid which tends, in the long-wavelength limit, *completely* to shield applied fields. Therefore $\epsilon(k)$ must display the following feature:

$$\lim_{k \rightarrow 0} [\epsilon(k)]^{-1} = 0. \quad (9)$$

The linear response of a real electrolyte to an applied

sinusoidal electrostatic potential may be regarded as composed additively of two effects. The first consists of pure dielectric response, without mass redistribution, and consists of:

- (a) induction of multipoles in both solvent molecules and the ions;
- (b) orientation of permanent dipoles;
- (c) interactions among the multipoles.

The second partial response involves ionic conduction (generally with solvent drag) to produce finally sinusoidally varying singlet densities for all species.

For heuristic purposes it is convenient to imagine that the ions in the solution have very large masses.³ Then it will indeed take very long for the ions to redistribute. The nearly immediate response of the system will hence be the purely dielectric response just described, and since the ions during this initial period essentially are stationary we may use the resultant average electrostatic potential to define a solution dielectric constant $\epsilon_0(k)$, exactly as in Eq. (7) for a nonelectrolytic fluid. Ultimately (over a span of time dependent on the ion masses assigned), the ions would move into position to reduce further the mean potential's amplitude, so that $\epsilon(k)$, rather than the initial response $\epsilon_0(k)$, obtains.

Though this infinite-ion-mass artifice serves to clarify the distinction between $\epsilon_0(k)$ and $\epsilon(k)$ for an electrolyte, it is scarcely applicable to real electrolytes. Using the fact that at sufficiently low frequency the mechanisms operating to produce $\epsilon_0(k)$ are nondissipative, whereas those producing the final shielding charge separation are dissipative, it is possible to measure $\epsilon_0(0)$. In fact, Hasted, Collie, and Ritson⁴ have determined this quantity for a number of salts dissolved in water. We shall proceed under the assumption that $\epsilon_0(0)$ for any electrolytic solution of interest could be measured. Of course $\epsilon_0(0)$ for the primitive electrolyte model is nothing but the k -independent dielectric constant of its continuum solvent.

In the final equilibrium state achieved by a conducting electrolyte under the perturbing influence of applied charge density $q_{\text{ap}}(\mathbf{r})$, the average force on any type α ion at position \mathbf{r} may be regarded as split into two parts,

$$\bar{\mathbf{F}}_\alpha(\mathbf{r}) = \bar{\mathbf{F}}_{p,\alpha}(\mathbf{r}) + \bar{\mathbf{F}}_{c,\alpha}(\mathbf{r}), \quad (10)$$

that correspond precisely to the two additive responses. The former, $\bar{\mathbf{F}}_{p,\alpha}(\mathbf{r})$, is the mean force due to the applied field and the dielectric polarization of the entire fluid (before mass redistribution), and the second, $\bar{\mathbf{F}}_{c,\alpha}(\mathbf{r})$, is the additional mean force that results when the final ionic charge distribution is in place. The

³ The classical ionic equilibrium distribution functions of interest are independent of these masses.

⁴ J. B. Hasted, D. M. Ritson, and C. H. Collie, *J. Chem. Phys.* **16**, 1 (1948).

² J. G. Kirkwood, *J. Chem. Phys.* **7**, 911 (1939).

shielding property expressed by Eq. (9) is equivalent to the statement that the ionic singlet potentials of mean force⁵ (for fixed ψ_0) vanish as $k \rightarrow 0$; in terms of the mean forces themselves one thus requires

$$\lim_{k \rightarrow 0} k^{-1} \bar{\mathbf{F}}_{\alpha}(\mathbf{r}) \equiv \lim_{k \rightarrow 0} k^{-1} [\bar{\mathbf{F}}_{p,\alpha}(\mathbf{r}) + \bar{\mathbf{F}}_{c,\alpha}(\mathbf{r})] = 0. \quad (11)$$

