SUPPLEMENTARY MATERIAL

"The Role of Charge Distribution in the Modeling of Polyatomic Ions: The Nitrate Anion Case."

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The Supplementary Material for the publication "*The Role of Charge Distribution in the Modeling of Polyatomic Ions: The Nitrate Anion Case*" contains a compilation of numerical (raw) data obtained from molecular dynamics (MD) simulations of aqueous nitrate solutions analyzed in the main text. The following properties are reported:

- Contributions to $G(r)$ arising from correlations between nitrate oxygen atoms (O_n) and nitrate nitrogen atoms (N_n) with H_w, O_w, O_n, K^+, and N_n for Models 3 and 4.

- Raw simulated densities as a function of temperature for aqueous $NaNO_3$ solutions at a concentration of 1 m and room pressure, for different values of the nitrate nitrogen charge (q_N). Cases presented: Model 1, $q_N = 0.6749e$ [1]; Model 2, $q_N = 0.3700e$; Model 3, $q_N = 0.1700e$; Model 4, $q_N = 0.0000e$; Model 5, $q_N = -0.1000e$; and Model 6, $q_N = -0.2125e$.

- Raw simulated temperature of maximum density (TMD) and the corresponding density at the TMD as a function of q_N for aqueous $NaNO_3$ solutions at a concentration of 1 m and room pressure. The MD simulations were performed using two reduced scaled charge, $q_{\text{scaled}} = \pm 0.85e$ and $\pm 0.80e$.

- Raw simulated densities as a function of temperature for aqueous salt solutions of KNO_3 and NH_4NO_3 at a concentration of 1 m and room pressure for Models 1 and 5. Cases presented: Model 1, $q_N = 0.6749e$ [1]; and Model 5, $q_N = -0.1000e$.

- Raw simulated densities as a function of molality for aqueous nitrate salt solutions ($NaNO_3$, KNO_3, NH_4NO_3, $Ca(NO_3)_2$, and $Mg(NO_3)_2$) at 298.15 K and 1 bar using the Model 5.

- Raw simulated self-diffusion coefficient of water (D_{H_2O}) as a function of molality in aqueous nitrate salt solutions ($NaNO_3$, KNO_3, and NH_4NO_3) at 298.15 K and 1 bar using the Model 5.

- Raw simulated shear viscosity (η) as a function of molality in aqueous nitrate salt solutions ($NaNO_3$, KNO_3, and NH_4NO_3) at 298.15 K and 1 bar using the Model 5.

- Raw simulated densities as a function of temperature for aqueous salt solutions of $CsNO_3$, $RbNO_3$, $LiNO_3$, $Ca(NO_3)_2$, and $Mg(NO_3)_2$ at a concentration of 1 m (except for $Ca(NO_3)_2$, which was simulated at 0.5 m) and room pressure for Model 5.

- Summary of the crossed Lennard-Jones (LJ) (σ_{ij}, ε_{ij}) parameters to the pair potential.

- Contributions to $G(r)$ arising from correlations between nitrate oxygen atoms (O_n) and nitrate nitrogen atoms (N_n) with H_w, O_w, O_n, K^+, and N_n for Models 1, 3, 3 (LJ new) and 4.

- Density as a function of molality for aqueous nitrate salt solutions ($NaNO_3$, KNO_3, and NH_4NO_3) at 298.15 K and 1 bar.

- Raw calculated values of the TMD and the corresponding density at the TMD ($\rho_{\max}$) for aqueous salt solutions at 1 m concentration and room pressure, for $NaNO_3$, KNO_3, and NH_4NO_3.

