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On the Second-Moment Condition of Stillinger and Lovett

D. J. Mitchell,[1] D. A. McQuarrie,[2] Attila Szabo,[2,4] and J. Groeneveld[3]

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The Stillinger–Lovett second-moment condition of electrolyte solutions is derived rigorously and simply from only some reasonable (but apparently never proven rigorously) assumptions concerning the asymptotic form of the direct correlation function and the Ornstein–Zernike equation. The derivation suggests that this condition is not the first member of a hierarchy of moment conditions and that there exists no simple result for a fourth-moment condition.

KEY WORDS: Ornstein–Zernike equation; direct correlation function; electrolytes; moment condition; solutions; Coulombic.

In 1968 Stillinger and Lovett$^{(1)}$ derived an exact second-moment condition for the ionic atmospheres in an electrolyte solution. This condition can be written in the form

$$S_2 = \sum_{i,j} q_i\rho_i q_j\rho_j \int_0^\infty h_{ij}(r) 4\pi r^4 \, dr = -3\epsilon/2\pi\beta \tag{1}$$

where q_i and ρ_i are the charge and average concentration, respectively, of the ith ionic species, $h_{ij}(r) = h_{ji}(r)$ is the total correlation function between species i and j, ϵ is the dielectric constant of the solvent, and $\beta = (kT)^{-1}$.

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[1] Department of Applied Mathematics, Research School of Physical Sciences, The Australian National University, Canberra, Australia.

[2] Department of Chemistry, Indiana University, Bloomington, Indiana.

[3] Instituut voor Theoretische Fysica der Rijksuniversiteit, Utrecht, The Netherlands.

[4] Alfred P. Sloan Fellow.

This so-called second-moment condition is to be compared with the conditions of electroneutrality (one for each species), which can be written as

$$\sum_j q_j\rho_j \int_0^\infty h_{ij}(r) 4\pi r^2\, dr = -q_i, \qquad i = 1, 2, \ldots, \sigma \tag{2}$$

The notation and form of Eq. (2) suggest that these conditions of electroneutrality be called the zero-moment condition.

To our knowledge the important condition, Eq. (1), has never been derived generally from within a rigorous statistical mechanical framework, although Outhwaite(2) has shown it to be equivalent to a normalization condition on the mean electrostatic potential of Debye–Hückel for an ideal solvent. In this note we shall derive Eq. (1) rigorously from only the Ornstein–Zernike equation and a commonly assumed[5] and reasonable, but apparently never proven rigorously, asymptotic form of the direct correlation function $c_{ij}(r)$. In addition to being straightforward and rigorous, our derivation suggests that Eqs. (2) and (1) are *not* the first two members of a hierarchy of moment conditions.

We start with the Ornstein–Zernike equation for σ components (see, e.g., Ref. 3)

$$h_{ij}(r) = c_{ij}(r) + \sum_{l=1}^{\sigma} \rho_l \int h_{il}(r') c_{lj}(|\mathbf{r} - \mathbf{r}'|)\, d\mathbf{r}' \tag{3}$$

and define(4)

$$\bar{f}_{ij}(k) = (\rho_i\rho_j)^{1/2} \int [\exp(-i\mathbf{k}\cdot\mathbf{r})] f_{ij}(r)\, d\mathbf{r} \tag{4}$$

By taking the Fourier transform of the Ornstein–Zernike equation and denoting the matrix whose ijth element is $\bar{f}_{ij}(k)$ by $\underset{\sim}{\bar{f}}(k)$, we find

$$\underset{\sim}{\bar{h}}(k) = \underset{\sim}{\bar{c}}(k) + \underset{\sim}{\bar{c}}(k)\underset{\sim}{\bar{h}}(k) \tag{5}$$

or

$$\underset{\sim}{\bar{h}}(k) = [\underset{\sim}{I} - \underset{\sim}{\bar{c}}(k)]^{-1}\underset{\sim}{\bar{c}}(k) \tag{6}$$

Now, our first assumption is that, asymptotically, the direct correlation function goes simply as the Coulomb potential, i.e.,

$$c_{ij}(r) \sim -\beta q_i q_j/\epsilon r \qquad \text{as} \quad r \to \infty \tag{7}$$

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[5] See, e.g., Mou and Mazo(8) for a recent use of this assumption.