In the small- k limit,

$$k^{-1} \bar{\mathbf{F}}_{p,\alpha}(\mathbf{r}) \sim - (Z_{\alpha} e / k) \nabla [\psi_0 / \epsilon_0(0)] \sin(\mathbf{k} \cdot \mathbf{r}), \quad (12)$$

so that the shielding phenomenon expressed by Eq. (11) may equally well be written thus,

$$\lim_{k \rightarrow 0} k^{-1} \{ - [Z_{\alpha} e / \epsilon_0(0)] \nabla \sin(\mathbf{k} \cdot \mathbf{r}) + \bar{\mathbf{F}}_{c,\alpha}(\mathbf{r}) \} = 0. \quad (13)$$

In the same small- k limit, $\bar{\mathbf{F}}_{c,\alpha}$ should likewise have a particularly simple form that is determined by the electric field \mathbf{E}_c established by the final density q_{in} of ionic charge induced in the solution by q_{ap} ,

$$\begin{aligned} \bar{\mathbf{F}}_{c,\alpha}(\mathbf{r}) &\sim Z_{\alpha} e \mathbf{E}_c(\mathbf{r}), \\ \nabla \cdot \mathbf{E}_c(\mathbf{r}) &= [4\pi / \epsilon_0(0)] q_{in}(\mathbf{r}). \end{aligned} \quad (14)$$

Therefore Eq. (13) may be modified to read

$$\lim_{k \rightarrow 0} k^{-1} [- \nabla \sin(\mathbf{k} \cdot \mathbf{r}) + \epsilon_0(0) \mathbf{E}_c(\mathbf{r})] = 0. \quad (15)$$

In the case of the primitive-model electrolyte, it is immediately possible to relate $q_{in}(\mathbf{r})$ to the ionic pair correlation functions, since the effect of $q_{ap}(\mathbf{r})$ on the system amounts precisely to a sum of single-ion potentials.¹ But a real electrolyte strictly speaking does not have this property; the effect of the interaction of the solution with the applied field involves overwhelmingly complicated many-molecule polarization interactions that could only be analytically expressed as many-body potential energies in the system's Hamiltonian.

Nevertheless, a certain flexibility in the choice of applied potentials should exist for which the shielding statement equation (15) remains valid. For example, the electrolyte could be perturbed instead by adding to its Hamiltonian,

$$\psi_0 \sum_{\alpha=1}^{\nu} \frac{Z_{\alpha} e}{\epsilon_0(0)} \sum_{j_{\alpha}=1}^{N_{\alpha}} \sin(\mathbf{k} \cdot \mathbf{r}_{j_{\alpha}}) \quad (16)$$

(the ions of type α are N_{α} in number) which directly affects *only* the ions, but whose magnitude has been selected by inclusion of $\epsilon_0(0)$ to agree precisely with the small- k polarization effect of the original electrostatic perturbation. Since the force on any ion produced by artificial perturbation (16) is therefore the same (for sufficiently small k) as the *average* external plus polarization force produced by the original "real" electrostatic

⁵ For definition of molecular correlation functions and potentials of mean force, see T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Co., New York, 1956), Chap. 6.

applied field, the shielding phenomenon should still occur. This means that Eq. (15) should be equally valid for the induced charge field \mathbf{E}_c produced by (16), as for that produced by the original $q_{ap}(\mathbf{r})$.

The analytic advantage of perturbation (16) is that $q_{in}(\mathbf{r})$ may now be written down in terms of the set of ion-ion pair correlation functions for the unperturbed solution, $g_{\alpha\beta}^{(2)}(\mathbf{r})$,⁶ since it is a straightforward matter to evaluate the linear ion density variations induced by (16) in standard canonical ensemble theory.⁵ The result has the following form:

$$\begin{aligned} q_{in}(\mathbf{r}) &= - [\psi_0 e^2 / k_B T \epsilon_0(0)] \sin(\mathbf{k} \cdot \mathbf{r}) \\ &\times \left[\sum_{\alpha=1}^{\nu} Z_{\alpha}^2 C_{\alpha} + \sum_{\alpha,\beta=1}^{\nu} Z_{\alpha} Z_{\beta} C_{\alpha} C_{\beta} \int_V g_{\alpha\beta}^{(2)}(s) \cos(\mathbf{k} \cdot \mathbf{s}) d\mathbf{s} \right], \end{aligned} \quad (17)$$

where the \mathbf{s} integration spans the periodicity volume V , and where k_B and T as usual are Boltzmann's constant and absolute temperature.