I. STRUCTURE FROM NEUTRON DIFFRACTION FOR MODELS 3 AND 4

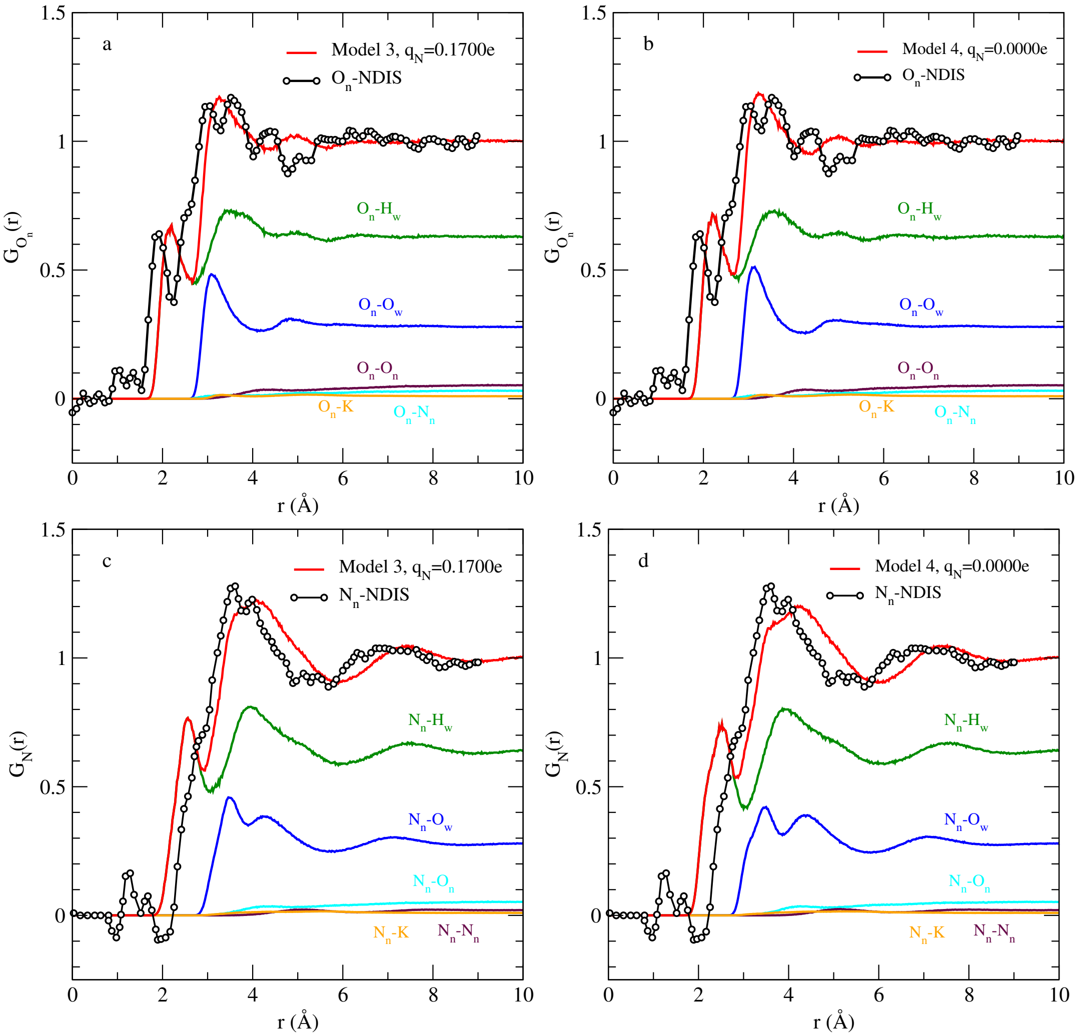

Fig. S 1. Panels (a) and (b): Contributions to $G(r)$ arising from correlations between nitrate oxygen atoms (O_n) and H_w, O_w, O_n, K^+, and N_n for Models 3 and 4, respectively. Panels (c) and (d): Same as panels (a) and (b), but for correlations involving the nitrate nitrogen atom (N_n) with the same species. Experimental data are taken from Ref. [2].

II. RAW DATA

A. Bulk densities

Table S I. Raw simulated densities as a function of temperature for aqueous $NaNO_3$ solutions at a concentration of 1 m and room pressure, for different values of the nitrate nitrogen charge (q_N). Cases presented: Model 1, $q_N = 0.6749e$ [1]; Model 2, $q_N = 0.3700e$; Model 3, $q_N = 0.1700e$; Model 4, $q_N = 0.0000e$; Model 5, $q_N = -0.1000e$; and Model 6, $q_N = -0.2125e$. Experimental data were taken from Ref. [3]. The relative percentage deviation defined as dev.(%)= $100 \cdot |\rho^{exp} - \rho^{sim}|/\rho^{exp}$.

