A new theoretical approach to 1:1 electrolytes at low temperature

Weimin Zhou\textsuperscript{1} and Jerome K. Percus\textsuperscript{1,2}

\textsuperscript{1}Department of Physics, New York University, 4 Washington Place, New York, New York 10003

\textsuperscript{2}Courant Institute of Mathematical Sciences, New York University, New York, NY, 10012

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A new theoretical approach to 1:1 electrolytes at low temperature is developed, RPM and SAPM are studied with this approach, and their critical points of first order phase transition are calculated.

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This report presents a new theoretical approach to ionic systems at low temperature. The systems under study are primitive models of electrolytes: Equal numbers, $N$, of positively and negatively charged hard spheres of diameter $a_+$ and $a_-$ in a volume $V$, carrying charges $+q_0$ and $-q_0$ respectively, interact via the Coulomb potential $\pm q_0^2/Dr$ in a medium of dielectric constant $D$. The size asymmetry of + and − ions is measured by $\lambda = a_-/a_+$, with $\lambda = 1$ being the special case of the Restricted Primitive model (RPM) and otherwise the Size Asymmetric Primitive Model (SAPM). Such systems undergo a first order phase transition at low temperature and moderately low density, they have received increasing attention in recent years (see, e.g. [1, 2, 3, 4, 5]). In the following, we define $a = \frac{1}{2}(a_++a_-)$ and the normalized reciprocal temperature $\beta = q_0^2/(k_BT D)$, which has a length dimension, we denote the total particle number density by $\rho$, and because of the symmetry with respect to the exchange of + and − ions, only $\lambda \leq 1$ is considered.

There are $2N^2 - N$ pairwise interactions in the system, among which $N^2$ are negative (between unlike ions), $N^2 - N$ are positive (between like ions). Intuitively, if the $N^2 - N$ positive interactions could be used to cancel $N^2 - N$ negative interactions, we would only have $N$ negative pairwise interactions left in the system. And this is desirable because it’s much more manageable to deal with $N$ than $2N^2 - N$ interactions, analytically or numerically. In this context, let’s review a pairing procedure first introduced by Stillinger and Lovett [6]. In their procedure, all the distances between two unlike ions are computed, the first pair is defined as the two unlike ions that have the closest distance, and this step is repeated, taking into account only ions that remain unpaired, until all the ions in the system are exhausted. If a certain prescription [5] is used on the situations (of zero weight) when one ion has more than one unlike ion at the same distance, the result of such procedure is that each positive ion has one and only one negative ion as its partner, and vice versa. We call this procedure ”Closest Pairing” (CP). The following numerical study was carried out to exam the energy profile of CP pairs: $N = 500$, $a_+ = a_- = 1$, ions are randomly placed in a cubic box of volume $V$, with hard wall boundary condition; pairs are formed through CP procedure, and the $N$ attractive inter-ion interactions of CP pairs are summed up, divided by $N$, denoted by $I_{cp}$, and then compared with $I$: the sum of all the $2N^2 - N$ pairwise interactions divided by $N$. We found that for a wide range of densities, at least for $\rho \in [0.01, 0.2]$, $I_{cp}$ is within close range of $I$ for configurations with $I \in [-1, -\rho^{1/3}]$: while for $I > -\rho^{1/3}$, $I_{cp}$ has a value less but around $-\rho^{1/3}$ and shows no significant change for different configurations; and of course, $I_{cp}$ cannot have values below $(-1/\alpha)$, here, $\alpha = 1$. A typical plot of $I_{cp}$ vs. $I$ is shown in Figure 1.

