Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Interfacial and bulk properties of concentrated solutions of ammonium nitrate

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Section I: Non-polarisable water models

Table S1. The molecular parameters for the three water models employed in the current study.

	σ (Å)	ε (kJ mol^{-1})	q ($\lvert e \rvert$)
SPC/E model[1]			
O	3.166	0.650	-0.8476
H	0	0	0.4238
O-H distance (Å)	1.0		
H-O-H angle (°)	109.47		
k_b (kJ (mol·Å^2)$^{-1}$)	2319.13	For **SPCE/F** model[2]	
k_θ (kJ (mol·rad^2)$^{-1}$)	191.5	For **SPCE/F** model[2]	
TIP4P/2005 model[3]			
O	3.1589	0.774	0
H	0	0	0.5564
M	0	0	-1.1128
O-H distance (Å)	0.9572		
H-O-H angle (°)	104.52		
O-M distance (Å)	0.1546		

Section II. Various properties of water with non-polarisable force fields

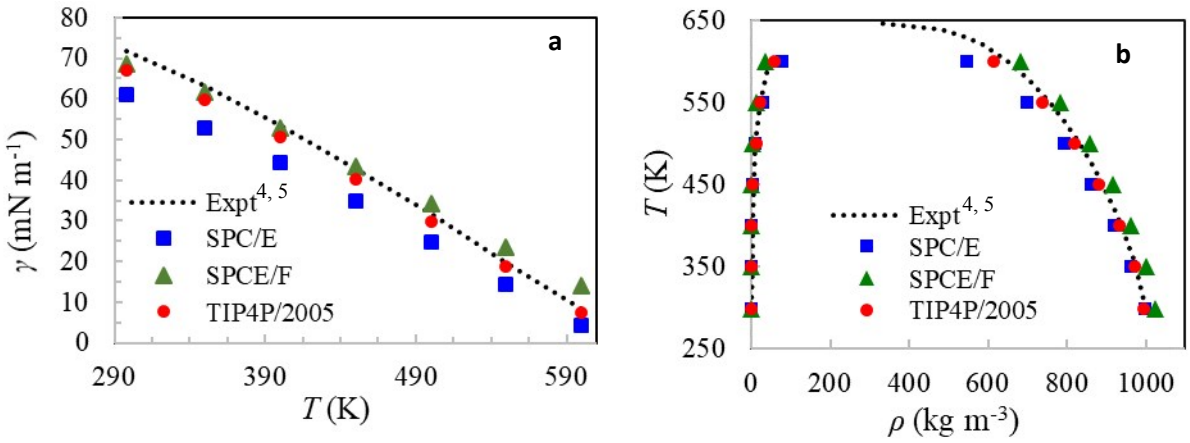

Figure S1. a) Values of the surface tension and b) the orthobaric densities of water. The dashed line represents the experimental values[4, 5], whereas the blue squares, green rectangles and red circles denote the present results with $N = 2133$ using SPC/E, SPCE/F and TIP4P/2005 models, respectively.