Exp. Data		Model 1		Model 2		Model 3	
T(K)	ρ (kg/m^3)	ρ (kg/m^3)	dev.(%)	ρ (kg/m^3)	dev.(%)	ρ (kg/m^3)	dev.(%)
240	–	1061.65	–	1061.15	–	1060.60	–
245	–	1062.41	–	1062.01	–	1061.45	–
250	1058.86	1062.62	0.36	1062.18	0.31	1062.00	0.30
255	1059.24	1062.44	0.30	1062.11	0.27	1061.93	0.25
260	1059.20	1061.90	0.26	1061.78	0.24	1060.73	0.14
265	1058.79	1061.18	0.23	1061.03	0.21	1060.90	0.20
270	1058.10	1060.07	0.19	1060.00	0.18	1059.96	0.18
275	1057.19	1058.81	0.15	1058.69	0.14	1058.82	0.15
280	1056.12	1057.23	0.11	1057.23	0.11	1057.45	0.13

Exp. Data		Model 4		Model 5		Model 6	
T(K)	ρ (kg/m^3)	ρ (kg/m^3)	dev.(%)	ρ (kg/m^3)	dev.(%)	ρ (kg/m^3)	dev.(%)
240	–	1060.73	–	1060.83	–	1061.42	–
245	–	1061.54	–	1061.93	–	1062.63	–
250	1058.86	1062.13	0.31	1062.36	0.33	1062.96	0.39
255	1059.24	1062.08	0.27	1062.65	0.32	1063.22	0.38
260	1059.20	1061.96	0.26	1062.31	0.29	1063.01	0.36
265	1058.79	1061.35	0.24	1061.77	0.28	1062.48	0.35
270	1058.10	1060.43	0.22	1060.91	0.27	1061.62	0.33
275	1057.19	1059.36	0.21	1059.79	0.25	1060.57	0.32
280	1056.12	1057.89	0.17	1058.43	0.22	1059.18	0.29

Table S II. Raw simulated temperature of maximum density (TMD) and the corresponding density at the TMD as a function of q_N for aqueous $NaNO_3$ solutions at a concentration of 1 m and room pressure. The MD simulations were performed using two reduced scaled charge, $q_{scaled} = \pm 0.85e$ and $\pm 0.80e$. Experimental data, $TMD^{exp} = 256.90$ K and $\rho^{exp} = 1059.30$ kg/m^3 at 1 bar, were taken from Ref. [3].

$q_{scaled} = \pm 0.85e$				
q_N (e)	TMD (K)	dev.(%)	ρ (kg/m^3)	dev.(%)
-0.2125	254.67	0.87	1063.22	0.37
-0.1000	254.30	1.01	1062.59	0.31
0.0000	253.57	1.29	1062.16	0.27
0.1700	252.66	1.65	1062.04	0.26
0.3700	251.65	2.04	1062.25	0.28
0.4740	251.06	2.27	1062.45	0.30
0.6749	250.65	2.43	1062.60	0.31
0.8000	250.84	2.36	1062.59	0.31
1.0000	251.10	2.26	1062.81	0.33
$q_{scaled} = \pm 0.80e$				
q_N (e)	TMD (K)	dev.(%)	ρ (kg/m^3)	dev.(%)
-0.0941	255.78	0.44	1060.64	0.13
0.6352	251.69	2.03	1062.41	0.29

Table S III. Raw simulated densities as a function of temperature for aqueous salt solutions of KNO_3 and NH_4NO_3 at a concentration of 1 m and room pressure for Models 1 and 5. Cases presented: Model 1, $q_N = 0.6749e$ [1]; and Model 5, $q_N = -0.1000e$. Experimental data were taken from Ref. [3]. The relative percentage deviation defined as dev.(%)= $100 \cdot |\rho^{exp} - \rho^{sim}|/\rho^{exp}$.