This asymptotic form of $c_{ij}(r)$ dictates that$^{(5)}$

$$\begin{aligned}\bar{c}_{ij}(k) &= \frac{4\pi}{k}(\rho_i\rho_j)^{1/2}\int_0^\infty c_{ij}(r)r \sin kr\, dr \\ &\sim -\frac{4\pi}{k^2}\frac{\beta q_i q_j(\rho_i\rho_j)^{1/2}}{\epsilon} \qquad \text{as} \quad k \to 0\end{aligned} \tag{8}$$

If, second, $k^2\bar{c}_{ij}(k)$ can be written as a power series in k, we can write

$$\bar{\underset{\sim}{c}}(k) = \underset{\sim}{c}^{(-2)}k^{-2} + \underset{\sim}{c}^{(0)} + \underset{\sim}{c}^{(2)}k^2 + \cdots \tag{9}$$

where $\underset{\sim}{c}^{(0)}$, $\underset{\sim}{c}^{(2)}$, etc. are undetermined matrices and the matrix elements of $\underset{\sim}{c}^{(-2)}$ are given by

$$-c_{ij}^{(-2)} = (4\pi\beta/\epsilon)q_i q_j(\rho_i\rho_j)^{1/2} \tag{10}$$

For future reference we note that

$$-\mathrm{Tr}[\underset{\sim}{c}^{(-2)}] = -\sum_i c_{ii}^{(-2)} = \kappa^2 \tag{11}$$

where

$$\kappa = \left[(4\pi\beta/\epsilon)\sum_j \rho_j q_j^2\right]^{1/2} \tag{12}$$

is the usual Debye–Hückel screening parameter.

Since $\underset{\sim}{c}^{(-2)}$ is singular, it is not possible to expand Eq. (6) in a power series in k in a simple manner, i.e., by using the expansion $(\underset{\sim}{A} + \underset{\sim}{B})^{-1} = \underset{\sim}{A}^{-1} - \underset{\sim}{A}^{-1}\underset{\sim}{B}\underset{\sim}{A}^{-1} + \cdots$. However, from our second assumption (9) and the Ornstein–Zernike equation (5) it can be deduced that also $\bar{\underset{\sim}{h}}(k)$ can be expanded in (now only positive) powers of k^2:

$$\bar{\underset{\sim}{h}}(k) = \underset{\sim}{h}^{(0)} + \underset{\sim}{h}^{(2)}k^2 + \underset{\sim}{h}^{(4)}k^4 + \cdots \tag{13}$$

and so the $2n$th moment, defined as

$$S_{2n} = \sum_{ij} q_i q_j \rho_i \rho_j \int_0^\infty h_{ij}(r) 4\pi r^{2n+2}\, dr \tag{14}$$

can be expressed in terms of $\underset{\sim}{h}^{(2n)}$ as

$$S_{2n} = (-)^n(2n + 1)! \sum_{ij} (\rho_i\rho_j)^{1/2} q_i q_j h_{ij}^{(2n)} \tag{15}$$

Using Eq. (10), this can be rewritten as

$$S_{2n} = \frac{(-)^{n+1}(2n + 1)!\,\epsilon}{4\pi\beta}\,\mathrm{Tr}[\underset{\sim}{c}^{(-2)}\underset{\sim}{h}^{(2n)}] \tag{16}$$

Substituting Eqs. (9) and (13) into (5) and collecting terms, we find

$$0 = \underset{\sim}{c}^{(-2)} + \underset{\sim}{c}^{(-2)}\underset{\sim}{h}^{(0)} \tag{17a}$$

$$\underset{\sim}{h}^{(0)} = \underset{\sim}{c}^{(0)} + \underset{\sim}{c}^{(0)}\underset{\sim}{h}^{(0)} + \underset{\sim}{c}^{(-2)}\underset{\sim}{h}^{(2)} \tag{17b}$$

$$\underset{\sim}{h}^{(2)} = \underset{\sim}{c}^{(2)} + \underset{\sim}{c}^{(2)}\underset{\sim}{h}^{(0)} + \underset{\sim}{c}^{(0)}\underset{\sim}{h}^{(2)} + \underset{\sim}{c}^{(-2)}\underset{\sim}{h}^{(4)} \tag{17c}$$

etc. Since the matrix $\underset{\sim}{c}^{(-2)}$ is separable, it is convenient to introduce Dirac notation. We set

