# The role of Coulomb interaction in the structural formation of molten Ytterium chloride

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*Abstract*

*We considered the ionic arrangement within liquid $YCl_3$ as an example of the strong ionic melts of lanthanide-metal-trichlorides. Numerical calculations of the correlation functions of the liquid based on an ionic model and a Busing pair potential were carried out. Parameters of the $Y^{3+}$ were fitted to the Y - Cl bond length in a $YCl_3$ crystal and the breathing mode frequency of the $(YCl_6)^{3-}$ octahedral unit. The optimized random phase approximation (ORPA) was adopted for the closure relations. Our results were in good agreement with the available experimental data at short-range order. It was also observed that the theoretical partial structure factor, as well as other pair correlation functions, would always provide insight into the origin and nature of the short-range and intermediate-range orders within this class of material.*

*Keywords*
> Coulomb interactions, correlations and liquid lanthanide-metal-trichlorides

## 1.0    Introduction

The knowledge of the structural properties of the trivalent metal chloride in its molten form from fundamental information on the inter-ionic interactions is still of theoretical and practical interest. This is so since important data on the melting mechanism and structural arrangements as well as phase equilibrium properties of these materials form the basis for a large number of mixtures and separations used by the processing industry.

$YCl_3$ is a trivalent metal chloride which transforms from ionic crystal structure into mostly ionic liquid with intermediate range order through melting. This transformation is fundamentally accomplished at low chemical activity parameter $X_m$ [6].

In this paper, we are particularly interested in the structural properties of the two component-liquid which require for its description the three radial distribution functions $g_{ij}(r), i, j = Y \text{ or } Cl$ with corresponding partial structure factor of form

$$S_{ij}(k) = \delta_{ij} + 4\pi (n_i n_j)^{\frac{1}{2}} \int_0^\infty \left[ g_{ij}(r) - 1 \right] \frac{\sin kr}{kr} r^2 dr \qquad (1.1)$$

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where the $n_i's$ are the number densities of species $i$ [3].

At the level of experiment, solid $YCl_3$ crystallizes in $Al$ structure. This is a layer structure derivable from small distortions of the face centred cubic *(fcc)* packing of chlorines intercalating metal ions at the octahedral sites. Specifically, each layer in its undistorted (idealized) form comprises two triangular lattices of chlorines, sandwiching the metal ions into edge-sharing $(YCl_6)^{3-}$ octahedra. The melting temperature $T_m$, of $YCl_3$ crystal is ~725°C with a moderate entropy change of about 1912 Cal./mol. °C and a negligible volume change. An extensive Raman scattering study of the mixed $YCl_3$ crystals as well as its pure form revealed the Raman modes of the $(YCl_6)^{3-}$ octahedron, observed at $v \approx 260 cm^{-1}$ from room temperature up to $T \gtrsim T_m$. Despite the high temperature range and the various stoichiometric compositions up to the pure $YCl_3$ melt, this value of Raman mode persists. This is a clue to strong stability of the $(YCl_6)^{3-}$ coordination [4 and 7].

In another development, neutron diffraction measurements of the Faber-Ziman structure factor of molten $Y YCl_3$ at 1020K confirmed the basic six-fold coordination of $Y$ by $Cl$ and thus revealed the existence of a first sharp diffraction peak (FSDP) at $k = 0 \cdot 95 \overline{A}^{-1}$ [11]. The total diffraction feature indicates a strongly structured liquid or glass with intermediate range order. Hence, the notion that the structure of molten $YCl_3$ is a loose ionic network of edge-sharing octahedral [2]. However, the possible remnants of layer-like structure and of interlayer correlations (mostly $Cl$-$Cl$)) in the $YCl_3$ melt are still issues of controversy in the Physics arena.

The present effort aims at a quantitative analysis of the partial structure factor of molten $YCl_3$ with a view to ascertaining the role of the Coulomb interactions among the constituents of $YCl_3$ within the total pair correlation functions. We are aware of a similar work by [8]. These authors premised their analysis on a charged-hard-sphere (CHS) model in a hyper-netted-chain approximation (HNC). On the contrary, the present attempt specifically recasts the inter-ionic potentials in a form that allows the optimized random phase approximation (ORPA) treatment (see [1], [9] and [10]. Our procedure is based on the scheme of extremum conditions and thermodynamic consistence for an arbitrary reference system. This becomes necessary in view of the fact that it is possible to prove the uniqueness of ORPA solutions unlike the HNC solutions. ORPA technique has a definite technical advantage over HNC and other integral equation methods which will always yield spurious results because of their tendency towards multiple results. An appreciable improvement of the results is achieved when this defiency is amended through the requirements of thermodynamic consistency as prescribed by the present ORPA version. We shall exclude the ionic polarization effect in our calculations to enable us make comparison with the results of [9].

