Mode Expansion in Equilibrium Statistical Mechanics. II. A Rapidly Convergent Theory of Ionic Solutions*

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The mode expansion theory, which was derived in a previous paper, is applied to the calculation of thermodynamic properties of an ionic solution. The specific system investigated is the 1–1 restricted primitive model aqueous electrolyte. In this model, the effective interactions (potentials of mean force at infinite dilution) between ions are a sum of pair potentials, and the pair potentials are hard-core repulsions (all with diameter 4.6 Å) plus a positive or negative Coulomb potential reduced by the dielectric constant of water. For this system, the mode expansion converges rapidly. At salt concentrations between 0.05 and 1.0M, only the first three terms in the expansion are needed to obtain osmotic coefficients and activity coefficients which agree very well with the accurate results obtained by integral equation methods. Due to the computational simplicity of the mode expansion, it is argued that the theory provides a convenient method for studying more realistic models for electrolytes.

I. INTRODUCTION

In the first paper of this series,1 a new expansion for the Helmholtz free energy of a classical system was introduced. The scope of that paper was limited to a description of the general theory of our method, which we call the mode expansion, and a demonstration of the correspondence between it and the ionic cluster theory.2 In this paper we apply the mode expansion to a system of experimental interest: an ionic solution. For salt concentrations between 0.05 and 1.0M, only the first three terms in the mode expansion need be retained to obtain exceptionally accurate thermodynamic properties for 1–1 electrolytes in water.

The specific system investigated in this paper is a 1–1 restricted primitive model electrolyte. That is, the effective interactions (potentials of mean force at infinite dilution) between ions are a sum of pair potentials, and the pair potentials are hard cores (all of the same diameter) plus a positive or negative Coulomb potential reduced by the dielectric constant of the solvent. This hypothetical system is not expected to yield a quantitative description of real ionic solutions. Both the pairwise additivity of the potentials of mean force and the infinite repulsion as a representation of the short-range forces are oversimplifications. However, this model is a frequently studied system; and recently, reliable thermodynamic data for the system have been
obtained from the solutions of integral equations and Monte Carlo calculations. Thus, the scope of this paper is limited to testing the usefulness of our ideas in duplicating the thermodynamics of model electrolytes. Though the model considered here is the simplest possible, we find no reason to doubt that our method will be accurate for more complicated and realistic models.

As described in I, the mode expansion is a perturbation theory which describes the effects of a perturbation energy, \( U \), on the equilibrium properties of a system whose total potential energy is \( W = U_0 + U \). The quantity \( U_0 \) is called the reference system potential energy. Our method differs from most perturbation theories in that we do not concern ourselves directly with interactions between particles. Rather, attention is focused on the correlations among a set of collective coordinates: the Fourier transforms of the particle density. We assume that the perturbation can be decomposed into a sum of pair potentials, and that the Fourier transforms of the pair potentials exist. The mode expansion expresses the total free energy minus the reference system free energy as an infinite series of terms involving the Fourier transforms of the perturbation potentials and correlation functions in the reference system. The first term neglects correlations among density Fourier components with different wave vectors. This is often called the random phase approximation. The higher-order terms give a systematic way of correcting that approximation.

In this paper, we choose the reference system to be a hard-sphere fluid. Thus, the perturbations are Coulomb interactions reduced by a dielectric constant. A similar separation of the potential energy into reference and perturbation parts for the restricted primitive model was used by Stell and Lebowitz. It should be noted that the value of the perturbation potential inside the hard core of the reference system can be chosen arbitrarily. Usually it is algebraically convenient to define the perturbation to be the Coulomb potential for distances greater and smaller than the hard-sphere diameter. We have found, however, that the convergence of the mode expansion is apparently greatly enhanced by a different choice of the perturbation for distances smaller than the hard-sphere diameter. The reason is that our corrections to the random phase approximation are functional of the Fourier transform of the perturbation. The series of these corrections appears to converge rapidly when the Fourier transform decays rapidly as a function of the wave vector, \( k \), for large \( k \); and the decay of this Fourier transform can be enhanced by changing the perturbation inside the hard core from a Coulomb interaction to another function. Of course, if the infinite series could be summed exactly, the result would not depend on the choice of perturbation potential for those physically inaccessible regions of phase space in which two particles are separated by less than a hard-core diameter. However, if a particular choice of this potential makes the infinite series converge rapidly, this choice will also make the first few terms in the series more useful for numerical calculations.

In this paper, we are not using the usual concept of “convergence of an infinite series.” We use this phrase in the less formal sense to describe a series if successive terms in the series decrease in numerical value rapidly and if truncation of the series after a few terms gives accurate numerical values of the function that the expansion is intended to represent.