KNO_3						NH_4NO_3					
Exp. Data		Model 1		Model 5		Exp. Data		Model 1		Model 5	
T (K)	ρ (kg/m^3)	ρ (kg/m^3)	dev.(%)	ρ (kg/m^3)	dev.(%)	T (K)	ρ (kg/m^3)	ρ (kg/m^3)	dev.(%)	ρ (kg/m^3)	dev.(%)
240	–	1064.05	–	1061.19	–	240	–	1030.32	–	1027.92	–
245	–	1065.18	–	1062.79	–	245	–	1032.40	–	1030.16	–
250	–	1065.76	–	1063.62	–	250	–	1033.58	–	1031.61	–
255	1062.60	1066.00	0.32	1064.13	0.14	255	–	1034.39	–	1032.80	–
260	1062.02	1065.84	0.36	1064.26	0.21	260	–	1034.74	–	1033.23	–
265	1061.35	1065.30	0.37	1063.99	0.25	265	1033.50	1034.66	0.11	1033.58	0.01
270	1060.43	1064.71	0.40	1063.47	0.29	270	1033.24	1034.25	0.10	1033.30	0.01
275	1059.36	1063.46	0.39	1062.67	0.31	275	1032.68	1033.46	0.08	1032.78	0.01
280	–	1062.16	–	1061.46	–	280	1031.84	–	–	1031.97	0.01

Table S IV. Raw simulated densities as a function of molality for aqueous nitrate salt solutions ($NaNO_3$, KNO_3, NH_4NO_3, $Ca(NO_3)_2$, and $Mg(NO_3)_2$) at 298.15 K and 1 bar using the Model 5. Experimental data were taken from Refs. [4–6]. The relative percentage deviation defined as dev.(%)= $100 \cdot |\rho^{exp} - \rho^{sim}|/\rho^{exp}$.

$NaNO_3$				KNO_3				NH_4NO_3			
m	ρ (kg/m^3)	ρ (kg/m^3)	dev.(%)	m	ρ (kg/m^3)	ρ (kg/m^3)	dev.(%)	m	ρ (kg/m^3)	ρ (kg/m^3)	dev.(%)
1.00	1059.29	1051.23	0.761	1.00	1055.31	1055.38	0.007	1.00	1027.16	1028.00	0.082
2.00	1098.53	1100.09	0.142	2.00	1107.60	1107.39	0.019	2.00	1053.67	1055.00	0.126
3.00	1142.26	1144.25	0.174	3.00	1154.40	1153.95	0.039	3.00	1077.82	1079.00	0.110
4.00	1182.00	1184.12	0.179					5.00	1119.04	1121.00	0.175
5.00	1219.10	1221.21	0.173					8.00	1168.13	1172.22	0.350
6.00	1254.40	1255.24	0.067					12.00	1217.70	1223.27	0.457
8.00	1316.03	1316.02	0.001								
10.00	1369.37	1368.67	0.051								

$Ca(NO_3)_2$				$Mg(NO_3)_2$			
m	ρ (kg/m^3)	ρ (kg/m^3)	dev.(%)	m	ρ (kg/m^3)	ρ (kg/m^3)	dev.(%)
1.00	1108.10	1111.17	0.277	1.00	1108.11	1097.51	0.957
2.00	1204.35	1206.69	0.194	2.00	1203.85	1185.49	1.525
3.00	1288.86	1287.92	0.073	3.00	1288.85	1264.23	1.910
4.00	1358.00	1357.63	0.027	4.00	1357.71	1335.25	1.654
5.00	1420.83	1416.26	0.322	5.00	1420.83	1398.39	1.579
6.00	1475.94	1465.33	0.719				
7.00	1524.91	1506.45	1.211				

B. Self-Diffusion Coefficient

Table S V. Raw simulated self-diffusion coefficient of water (D_{H_2O}), as a function of molality in aqueous nitrate salt solutions ($NaNO_3$, KNO_3, and NH_4NO_3) at 298.15 K and 1 bar using the Model 5.

	$NaNO_3$	KNO_3	NH_4NO_3
m	$D_{H_2O} \cdot 10^{-5}$ (cm^2/s)	$D_{H_2O} \cdot 10^{-5}$ (cm^2/s)	$D_{H_2O} \cdot 10^{-5}$ (cm^2/s)
1.00	2.16	2.35	2.29
2.00	2.03	2.35	2.29
3.00	–	2.31	2.19
4.00	1.66	–	–
5.00	–	–	2.06

C. Shear viscosity

Table S VI. Raw simulated shear viscosity (η) as a function of molality in aqueous nitrate salt solutions ($NaNO_3$, KNO_3, and NH_4NO_3) at 298.15 K and 1 bar using the Model 5.

