

Atomistic Polarizable Potential for Liquids, Electrolytes, & Polymers (APPLE&P)

WMI has recently developed highly accurate and transferable force field that allows simulations of a wide range of materials, including liquid and polymer electrolytes and ionic liquids (ILs). Molecular dynamics (MD) simulations using APPLE&P provide unprecedented (for molecular simulations) accuracy of prediction thermodynamic and transport properties. Below we provide few examples of the APPLE&P validation.

Systems used in APPLE&P parameterization.

A set of ILs for which density, heat of vaporization, ion self-diffusion coefficient, ionic and thermal conductivity, viscosity and crystal structure data are available in the literature has been selected for validation. Figure 1 shows the anions and cations of the ILs for which have been used in the APPLE&P parameterization. One of the reasons for choosing this particular set of cations and anions is that it allows us to thoroughly investigate the force field transferability by combining various groups in a number of ways. Such transferability is of paramount importance because tailoring of IL properties critically depends on anion and cation modifications in addition to combining various charged groups. Many of the chosen anions such as TFSI⁻ and FSI⁻ with broad charge delocalization have been chosen because they yield ILs with low melting and glass transition temperatures, relatively low viscosity and fast ion transport which are desired in many applications.

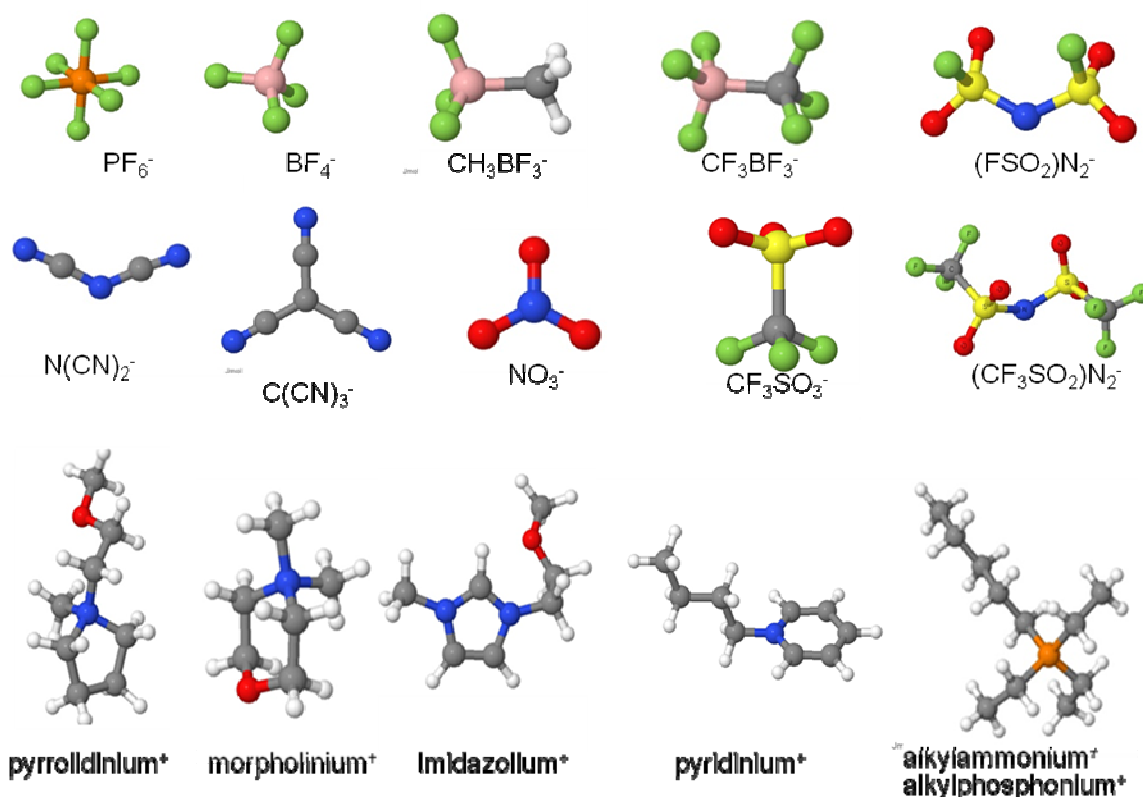


Fig. 1. A set of anions and cations used in parameterization and validation of APPLE&P. Note, that while pyrrolidinium⁺ and imidazolium⁺ cations are shown only with oligoether modifying groups, the force field has been tested for these cations with both oligoether and alkane modifying groups. Different attachment positions of alkyl chains to the imidazolium⁺ ring have been tested.