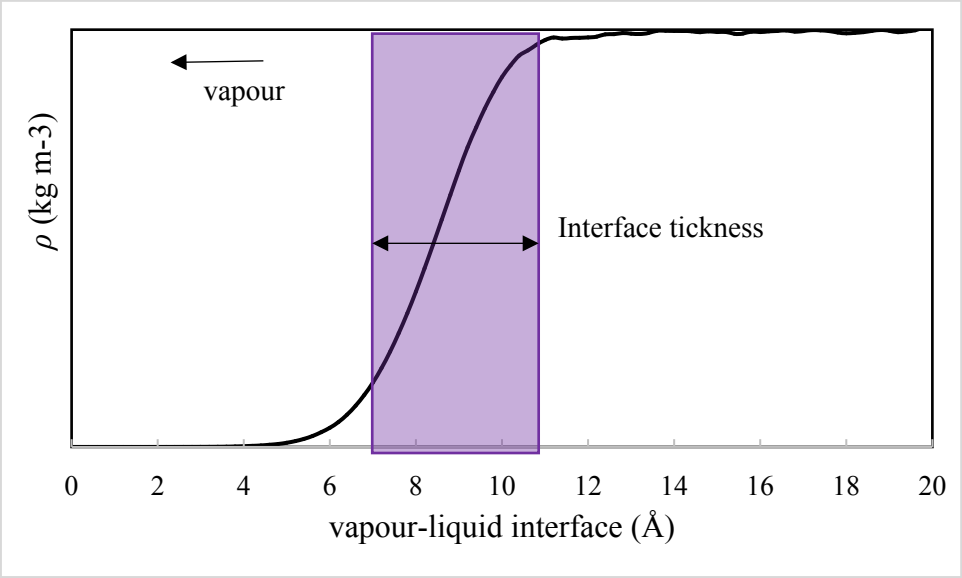

Figure S2. A schematic diagram of the density profile across the vapour-liquid interface and thickness of the interface for the SPC/E water model at 350 K.

Table S2. Liquid and vapour density, interfacial thickness and surface tension of SPC/E, SPCE/F and TIP4P/2005 water at the temperature range of 298.15 – 600 K. The interfacial thickness was calculated by fitting the hyperbolic tangent function to the density profiles. The numbers in parentheses represent one standard deviation.

T (K)	ρ_{liq} (kg m^{-3})	ρ_{vap} (kg m^{-3})	$\delta^{t}_{10\text{-}90}$ (Å)	γ (mN m^{-1})
SPC/E				
298.15	996.6 (0.1)	0.0	3.550 (0.008)	61.2 (0.1)
350	963.2 (0.1)	0.11 (0.03)	4.513 (0.007)	52.9 (0.1)
400	918.4 (0.1)	0.62 (0.02)	5.670 (0.008)	44.4 (0.1)
450	861.3 (0.2)	2.8 (0.1)	6.591 (0.022)	34.8 (0.2)
500	791.3 (0.1)	9.4 (0.1)	9.003 (0.012)	24.7 (0.1)
550	699.5 (0.2)	30.7 (1.1)	15.448 (0.018)	14.4 (0.2)
600	546.0 (1.1)	76.8 (0.9)	27.860 (0.044)	4.2 (0.2)
SPCE/F				
298.15	1025.2 (0.1)	0.0	3.131 (0.021)	68.7 (0.2)
350	999.6 (0.1)	0.0	4.001 (0.006)	61.8 (0.1)
400	961.8 (0.2)	0.21 (0.01)	4.816 (0.006)	52.8 (0.2)
450	915.0 (0.1)	1.3 (0.1)	6.771 (0.008)	43.4 (0.1)
500	857.4 (0.3)	4.4 (0.1)	7.329 (0.008)	34.1 (0.2)
550	783.4 (0.1)	12.2 (0.1)	12.150 (0.029)	23.6 (0.2)
600	683.1 (0.5)	35.0 (0.4)	17.797 (0.027)	14.2 (0.2)
TIP4P/2005				
298.15	995.0 (0.1)	0.0	3.405 (0.008)	67.2 (0.1)
350	970.4 (0.2)	0.0	4.293 (0.009)	59.8 (0.1)
400	932.0 (0.1)	0.61 (0.01)	5.150 (0.009)	50.5 (0.1)
450	881.4 (0.1)	2.4 (0.1)	7.193 (0.008)	40.4 (0.2)
500	818.2 (0.7)	13.2 (1.5)	10.590 (0.045)	29.9 (0.2)
550	737.5 (0.3)	21.4 (0.4)	15.318 (0.039)	19.0 (0.1)
600	614.0 (1.8)	58.9 (0.2)	26.691 (0.051)	7.5 (0.1)

Section III. Coordination numbers and comparison of OPLS and OPLS/ECC models

Table S3. The calculated coordination numbers (*CN*) for the first minima in $g(r)$ of Figure 4.