In Sec. II, the mode expansion theory for the restricted primitive model electrolyte is discussed. A comparison is made with the ionic cluster theory. Also, our method of treating the Coulomb potential is discussed. In Sec. III, numerical results are presented and compared with the integral equation results. The paper is concluded in Sec. IV with a discussion of our work.

II. THE THEORY FOR THE 1–1 RESTRICTED PRIMITIVE MODEL

A. Definition of the Problem

Following the development in I, the total potential energy of our system is separated into a reference system part, \( U_0 \), and a perturbation \( U \):

\[ W = U_0 + U. \]  

(2.1)

As a result, the excess Helmholtz free energy \( \Delta A \) can be expressed in terms of the reference-system excess Helmholtz free energy \( \Delta A_0 \) and the reference system average of the perturbation Boltzmann factor:

\[ -\beta \Delta A = -\beta \Delta A_0 + \ln(\exp[-\beta U]). \]  

(2.2)

Here \( \beta \) is the reciprocal of Boltzmann’s constant times the temperature, and the angle brackets \( \langle \cdots \rangle \) denote the configurational average in the reference system [see Eq. (2.3) in I].

The actual interactions in an ionic solution are very complicated. It is therefore convenient to make use of the McMillan-Mayer solution theory, and thereby avoid dealing with the real solvent–solvent and solute–solvent interactions. Thus, whenever we use the terminology “interaction” or “potential energy” we are referring to effective potentials, namely potentials of mean force at infinite dilution. The thermodynamic quantities derived in this way are osmotic quantities. For example, the excess osmotic pressure \( \Delta P \) is given by

\[ -\Delta P = (\partial \Delta A / \partial N)_V, \]  

(2.3)

where \( V \) is the volume of our ionic solution.

The system treated in this paper is the restricted primitive model for a 1–1 electrolyte, which is defined by the effective interactions between the solute particles. For a system in which \( N \) salt molecules are dissociated there are \( 2N \) ions in solution, and the model inter-
actions are
\[ W = \sum_{i<j}^{2N} w_{ij}(r_{ij}), \quad r_{ij} = |r_i - r_j|, \quad (2.4a) \]
where
\[ w_{ij}(r) = \infty, \quad r < \sigma, \]
\[ = z_j e^r (e^r/D) r^{-1}, \quad r \geq \sigma. \quad (2.4b) \]
Here \( r_i \) is the position of the \( i \)th ion, \( z_i \) is the sign of the charge on the \( i \)th ion \((\pm 1)\), \( -e \) is the electronic charge, and \( D \) is the dielectric constant of the solvent. In our development, the reference system is a fluid composed of \( 2N \) hard spheres of diameter \( \sigma \):
\[ U_0 = \sum_{i<j}^{2N} u_0(r_{ij}), \quad (2.5a) \]
\[ u_0(r) = \infty, \quad r < \sigma, \]
\[ = 0, \quad r \geq \sigma. \quad (2.5b) \]
Thus, the perturbation is
\[ U = \sum_{i<j}^{2N} z_i z_j u(r_{ij}), \quad (2.6) \]
where
\[ u(r) = e^r / D r, \quad r \geq \sigma. \quad (2.7) \]
For \( r < \sigma \), \( u(r) \) can be any finite function. The choice of a particular form of the perturbation inside the hard core will be described in a later part of this section when the reasons for the choice can be discussed.

**B. The Mode Expansion**

Since the mode expansion deals with the correlations among Fourier components of the particle density, we first express the perturbation potential energy in terms of these Fourier components. Imposing periodic boundary conditions on the \( 2N \)-particle system in a cubic box of volume \( V \), we obtain
\[ U = V^{-1} \sum_k \hat{A}(k) [\hat{q}(k) q(-k) - 2N], \quad (2.8) \]
where
\[ \hat{A}(k) = \int dr u(r) \exp(-ik \cdot r) \quad (2.9) \]
and
\[ \hat{q}(k) = \sum_{j=1}^{2N} z_j \exp(-ik \cdot r_j) \quad (2.10) \]
is the two-component generalization of the Fourier component defined in Eq. (2.9) of I. As in that paper, \( \sum_{k'} \) denotes a sum over half of \( k \) space with \( k = 0 \) omitted. Unlike Eq. (2.10) of I, a mean field term does not appear in \( U \) since it vanishes for ionic systems in the thermodynamic limit due to the neutrality condition:
\[ \sum_{j=1}^{2N} z_j = 0. \]
Equations (2.8) and (2.2) are combined to give the analogs of Eqs. (2.11) and (2.12) in I:
\[ -\beta \Delta A = -\beta \Delta A_0 + \sum_k 2p(k) + \ln \left( \sum_k \hat{q}(k) \right), \quad (2.11) \]
where
\[ p(k) = \frac{z_0 q(k)}{c}, \quad (2.12) \]
is the salt concentration, and
\[ \hat{s}(k) = \exp \left[ -\beta \hat{q}(k) q(-k) / N \right] \quad (2.14) \]
is the \( k \)th mode. The notation \( \prod_{k'} \) denotes a product over half of \( k \) space with \( k = 0 \) omitted.