	$NaNO_3$	KNO_3	NH_4NO_3
m	η (mPa·s)	η (mPa·s)	η (mPa·s)
1.00	0.94	0.86	0.87
2.00	1.02	0.91	0.89
3.00	–	0.93	0.95
4.00	1.33	–	–
5.00	–	–	1.10

Table S VII. Raw simulated densities as a function of temperature for aqueous salt solutions of $CsNO_3$, $RbNO_3$, $LiNO_3$, $Ca(NO_3)_2$, and $Mg(NO_3)_2$ at a concentration of 1 m (except for $Ca(NO_3)_2$, which was simulated at 0.5 m) and room pressure for Model 5.

$CsNO_3$		$RbNO_3$		$LiNO_3$	
T (K)	ρ (kg/m^3)	T (K)	ρ (kg/m^3)	T (K)	ρ (kg/m^3)
240	1132.72	240	1090.84	240	1037.23
245	1135.19	245	1094.16	245	1038.73
250	1136.95	250	1096.25	250	1040.30
255	1138.14	255	1097.56	255	1041.08
260	1138.78	260	1098.19	260	1041.57
265	1138.87	265	1098.44	265	1041.69
270	1138.46	270	1098.23	270	1041.31
275	1137.99	275	1097.70	275	1040.72
280	1136.91	280	1096.78	280	1039.91
285	1135.74	285	1095.58	285	1038.70
298	1131.19	298	1091.31	298	1034.70

$Ca(NO_3)_2$		$Mg(NO_3)_2$	
T (K)	ρ (kg/m^3)	T (K)	ρ (kg/m^3)
240	1063.05	240	1107.50
245	1064.62	245	1108.34
250	1065.58	250	1108.80
255	1066.02	255	1108.45
260	1065.93	260	1108.19
265	1065.60	265	1107.65
270	1065.07	270	1106.70
275	1064.28	275	1105.52
280	1062.96	280	1104.18
285	1061.68	285	1102.58
298	1056.91	298	1097.65

III. MODIFICATION OF LJ PARAMETERS FOR MODEL 3

In this work the LJ parameters of the original parameterization [1] (optimized for Model 1) were used for all the results. Here, we will briefly explore how the structure, the densities and the TMD would be affected by a modification of the LJ parameters when using Model 3. We will modify only the LJ interactions between the atoms of the nitrate group and those of water with the goal of improving slightly the structural predictions from NDIS (by shifting the initial raise of $G_N(r)$ to slightly larger distances). These new LJ parameters will be labeled as LJ mod. The LJ parameters of the original force field and from this slightly modified version (LJ mod) are presented in Table VIII

Table S VIII. Summary of the crossed Lennard-Jones (LJ) (σ_{ij}, ε_{ij}) parameters between the atoms of the nitrate group and water for the original parametrization [1] and for a modified one designed for Model 3. The geometry of the NO_3^- is defined by a $\widehat{O_n N_n O_n}$ angle of 120° and, a O_n-N_n distance of 1.256 Å being O_n and N_n the oxygen and nitrogen atoms of the nitrate anion, respectively, as reported in Ref. [1]. The σ_{ij} and ε_{ij} parameters of the LJ pair potential are presented in units of Å and kJ/mol, respectively. The charge of the nitrate anion is $\pm 0.85e$ in accordance with the Madrid 2019 force field. The ε_{ij} interaction parameters obey the Lorentz-Berthelot (LB) combining rules.

Original parametrization from Ref. [1]			
i	j	σ_{ij} (Å)	ε_{ij} (kJ/mol)
N_n	O_w	3.1545(LB)	LB
O_n	O_w	3.2300	LB
Modified (LJ mod)			
i	j	σ_{ij} (Å)	ε_{ij} (kJ/mol)
N_n	O_w	3.3800	LB
O_n	O_w	3.2000	LB

The results for the structure for all the models of this work, including Model 3 with slightly different LJ parameters (LJ mod) are presented in Fig. S.2 As can be seen, modification of the LJ parameters improves the structural predictions somewhat (especially for $G_N(r)$).