Concentration (mol kg^{-1})	First minima							
	N_n-O_w		N_n-H_w		N_a-O_w		N_a-H_w	
	***r* (Å)**	***CN*(*r*)**	***r* (Å)**	***CN*(*r*)**	***r* (Å)**	***CN*(*r*)**	***r* (Å)**	***CN*(*r*)**
0.65	5.10	16.17	3.25	6.20	3.75	6.67	4.45	21.53
2.5	5.10	14.67	3.25	5.55	3.75	6.04	4.45	19.85
4.1	5.10	13.57	3.25	5.12	3.75	5.60	4.45	18.55
5.9	5.10	12.52	3.25	4.72	3.75	5.18	4.45	17.23
13.6	5.10	9.57	3.25	3.59	3.75	3.97	4.45	13.40
18.7	5.10	8.50	3.25	3.20	3.75	3.55	4.45	11.95

RDF using OPLS and OPLS/ECC models

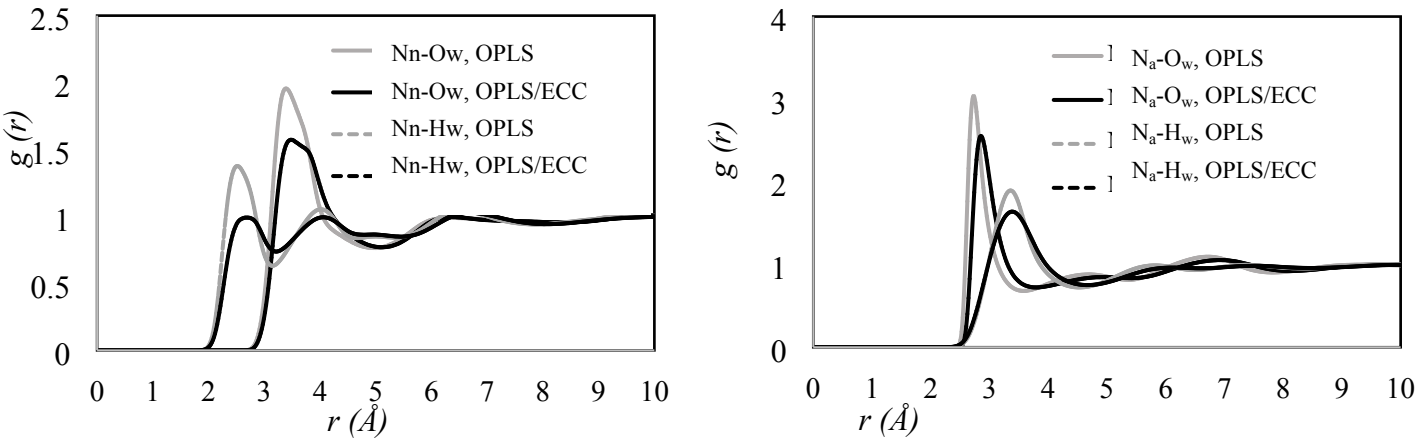

Figure S3. Nitrogen of ions-water radial distribution functions for 18.7 mol kg^{-1} AN solution using the OPLS and OPLS/ECC models and the TIP4P/2005 force field for water at 298.15 K.

Section IV. Experimental values of surface tension of AN solutions

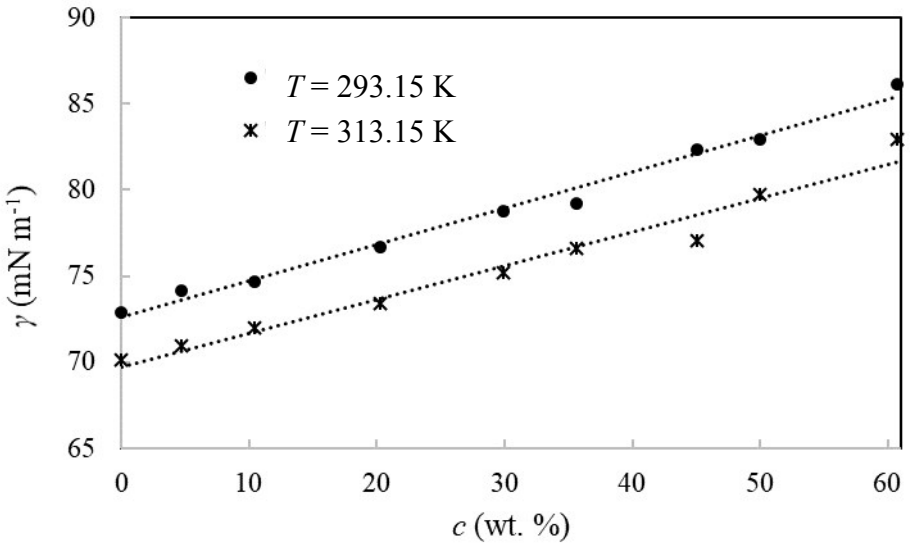

Figure S4. Experimental values of surface tension of AN solutions at temperatures of 293.15 K and 313.15 K.[6]