The remaining part of this work is planned as follows: section 2 gives the main theoretical expressions needed while section 3 outlines the calculation procedures. In the meantime, numerical results obtained for molten $YCl_3$ (and consequently it is the case for other molten tri-halide salts) are presented and discussed in section 4 before conclusion.

## 2.0    Theory

The ionic potential model for $YCl_3$ takes into consideration the molecular shape, metal-halogen bond length and vibrational frequencies in the molten state. This is modeled by the Busing-type effective interactions where the sum of the pair potential between ions of types $i$ and $j$ at separation $r$ is given by

$$\Phi(r_{ij}) = \sum_{i<j=1}^{N} \varphi_{ij}(r) \tag{2.1}$$

and

$$\varphi_{ij}(r) = Z_i Z_j \frac{e^2}{r} + f(\rho_i + \rho_j) \exp\left(\frac{R_i + R_j - r}{\rho_i + \rho_j}\right) \tag{2.2}$$

Equation (2.2) comprises the Coulomb interactions and a short-range overlap repulsion; it ascribes to each ion a valence $Z_i$, an effective radius $R_i$ and a hardness $\rho_i$. Ideally, a full determination of the effective interactions for the family of trivalent-metal-halide chlorides should aim at configuring the model in a manner that includes the ionic polarization effects of any structural distortions.

The system of charged hard spheres (CHS) contains particles having charge $Ze$ of diameter $\sigma_{ij}$ such that the overall charge neutrality of the system is maintained. The particles interact among themselves via a Coulomb repulsion of form

$$\varphi_0 = \begin{cases} (Z_i e)^2/\varepsilon a k_\beta T, & r > \sigma_{ij} \\ \infty, & r < \sigma_{ij} \end{cases} \tag{2.3}$$

In (2.3), $T$=temperature, $a = (4\pi n/3)^{-\frac{1}{3}}$, $\eta_{ij} = 6\pi n \sigma_{ij}^3$ (parking fraction), $Z_i$= effective valence of specie $i$ and $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ such that $\lambda_{ij} = \frac{1}{2}(\sigma_j - \sigma_i)$. The CHS model facilitates the study of the interplay between the short-range repulsion (overlap) and the long-range Coulomb interactions.

The model potential readily makes possible the evaluation of the partial structure factor through equation

$$S_{ij}(k) = \delta_{ij} + n(x_i x_j)^{\frac{1}{2}} \int dr \left[g_{ij}(r) - 1\right] \exp(ik \cdot r) \tag{2.4}$$

where $n$ represents the number density and $x_i$ the number of ions of type $i$ in the formula units. The direct and total correlation functions $c_{ij}(r)$ and $h_{ij}(r)$ respectively are related through the Orstein-Zernike equation

$$h_{ij}(r) = c_{ij}(r) + n \sum_i x_i \int dr' \, h_{ij}(r')c_{ij}(r - r') \tag{2.5}$$

where $h_{ij}(r) = g_{ij}(r) - 1$. Thus, Faber-Ziman structure factor, $S_n(k)$ becomes

$$S_{FZ}(k) = \left(\sum_i x_i b_i^2\right)^{-1} \left[\sum_{ij} (x_i x_j)^{\frac{1}{2}} b_i b_j \, S_{ij}(k)\right] \tag{2.6}$$

where $b_i$ represents the neutron scattering length of ion $i$. The total pair correlation function is then defined as

$$T(r) = 4\pi n r + (2/\pi) \int_0^{k_{max}} [S_{FZ}(k) - 1] \sin(kr) \, k dk \tag{2.7}$$

Also, the running coordination number may be calculated from

$$N_{ij}(r) = 4\pi n x_j \int_0^r g_{ij}(r')(r')^2 dr' \tag{2.8}$$

The optimized random phase approximation (ORPA) technique is a perturbation process that has been used severally and successfully to determine the structures of liquids with strongly repulsive

$$\tag{2.9}$$

core potentials, including liquid metals [5]. In an earlier development, [10] established that the ORPA method can also be used to evaluate the structural properties of multi-component liquids for desirable high precision. The original ORPA method relies on the inter-atomic potential being separated into a reference potential term and a perturbation as in [1].