The last expression permits explicit integration of the second equation (14) to be carried out for \mathbf{E}_c . Then if that \mathbf{E}_c is utilized in Eq. (15), it is established that

$$\begin{aligned} 0 &= \lim_{k \rightarrow 0} \left\{ 1 - \frac{\kappa^2}{k^2} \left[1 + \left(\sum_{\alpha=1}^{\nu} Z_{\alpha}^2 C_{\alpha} \right)^{-1} \sum_{\beta,\gamma=1}^{\nu} Z_{\beta} Z_{\gamma} C_{\beta} C_{\gamma} \right. \right. \\ &\quad \left. \left. \times \int_V g_{\beta\gamma}^{(2)}(s) \cos(\mathbf{k} \cdot \mathbf{s}) ds \right] \right\}. \end{aligned} \quad (18)$$

In writing Eq. (18), we have introduced the Debye parameter

$$\kappa^2 = \frac{4\pi e^2}{k_B T \epsilon_0(0)} \sum_{\alpha=1}^{\nu} Z_{\alpha}^2 C_{\alpha}, \quad (19)$$

including the correct solution dielectric constant $\epsilon_0(0)$. The $g_{\beta\gamma}^{(2)}$ should approach their limiting values at large s sufficiently rapidly that it is possible to commute the summation and integration operations in (18), as well as to replace $\cos(\mathbf{k} \cdot \mathbf{s})$ by its angular average,

$$\begin{aligned} 0 &= \lim_{k \rightarrow 0} \left(1 - \frac{\kappa^2}{k^2} \left\{ 1 + \left(\sum_{\alpha=1}^{\nu} Z_{\alpha}^2 C_{\alpha} \right)^{-1} \int \frac{\sin(ks)}{ks} \right. \right. \\ &\quad \left. \left. \times \left[\sum_{\beta,\gamma=1}^{\nu} Z_{\beta} Z_{\gamma} C_{\beta} C_{\gamma} g_{\beta\gamma}^{(2)}(s) \right] ds \right\} \right). \end{aligned} \quad (20)$$

The over-all electroneutrality condition

$$\sum_{\gamma=1}^{\nu} Z_{\gamma} C_{\gamma} = 0 \quad (21)$$

permits us to extend the \mathbf{s} integral in Eq. (20) over all space.

The portion of Eq. (20) in braces possesses a formal

⁶ As usual, each of these functions approach unity as r approaches infinity.

expansion in even powers of k by virtue of the series

$$\sin(ks)/ks = 1 - \frac{1}{6}(k^2s^2) + (k^4s^4/120) - \dots$$

In order that the zero limit specified by Eq. (20) obtain, the k -independent and k^2 orders of that quantity with braces must both be suitably constrained. The requisite conditions are, first from the k^0 order,

$$- \sum_{\alpha=1}^{\nu} Z_{\alpha}^2 C_{\alpha} = \sum_{\alpha=1}^{\nu} Z_{\alpha} C_{\alpha} \int \left[\sum_{\beta=1}^{\nu} Z_{\beta} C_{\beta} g_{\alpha\beta}^{(2)}(s) \right] ds, \quad (22)$$

and second from the k^2 order,

$$-6\kappa^{-2} = \left(\sum_{\alpha=1}^{\nu} Z_{\alpha}^2 C_{\alpha} \right)^{-1} \int \left[\sum_{\beta,\gamma=1}^{\nu} Z_{\beta} Z_{\gamma} C_{\beta} C_{\gamma} g_{\beta\gamma}^{(2)}(s) \right] s^2 ds. \quad (23)$$

The first of these is nothing but a linear combination of the well-known local electroneutrality conditions,

$$-Z_{\alpha}e = \int \left[\sum_{\gamma=1}^{\nu} Z_{\gamma} e C_{\gamma} g_{\alpha\gamma}^{(2)}(s) \right] ds, \quad (24)$$

specifying that the total mean charge in the ion atmosphere around an α ion is precisely $-Z_{\alpha}e$. The second, Eq. (23), is the desired general second-moment condition