It is then adequate to approximate $I$ by $I_{cp}$ in the low temperature regime: $\beta \gg a$, when, expectedly, most unlike ions are closely paired up and the value of $I$ is in the close neighborhood of $(-1/\alpha)$. For clarity of presentation, we call such approximation ”CP Approximation (CPA)”. But configurations with $I > -\rho^{1/3}$ do pose a potential problem for us. Although in the thermodynamic limit when $N, V \rightarrow \infty$, such configurations would have virtually no contribution to any physical phenomenon we are interested here, they do occupy a relatively very large volume in phase space because they allow particles to move much more freely. Thus if no precautions are taken in the calculation of the partition function with $I$ approximated by $I_{cp}$, this large but ought to be insignificant phase space volume would be associated with a significantly magnified Boltzmann factor, and this could significantly affect the result quantitatively, if not

![FIG. 1: $I_{cp}$ vs. $I$ for 1000 random sampling configurations at $\rho = 0.05$. cross: with no restrictions on the selection of configurations; circle: with DNR imposed on the selection of configurations; dashed line: $I$, as reference.](image-url)
qualitatively. In order to prevent this from happening, we put a restriction on the selection of the allowed configurations, called "Detailed Negativity Requirement" (DNR): two like ions can not get closer than a distance \( D \) unless at least one of them has at least one unlike ion at a position that is closer than \( D \). A similar numerical study was carried out in which only the configurations that comply with DNR are sampled, and we found that DNR does eliminate unwanted configurations \( \Xi \); a corresponding plot of \( I_{CP} \) vs. \( I \) is also presented in Figure \( \Xi \) (we see that DNR also limits local energy fluctuations and admittedly deserves further study).

In the following, we present an analytical scheme that employs CPA with DNR.

In the Grand Canonical Ensemble, the system is described by five parameters \((a, \lambda, z_+, z_-, \beta)\). The partition function is:

\[
\Xi = \sum_{N_+ = 0}^{\infty} \sum_{N_- = 0}^{\infty} \frac{z_+^{N_+} z_-^{N_-}}{N_+! N_-!} \int \cdots \int d\mathbf{r}^{N_+ + N_-} \times \exp\{-\frac{\beta}{2} \sum_{i,j=1}^{N_+ + N_-} \left[ \frac{\sigma_i \sigma_j}{r_{i,j}} + V_{hc}(r_{i,j}, \sigma_i, \sigma_j | a, \lambda) \right] \}
\]

\( \beta \) is the sign of ion \( i \) and \( r_{i,j} = |\mathbf{r}_i - \mathbf{r}_j| \) is the distance between ion \( i \) and ion \( j \). The hard core interaction \( V_{hc} \) has the usual meaning, here we have to specify the signs of the two ions involved because of the size asymmetry.

We now carry out the CP procedure on any configuration of the system, and group pairs that have the ion-ion distance in \([a, a + \xi]\), \( \xi \) being infinitesimal; denote the number of such pairs by \( N_0 \). For the rest of the ions in the system, this operation and DNR would change the first two system parameters from \((a, \lambda)\) to \((a + \xi, \tilde{\lambda})\), where \( \tilde{\lambda} = \min(1, \lambda + \xi(1 + \lambda)/a) \). Now we have:

\[
\Xi = \sum_{N_+ = 0}^{\infty} \sum_{N_- = 0}^{\infty} \frac{z_+^{N_+} z_-^{N_-}}{N_+! N_-!} \int \cdots \int d\mathbf{r}^{N_+ + N_-} \times \exp\{-\frac{\beta}{2} \sum_{i,j=1}^{N_+ + N_-} \left[ \frac{\sigma_i \sigma_j}{r_{i,j}} + V_{hc}(r_{i,j}, \sigma_i, \sigma_j | a, \lambda) \right] \}
\]

\[
\times \sum_{N_0 = 0}^{\infty} \frac{(z_+ z_-)^{N_0}}{N_0!} \int \cdots \int d\mathbf{r}^{N_0} \exp\left\{ \sum_{k=1}^{N_0} \frac{\beta}{2} s_k \right\}
\]

\[
\times \exp\{-\beta \sum_{l=1}^{N_0} \left[ \sum_{m=1}^{N_0} V_{ps, l, m} + \sum_{n=1}^{N_0} \frac{V_{pp, l, n} + V_{pp, l, n'}^\ast}{2} \right]\}
\]

(2)

where \( \mathbf{X} = \mathbf{R} \oplus \mathbf{s} \) is the six-component vector comprising the position of the center of a pair, \( \mathbf{R} \), and the relative displacement vector, \( \mathbf{s} \), which points from \(-\) ion to \(+\) ion of this pair. In the integration range of \( \mathbf{X}, v \) is the range of \( \mathbf{s} \) delimited by the requirement that \( s \in [a, a + \xi] \).