APPLE&P Validation

WMI has extensively validated the ability of MD simulations utilizing APPLE&P to accurately predict thermodynamic, transport and structural properties for a variety of compounds. In addition to 29 ILs we have also investigated a variety of non-ionic compounds that are commonly used for IL cation and anion modification such as alkyl, fluoroalkyl, oligoether, nitrate, $-\text{NO}_2$. Below we give few examples of properties predicted from simulations using APPLE&P both for ionic and non-ionic compounds.

Non-ionic materials. In Table 1 we compare densities, heat of vaporization, and self-diffusion coefficient as obtained from experiments and predicted from simulations using APPLE&P for a number of non-ionic liquids. We found an excellent agreement between simulation predictions/descriptions and experiment for a wide class of liquids, including energetic materials such as dimethylnitramine (DMNA), alkyl nitrates. We also observed an excellent prediction of surface tension for n-alkanes and fluoroalkanes and diblocks of hydrogenated/fluorinated alkanes.

Table 1. Liquid density (ρ), heat of vaporization (ΔH) and self-diffusion coefficient (D). All data are for liquids at 1 atm. Experimental data are given in parentheses.

liquid	T (K)	ρ (kg/m ³)	erro r ρ (%)	ΔH (kcal/mol)	error ΔH (%)	D (10 ⁻¹⁰ m/s ²)	error D (%)
C ₃ H ₈	321	575 (581)	-1.0	4.29 (4.55)	-6	57.3 (54.7)	-5
C ₅ H ₁₂	298	617 (621)	-0.6	6.09 (6.39)	-5	59 (56.2)	-5
C ₆ H ₁₄	298	651 (655)	-0.6	7.33 (7.58)	-3		
C ₁₀ H ₂₂	298	729 (727)	0.3	12.25 (12.28)	0	13.1 (14)	-6
C ₄ F ₁₀	273	1557 (1585)	-1.7	5.35 (5.46)	-2		
C ₆ F ₁₄	298	1663 (1675)	-0.7	7.31 (7.51)	-3		
C ₉ F ₂₀	295	1785 (1769)	0.9				
1,2- dimethoxyethane	298	851.2 (861)	-1.1	8.63 (8.70)	-1	32.9 (31.5)	4
diglyme	298	928 (934)	-0.6			13.7 (13)	5
DMNA	345	1116 (1109)	0.6				
ethyl nitrate	293	1102 (1108)	-0.6	8.17 (8.67)	-6	23	
butyl nitrate	298	1020 (1023)	-0.3	10.26 (10.42)	2	13.5	
dimethyl ketone	298	778 (785)	-0.8	6.90 (7.47)	-8	46.7 (37.5- 40.9)	15

Ionic Liquids. Twenty nine ILs composed from cations and anions shown in Fig. 1 have been simulated at 298 K, 333 K and 393 K. Table 2 summarizes density of ILs predicted from MD simulations using APPLE&P and its deviations from experiments. In most cases we observed excellent predictive capabilities of APPLE&P force field with the difference between predicted and measured values of less than 1%. For a few ILs density from MD simulations deviated up to 2%, however, for those ILs experimental data contained only three digits such as 1.06 g/cm³ for [mepy][N(CN)₂] indicating at least 1% error bar. Thus, we suspect that the larger deviation between experimental densities and those from simulations could be due to poor accuracy of experimental values.

Table 2. Density (in kg m^{-3}) of 29 ILs predicted from MD simulations performed in Phase I, experimental values (in parenthesis) followed by the deviation in % of MD simulation predictions from experimental values.