III. DISCUSSION

The existence of a second-moment condition (23) on electrolyte correlation functions, as well as the existence of the standard "zereth-moment" local electroneutrality conditions (24) is of course intimately related to the long-range character of Coulomb interactions. For that reason no analogous conditions can be derived relating the correlation functions in nonelectrolytes. It is interesting to note that the shielding of each ion expressed by the local electroneutrality conditions (24) would obtain even if the Coulomb potential between pairs of ions varied spatially as r^{-p} , with any $1 \leq p \leq 3$, but only at the lower p limit 1 would the second-moment condition necessarily apply.⁷

The linear Debye-Hückel point-ion theory specifies the ionic pair correlation functions to be the following⁸:

$$g_{\beta\gamma}^{(2)}(s) \cong 1 - [Z_{\beta} Z_{\gamma} e^2 \exp(-\kappa s)] [k_B T \epsilon_0(0) s]^{-1}. \quad (25)$$

One easily verifies by substitution that this set of approximate correlation functions exactly satisfies the general second-moment condition. The version of the theory in which ion sizes are inserted however does not generally satisfy the condition.⁹

⁷ The denominator k^2 in Eq. (20) in this more general circumstance would become k^{2-p} , and unless $p=1$ precisely, no condition on the $O(k^2)$ part of the quantity in braces in this equation is required.

⁸ P. Debye and E. Hückel, *Z. Physik* **24**, 185, 305 (1923).

⁹ It could, though, if one is prepared to admit an effective decay constant in the pair correlation functions differing slightly from the conventional κ as defined in Eq. (19).

From time to time, theories of ionic correlation functions are proposed which purport to extend the Debye-Hückel results to moderate or high concentration.¹⁰ The long-range character of the Coulomb interactions makes it especially unclear how the approximations used in these theories affect the results. It therefore seems desirable and important to check the results of such theories, past and future, for consistency with the general second-moment condition.

In the case of a weakly ionizing substance such as water, the second-moment condition may prove valuable in assessing dielectric properties at distances comparable to molecular size. At room temperature, κ^{-1} for water is about 1300 Å, owing to the extremely low concentration of H^+ and OH^- . Except at small distances (below about 20 Å probably), the four ionic pair correlation functions should be essentially exactly specified by the Debye-Hückel theory with the ordinary macroscopic dielectric constant. At the smaller distances, however, the principal modification will be deviation of the local dielectric constant from the macroscopic value. We speculate that the application of the second-moment condition to pure water will prove valuable in unraveling the relation between local hydrogen-bond order and general dielectric behavior.

The existence of complex ions in some electrolytes illustrates in a way the power and breadth of applicability of the general second-moment condition. For these electrolytes in fact there is considerable flexibility in choice of definition of the separate species $1 \dots \nu$ in condition (23). In the case of aqueous $MgSO_4$, for instance, one either may regard the uncharged ion pair to be a separate chemical entity or not, depending on convenience, but in either event condition (23) must be obeyed. Of course the concentrations to be inserted into that relation, and the functional forms of the $g_{\beta\gamma}^{(2)}$'s are very much dependent on whether (and precisely how) the ion-pair species is defined and distinguished. Nevertheless the equality shown must obtain as an invariant relation. This fact may indeed help clarify the ambiguities that sometimes surround attempts at a precise statistical-mechanical definition of complex ions in concentrated solutions.

Finally, we stress the fact that phenomenological notions about the response of conductors to external fields have been a basic ingredient in our second-moment-condition derivation. It is desirable to seek an alternative derivation utilizing solely the microscopic theory that proceeds merely from knowledge of the electrolyte's Hamiltonian. The construction of such an alternative proof would very likely constitute a major theoretical advance in the understanding of concentrated electrolytes.

¹⁰ A representative list of such attempts is provided by J. C. Poirier in a contributed chapter to: B. E. Conway and R. G. Barradas, *Chemical Physics of Ionic Solutions* (John Wiley & Sons, Inc., New York, 1966).