$$\Phi(r) = \varphi_{ref}(r) + \varphi_{per}(r) \tag{10}$$

Equation (2.9) naturally leads to similar decomposition for the total and direct correlation functions i.e.

$$h_{ij}(r) = h_{ref}(r) + \Delta h_{ij}(r) \tag{2.10}$$

$$c_{ij}(r) = c_{ref}(r) + \Delta c_{ij}(r) \tag{2.11}$$

The fact that $h_{ref}(r)$ and $c_{ref}(r)$ satisfy the same equation results in

$$\Delta \hat{h}_{ij}(k) = \frac{\Delta \hat{c}_{ij}(k)[S_{ref}(k)]^2}{1 - n\Delta \hat{c}_{ij}(k)S_{ref}(k)} \tag{2.12}$$

and

$$S_{ref}(k) = 1 + n\hat{h}_{ref}(k) \tag{2.13}$$

(A hat on a function of $k$ indicates the 3-dimensional Fourier transform of the corresponding function in r-space). In particular, ORPA closure corresponds to

$$\Delta c_{ij}(r) = -\beta\varphi_{per}(r) \quad for \quad r > \sigma_{ij} \tag{2.14}$$

$$\Delta h_{ij}(r) = 0 \quad for \quad r < \sigma_{ij} \tag{2.15}$$

Equation (2.15) corresponds to the extremum condition for the free energy functional.

To calculate $S_{ij}(k)$ successfully for $YCl_3$, the choice of a reference system that reproduces well the basic features of the real system is very necessary. The version of ORPA adopted here (Pastore et. al. [10]) allows any convenient (arbitrary) reference system. Consequently, we shall regard the dominant part of the inter-atomic potential as the Madelung term and then treat the overlap as a perturbation. We shall seek an ORPA variational procedure where a free energy functional is defined as

$$F_{ring}[\Delta c(r)] = -1/[n(2\pi)^3] \int d^3k \, [n S_{ref}(k)\Delta \hat{c}_{ij}(k)$$

$$+ log\{1 - nS_{ref}(k)\Delta \hat{c}_{ij}(k)\}] \tag{2.16}$$

In (2.16), $\Delta c(r) = 0$ implies a violation of Equation (2.16) (random phase approximation (RPA)). Hence we demand for the variation of $c(r)$ inside the exclusion hole via the partial derivatives of $F_{ring}$ with respect to $\Delta \hat{c}_{ij}(k)$ as in

$$\frac{\partial F_{ring}}{\partial \Delta \hat{c}_{ij}(k)} = \frac{-n}{(2\pi)^3} \Delta \hat{h}_{ij}(k) \tag{2.17}$$

Fourier transform of (2.17) yields

$$\frac{\partial F_{ring}}{\partial \Delta \hat{c}_{ij}(r)} = -n \Delta \hat{h}_{ij}(r) \tag{2.18}$$

Equation (2.18) is the required variational condition needed to determine the unknown $\Delta c(r)$; it is equivalent to imposing an extremum condition on $F_{ring}$ with respect to the variations of $\Delta c(r)$ inside $\sigma_{ij}$. Note that the Helmholz free energy functional has been written in terms of the direct correlation function $c_{ij}(r)$. Thus $g_{ref}(r) \approx 0 \, for \, r < \sigma_{ij}$ implies the variation of $\Delta c_{ij}(r)$ inside $\sigma_{ij}$. Consequently, we define the radius $\sigma_{ij}$ of this region as the value of $r$ below which $g_{ref}(r)$ is too small in computer simulation. The plasma parameter ($\Gamma$) and all the grid

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points within $\sigma_i$, $\sigma_j$ and $\sigma_{ij}$ could be treated as unknowns instead of expressing $\Delta c_{ij}(r)$ in Taylor series or Legendre polynomials which have few parameters and therefore are not very efficient. It should be mentioned that large number of meshes implies more degrees of freedom and enhanced accuracy.

## 3.0     Calculation procedure

We took the overlap parameters of $Cl^-$ from the data of Yuen et. al. (as in.[7]) and proceeded in the manner of [8] to evaluate the overlap parameters for $YCl_3$ by a fit to the $Y-Cl$ bond length (2.63Å) and the breathing mode frequency (260 cm$^{-1}$) of $(YCl_6)^{3-}$.