Section V. RDF and snapshots of coordination shell around one nitrogen of nitrate in the bulk and at the interface of the slab

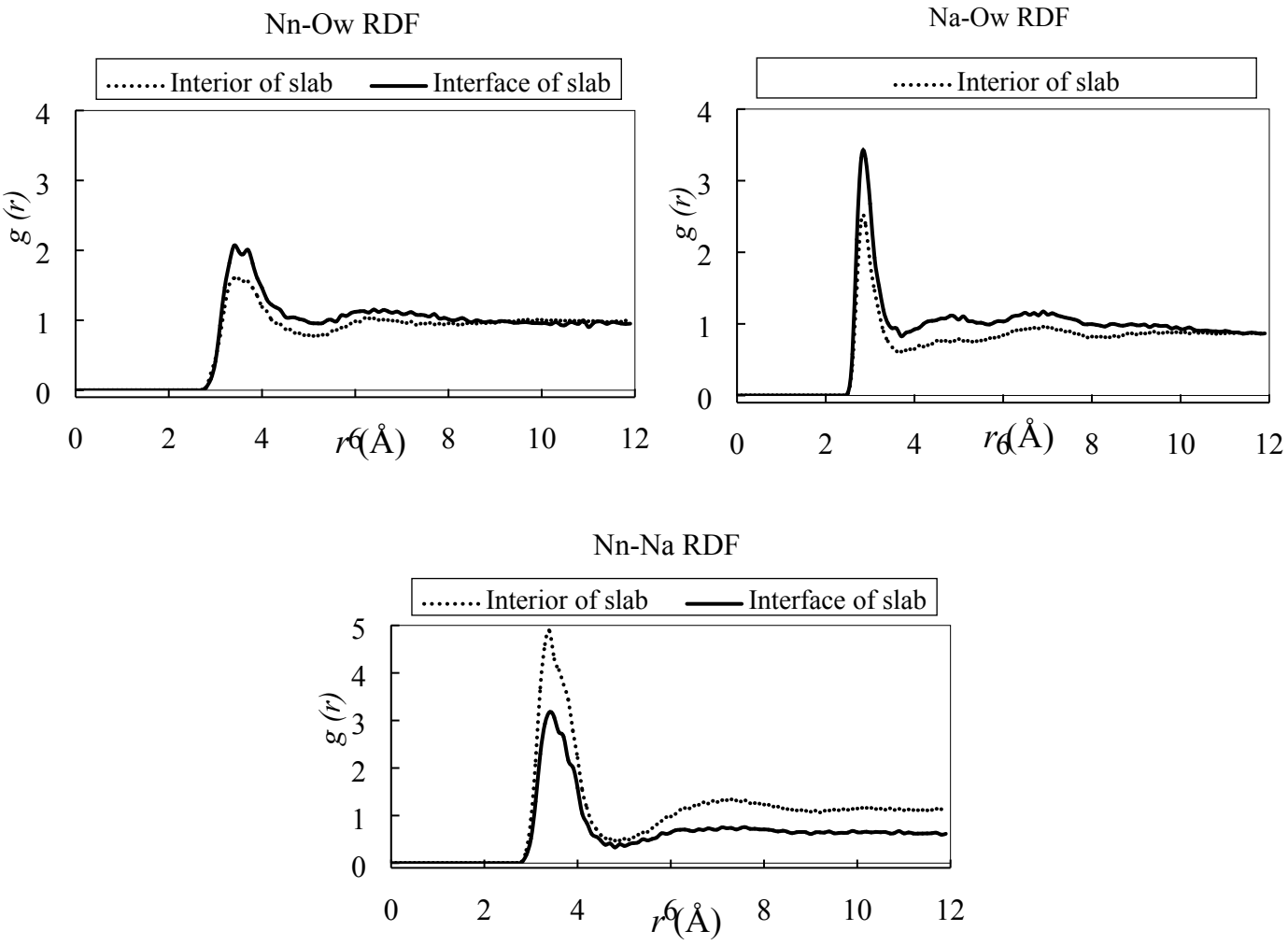

Figure S5. Radial distribution functions for the molality of AN solution of 18.7 mol kg^{-1}, for the OPLS/ECC model for the ions and the TIP4P/2005 model for water at 298.15 K; N_n and N_a denote nitrogen atoms in nitrate and ammonium ions and O_w signifies the oxygen atoms in water.

