Exact relations between charge-density functions determining the total Coulomb energy and the dielectric constant for a mixture of neutral and charged site-site molecules

Jocelyn M. Rodgers\(^1,2\)\(^\ast\) and John D. Weeks\(^1,3\)\(^†\)

\(^1\)Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742
\(^2\)Chemical Physics Program, University of Maryland, College Park, Maryland 20742
\(^3\)Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

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We extend results developed by Chandler [J. Chem. Phys. 65, 2925 (1976)] for the dielectric constant of neutral site-site molecular models to mixtures of both charged and uncharged molecules. This provides a unified derivation connecting the Stillinger-Lovett moment conditions for ions to standard results for the dielectric constant for polar species and yields exact expressions for the small-\(k\) expansion of the two-point intermolecular charge-density function used to determine the total Coulomb energy. The latter is useful in determining corrections to the thermodynamics of uniform site-site molecular models simulated with spherically truncated Coulomb interactions.

I. DERIVATION OF ZEROTH AND SECOND MOMENT CONDITIONS FOR A MIXTURE OF NEUTRAL AND CHARGED SITE-SITE MOLECULES

The total Coulomb energy obtained during simulation of a mixture of small site-site molecular species without any intramolecular charge-charge interactions is

\[
U^q = \left\langle \frac{1}{2} \sum_M \sum_{M'} \sum_{i=1}^{N_M} \sum_{j=1}^{N_{M'}} \left( 1 - \delta_{MM'} \delta_{ij} \right) \sum_{\alpha=1}^{n_M} \sum_{\gamma=1}^{n_{M'}} q_{\alpha M} q_{\gamma M'} \frac{|r_{(\alpha) i M} - r_{(\gamma) j M'}|}{|r - r'|} \right\rangle.
\]

(1)

where \(\rho_{qq}\) is a two-point intermolecular charge-density function that explicitly excludes any purely intramolecular charge correlations, as implied by Eq. (1) and detailed below.

The composite function \(\rho_{qq}(r, r')\) is a charge-weighted linear combination of all intermolecular, two-point site-site distribution functions,

\[
\rho_{qq}(r, r') = \sum_{\alpha M} \sum_{\gamma M'} q_{\alpha M} q_{\gamma M'} \rho_{\alpha M \gamma M'}(r, r').
\]

(3)

We now relate this function to the basic charge-charge linear response function used in the theory of the dielectric constant.
For solutions of primitive model ions, charge neutrality and screening place specific requirements on the behavior of \( \rho^{qq} \) in \( k \)-space at small \( k \) values \cite{4}. More generally, for a fluid composed of charged and polar molecules, the dielectric screening behavior of the molecules places restrictions on the decay of this two-point charge density. Based on this observation, we are able to harness a theoretical development of Chandler \cite{1} that expresses the dielectric constant in terms of an exact sum of charge-density-weighted pair correlation functions. We generalize the derivation to include both charged and neutral site-site molecules and we take the dielectric constant as a given. From this vantage point, we may instead use these relations to place requirements on the decay of the two-point charge density \( \rho^{qq} \).

We first define the instantaneous single-point charge-density \( \rho^q(r, \mathbf{R}) \), a function of both a given external position \( r \) and the set of positions of all mobile particles \( \mathbf{R} \equiv \{ \mathbf{R}_M \} \equiv \{ \mathbf{r}_{iM}^{(\alpha)} \} \), as

\[
\rho^q(r, \mathbf{R}) = \sum_M \sum_i^{N_M} \sum_{\alpha=1}^{n_M} q_{iM} \delta(r - \mathbf{r}_{iM}^{(\alpha)}).
\]  

(4)

With such a definition, the ensemble-averaged charge-density profile \( \rho^q(r) \) is

\[
\rho^q(r) = \left\langle \rho^q(r, \mathbf{R}) \right\rangle.
\]  

(5)

In the case of a uniform system, \( \rho^q(r) = 0 \). Comparing Eqs. (1) and (2) and using Eq. (1), we may also express \( \rho^{qq}(|r - r'|) \) for a uniform system as

\[
\rho^{qq}(|r - r'|) = \left\langle \rho^q(r, \mathbf{R})\rho^q(r', \mathbf{R}) \right\rangle - \left\langle \sum_M \sum_i^{N_M} \sum_{\alpha=1}^{n_M} q_{iM} \delta(r - \mathbf{r}_{iM}^{(\alpha)}) \delta(r' - \mathbf{r}_{1M}^{(\gamma)}) \right\rangle.
\]  

(6)