The mode expansion is a systematic way of approximating the free energy as expressed in Eq. (2.11). As derived in Sec. III of I, the expansion is
\[ -\beta \Delta A / V = \alpha - \alpha_0 + \sum_{n=1}^{N} \alpha_n, \quad (2.15a) \]
where
\[ \alpha_1 = V^{-1} \sum_k \left[ 2p(k) + \ln B_1(k) \right], \quad (2.15b) \]
and
\[ B_1(k) = \langle \hat{s}(k) \rangle, \]
\[ B_2(k^2) = \langle \hat{s}_1\hat{s}_2 \rangle / \langle \hat{s}_1 \rangle \langle \hat{s}_2 \rangle, \]
\[ B_3(k^3) = \langle \hat{s}_1\hat{s}_2\hat{s}_3 \rangle / \langle \hat{s}_1 \rangle \langle \hat{s}_2 \rangle \langle \hat{s}_3 \rangle \langle \hat{s}_4 \rangle \langle \hat{s}_5 \rangle \langle \hat{s}_6 \rangle, \quad (2.15c) \]
etc., \( s_i \) denotes \( s(k_i) \), \( \alpha_0 \) is minus \( \beta \) times the excess free energy per unit volume of the reference system, and \( \sum_{k'} \) denotes the \( n \)-fold sum subject to the constraint that no two \( k \) vectors in a particular term can be equal. The quantity \( \alpha_n \) gives the contribution to \( \alpha \) due to the correlations among \( n \) modes. The series in Eq. (2.15a) is formally exact in that it is an exact representation of \( \alpha \) when carried to infinite order.

**C. Results**

To use the mode expansion, we must first express \( B_n(k^r) \) in terms of \( \hat{A}(k) \) and correlation functions in the reference system. This is accomplished by introducing the \( c_m \) functions defined in Eq. (3.5) of I, and following the procedure outlined at the end of Sec. III of I. The

![Fig. 1. Cluster diagrams for terms appearing in \( \alpha_1 \) and \( \alpha_2 \) of the mode expansion. The dts represent particles (integration variables), the dashed lines represent Friedman's q bonds (Ref. 2), the solid lines represent the two-particle correlation in the reference system, \( h_{2n} \) bonding two particles, and the triangle represents the reference system \( h_{23} \) bonding three particles. Both \( h_{2n} \) and \( h_{23} \) themselves can be expanded in terms of graphs involving Friedman's kij=exp[-\beta \hat{q}(r_{ij})] bonds. Using Friedman's conventions for combinational factors, the two-mode term, \( \alpha_2 \), is equal to graph (a), and the three-mode term, \( \alpha_3 \), is the sum of graphs (b) and (c).]
expression for $B_0(k^2)$ is then inserted into Eq. (2.15b) and the sums over $k$ vectors are converted to integrals in the usual way. The algebraic details of the procedure are tedious but straightforward, if proper care is used when taking the thermodynamic limit. The results for the 1–1 restricted primitive model in the thermodynamic limit are

$$a_1 = \left[1/2(2\pi)^2\right] jdk^2 \int [2\rho(k) - \ln[1+2p(k)]]$$ (2.16)

$$a_2 = \left[1/8(2\pi)^3\right] jdk^2 \int \left( \sum_{j=1}^{2} \beta \hat{\phi}(k_j) \right) \hat{e}_1(k_1, k_2)$$ (2.17)

$$a_3 = \left[1/48(2\pi)^9\right] jdk^2 \int \left( \sum_{j=1}^{3} \beta \delta(k_j) \right) \hat{e}_5(k_1, k_2, k_3)$$ (2.18)

where

$$\hat{v}(k) = \hat{a}(k)/[1+2p(k)]$$ (2.19)

is the Fourier transform of a screened potential, and

$$\hat{e}_1(k_1, k_2) = \left(8\hat{v}/V\right) jdk_1dk_2 \cos(k_1\cdot r_{12}) \cos(k_2\cdot r_{12})$$

$$\hat{e}_5(k_1, k_2, k_3) = \left(4\hat{v}/V\right) jdk_1dk_2dk_3 \cos(k_1\cdot r_{12}) \cos(k_2\cdot r_{13}) \cos(k_3\cdot r_{13})$$

Here the quantities $h_{12}$ and $h_{123}$ are the usual two- and three-particle correlation functions for the reference system.  