The variational treatment of the grid points within the excluded volume region of the pair distribution function was adapted to the necessary data on $YCl_3$. We employed the steepest descent method of optimization where the extremum condition assumed

$$\Lambda^{l+1}(r) = \Lambda^l(r) - \gamma \left[\frac{\partial F_{ring}}{\partial \Lambda(r)}\right] \quad for \ \Lambda^{l+1} = \Lambda^l \tag{3.1)}$$

Using (3.1), the search for the minimum began at certain point and moved stepwise by varying $\Lambda(r)$ along the direction of the local gradient of the ORPA free energy functional. The displacement was put at a fixed quantity $\gamma$ which we determined by trial and error in a manner that decreased the value monotonically. Our algorithm solved (3.1) numerically on a grid of 2053 points with $\Delta r = 0.025a$Å, $a = (3/4\pi n)^{-1/4}$. The operations required by the steepest descent procedure were performed efficiently with the aid of the Fast Fourier Transform (FFT).

## 4.0     Results and discussions

The overlap parameters of the model interaction calculated in this work were listed on Table 4.1. These values facilitated the evaluation of $g_{ij}(r)$ and hence Equations (2.4),(2.6), (2.7)

and (2.8) at $T = 1020K \ and \ n = 2.56g/cm^3$; the calculated results were plotted in Figures

(4.1)- (4.5). Some important structural parameters emanating from our numerical calculations were also summarized in tables 2.

The Faber-Ziman structure factor obtained in this work (Figure 4.1) indicated that the

first sharp diffraction peak (FSDP) is at $k_{FZ} \approx 0.998$Å$^{-1}$ compared to its experimental value at

$k_{FZ} = 0.95$Å$^{-1}$ measured by [11] and compared with $k_{FZ} = 1.25$ obtained in [10] using CHS

reference in HNC approximation.

As observed from Figure 4.2 for $N_{ij}(r)$, the model potential (Busing type) accounted for

the short-range correlation in molten $YCl_3$ satisfactorily up to 2$^{nd}$ neighbour shell. The full-line

represented the coordination of $Y$ by $Cl$ which should be thrice as large as that of $Cl$ by $Y$.

We also observed in Figure 4.3 that $g_{Y-Cl}(r)$ attained a very low value (~ 0.065) at its

first minimum which was rather long-lived, an indication that the first peak in $T(r)$ (Figure 4.4) was due to $Y-Cl$ (nearest neighbour) correlation with a running coordination number,

$N_{Y-Cl}(r)$ ~ 5.87 above 3Å (see first intersection in Figure 4.2). It was also seen that the bond

length expanded in the liquid phase as it should and the 2$^{nd}$ peak in $T(r)$ was largely due to

$Cl - Cl$ correlation (see Figure 4.4). This became apparent from the fact that no special structure was exhibited by $N_{Cl-Cl}(r)$ but attained value ~ 13.6 at the position of minimum in $g_{Cl-Cl}(r)$ compared to $N_{Cl-Cl}(r)$ = 8.2 reported by some other calculations through a fit of Gaussian function to the second peak in the experimental $T(r)$. Our observation supported the fact that the interlayer correlation was substantially relaxed on melting. To evaluate $T(r)$, a Fourier integral transform, its upper cut-off ($k_{max}$) was put at ~ 8Å$^{-1}$ which was the same as the