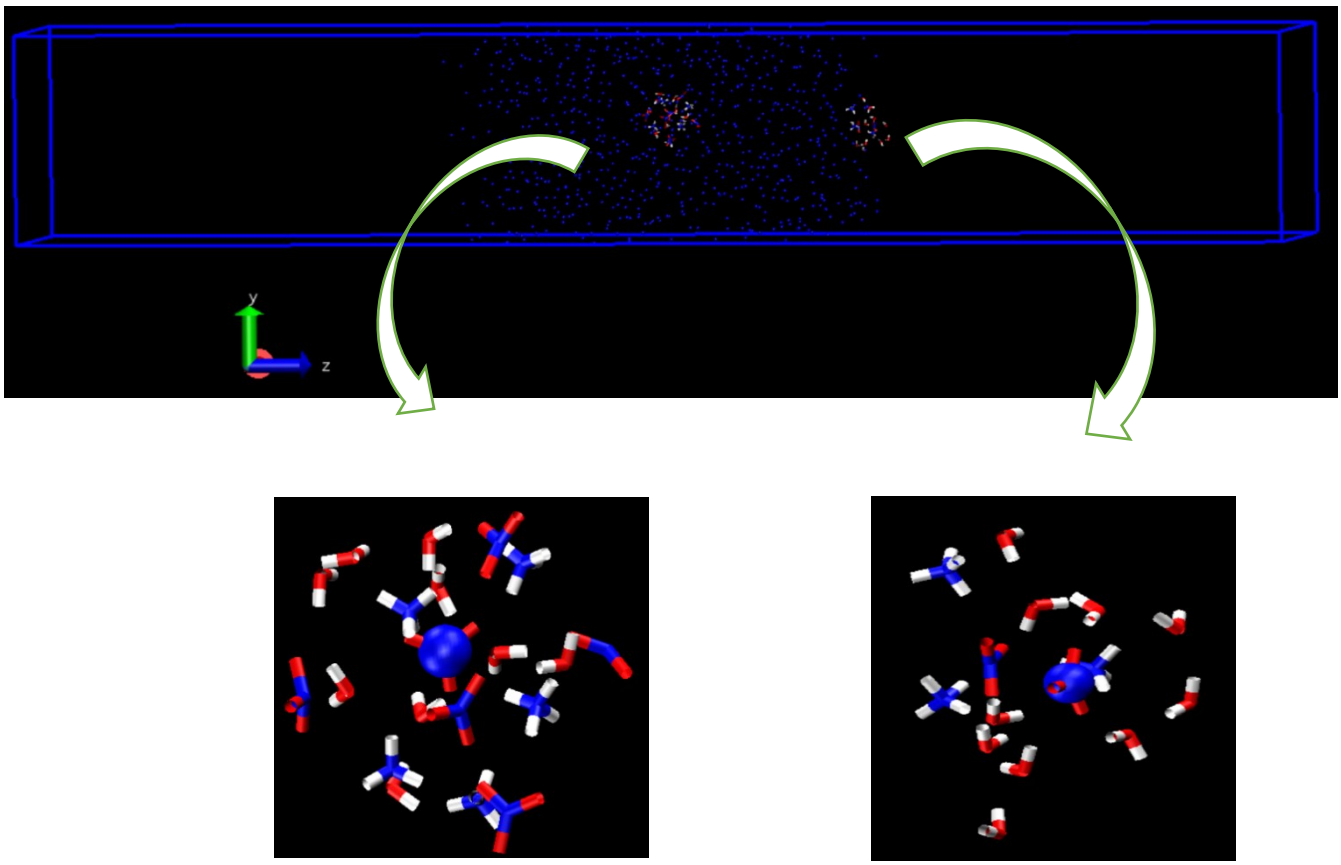

Figure S6. Solvation shells around nitrogen atoms in a nitrate anion (all water molecules and ions are within 5.1 Å of the target nitrogen atom) in the bulk and at the interface for the AN molality of 18.7 mol kg^{-1}. The water molecules, nitrate anions and ammonium cations are illustrated in red – white, blue – red and blue – white, respectively.