These equations can be written in a form which is more amenable to comparison with other theories by introducing

$$\nu(r) = \left[1/(2\pi)^3\right] jdk^2 \hat{v}(k) \exp(ik\cdot r)$$ (2.21)

and applying Fourier's integral theorem. In so doing, we obtain

$$a_2 = \left(2\hat{v}/V\right) jdk_1dk_2 \cos(k_1\cdot r_{12}) \cos(k_2\cdot r_{12})$$

$$a_3 = \left(-4\hat{v}/V\right) jdk_1dk_2dk_3 \cos(k_1\cdot r_{12}) \cos(k_2\cdot r_{13}) \cos(k_3\cdot r_{13})$$

(2.22)

(2.23)

As mentioned in I, the theoretical (and numerical) evaluation of further terms in the mode expansion ($a_n, n>3$) is difficult and has been performed only for the special case of a one-component system where the reference system is an ideal gas. However, we can make some statements about $a_n$ for $n>3$ that may be of interest. First, $a_n$ is in general a functional of order $n$ (and higher) of the screened potential, $\nu(r)$. The smallness of $\nu(r)$ produces the convergence in the calculations presented in the next section. Furthermore, we strongly believe that all the $a_n$ will be finite for the system considered in this paper. The mode expansion seems to be an analytic, nondiagramatic way of summing over Coulomb chains to eliminate the long-range divergences associated with the Coulomb potential; and the reference interactions exclude the possibility of the short-range divergences encountered in the electron gas (Sec. I).

The case considered here, namely the 1–1 symmetric primitive model electrolyte, is by far the simplest electrolyte model to which to apply the mode expansion. For other cases, such as multicomponent solutions and unsymmetrical electrolytes, additional complexities associated with the number of different ionic species arise, making the terms in the mode expansion more difficult to evaluate. However, the other combinatorial difficulties associated with graph theoretical treatments do not appear in evaluating the first few terms.

If the perturbation pair potential, $u(r)$, is taken to be the Coulomb potential for $r<\sigma$ as well as $r \geq \sigma$, we are able to make contact with previous work in the field. For this choice of $u(r)$, $2p(k)$ is $\kappa^2/k^2$, where $\kappa$ is the inverse Debye screening length,

$$\kappa^2 = \left(\frac{4\pi \beta \epsilon^2}{D} \right) \sum_{i=1}^{n} \sigma_i^2 = \frac{8\pi \beta \epsilon^2 c}{D}. \tag{2.24}$$

Then $a_1$ is the Debye–Hückel Limiting Law for $\alpha$, $\kappa^2/12\pi$, which is equal to the sum over ring graphs in the ionic cluster theory. Furthermore, $v(r)$ for this case is the Debye potential ($\epsilon/Dr \exp(-\sigma r)$; and $-\beta \hat{\epsilon}(\sigma r)$ becomes the function which Friedman denotes by $G_0(r)$. The quantities $a_2$ and $a_3$ then correspond to particular graphs in the ionic cluster theory. These diagrams are shown in Fig. 1. Stell and Lebowitz have shown that only these diagrams contribute to the free energy to the lowest few orders in $\beta \epsilon^2/D$. [If we expand $a_2$ and $a_3$ in powers of $\beta \epsilon^2/D$, Eqs. (2.11) of Ref. 6 are obtained.]

D. The Choice of $u(r)$ for $r<\sigma$

From Eqs. (2.17) and (2.18) it is seen that if $p(k)$, and thus $\hat{v}(k)$, is small in some sense and decays rapidly as $k$ increases, the mode expansion will probably converge rapidly. We now discuss a choice of $u(r)$ which will aid this convergence.

The Coulomb potential is drawn schematically in Fig. 2(a). As we have mentioned, for this potential $2p(k) = k^2/\kappa^2$, which decays as $k^4$. Since the large value of the Coulomb potential for small $r$ probably requires some large Fourier components to describe it in a Fourier series, we might expect $p(k)$ to be smaller if we choose $u(r)$ to be zero for $r<\sigma$. This choice is depicted in Fig. 2(b). It is the one used by Eisenhal and McMillan. However, it will not serve our purpose since it produces a discontinuity in $u(r)$ at $r=\sigma$, and discontinuities produce large $k$ Fourier components. In fact this choice gives $2p(k) = k^2(\cos \sigma)/\kappa^2$.