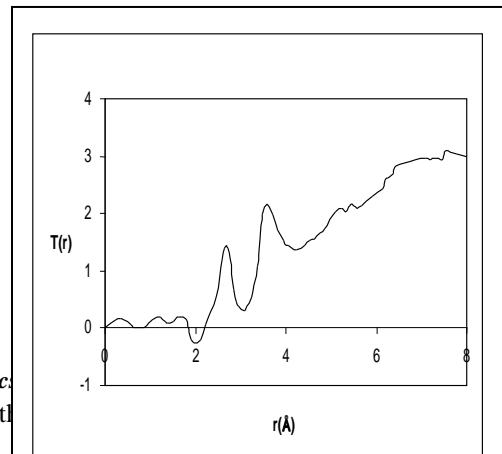experimental value. Hence, oscillations below 8Å$^{-1}$ would be due to the finite cut-off.
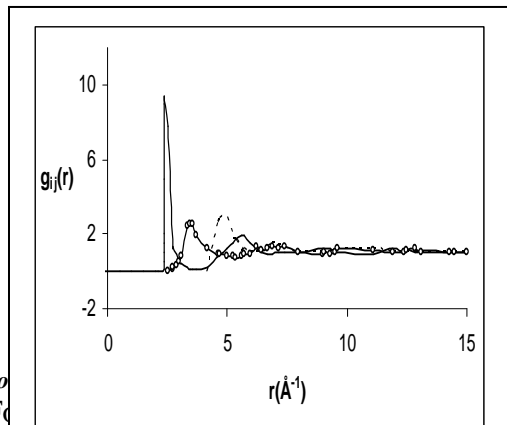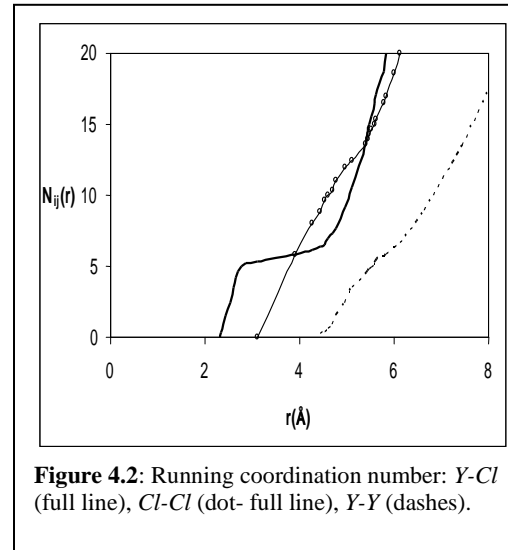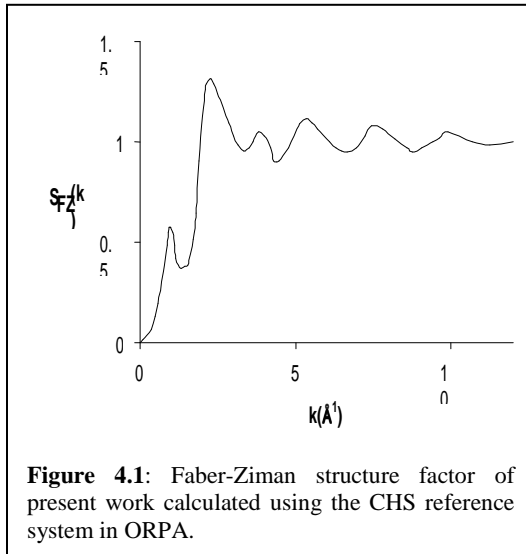
Furthermore, $g_{Y-Y}(r)$ had its main peak at ~5Å (Fig.3) which was a consequence of a strong Coulomb repulsion between the $Y^{3+}$ ions in the model potential. In Figure 4.5, a subsidiary peak in $S_{YY}(k)$, a main peak in $S_{Cl-Cl}(k)$ and a deep trough in $S_{YCl}(k)$ were seen at about $2Å^{-1}$. These were recognized as signatures of the alternation of the components in the molten salt.
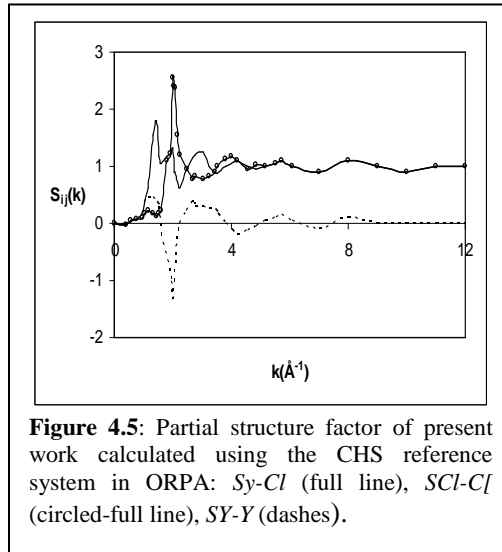
**Table 4.1**: Overlap parameters of the Busing pair potential calculated in this work.

| $Z_Y$ | $Z_{Cl}$ | $f(e^2/\text{Å}^2)$ Type equation here. | $R_Y(\text{Å})$ | $R_{Cl}(\text{Å})$ | $\rho_Y$ | $\rho_{Cl}$ |
|---|---|---|---|---|---|---|
| 3 | -1 | -0.05 | 1.12 | 1.71 | 0.007 | 0.238 |

Table 4.2: Important structural parameters of present work in comparison with other results:

| Parameter | $r_{ij}$ (main peak in $g_{ij}(r)$) | | $k_{ij}$ (FSDP in $S_{ij}(k)$) | | $N_{ij}(r)$ | |
|---|---|---|---|---|---|---|
| | This work | Theory Ref.[10] | This work | Theory Ref.[10] | This work | Theory Ref.[10] |
| $Y-Cl$ | 2.38Å | 2.35Å | 0.999Å$^{-1}$ | 1.260Å$^{-1}$ | 5.89 | 5.87 |
| $Cl-Cl$ | 3.52Å | 3.55Å | 2.010 Å$^{-1}$ | 2.000Å$^{-1}$ | 13.46 | 13.8 |
| $Y-Y$ | 4.79Å | 5Å | 1.400Å$^{-1}$ | 1.300Å$^{-1}$ | - | - |