Section VI. Lammps code for calculating surface tension-Part 1

```
units                real
atom_style           full
dimension       3
boundary        p p f



pair_style      lj/long/tip4p/long long long 6 2 2 2 0.1546 12
kspace_style    pppm/disp/tip4p 1e-4
kspace_modify force/disp/real 0.0001
kspace_modify force/disp/kspace  0.002
kspace_modify slab 3.0


bond_style     harmonic
angle_style    harmonic
improper_style  cvff

special_bonds             lj/coul 0.0 0.0 0.5

read_data      0-65.data

pair_coeff 1 1 0 0
pair_coeff 1 2 0 0
pair_coeff 1 3 0 0
pair_coeff 1 4 0 0
pair_coeff 1 5 0 0
pair_coeff 1 6 0 0
pair_coeff 2 2 0 0
pair_coeff 2 3 0 0
pair_coeff 2 4 0 0
pair_coeff 2 5 0 0
pair_coeff 2 6 0 0
pair_coeff 3 3 0.17 3.25
pair_coeff 3 4 0.17 3.19961
pair_coeff 3 5 0.188944 3.04877
pair_coeff 3 6 0.177437 3.20413
pair_coeff 4 4 0.17 3.15
pair_coeff 4 5 0.188944 3.0015
pair_coeff 4 6 0.177437 3.15445
pair_coeff 5 5 0.21 2.86
pair_coeff 5 6 0.197211 3.00574
pair_coeff 6 6 0.1852 3.1589

set type 1 charge 0.2625
```

```
set type 2 charge 0.5564
set type 3 charge -0.3
set type 4 charge 0.5955
set type 5 charge -0.4485
set type 6 charge -1.1128

group  nitrate  type 4 5 # Nn On
group  ammonium  type 1 3 # Ha Na
group  water   type 2 6 # Hw Ow



# neighbor skin
neighbor 2.0 bin
neigh_modify  every 1 delay 0 check yes



compute   pe all pe
compute   ke all ke
compute  1      all     chunk/atom  bin/1d  z center 0.2  units box

fix      23      water     ave/chunk  1 500000 1000000 13  density/mass  density/number file
density_water.txt
fix      2       all       ave/chunk  1 500000 1000000 1   density/mass  density/number file
density_all.txt

thermo    1000
thermo_style    multi
#-----------------Energy minimization----------------
#min_style cg
minimize 1.0e-8 1.0e-8 5000 10000
fix 3 all shake 0.0001 20 0 b 2 a 2
fix walls all wall/reflect zlo 40.5 zhi 82.5 units box

thermo    1000
thermo_style         custom  step spcpu temp density press ke pe etotal  lx ly lz
dump 1 all           custom 10000 traj.lammpstrj id mol type mass q xu yu zu ix iy iz vx vy vz
dump_modify    1 sort id
restart  1000000  ANwater.restart
#
#-----------------Initial velocity-------------------
velocity             all  create   298.15  123456 dist gaussian
#
#-----------------Equilibrium-----------------------
fix          5   all npt temp 298.15 298.15  100.0 x 1.0 1.0 1000.0 y 1.0 1.0 1000.0 couple xy
timestep 1
run           500000
```

```
write_data  npt_wall_1run.data
write_coeff  pair.coeff
```