\( V_{ps, l, m} \) denotes the interaction between pair \( l \) and single ion \( m \), written explicitly:

\[
V_{ps, l, m} = V_{ps}(\mathbf{X}_l, \mathbf{r}_m, \sigma_m | a, \lambda) = V_{ps}(\mathbf{R}_l, \mathbf{s}_l, \mathbf{r}_m, \sigma_m | a, \lambda)
\]

\[
= V_{hc}(\left(\mathbf{R}_l + \frac{\mathbf{s}_l}{2}\right) - \mathbf{r}_m |, +1, \sigma_m | a, \lambda)
\]

\[
+ V_{hc}(\left(\mathbf{R}_l - \frac{\mathbf{s}_l}{2}\right) - \mathbf{r}_m |, -1, \sigma_m | a, \lambda)
\]

\[
+ V_{cd}(\mathbf{R}_l, \mathbf{s}_l, \mathbf{r}_m, \sigma_m);
\]

where \( V_{cd} \) is the extra spatial exclusion imposed by CP and DNR:

\[
V_{cd}(\mathbf{R}_l, \mathbf{s}_l, \mathbf{r}_m, \sigma_m) = \left\{ \begin{array}{ll}
\infty & \text{if } |\mathbf{R} \pm \mathbf{s}_m(\frac{\mathbf{d}_l}{2}) - \mathbf{r}_m| < s_l; \\
0 & \text{otherwise.}
\end{array} \right.
\]

Notice that in the expression of \( V_{ps} \) there are no electric interaction terms because of CPA, and this makes \( V_{ps} \) a short-ranged interaction. \( V_{pp} \) is the interactions between two CP pairs, \( l \) and \( n \), which is also short-ranged because of CPA. Since \( \xi \) is infinitesimal, configurations with more than one chosen pair in any finite region can be neglected, so can \( V_{pp} \) and the summation over \( N_0 \) in Equation (2) can be replaced by an exponential form:

\[
\exp\{\xi z + z^- e^{-\frac{\beta}{2} a^2} M\}
\]

(3)

where

\[
M = \int_V d\mathbf{R} \int_{4\pi} d\omega \exp\{-\beta \sum_{m=1}^{N_+ + N_-} V_{ps}(\mathbf{R}, \mathbf{a}(\omega), \mathbf{r}_m, \sigma_m | a, \lambda)\}
\]

(4)

\( \omega \) is the orientation of the pair supplying the direction of \( \mathbf{a}(\omega) \) whose magnitude is \( a \).

To evaluate Equation (3), we decompose the exponential form in the usual way:

\[
M = \int_V d\mathbf{R} \int_{4\pi} d\omega \prod_{m=1}^{N_+ + N_-} (f_m + 1)
\]

(5)

\[
= N \cdot \sum_{m=1}^{N_+ + N_-} S_m + \sum_{n,n' = 1}^{N_+ + N_-} D_{n,n'} + \ldots
\]

where:

\[
f_m = \exp\{-\beta V_{ps}(\mathbf{R}, \mathbf{a}(\omega), \mathbf{r}_m, \sigma_m | a, \lambda)\} - 1;
\]

\[
N = \int_V d\mathbf{R} \int_{4\pi} d\omega f_m;
\]

\[
S_m = \int_V d\mathbf{R} \int_{4\pi} d\omega f_m;
\]

\[
D_{n,n'} = \int_V d\mathbf{R} \int_{4\pi} d\omega f_n \times f_{n'}.
\]
Higher order terms which involve more than two $f$’s can be defined similarly. Notice that $S$ is the same for all ions of the same sign, in the following we’ll use $S_+(a, \lambda)$ and $S_-(a, \lambda)$ to denote them respectively. $D_{n,n'}$ depends on the value of $(a, \lambda)$ and the relative position and signs of the ion $n$ and $n'$; it acts like an extra 2-body interaction for the rest of the ions in the system. Similarly higher order terms act like extra multi-body interactions. Now the partition function becomes:

$$\Xi \equiv \exp\{\xi z_+ z_- e^{\frac{\beta}{2}} a^2 \times N\} \times \sum_{N_+ = 0}^{\infty} \sum_{N_- = 0}^{\infty} \frac{\hat{Z}_+^{N_+} \hat{Z}_-^{N_-}}{N_+! N_-!} \int \ldots \int d\{N_+ + N_-\} \times \exp\{-\frac{\beta}{2} \sum_{i,j = 1}^{N_+ + N_-} \frac{\sigma_i \sigma_j}{r_{i,j}} + V_{h.c.}(\sigma_i, \sigma_j, r_{i,j}[a + \xi, \tilde{\lambda}])\} \times \exp\{\xi z_+ z_- e^{\frac{\beta}{2}} a^2 \times \sum_{n, n' = 1}^{N_+ + N_-} D_{n,n'} + \ldots\}$$

(6)

where $\hat{Z}_\pm = z_\pm \exp\{\xi z_\pm z_- e^{\frac{\beta}{2}} a^2 \times S_\pm(a, \lambda)\}$.

We see an interesting pattern in Equation (6): the LHS denotes the partition function with system parameter $(a, \lambda, z_+, z_-, \tilde{\lambda})$, while the RHS has an exponential term followed by the expression of a partition function with system parameter $(a + \xi, \tilde{\lambda}, z_+, z_-, \beta)$ and the extra interactions introduced by $D$ and high order terms of $\mathcal{M}$. We can of course assume that there are also these extra interactions on the LHS, but they have the special initial value of 0. Because of this similarity, the same procedure we performed on the original partition function can be carried out on the new partition function on the RHS and then repeated: a differential procedure that resembles the Renormalization Group Theory, except that no fixed point of the system parameters is expected. Since $V_{ps}$ is short-ranged, we will neglect $D$ and all the higher order terms of $\mathcal{M}$ in the following for simplicity; their effects will be discussed later in this report. The system parameters are now interpreted as variables to be “scaled up” in this procedure, with no confusion, denoted as $(\hat{a}, \hat{\lambda}, \hat{z}_+, \hat{z}_-, \hat{\beta})$ that take the initial values of $(a, \lambda, z_+, z_-, \beta)$, and $\hat{a}$ serves as the scaling factor. From the above derivation, the differential equations of the other system parameters with respect to $\hat{a}$ are:

$$\begin{align*}
\hat{\lambda}'(\hat{a}) &= \left\{ \begin{array}{ll}
(1 + \hat{\lambda})/\hat{a} & \text{if } \hat{\lambda} < 1; \\
0 & \text{otherwise};
\end{array} \right.\\
\hat{z}'_\pm(\hat{a}) &= \hat{z}_\pm \times \hat{z}_\pm e^{\frac{\beta}{2} \hat{a}^2} \times S_\pm(\hat{a}, \hat{\lambda}); \\
\hat{\beta}'(\hat{a}) &= 0.
\end{align*}$$

(7)

which are easily solved. This procedure can be carried out until the temperature is not considered low anymore when $\hat{a} = \Lambda \sim \beta$, and we have:

$$\Xi \equiv \exp\{V \int z_+ \hat{a} \hat{z}_+(\hat{a}) \hat{z}_-(\hat{a}) e^{\frac{\beta}{2} 4\pi \hat{a}^2 d\hat{a}}\} \times \Xi(\Lambda, \hat{\lambda}(\Lambda), \hat{z}_+(\Lambda), \hat{z}_-(\Lambda), \beta).$$

(8)

where $\Xi(\Lambda, \hat{\lambda}(\Lambda), \hat{z}_+(\Lambda), \hat{z}_-(\Lambda), \beta)$ is the contribution from “free moving” ions, which can be evaluated by linearized theories such as the Mean Spherical Approximation (MSA) or the Debye-Huckle (DH) Theory. The exact value of $\Lambda$ is, of course, not important; in this report, we set $\Lambda = \beta/2$.