**Figure 4.1**: Faber-Ziman structure factor of present work calculated using the CHS reference system in ORPA.



**Figure 4.2**: Running coordination number: *Y-Cl* (full line), *Cl-Cl* (dot- full line), *Y-Y* (dashes).



**Figure 4.3**: Pair distribution function of present work calculated using the CHS reference system in ORPA: *gy-Cl* (full line), *gCl-Cl* (dot-



**Figure 4.4:** *T(r)* of present work calculated using CHS reference system in ORPA.

**Figure 4.5**: Partial structure factor of present work calculated using the CHS reference system in ORPA: *Sy-Cl* (full line), *SCl-C[* (circled-full line), *SY-Y* (dashes).

## 5.0    Conclusion

By adjusting the average $Y - Cl$ bond length in the $YCl_3$ melt to $2.63\text{Å}$ as in the crystalline state, we have been able to determine the parameters of a simple interaction model for the 3:1 ionic liquid. This knowledge, in turn, enabled us determine, to a reasonable extent, some notable structural properties of the melt. The Faber-Ziman structure factor (Fig. 1) of present work yielded a first sharp diffraction peak (FSDP) which compared favourably with experimental value.

$$Ratio = \frac{position\ of\ main\ peak\ in\ g_{Cl-Cl}}{position\ of\ main\ peak\ in\ g_{Y-Cl}} \cong \sqrt{2}$$

is appropriate for octahedral coordination. Obviously, the Coulomb interactions between the trivalent cations and the monovalent ions suffice to establish a rather stable coordination of the octahedral type in the melt. That is, the Busing–type potential suffices to induce a long-lived octahedral coordination between nearest neighbours and up to the intermediate range. It should

also be emphasized that the present attempt is suitable for predicting short-range order in molten $YCl_3$.

## 6.0    Acknowledgement

### *References*

[1]    Andersen, H. C., Chandler, D. and Weeks, J. D. (1972), 'Role of repulsive and attractive forces in determining the equilibrium structure of simple liquids', *J. Chemical Phys.* 56, № 8, pp. 3812-3823.

[2]     Egelstaff, P. A. (1969), 'In *Introduction to liquid state*', Ch. 4, pp. 40-52, US ed. Academic Press: New- York.

[3]     Hansen, J. P. and McDonald, I. R. (1986), 'Theory of simple liquids', *2$^{nd}$ ed. Academic   Press: London*, Ch. 10.

[4]     Igarashi, K. and Mochinaga, J. (1987), 'The molten state of halides', *Naturforsch*, № 42a, pp. 777-787.

[5]     Matthew-Ojelabi, F. (2006), 'Electrical resistivity of liquid metals from a charged-hard reference system in the optimized random phase approximation', *J. Ass. for Advancement of Modeling and Simulation (AMSE)*, A, Vol. 79, № 4, page 65.

[6]     Matthew-Ojelabi, F. (2008), 'Empirical Formula for the Parameters of Metallic Monovalent Salts', *J. Nig. Ass. Math. Phys.* (in press).

[7]     Papatheodorou, G. N. (1977), 'Thermodynamic properties of inorganic substances', *J. Chem. Phys.* № 69, pp. 3159-3163.

[8]     Pastore, G., Adkenis, Z. and Tosi, M. P. (1991), 'Structures of molten yttrium chloride in an ionic model', Pre-print of ICTP Ref. № IC/91/123.

[9]     Pastore, G., Matthew F., Akinlade, O. and Badirkhan, Z. (1995), 'Numerical solution of  the optimized random-phase approximation', *Molecular Physics.* 84, № 1, pp. 653-661.

[10]    Pastore, G., Akinlade, O., Matthew, F.  and Badirkhan, Z. (1998), 'Optimized random phase approximation for arbitrary reference systems: extremum conditions and  thermodynamic consistence', *Physical Rev. E.* 57, № 1, pp. 460-464.

[11]    Saboungi, M. -L., Price, D. L. Scamehon, C and Tosi, M. P. (1991), 'Computer simulation  studies of molten $BiI_3$', *Europhys. Lett.* № 15, pp. 283-295.