We have used the equivalence of all molecules of type \( M \) in the last term. This term removes purely intramolecular charge-density correlations; we shall determine the small-\( k \) contributions from that term based on well-known molecular properties using the approach of Chandler \cite{1} later in this note. The first term, in contrast, is exactly the charge-charge linear response function for a uniform neutral system:

\[
\left\langle \rho^q(r, \mathbf{R})\rho^q(r', \mathbf{R}) \right\rangle = \left\langle \delta \rho^q(r, \mathbf{R})\delta \rho^q(r', \mathbf{R}) \right\rangle \equiv \chi^{qq}(|r - r'|).
\]  

(7)

Here \( \delta \rho^q(r, \mathbf{R}) \equiv \rho^q(r, \mathbf{R}) - \left\langle \rho^q(r, \mathbf{R}) \right\rangle \). Physically \( \chi^{qq} \) describes the coupling between charge-density fluctuations at positions \( r \) and \( r' \). As is well established \cite{1, 5}, such a function is intimately related to the dielectric behavior of the fluid at long distances, and furthermore, may be easily analyzed using basic electrostatics and standard definitions of the functional derivative.

The electrostatic potential at \( r \) induced by a fixed external charge distribution \( \rho^{q}_\text{ext}(r') \) (e.g., a test charge \( Q \) placed at the origin, as considered by Chandler) is given by

\[
\mathcal{V}_\text{ext}(r) = \int \frac{\rho^{q}_\text{ext}(r')}{|r - r'|} dr',
\]  

(8)

and the associated electrostatic energy for a particular microscopic configuration characterized by the set of molecular positions \( \mathbf{R} \) is then

\[
U^{q}_\text{ext}(\mathbf{R}) = \int \rho^q(r, \mathbf{R}) \mathcal{V}_\text{ext}(r) dr.
\]  

(9)

This energy contribution will appear in the nonuniform system’s Hamiltonian when \( \mathcal{V}_\text{ext}(r) \) is nonzero. As such, we know from standard definitions of functional differentiation of free energies \cite{5, 6} that

\[
\frac{\delta [-\beta A]}{\delta [-\beta \mathcal{V}_\text{ext}(r)]} = \left\langle \frac{\delta \rho^q(r, \mathbf{R})}{\delta \mathcal{V}_\text{ext}(r)} \right\rangle \mathcal{V} \equiv \rho^{q}_V(r),
\]  

(10)

where \( \beta \equiv (k_B T)^{-1} \) and the subscript \( \mathcal{V} \) indicates that the ensemble average is taken in the presence of an external potential. Similarly we have

\[
\frac{\delta \rho^{q}_V(r)}{\delta [-\beta \mathcal{V}_\text{ext}(r')]} = \frac{\delta [-\beta A]}{\delta [-\beta \mathcal{V}_\text{ext}(r)]} \frac{\delta [-\beta A]}{\delta [-\beta \mathcal{V}_\text{ext}(r')]} = \chi^{qq}(r, r').
\]  

(11)
The total electrostatic potential at position \( \mathbf{r} \) in the nonuniform fluid is then given by the sum of the external potential and the induced polarization potential:

\[
V_{\text{tot}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \mathcal{V}_{\text{pol}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho_0^q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{12}
\]

To get a formula for the dielectric constant we expand about the uniform neutral system and evaluate \( \mathcal{V}_{\text{pol}} \) to linear order in \( V_{\text{ext}} \) using Eq. (11) and find

\[
\begin{align*}
V_{\text{tot}}(\mathbf{r}) &\approx V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \int d\mathbf{r}'' \frac{\delta \rho^q(\mathbf{r}')}{\delta [-\beta V_{\text{ext}}(\mathbf{r}'')]} [-\beta V_{\text{ext}}(\mathbf{r}'')], \\
&= V_{\text{ext}}(\mathbf{r}) - \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \int d\mathbf{r}'' \beta \chi^{qq}(|\mathbf{r}' - \mathbf{r}''|) V_{\text{ext}}(\mathbf{r}''). \tag{13}
\end{align*}
\]

Here \( \chi^{qq} \) is the linear response function in the uniform fluid as in Eq. (7). Taking the Fourier transform of the final equation, we find

\[
\hat{V}_{\text{tot}}(\mathbf{k}) = \hat{V}_{\text{ext}}(\mathbf{k}) - \frac{4\pi}{k^2} \beta \hat{\chi}^{qq}(\mathbf{k}) \hat{V}_{\text{ext}}(\mathbf{k}). \tag{15}
\]

Thus to linear order we have

\[
\frac{\hat{V}_{\text{tot}}(\mathbf{k})}{\hat{V}_{\text{ext}}(\mathbf{k})} = 1 - \frac{4\pi \beta}{k^2} \hat{\chi}^{qq}(\mathbf{k}). \tag{16}
\]