Ionic Liquid	393 K	333 K	298 K	exp. ref
	ρ^{MD} (ρ^{exp}) error	ρ^{MD} (ρ^{exp}) error	ρ^{MD} (ρ^{exp}) error	
[emim][BF ₄]	1198 (1206) -0.6	1243 (1253) -0.8	1262 (1280) -1.4	133
[bmim][BF ₄]	1128 (1135) -0.6	1169 (1178) -0.9	1193 (1204) -0.9	49
[bmim][PF ₆]	1286 (1288) -0.2	1336 (1341) -0.3	1365 (1371) -0.4	49
[emim][Ntf ₂]	1426 (1427) -0.1	1479 (1487) -0.6	1511 (1522) -0.7	47
[bmim][Ntf ₂]	1349 (1348) 0.1	1401 (1404) -0.2	1433 (1437) -0.2	134
[C ₆ mim][Ntf ₂]	1290	1342 (1330) 0.9	1373 (1366) 0.5	47
[C ₇ mim][Ntf ₂]	1266 (1262) 0.3	1317 (1314) 0.2	1346 (1348) 0.1	135
[bmmim][Ntf ₂]	1332	1383 (1386) -0.2	1413 (1420) -0.5	136
[bmim][CF ₃ SO ₃]	1217 (1226) -0.7	1262 (1274) -0.9	1287 (1302) -1.1	49
[bmim][NO ₃]	1106 (1092) 1.3	1141 (1131) 0.9	1166 (1154) 1.1	137
[emim][CF ₃ BF ₃]	1246	1291	1321	
[emim][CH ₃ BF ₃]	1094 (1091) 0.3	1130 (1130) 0.0	1155 (1153) 0.2	138
[emim][N(CN) ₂]	1020	1064	1082 (1080) 0.2	139
[emim][C ₄ H ₉ SO ₃]		1115	1134	
[emim][C(CN) ₃]		1059	1084 (1110 at 293K)	140
[(C ₅ O ₂)mim][BF ₄]	1186	1232	1259 (1260) 0.1	141
[(C ₅ O ₂)mim][Ntf ₂]	1368	1423	1457 (1450) 0.5	141
[emim][FSI]	1310	1351	1380	
[mppy][Ntf ₂]	1348 (1343) 0.4	1396 (1386) 0.7	1427 (1408-1447)	142, 143
[mbpy][Ntf ₂]	1315 (1313) 0.1	1369 (1367) 0.1	1393 (1399) -0.5	144
[mepy][N(CN) ₂]	987	1019	1040 (1060) -1.8	139
[P _{2,2,2,5}][Ntf ₂]			1296 (1320) -1.9	145
[Phosphl _{1,2}][C(CN) ₃]			1062	
[N _{1,1,1,4}][Ntf ₂]	1328	1381 (1357) 1.7	1410 (1393) 1.2	144
[N _{4,4,4,1}][Ntf ₂]	1193	1233	1263	
[piperid _{1,4}][Ntf ₂]	1302	1350	1381 (1378.6-1380) <0.3	136, 146
[b-pyrid][Ntf ₂]	1368 (1366) 0.2	1422 (1422) 0.0	1454 (1454) 0.0	144
[b-pyrid][BF ₄]	1144	1189 (1192.2) -0.3	1213 (1214.4) -0.1	147
[MO _{1,2}][Ntf ₂]	1357	1407	1438 (1440.5) -0.2	146

Fig. 2 shows comparison of heat of vaporization predicted from MD simulation with experimental data for a family of imidazolium-based ILs. Unlike simulations utilizing Padua’s force field, simulations using APPLE&P are in excellent agreement with the heat of vaporization values derived from analysis of three different experiments.

Accurate prediction of ILs transport properties is quite important for multiple applications as low viscosity, high conductivity and ion transport ILs are desired. Table 3 summarizes root mean square (RMS) deviation of the ion self-diffusion coefficients predicted using MD simulations from experimental data indicating consistent and excellent predictive capabilities. Moreover, Fig. 3 demonstrates for a representative subset of ILs that the temperature dependence of ion self-diffusion coefficients is also accurately predicted. Similar quality predictions were obtained for ion conductivity. An extension of the force field to ILs doped with lithium salts has been also explored. In these systems MD simulation predicted ion self-diffusion coefficients were found to be in excellent agreement with the pgf-NMR experimental data.

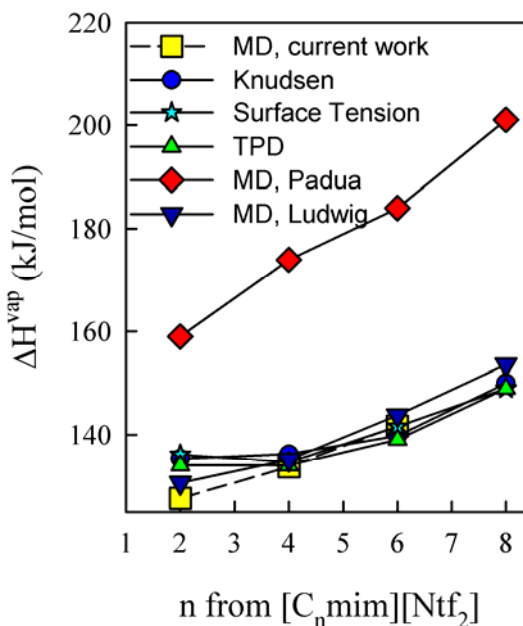


Fig.2. Heat of vaporization for ILs from experiments (Knudsen, Surface Tension, TPD) compared to MD simulation predictions by other groups (Padua and Ludwig) and MD predictions using APPLE&P (current work).

Table 3. The root mean square (RMS) deviation of ion self-diffusion coefficients of ILs predicted using MD simulations from experimental data.