A remaining simple choice is one which sets $u(r)$ for $r<\sigma$ equal to the Coulomb potential at $r=\sigma$ [see Fig. 2(c)]. That is, if we take

$$u(r) = \epsilon/Dr, \quad r<\sigma, \tag{2.25}$$
TABLE I. Excess free energy of a model ionic solution.

<table>
<thead>
<tr>
<th>I*</th>
<th>a₀/c</th>
<th>a₁/c</th>
<th>a₂/c</th>
<th>a₃/c</th>
<th>HNC a/c</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>-0.0247</td>
<td>0.2299</td>
<td>-0.0157</td>
<td>0.2587</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>-0.0495</td>
<td>0.3990</td>
<td>-0.0249</td>
<td>0.3247</td>
<td>0.3262</td>
<td>-0.0015</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.0998</td>
<td>0.5225</td>
<td>-0.0362</td>
<td>0.3866</td>
<td>0.3854</td>
<td>+0.0012</td>
</tr>
<tr>
<td>0.3</td>
<td>-0.1508</td>
<td>0.6055</td>
<td>-0.0431</td>
<td>0.4117</td>
<td>0.4078</td>
<td>+0.0039</td>
</tr>
<tr>
<td>0.5</td>
<td>-0.2553</td>
<td>0.7203</td>
<td>-0.0506</td>
<td>0.4143</td>
<td>0.408</td>
<td>+0.006</td>
</tr>
<tr>
<td>0.7</td>
<td>-0.3633</td>
<td>0.8011</td>
<td>-0.0541</td>
<td>0.3837</td>
<td>0.376</td>
<td>+0.008</td>
</tr>
<tr>
<td>0.8</td>
<td>-0.4185</td>
<td>0.8341</td>
<td>-0.0551</td>
<td>0.3605</td>
<td>0.352</td>
<td>+0.009</td>
</tr>
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<td>0.9</td>
<td>-0.4747</td>
<td>0.8636</td>
<td>-0.0556</td>
<td>0.3333</td>
<td>0.328</td>
<td>+0.005</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.5318</td>
<td>0.8902</td>
<td>-0.0558</td>
<td>0.3025</td>
<td>0.298</td>
<td>+0.005</td>
</tr>
</tbody>
</table>

* Ionic strength or concentration in moles/liter.

* These numbers are the sum of reference system, one-mode, and two-mode contributions. They contain computational errors in the fourth decimal place. See the text for a discussion of sources of error.

Then

\[ 2p(k) = (\kappa \sigma)^2 \sin \kappa \sigma / (\kappa \sigma)^2, \quad (2.26) \]

which decays faster than the usual k⁻². Clearly, we could continue, and search for another form for \( \kappa(r) \) inside the bare core which would increase the decay even further. However, the choice defined by Eq. (2.25) is all that is needed to produce rapid convergence of the mode expansion.

III. NUMERICAL RESULTS

Rasaiah and Friedman have solved the analogs of the hypernetted chain (HNC) and Percus–Yevick integral equations due to Allnatt. On the basis of consistency checks and comparison with recent Monte Carlo calculations, they concluded that their solutions of the HNC equation give very accurate results for the primitive model of an aqueous 1-1 electrolyte for concentrations at least up to 1M. One system they considered is a symmetric 1-1 electrolyte in water at 25°C. The hard-sphere radii were chosen to be 4.6 Å. For concentrations between 0.05 and 1M, they tabulate the osmotic coefficient \( \varphi \) and the natural logarithm of the mean activity coefficient, ln\( \gamma_{\pm} \), as a function of concentration. These quantities are related to \( a/c \), defined in Sec. II, in the following way:

\[ \varphi = 1 - \frac{1}{2} \frac{\partial}{\partial c} \left( \frac{a}{c} \right), \quad (3.1) \]
\[ \ln \gamma_{\pm} = \varphi - 1 - \frac{a}{c}. \quad (3.2) \]

The basis for Eq. (3.1) is discussed in Sec. II [see Eq. (2.3)], and (3.2) follows from an analog of the Gibbs–Duhem equation. From Eq. (3.2) and the tabulated values of \( \varphi \) and ln\( \gamma_{\pm} \) of Rasaiah and Friedman, their values for \( a/c \) can be calculated.

We have calculated \( a/c \), \( \varphi \), and ln\( \gamma_{\pm} \) for the same model using the mode expansion. All values are for McMillan–Mayer reference states. The hard-core reference system free energy was calculated up to and including the contribution of the fifth virial coefficient. For the concentration range of interest, this series gives an essentially exact result for the reference system free energy. The one and two mode terms were evaluated by numerical integration using Simpson's rule and truncating the integrals at a finite upper limit. All calculations were performed to double precision (approximately 17 significant figures) on the IBM 360/67 computer at the Stanford Computation Center.