Phenomenologically, we know that in the limit of \( k \to 0 \), this ratio of the total electrostatic potential to the externally-imposed potential is exactly \( 1/\epsilon \). Therefore, we find for our molecular mixture the general result

\[
\lim_{k \to 0} \left( 1 - \frac{4\pi \beta}{k^2} \hat{\chi}^{qq}(\mathbf{k}) \right) = \frac{1}{\epsilon}. \tag{17}
\]

Based on the limit in Eq. (17), and expanding \( \hat{\chi}^{qq} \) for small \( k \) as \( \hat{\chi}^{(0)qq} + \hat{\chi}^{(2)qq} k^2 \), we have

\[
\begin{align*}
\hat{\chi}^{(0)qq} &= 0, \\
4\pi \beta \hat{\chi}^{(2)qq} &= 1 - \frac{1}{\epsilon}.
\end{align*} \tag{18}
\]

Any mixture with mobile ions acts as a conductor with \( \epsilon = \infty \) in Eq. (18), independent of the nature of the neutral components.

Our goal is to write a small-\( k \) expansion of the two-point intermolecular charge density,

\[
\hat{\rho}^{qq}(\mathbf{k}) \approx \hat{\rho}^{(0)qq} + k^2 \hat{\rho}^{(2)qq} + \mathcal{O}(k^4). \tag{19}
\]

As stated at the beginning of this derivation,

\[
\rho^{qq}(|\mathbf{r} - \mathbf{r}'|) = \chi^{qq}(|\mathbf{r} - \mathbf{r}'|) - \sum_M \sum_{\alpha=1}^{n_M} \sum_{\gamma=1}^{n_M} q_{\alpha M} q_{\gamma M} \delta(\mathbf{r} - \mathbf{r}_{1M}^{(\alpha)}) \delta(\mathbf{r}' - \mathbf{r}_{1M}^{(\gamma)}). \tag{20}
\]

We already have results for the small-\( k \) expansion of the charge-charge linear response function \( \hat{\chi}^{qq} \). Now we must remove the intramolecular contributions as described by the second term in the equation above. Defining the conditional singlet intramolecular site density functions \( \hat{\rho}_{\alpha\gamma M}(\mathbf{r} | \mathbf{r}') \) for \( \alpha \neq \gamma \) as

\[
\rho_{\gamma M}(\mathbf{r}') \hat{\rho}_{\alpha\gamma M}(\mathbf{r} | \mathbf{r}') = \left( N_M \delta(\mathbf{r} - \mathbf{r}_{1M}^{(\alpha)}) \delta(\mathbf{r}' - \mathbf{r}_{1M}^{(\gamma)}) \right), \tag{20}
\]

and applying consequences of uniformity, we find

\[
\rho^{qq}(|\mathbf{r} - \mathbf{r}'|) = \chi^{qq}(|\mathbf{r} - \mathbf{r}'|) - \sum_M \rho_M \sum_{\alpha, \gamma} q_{\alpha M} q_{\gamma M} \left[ \delta_{\alpha, \gamma} \delta(\mathbf{r} - \mathbf{r}') + 2 \delta_{\alpha, \gamma} (|\mathbf{r} - \mathbf{r}'|) \right]. \tag{21}
\]
Using the notation of Chandler for the term in square brackets \[^1\], we may write this expression more compactly as

$$
\rho^{qq}(|r - r'|) = \chi^{qq}(|r - r'|) - \sum_M \rho_M \sum_{\alpha,\gamma} q_{\alpha M} q_{\gamma M} \omega_{\alpha \gamma M} (|r - r'|).
$$

(22)

For neutral molecules, Chandler demonstrated that the small-\(k\) components of \(\hat{\omega}_{\alpha \gamma M}(k)\) are related to simple properties of the molecule. For both charged and uncharged molecules, the zeroth moment of \(\hat{\omega}_{\alpha \gamma M}\) is simply

$$
\hat{\omega}^{(0)}_{\alpha \gamma M} = \delta_{\alpha \gamma} + \int dr \rho_{\alpha |\gamma M}(r) = \delta_{\alpha \gamma} + (1 - \delta_{\alpha \gamma}) = 1.
$$

(23)

Using this exact expression in Eq. (22) yields

$$
\hat{\rho}^{(0)qq} = \hat{\chi}^{(0)qq} - \sum_M \rho_M \sum_{\alpha,\gamma} q_{\alpha M} q_{\gamma M} = - \sum_M \rho_M q_M^2,
$$

(24)

an expression encompassing the standard zeroth moment condition for ions \[^4\] and the zeroth moment for neutral molecular species \[^1\].