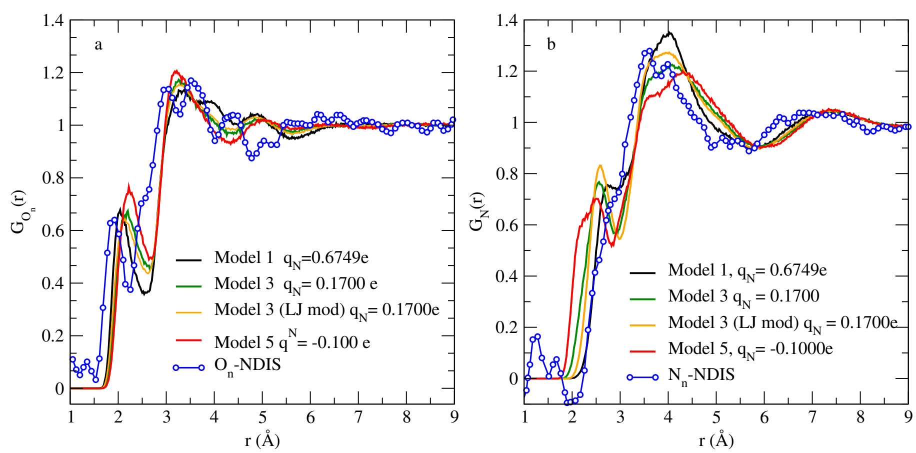

Fig. S 2. Panel (a): Contributions to $G(r)$ arising from correlations between the nitrate oxygen atoms (O_n) and H_w, O_w, O_n, K^+, and N_n for Models 1, 3, 3 (LJ mod), and 5, respectively. Panel (b): the same as in panel (a) but for the corresponding contributions involving the nitrate nitrogen atom (N_n) and the same species. The results correspond to a KNO_3 aqueous solution at a concentration of 3.4 m. Experimental data are taken from Ref. [2].

Let us now analyze the density predictions. They are presented in Fig. S3. As can be seen, the modification of the LJ parameters deteriorates slightly the density predictions at high concentrations (although the predictions are still reasonable). Thus trying to improve the structure for Model 3 by modifying the LJ parameters results in slightly worse density predictions. Thus it is not possible to improve much more Model 3 by modifying the LJ parameters.

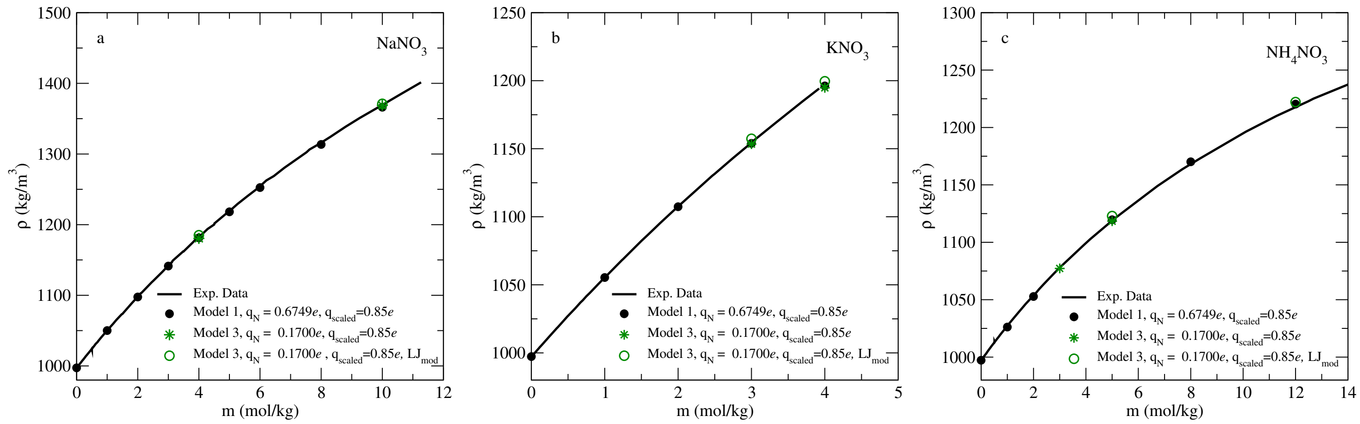

Fig. S 3. Density as a function of molality for aqueous nitrate salt solutions at 298.15 K and 1 bar. Panel (a): $NaNO_3$, panel (b) KNO_3, and panel (c) NH_4NO_3; The simulation results are shown with symbols, while continuous lines stand for the experimental data taken from Refs.[4–6]. The MD simulations were performed using the Models 1 (black circles) , Model 3 (green asterisks) and Model 3 with the LJ modified parameters (green open circles) using a net scaled charge of $q_{\text{scaled}} = \pm 0.85e$ for both the nitrate anion and the cation [1].