$$\underset{\sim}{c}^{(-2)} \equiv -|c\rangle\langle c| \tag{18}$$

so that $c_{ij}^{(-2)} = -\langle i|c\rangle\langle c|j\rangle$. In this notation Eq. (11) becomes

$$\begin{aligned} -\mathrm{Tr}[\underset{\sim}{c}^{(-2)}] &= \mathrm{Tr}[|c\rangle\langle c|] = \sum_i \langle i|c\rangle\langle c|i\rangle \\ &= \sum_i \langle c|i\rangle\langle i|c\rangle = \langle c|c\rangle = \kappa^2 \end{aligned} \tag{19}$$

and

$$-\mathrm{Tr}[\underset{\sim}{c}^{(-2)}\underset{\sim}{h}^{(2n)}] = \langle c|\underset{\sim}{h}^{(2n)}|c\rangle \tag{20}$$

so that

$$S_{2n} = \frac{(2n+1)!\,(-)^n\epsilon}{4\pi\beta}\langle c|\underset{\sim}{h}^{(2n)}|c\rangle \tag{21}$$

We now rewrite Eqs. (17) using the above notation. Equation (17a) becomes

$$0 = |c\rangle\langle c| + |c\rangle\langle c|\underset{\sim}{h}^{(0)} \tag{22}$$

Since $|c\rangle \neq 0$, this implies that

$$\underset{\sim}{h}^{(0)}|c\rangle = -|c\rangle \tag{23}$$

which is just another way of saying that the zeroth-moment conditions (2) hold.

Using Eqs. (22) and (19), we also note that

$$\langle c|h^{(0)}|c\rangle = -\langle c|c\rangle = -\kappa^2 \tag{24}$$

and so Eq. (21) with $n = 0$ gives

$$S_0 = -\kappa^2\epsilon/4\pi\beta \tag{25}$$

which is an alternative form of the electroneutrality condition.

To find the corresponding expression for S_2, we multiply both sides of Eq. (17b) from the left by $\langle c|$ and from the right by $|c\rangle$ and see that the two terms involving the unknown matrix $\underset{\sim}{c}^{(0)}$ cancel, so that we are left with simply

$$-\langle c|c\rangle = -\langle c|c\rangle\langle c|h^{(2)}|c\rangle \tag{26}$$

or

$$\langle c|h^{(2)}|c\rangle = 1 \tag{27}$$

Substituting this into Eq. (21) with $n = 1$ gives

$$S_2 = -3\epsilon/2\pi\beta \tag{28}$$

One readily shows that (27) and (28) are equivalent to the second-moment condition, Eq. (1). It is interesting to note in this case that the unknown matrix $\underset{\sim}{c}^{(0)}$ that appears in Eq. (17b) drops out of the final result and so S_2 has the simple form given by Eq. (28).

Let us go on and see what the result for S_4 will appear like. Again, multiplying Eq. (17c) from the left by $\langle c|$ and from the right by $|c\rangle$, we find

$$\langle c|\underset{\sim}{h}^{(2)}|c\rangle = \langle c|\underset{\sim}{c}^{(0)}\underset{\sim}{h}^{(2)}|c\rangle - \langle c|c\rangle\langle c|\underset{\sim}{h}^{(4)}|c\rangle \tag{29}$$

Unlike the case for S_2, the undetermined matrix $\underset{\sim}{c}^{(0)}$ does not cancel out of the problem, and so S_4, which, according to Eq. (21), is related to $\langle c|\underset{\sim}{h}^{(4)}|c\rangle$ in the above expression, is not given in terms of known, simple quantities, by which we mean quantities that do not depend on the details of the shorter range molecular interactions, but only on the long-range (i.e., Coulomb) part of it. On the other hand, it is interesting to observe that $\underset{\sim}{c}^{(2)}$ in Eq. (29) does drop out just as $\underset{\sim}{c}^{(0)}$ drops out of Eq. (26). It can be shown, however, that there is no simple expression in the above sense for S_4 as there is for S_0 and S_2.

In summary, then, we have derived the Stillinger–Lovett condition of electrolyte solutions rigorously from only an asymptotic form of the direct correlation function and the Ornstein–Zernike equation. In addition, we suggest that this expression results from the fortuitous cancellation of an unknown quantity and is not the first member of a hierarchy.

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[6] See, e.g., Refs. 6 and 7.

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