The hard-core pair correlation functions needed for the evaluation of the two-mode term were obtained from the exact solution of the Percus–Yevick equation for hard spheres. These correlation functions should be

![Fig. 2](image_url)

**FIG. 2.** Schematic graphs representing different choices for \( u(r) \) inside the hard core. Graph (a) is the usual choice taken for theoretical studies of ionic systems. Graphs (b) and (c) represent alternatives. Graph (c) depicts the choice used in this work for the application of the mode expansion to ionic systems.
essentially exact at the concentrations under consideration. Differentiation of $\alpha/c$ to obtain $\varphi$ was performed by analytic differentiation of polynomial fits. The only significant sources of numerical error were the truncation of the integrals, the finite step size in the numerical integration, and the differentiation procedure. These errors were estimated by numerical and analytic methods and their magnitudes are indicated in the tables.

Table I contains the reference system, one-mode, and two-mode contributions to $\alpha/c$, together with their sum and comparison with the HNC results obtained by Rasaiah and Friedman. For the concentration range 0.05–1M, the two-mode term is less than a tenth of the one-mode term, and these two terms plus the reference system contribution give very accurate results for the total $\alpha/c$. This illustrates the rapid convergence of the mode expansion and is a numerical confirmation of the usefulness of treating the Coulomb potential in the manner described in the previous section.

In Table II and Fig. 3, the mode expansion results for osmotic coefficient $\varphi$ are compared with those obtained from integral equation solutions. This is a more sensitive test of the mode expansion because $\varphi$ is related to the derivative of the free energy with respect to density. From the table it can be seen that inclusion of terms up to and including the two-mode term gives an accurate representation of the HNC results. To illustrate the convergence of the mode expansion, Fig. 3 also contains the mode expansion results when the series is truncated after the reference system and one mode terms, respectively. For comparison, this figure also contains the Debye–Hückel limiting law (DHL) as well as the results of the widely used DHL+$B_2$ approximation which denotes the sum of all ring diagrams and all two-particle cluster diagrams in the ionic cluster theory. The mode expansion truncated even after the one-mode term (denoted M1 in the figure) provides a much more accurate representation of $\varphi$ than does the DHL+$B_2$ approximation.

Table III and Fig. 4 contain the same comparison for the logarithm of the mean ionic activity coefficient. Once again the mode expansion gives remarkably accurate results. On the scale of Fig. 4, the integral equation and mode expansion curves are not distinguishable.

Thus for a 1–1 restricted primitive model electrolyte in water at 25°C with hard-core diameter 4.6 Å, the mode expansion provides an accurate description of the thermodynamic properties for the concentration range 0.05 to 1M.

We have evaluated the terms in the mode expansion in a rather elaborate way, making use of four virial coefficients and the Percus–Yevick pair correlation function for the reference system. The purpose of this was to ensure that the error in the calculation be smaller than the discrepancy between our results and the exact results. This provides a critical test of the mode expansion. However, for practical calculations, accuracy comparable to that shown in Tables I, II, and III can still be obtained with less information about the reference system. For example, if only the second and third virial coefficients of the reference system are used for $\alpha_0$ and if the reference system pair correlation function is approximated by its low density limit in evaluating $\alpha_0$, the values of $G/c$, $\varphi$, and $\ln\alpha_0$ are affected only by a few numbers in the third decimal place. Since the absolute error of the accurately calculated mode expansion results is in the third decimal place, this

### Table III. Mean ionic activity coefficient of a model ionic solution.

<table>
<thead>
<tr>
<th>$J^*$</th>
<th>$\ln\gamma_0^a$</th>
<th>HNC $\ln\gamma_0^a$</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>$-0.2104$</td>
<td>$-0.2191$</td>
<td>$-0.0087$</td>
</tr>
<tr>
<td>0.2</td>
<td>$-0.3235$</td>
<td>$-0.3286$</td>
<td>$0.0051$</td>
</tr>
<tr>
<td>0.3</td>
<td>$-0.2275$</td>
<td>$-0.2221$</td>
<td>$0.0054$</td>
</tr>
<tr>
<td>0.5</td>
<td>$-0.1854$</td>
<td>$-0.1776$</td>
<td>$0.0078$</td>
</tr>
<tr>
<td>0.7</td>
<td>$-0.1186$</td>
<td>$-0.1099$</td>
<td>$0.0087$</td>
</tr>
<tr>
<td>0.8</td>
<td>$-0.0789$</td>
<td>$-0.0704$</td>
<td>$0.0085$</td>
</tr>
<tr>
<td>0.9</td>
<td>$-0.0358$</td>
<td>$-0.0277$</td>
<td>$0.0081$</td>
</tr>
<tr>
<td>1.0</td>
<td>$+0.0104$</td>
<td>$+0.0181$</td>
<td>$0.0077$</td>
</tr>
</tbody>
</table>

*a Ionic strength or concentration in moles/liter.

b These results are the sum of reference system, one-mode, and two-mode contributions. They contain computational errors in the fourth decimal place. See the text for a discussion of errors.

c Reference 3. Obtained from solutions of the hypernetted chain equation.