Equation (8) concludes the above derivation, with simplifications of course: recall that $D$ and higher order terms of $\mathcal{M}$ have been neglected. If these terms are included in the derivation, theoretically speaking, a similar differential procedure can still be constructed, but it will have greater complication. Such simplification overestimates the repulsion between the CP pair and single ions at each step of the derivation, consequently, the value of pressure is raised; and the contribution from $\Xi(\Lambda, \hat{\lambda}(\Lambda), \hat{z}_+(\Lambda), \hat{z}_-(\Lambda), \beta)$ is lower estimated because $\hat{z}_\pm(\hat{a})$ is decreasing faster than it ought to be. But if the density of the system is not too high, it should not significantly affect the result. And if we are interested in situations with very low temperature: $\beta \gg \rho^{-1/3}$, how it is when the system is close to the critical point of the phase transition, the contribution from “free moving” ions can be neglected, because, not surprisingly, almost all ions would be closely paired up at such a low temperature; this can also be seen from the fact that, when $\beta \gg a$ and $z_\pm$ is sufficiently big (so that $\rho^{-1/3} \ll \beta$), if $\Xi(\Lambda, \hat{\lambda}(\Lambda), \hat{z}_+(\Lambda), \hat{z}_-(\Lambda), \beta)$ is evaluated in the same fashion as above (the integration with respect to $\hat{a}$ now goes from $\Lambda$ to $\infty$), with CPA but without DNR: a clear over-estimation, its contribution is still negligible. The partition function then takes a very simple form, written explicitly:

$$\Xi \equiv \exp\{V \int z e^{\frac{\beta}{2} 4\pi \hat{a}^2 d\hat{a}}\} \times \Xi(\hat{\lambda}(\hat{\lambda}(x)), \hat{z}_+(\hat{\lambda}(x)) + \hat{z}_-(\hat{\lambda}(x)))$$

(9)

where $z = z_+ z_-,$ and:

$$g(x) = a^2 e^{\beta/x}[S_+(x, \hat{\lambda}(x)) + S_-(x, \hat{\lambda}(x))]$$

(10)

The description of the system by Equation (9), however, does not exhibit a phase transition. Physically, we have seen that when CP pairs are evenly (randomly) distributed, $I \approx I_{ep}$ and the electric interaction between CP pairs, denoted by $V_{ppe}$ in the following, overall doesn’t have significant effects due to cancellation. But this ceases to be true for CP pairs in clusters, which are shown by MC simulations (e.g. (41)) to form abundantly when the system is close to phase transition. Recall the well-known relationship: $U = \frac{1}{2\tilde{\pi}} \int \mathbf{E}^2(r)dr$, for two CP pairs, lowering $V_{ppe}$ would lower $U$, which in turn lowers their
electric field as a whole and also makes the "shape" of their \( \mathbf{E}(\mathbf{r}) \) more concentrated. Because their electric field serves as the agent of the interaction between the two CP pairs and the rest of the system, lowering \( V_{ppe} \) would then make them more isolated from the rest of the system and their negative interaction less likely to be cancelled by positive interactions. For larger clusters, this effect becomes even more significant. In the following, we construct a VdW-like term to estimate the effect of this "extra" attraction between CP pairs and extend the scheme to exhibit phase transition.

The previous derivation is treated as the leading order calculation, from which the mean inter-ion separation of CP pairs is found to be \( \bar{\alpha} \):

\[
\langle s \rangle = \frac{2}{\bar{\rho}} \int_{\bar{a}}^{\Lambda} \frac{z e^{\bar{a}} [1 - z \int_{\bar{a}}^{\bar{\alpha}} g(y)(1 - \frac{y}{\bar{a}}) dy] 4\pi \bar{\alpha}^3}{[1 - z \int_{\bar{a}}^{\bar{\alpha}} g(x) dx]^2} d\bar{a}
\]

(11)

The change of pressure as the result of including this "extra" pair attraction is then estimated to be:

\[
\Delta P_2 = \frac{1}{\beta} B_{2,e}(\langle s \rangle, \lambda, \beta)(\frac{\bar{\rho}}{2})^2
\]