Lammps code for calculating surface tension-Part 2

```
units                real
atom_style           full
dimension       3
boundary        p p p

pair_style      lj/long/tip4p/long long long 6 2 2 2 0.1546 12
kspace_style    pppm/disp/tip4p 1e-6
kspace_modify force/disp/real 0.0001
kspace_modify force/disp/kspace  0.002
#kspace_modify slab 3.0

bond_style     harmonic
angle_style    harmonic
improper_style  cvff

special_bonds             lj/coul 0.0 0.0 0.5

read_data       npt_wall_1run.data

pair_coeff 1 1 0 0
pair_coeff 1 2 0 0
pair_coeff 1 3 0 0
pair_coeff 1 4 0 0
pair_coeff 1 5 0 0
pair_coeff 1 6 0 0
pair_coeff 2 2 0 0
pair_coeff 2 3 0 0
pair_coeff 2 4 0 0
pair_coeff 2 5 0 0
pair_coeff 2 6 0 0
pair_coeff 3 3 0.17 3.25
pair_coeff 3 4 0.17 3.19961
pair_coeff 3 5 0.188944 3.04877
pair_coeff 3 6 0.177437 3.20413
pair_coeff 4 4 0.17 3.15
pair_coeff 4 5 0.188944 3.0015
pair_coeff 4 6 0.177437 3.15445
pair_coeff 5 5 0.21 2.86
pair_coeff 5 6 0.197211 3.00574
pair_coeff 6 6 0.1852 3.1589
```

```
set type 1 charge 0.2625
set type 2 charge 0.5564
set type 3 charge -0.3
set type 4 charge 0.5955
set type 5 charge -0.4485
set type 6 charge -1.1128

group  nitrate  type 4 5 # Nn On
group  ammonium  type 1 3 # Ha Na
group  water   type 2 6 # Hw Ow
group oxygen  type 6 #Owater


# neighbor skin
neighbor 2.0 bin
neigh_modify  every 1 delay 0 check yes


compute   pe all pe
compute   ke all ke
compute  1      all     chunk/atom  bin/1d  z center 0.2  units box

fix      23      water     ave/chunk  1 1000000 1000000 13  density/mass  density/number file density_water.txt
fix      21      nitrate   ave/chunk  1 1000000 1000000 11  density/mass  density/number file density_nitrate.txt
fix      22      ammonium  ave/chunk  1 1000000 1000000 12  density/mass  density/number file density_ammonium.txt
fix      2       all       ave/chunk  1 1000000 1000000 1   density/mass  density/number file density_all.txt
fix      24      oxygen    ave/chunk  1 1000000 1000000 14   density/mass  density/number file density_oxygen.txt


# Set up pressure tensor components
# c_thermo_press[1] is the XX component of the pressure tensor
variable xPress equal c_thermo_press[1]
variable yPress equal c_thermo_press[2]
variable zPress equal c_thermo_press[3]

# Computes the symmetric per-atom stress tensor
compute CC2 all chunk/atom bin/1d z center 0.5 units box
compute stpa all stress/atom NULL
fix stress all ave/chunk 1 1000000 1000000 CC2 c_stpa[1] c_stpa[2] c_stpa[3] &
    c_stpa[4] c_stpa[5] c_stpa[6] file "out.stress.zProfile.txt"

# Compute surface tension
```

```
variable A_in_m equal 1e-10 # Angstrom in meter
variable atm_in_Pa equal 101325 # note: 1 Pa = 1 N/m^2
variable N_in_mN equal 1e3 # Newton in milliNewton
variable convFac equal ${A_in_m}*${atm_in_Pa}*${N_in_mN}
# lz is the box length in the z-dimention
variable st equal 0.5*lz*(v_zPress-0.5*(v_xPress+v_yPress))*${convFac} # in mN/m
fix st all ave/time 1 500 500 v_st file "out.surfTension.txt"
fix staverage all ave/time 1 500 500 v_st file "out.AVesurfTension.txt" ave running

thermo    1000
thermo_style    multi
#-----------------Energy minimization----------------
#min_style cg
minimize 1.0e-8 1.0e-8 5000 10000
fix 3 all shake 0.0001 20 0 b 2 a 2
#fix walls all wall/reflect zlo 69.5 zhi 140.5 units box

thermo    1000
thermo_style        custom  step spcpu temp density press ke pe etotal  lx ly lz pxx pyy pzz
dump 1 all          custom 10000 traj.lammpstrj id mol type mass q xu yu zu ix iy iz vx vy vz
dump_modify    1 sort id
restart  1000000  ANwater.restart
#
#-----------------Initial velocity-------------------
#velocity            all  create   298.15  123456 dist gaussian
#
#-----------------Equilibrium------------------------
fix          5   all nvt temp 298.15 298.15  100.0
timestep 1
run          20000000
write_data  nvt_final_1.data
write_coeff  pair.coeff
```

References

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4. Vargaftik, N. B.; Volkov, B. N.; Voljak, L. D., International Tables of the Surface Tension of Water. *J. Phys. Chem. Ref. Data* **1983,** *12* (3), 817-820.

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