![Fig. 3. The osmotic coefficient, $\varphi$, for an aqueous 1–1 restricted primitive model electrolyte with hard-sphere diameter 4.6 Å, obtained in various ways. DHL denotes the Debye–Hückel limiting law (sum of ring diagrams in cluster theory). DHL+$B_2$ denotes the sum of all ring diagrams and all two-particle cluster diagrams. M0, M1, and M2 denote the mode expansion truncated after the reference system, one-mode, and two-mode contributions, respectively. HNC denotes the solution of the hypernetted-chain integral equation (Ref. 3).](image-url)
extra source of error does not appreciably affect the usefulness of the results.

IV. DISCUSSION

In this section we will discuss the factors affecting the convergence of the mode expansion and the relationship between the mode expansion and the ionic cluster theory.

A. Convergence of the Mode Expansion

A "mode," as defined in Sec. II for the 1-1 electrolyte, can be written as

\[ s(k) = \exp[-\beta \hat{u}(k) \cdot q(k) / |V|] \]

(4.1)

where

\[ q(k) = \sum_{i=1}^{N} z_i \exp(ik \cdot r_i). \]

For a simple one-component fluid, Eq. (4.1) also holds with a simpler definition of \( q(k) \):

\[ q(k) = \sum_{i=1}^{N} \exp(ik \cdot r_i) \]

[see 1]. For a reference system at equilibrium, the various modes are fluctuating quantities, since they depend on the fluctuating positions of many particles. The basic physical idea which motivates the mode expansion is the hypothesis that fluctuations of different modes are statistically uncorrelated (or weakly correlated) in the reference system at equilibrium. Thus, for example,

\[ \langle s(k_1) s(k_2) \rangle \approx \langle s(k_1) \rangle \langle s(k_2) \rangle \]

implies that

\[ \ln[\langle s(k_1) s(k_2) \rangle / \langle s(k_1) \rangle \langle s(k_2) \rangle] \approx 0, \]

which implies that the two-mode term is small [see Eq. (2.15)].

There are two conditions under which one might expect weak correlations among the modes. The first is that the quantities, \( |q(k)|^2 \), which appear in the exponents of the modes, are statistically weakly correlated with each other. The second is that \( \hat{u}(k) \) is small, since this would imply that

\[ s(k) \approx 1 \]

and the fluctuations of \( s(k) \) (and hence the correlations among the fluctuations) are small. Both of these conditions are crucial for understanding the convergence of the mode expansion.

The first condition, namely that the \( |q(k)|^2 \) quantities be weakly correlated, is probably satisfied for very small \( k \). Consider the following intuitive argument, which is not intended to be a rigorous proof. If one makes the very reasonable assumption that a hard-core fluid can support sound waves for wavelengths large compared with the hard-core diameter \( \sigma \) (or for \( k \) vectors small compared with \( 2\pi / \sigma \)), then, in principle, a canonical transformation of the fluid Hamiltonian could be performed to give an expression in which the normal coordinates of the sound waves and their conjugate momenta are the canonical coordinates. To a good approximation, for each small \( k \) there would be one separate part in the Hamiltonian and the terms which couple normal coordinates for different small \( k \) would be small since these coupling terms are responsible for the slow decay of the sound wave. If one were to use this transformed Hamiltonian to calculate the equilibrium correlations of the different normal coordinates, it would be seen that these correlations are small. The normal coordinates are simply related to the \( q(k) \) defined above. (For a one-component fluid, they are identical.) Thus the existence of weakly damped sound waves in the reference fluid implies that the equilibrium fluctuations of the modes are weakly correlated. This intuitive argument makes it reasonable that for small \( k \), i.e., \( k \ll 2\pi / \sigma \), the modes are weakly correlated.