Finally we shall now present the predictions for the TMD for both Model 3, and Model 3 with LJ modified parameters. Results are presented in Table S. IX. As can be seen the modification of the LJ parameters for Model 3 does not change much the TMD with respect to the original Model 3 (remind that the estimated error in the TMD is of about 0.5 K).

Table S IX. Results for Models 1, 3, and 5 of this work with the original LJ parameters and for the model 3 (in parenthesis) with slightly different LJ parameters (LJ mod) for the TMD and the density at the TMD ($\rho_{\max}$) of aqueous salt solutions at a concentration of 1 m and room pressure. The systems considered are $NaNO_3$, KNO_3, and NH_4NO_3. Experimental data were taken from Ref. [3]. The quantities *dev.* and *dev.*(%) denote the absolute deviation between experimental and simulated values and the corresponding relative percentage deviation, respectively, defined for TMD as *dev.*(%)= $100|\text{TMD}^{\text{exp}} - \text{TMD}^{\text{sim}}|/\text{TMD}^{\text{exp}}$. Uncertainties of the TMD from simulation are of about 0.5K.

Salt	Model	TMD^{sim} (K)	TMD^{exp} (K)	*dev.*	*dev.*(%)	ρ^{sim} (kg/m^3)	ρ^{exp} (kg/m^3)	*dev.*	*dev.*(%)
$NaNO_3$	1	250.60	256.90	6.3	2.5	1062.6	1059.3	-3.3	0.3
	3	252.7(252.6)	256.90	4.2(4.3)	1.6(1.7)	1062.0 (1063.7)	1059.3	-2.7	0.2
	5	254.30	256.90	2.6	1.0	1062.6	1059.3	-3.3	0.3
KNO_3	1	255.70	261.10	5.4	2.1	1066.0	1062.8	-3.2	0.3
	3	257.8(257.3)	261.10	3.3(3.8)	1.3(1.4)	1065.3(1067.1)	1062.8	-2.5	0.2
	5	259.10	261.10	2.0	0.8	1064.3	1062.8	-1.5	0.1
NH_4NO_3	1	261.20	263.40	2.2	0.8	1034.8	1033.5	-1.3	0.1
	3	263.9(263.0)	263.40	-0.5(0.4)	0.2(0.1)	1034.4(1036.05)	1033.5	-0.9	0.1
	5	264.60	263.40	-1.2	0.5	1033.5	1033.5	0.0	0.0

The results presented here show that minor modifications of the LJ parameters for Model 3 will not change much the main conclusions of this work and besides that there is not much more room for improvement as attempts to improve the structural predictions by modifying the LJ parameters will deteriorate slightly the density predictions.

[1] V. M. Trejos, M. de Lucas, C. Vega, S. Blazquez, and F. Gámez, "Further extension of the Madrid-2019 force field: Parametrization of nitrate (NO_3^-) and ammonium (NH_4^+) ions," *J. Chem. Phys.*, vol. 159, no. 22, p. 224501, 2023.

[2] H. Wang, L. Vlcek, J. C. Neuefeind, K. Page, S. Irle, J. M. Simonson, and A. G. Stack, "Decoding oxyanion aqueous solvation structure: A potassium nitrate example at saturation," *J. Phys. Chem. B*, vol. 122, pp. 7584–7589, 2018.

[3] S. Blazquez, M. de Lucas, C. Vega, J. Troncoso, and F. Gámez, "The temperature of maximum in density of aqueous solutions of nitrate and ammonium salts: Testing the Madrid-2019 force field.," *J. Chem. Phys.*, vol. 161, no. 4, p. 046103, 2024.

[4] M. Laliberte and W. E. Cooper, "Model for calculating the density of aqueous electrolyte solutions," *J. Chem. Eng. Data*, vol. 49, no. 5, pp. 1141–1151, 2004.

[5] M. Laliberte, "Model for calculating the viscosity of aqueous solutions,," *J. Chem. Eng. Data*, vol. 52, no. 4, pp. 1507–1508, 2007.

[6] M. Laliberte, "A model for calculating the heat capacity of aqueous solutions, with updated density and viscosity data," *J. Chem. Eng. Data*, vol. 54, pp. 1725–1760, 2009.