The expression for \(\hat{\omega}_M^{(2)}\) determined by Chandler \[^1\] may be written most generally as

$$
\hat{\omega}_M^{(2)} = \sum_{\alpha,\gamma} q_{\alpha M} q_{\gamma M} \hat{\omega}^{(2)}_{\alpha \gamma M} = - \frac{1}{6} \int d\mathbf{r} \sum_{\alpha,\gamma} q_{\alpha M} q_{\gamma M} \rho_{\alpha |\gamma M}(r) r^2 = - \frac{1}{6} \sum_{\alpha,\gamma} q_{\alpha M} q_{\gamma M} \langle q^2_{\alpha \gamma M} \rangle,
$$

(25)

where \(l_{\alpha \gamma M}\) is the bondlength between sites \(\alpha\) and \(\gamma\) for a molecule of species \(M\). As shown in Ref. \(^1\) for a neutral molecule indicated by \(N\) below, the final summation in the above equation is simply related to the molecular dipole moment \(\mu_N\) and the molecular polarizability \(\alpha_N\) as

$$
\hat{\omega}_N^{(2)} = \sum_{\alpha \neq \gamma} q_{\alpha N} q_{\gamma N} \hat{\omega}^{(2)}_{\alpha \gamma N} = \frac{1}{3} \mu_N^2 + k_B T \alpha_N.
$$

(26)

This relationship does not hold for a charged molecule since the dipole moment then depends on the choice of coordinate system.

Distinguishing charged species \((C)\) and neutral species \((N)\) where \(\{M\} = \{N\} \cup \{C\}\), and without substituting for \(\hat{\omega}_N^{(2)}\) and \(\hat{\omega}_C^{(2)}\), we find

$$
\hat{\rho}^{(2)qq} = \frac{k_B T}{4\pi} \frac{\epsilon - 1}{\epsilon} - \sum_M \rho_M \sum_{\alpha \neq \gamma} q_{\alpha M} q_{\gamma M} \hat{\omega}^{(2)}_{\alpha \gamma M} = \frac{k_B T}{4\pi} \frac{\epsilon - 1}{\epsilon} - \sum_N \rho_N \hat{\omega}_N^{(2)} - \sum_C \rho_C \hat{\omega}_C^{(2)}.
$$

(27)

Thus, we may write a general expression for \(\hat{\rho}^{qq}\) in \(k\)-space. Utilizing the expressions for \(\hat{\omega}_N^{(2)}\) and \(\hat{\omega}_C^{(2)}\), we have

$$
\hat{\rho}^{qq}(k) = - \sum_C \rho_C q_C^2 + k^2 \frac{k_B T}{4\pi} \frac{\epsilon - 1}{\epsilon} - k^2 \sum_N \rho_N \left\{ \frac{1}{3} \mu_N^2 + k_B T \alpha_N \right\} + k^2 \sum_C \rho_C \sum_{\alpha \neq \gamma} q_{\alpha C} q_{\gamma C} \langle l_{\alpha \gamma C}^2 \rangle + \mathcal{O}(k^4).
$$

(28)

Unlike \(\chi^{qq}\) in Eq. (18), we see that the small-\(k\) behavior of this two-point intermolecular charge-density function depends on several simple properties of the solution as a whole, like the dipole moment and polarizability of individual neutral molecules, and the net molecular charge and the average square bond lengths of charged molecules, as well as the dielectric constant. Thus by knowing simple single molecule properties and the long wavelength dielectric constant, we know how intermolecular charge-charge correlations decay in solution. This is the essential equation used to develop energy and pressure corrections for simulations of bulk liquids using molecular models with truncated Coulomb interactions \[^2\]. A related expression may be developed for larger molecular species with intramolecular charge-charge interactions.

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\[^1\] D. Chandler, J. Chem. Phys. \textbf{67}, 1113 (1977).

\[^2\] J.M. Rodgers and J. D. Weeks, (to be published)

\[^3\] D. Chandler and L. R. Pratt, J. Chem. Phys. \textbf{65}, 2925 (1976).

\[^4\] F. H. Stillinger and R. Lovett, J. Chem. Phys. \textbf{49}, 1991 (1968).

\[^5\] J.-P. Hansen and I. R. McDonald, \textit{Theory of Simple Liquids} (Academic Press, New York, 2006), 3rd ed.

\[^6\] J. K. Percus, The pair distribution function in classical statistical mechanics, In \textit{The Equilibrium Theory of Classical Fluids} (W. A. Benjamin, Inc., New York, 1964). Our definition of \(\chi^{qq}\) is consistent with notation in this reference and Ref. \(^1\).