The second condition under which the modes are weakly correlated is that the various \( \hat{u}(k) \) quantities are small. Then the modes are close to unity and the value of a mode \( s(k) \) is insensitive to fluctuations in \( q(k) \). A glance at the Eqs. (2.17)–(2.18) shows that the quantity which effectively "couples" the modes together is the renormalized potential, \( \beta \hat{v}(k) \), which is the Fourier transform of \( \beta \hat{v}(r) \). Hence, if \( \beta \hat{v} \) is small in some sense, the mode expansion should converge rapidly.

Thus, the mode expansion should converge best if the Fourier transform of the perturbation potential is appreciable only for small \( k \) and if the renormalized potential is as small as possible. It should be possible, in principle, to choose the perturbation potential within
the hard core to satisfy these conditions in some optimum way and obtain a most rapidly converging mode expansion. We have not attempted such an optimization procedure, but our choice of perturbation, as discussed in Sec. II, apparently provides satisfactory convergence and satisfies the first of these conditions better than the usual choice or the choice of Eisenthal and McMillan.\textsuperscript{9} The renormalized potential is bounded for our choice of potential, and so our choice also satisfies the second condition better than does the usual choice.

B. Relationship between the Mode Expansion and Ionic Cluster Theory

In discussing the relationship between the ionic cluster theory and the mode expansion it is important to note that the structure of the mode expansion is not dependent upon any particular choice of perturbation potential. In addition, the structure of ionic cluster theory is not dependent upon separation of the potential into a Coulomb potential (i.e., a potential that is Coulombic for all \( r \)) and a short-range part. Ring diagrams and chains of potential bonds could be summed even for a general long-range potential, such as the type we have chosen to use.

When the cluster theory and the mode expansion are compared for the same perturbation, the two are seen to be equivalent in the sense that every part of each term in the mode expansion is precisely equal to the contribution of a set of diagrams in the cluster theory. [The formulation of ionic cluster theory to use in making the comparison is that given in Friedman's book\textsuperscript{2} in Eqs. (13.43b) and (13.37b) and the definitions following this latter equation. In these diagrams, any pair of vertices may be connected by any number of Debye–Hückel bonds (\( q \) bonds).] For the 1–1 electrolyte, the reference system \( \mathcal{A} \) is the sum of all diagrams which contain no \( q \) bonds. The single mode term is equal to the sum of ring diagrams. The diagrammatic description of the two- and three-mode terms was discussed in Sec. II. This is as far as we have evaluated the mode expansion for the 1–1 electrolyte. For the electron gas, however, we have established this correspondence for terms up to and including the seven mode contribution (see I).

The major difference between the cluster theory and the mode expansion is that while the structure of the cluster theory suggests no unique way of ordering the infinite series of terms, the mode expansion does provide an unambiguous sequence of terms, a sequence that seems to converge rapidly in the present instance. In cluster theory there are three types of reasons for grouping terms together. The first type of reason is the desire to eliminate long- and short-range divergences. The second reason is the desire to obtain a series in which a hopefully small ordering parameter appears explicitly. The concentration \( c \) is sometimes used as such a parameter. Stell and Lebowitz\textsuperscript{2} have used \( \beta \varepsilon / D \), or equivalently \( \kappa \sigma \), as an ordering parameter. A third approach is to group diagrams according to the number of particles appearing in them. (The DHLLE+\( B_2 \) approximation is an example of this approach.) It is unfortunately the case, however, that the ordering parameters are often not small for systems of interest. For example, for the electrolyte solution we have been discussing, the dimensionless parameter \( \kappa \sigma \) is about 1.5 for a concentration of 1MF.

It is certainly worth mentioning here that cluster theory has motivated at least one simple approximation which gives accuracy for the present problem comparable to that obtained with the mode expansion with a comparable amount of computational effort, namely the \( g(A) \) approximation of Rasaiyah and Friedman.\textsuperscript{3} In this approximation the infinite series cluster expansion for the ionic pair correlation function is truncated after a certain set of terms and the resulting function is used with the ionic equivalent of the compressibility equation to evaluate \( \partial \ln \gamma_{12} / \partial c \), from which the other thermodynamic properties can be evaluated. This approximation is, however, inconsistent in the sense that if the pressure equation rather than the compressibility equation is used, different and less accurate thermodynamic properties are obtained.

At present we do not know if the mode expansion can be obtained from the cluster theory by use of an as yet unknown ordering parameter. This will be a topic for future investigation. Nevertheless, the mode expansion does provide an unambiguous ordering of terms, and the arguments in the first part of this section indicate that for perturbations of the right type the series should converge rapidly. Our numerical results show that for the specific problem considered in this paper the convergence is indeed rapid.

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\textsuperscript{10} R. A. Allnatt, Mol. Phys. 8, 533 (1964).
\textsuperscript{11} For example, see Eq. (4.11) of Ref. 3.