(12)

where

\[
B_{2,e}(\langle s \rangle, \lambda, \beta) = -\frac{1}{2V} \int_{V_{ppe}} d\mathbf{R}_1 \frac{d\omega_1}{4\pi} \times \int_{V_{ppe} \leq \mathcal{E}_2} d\mathbf{R}_2 \frac{d\omega_2}{4\pi} \{ e^{-\beta V_{ppe}} - 1 \}
\]

(13)

where \( V_{ppe} \equiv V_{ppe}(\mathbf{R}_1, \omega_1, \mathbf{R}_2, \omega_2 | \langle s \rangle, \lambda) \) gives the electric interaction between two identical CP pairs of inter-connection \( \langle s \rangle \) for configurations allowed by CP and DNR, and otherwise 0. Here, \( B_{2,e} \) accounts for the "extra" attraction introduced by 4-ion (two CP pairs) clusters, and, following the spirit of the above discussion, we propose the use of energy standard in defining clusters: \( \mathcal{E}_2 \) is the maximum electric interaction between two pairs for them to be considered as a 4-ion cluster, bigger clusters can be defined in a similar fashion. The values of \( \mathcal{E}_2 \) and \( \mathcal{E}_s \) for clusters involving more than two CP pairs are chosen so that, in the sense of statistical average, \( I < (-1/a) \) (recall \( I_{cp} \geq (-1/a) \), \( I_{cp+I_{cluster}} \) "closely" approximate \( I \), where \( I_{cluster} \) denotes the "extra" attraction introduced by clusters. \( \mathcal{E}_s \) would of course depend on the temperature and the density of the system. Here, we take a short cut and choose \( \mathcal{E}_2 = -0.48/\langle s \rangle \) so that the critical temperature of RPM matches the result of MC simulations, which has converged to \( \sim 0.050 (q_{06}^2/k_B Da) \) in recent years.

Since the big asymmetry cases raise new problems with the formation of special micro-structures \([4]\) and is still under investigation, here we focus on situations with only moderate asymmetry. Some of the critical points obtained from this work are reported in Table I in which \( T_c = k_B T_c Da/q_{06}^2 \) and \( \rho_c = \rho_{00} a^3 \) are the reduced critical temperature and reduced critical density respectively, values from the MC simulation of \([4]\), if available, are also listed in the table as comparison, they are denoted by \( T_{c,Y} \) and \( \rho_{c,Y} \).

| \( \lambda \) | \( T_c^* \) | \( \rho_c^* \) | \( T_{c,Y} \) | \( \rho_{c,Y} \) |
|---|---|---|---|---|
| 1.00 | 0.049(6) | 0.070(3) | 0.0492(2) | 0.073(2) |
| 0.75 | 0.049(2) | 0.063(4) | 0.0488(2) | 0.072(2) |
| 0.50 | 0.048(2) | 0.053(5) | 0.0475(3) | 0.070(2) |
| 0.45 | 0.047(7) | 0.051(2) | - | - |
| 0.40 | 0.047(0) | 0.048(6) | - | - |
| 0.35 | 0.045(9) | 0.046(1) | - | - |
| 0.30 | 0.044(3) | 0.043(5) | - | - |
| 0.25 | 0.041(6) | 0.040(6) | 0.0422(3) | 0.050(3) |
| 0.20 | 0.036(7) | 0.038(0) | 0.0386(4) | 0.051(3) |

For the critical density of RPM, recent MC simulations have converged to \( \rho_c^* \sim 0.075 \), the result of this work (the case with \( \lambda = 1.00 \)) has a discrepancy of less than 10%. For the critical temperatures of all the values of \( \lambda \), we see a very good agreement (less than 10% of discrepancy) with the simulation results of \([4]\). More importantly, the result shows that both critical temperature and critical density decrease as the size asymmetry increases, and the decrease is small until \( \lambda \sim 0.4 \), after which they decrease more dramatically, these features are consistent with the results of MC simulations \([2,4]\); to our knowledge, it has not been shown before theoretically.

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[7] for details see the Doctoral Thesis of Weimin Zhou.