	RMS Self-Diffusion Coefficient Deviation (%)		RMS Self-Diffusion Coefficient Deviation (%)		
	cation	anion	cation	anion	
[emim][BF ₄]	13	18	[bmim][CF ₃ SO ₃]	18	32
[bmim][BF ₄]	12	20	[emim][FSI]	15	19
[bmim][PF ₆]	15	20	[mppy][Ntf ₂]	22	13
[emim][Ntf ₂]	21	17	[mbpy][Ntf ₂]	7	5
[bmim][Ntf ₂]	22	20	[c ₄ ,c ₁ ,c ₁ ,c ₁ -N][Ntf ₂]	9	13
[C ₆ mim][Ntf ₂]	11	17	[b-pyrid][Ntf ₂]	5	9

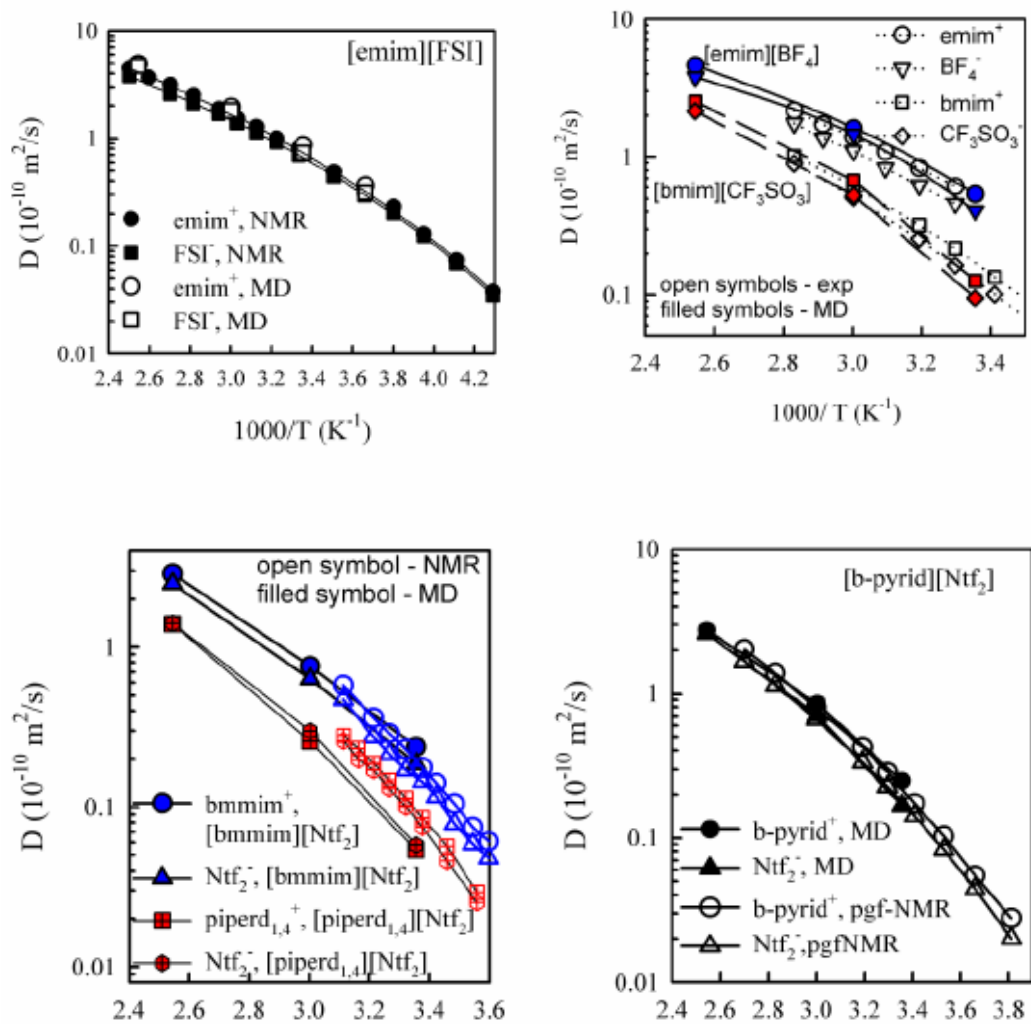


Fig. 3. Ion self-diffusion coefficients of ionic liquids obtained from MD simulations and pgf-NMR experiments listed below:

Table 4. Viscosity of selected ILs from MD simulations using APPLE&P and experiments.

	T, K	viscosity (mPa s)	
		MD	exp
[emim][TFSI]	393	4.2	4.4
[C ₅ O ₂ im][TFSI]	303	51.8	48.4
[C ₇ mim][TFSI]	303	65.5	63-66.8