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

Electronic Supporting Information

Accurate prediction of bulk properties in hydrogen bonded liquids: amides as case studies

Marina Macchiagodena[1], Giordano Mancini[1,2,*], Marco Pagliai[1,*], Vincenzo Barone[1,2]

[1] Scuola Normale Superiore di Pisa, Piazza dei Cavalieri 7, 56126, Pisa, Italy

[2] Istituto Nazionale di Fisica Nucleare (INFN) sezione di Pisa, Largo Bruno Pontecorvo 3, 56127 Pisa, Italy

Table S1: CM5 population analysis for formamide molecule. The calculations have been performed using the B3LYP exchange and correlation functional and 6-31+G(d), 6-311++G(d,p) and aug-cc-pVTZ basis sets, respectively.

	CM5 Charges (e)		
Atom	6-31+G(d) (used)	6-311++G(d,p)	aug-cc-pVTZ
C1	0.191055	0.190976	0.191509
H2	0.131902	0.129095	0.127973
N	-0.566816	-0.566023	-0.568819
H4	0.339036	0.336867	0.338320
H5	0.345109	0.342799	0.342886
O	-0.440286	-0.433714	-0.431869

Figure S1. Representation of HCO-NH_2, HCO-$NHCH_3$, HCO-$N(CH_3)_2$ with atom indexes used for specifying the force field.

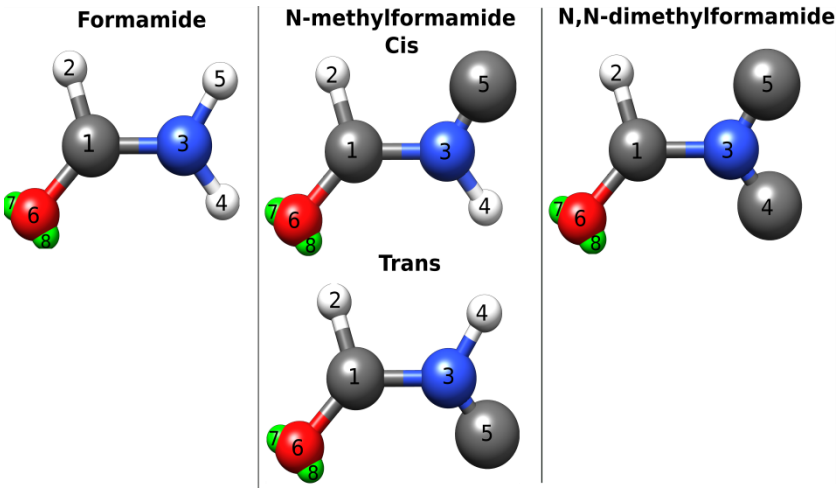

Table S2: Force field details for formamide, N-methylformamide and N,N-dimethylformamide.

Atom	Formamide			
	Mass (u)	Charge (e)	σ (nm)	ε (kJ/mol)
1	12.0110	0.154544	3.75000e-01	4.39320e-01
2	1.00800	0.131902	2.42000e-01	6.27600e-02
3	14.00670	-0.566816	3.25000e-01	7.11280e-01
4	1.00800	0.339036	0.00000e+00	0.00000e+00
5	1.00800	0.345109	0.00000e+00	0.00000e+00
6	15.99940	0.000000	2.96000e-01	8.78640e-01
7	0.00000	-0.201887	0.00000e+00	0.00000e+00
8	0.00000	-0.201887	0.00000e+00	0.00000e+00

Atom	N-methylformamide -CIS-			
	Mass (u)	Charge (e)	σ (nm)	ε (kJ/mol)
1	12.0110	0.146569	3.75000e-01	4.39320e-01
2	1.00800	0.127781	2.42000e-01	6.27600e-02
3	14.00670	-0.429268	3.25000e-01	7.11280e-01
4	1.00800	0.339814	0.00000e+00	0.00000e+00
5	15.03500	0.230849	3.80000e-01	7.11280e-01
6	15.99940	0.000000	2.96000e-01	8.78640e-01
7	0.00000	-0.207872	0.00000e+00	0.00000e+00
8	0.00000	-0.207872	0.00000e+00	0.00000e+00

Atom	N-methylformamide -TRANS-			
	Mass (u)	Charge (e)	σ (nm)	ε (kJ/mol)
1	12.0110	0.148973	3.75000e-01	4.39320e-01
2	1.00800	0.127948	2.42000e-01	6.27600e-02
3	14.00670	-0.430660	3.25000e-01	7.11280e-01
4	1.00800	0.345317	0.00000e+00	0.00000e+00
5	15.03500	0.211743	3.80000e-01	7.11280e-01
6	15.99940	0.000000	2.96000e-01	8.78640e-01
7	0.00000	-0.201661	0.00000e+00	0.00000e+00
8	0.00000	-0.201661	0.00000e+00	0.00000e+00

Atom	N,N-dimethylformamide			
	Mass (u)	Charge (e)	σ (nm)	ε (kJ/mol)
1	12.0110	0.146489	3.80000e-01	4.81160e-01
2	1.00800	0.124365	2.42000e-01	6.27600e-02
3	14.00670	-0.298481	3.25000e-01	7.11280e-01
4	15.03500	0.224764	3.80000e-01	7.11280e-01
5	15.03500	0.207582	3.80000e-01	7.11280e-01
6	15.99940	0.000000	2.96000e-01	8.78640e-01
7	0.00000	-0.202359	0.00000e+00	0.00000e+00
8	0.00000	-0.202359	0.00000e+00	0.00000e+00

Formamide

Bonds

ai	aj	type	r_{eq} (nm)	kr (kJ/mol nm^2)			
1	2	1	0.1102	303447.825			
1	3	1	0.1345	394511.707			
3	4	1	0.1012	439298.529			
3	5	1	0.1014	439298.529			
1	6	1	0.1235	519324.976			

Angles

ai	aj	ak	type	θ_{eq} (degr)	kθ (kJ/mol rad^2)		
2	1	3	1	113.34	335.5886		
2	1	6	1	121.75	487.8341		
1	3	4	1	121.05	382.3045		
1	3	5	1	120.71	382.3045		
3	1	6	1	124.92	825.6435		
4	3	5	1	118.24	245.6576		

Dihedrals

ai	aj	ak	al	type	gamma	kj (kJ/mol)	n
2	1	3	5	1	180.00	13.647	2
2	1	3	5	1	180.00	-3.400	4
2	1	3	5	1	180.00	1.258	6
2	1	3	5	1	180.00	-0.666	8
6	1	3	5	1	180.00	13.647	2
6	1	3	5	1	180.00	-3.400	4
6	1	3	5	1	180.00	1.258	6
6	1	3	5	1	180.00	-0.666	8
1	2	6	3	2	0.0	585.095	
3	1	4	5	2	0.0	30.047	

Virtual sites

Site	from			funct	theta	d
7	6	1	2	3	111.195	0.0312
8	6	1	3	3	110.518	0.0316

N-methylformamide -CIS-

Bonds

ai	aj	type	r_{eq} (nm)	kr (kJ/mol nm^2)			
1	2	1	0.1102	300951.897			
1	3	1	0.1343	378833.870			
3	4	1	0.1016	424492.396			
3	5	1	0.1459	240898.266			
1	6	1	0.1239	516162.657			

Angles

ai	aj	ak	type	θ_{eq} (degr)	kθ (kJ/mol rad^2)		
2	1	3	1	113.44	277.3539		
2	1	6	1	121.53	450.0066		
1	3	4	1	116.88	321.4647		
1	3	5	1	124.97	625.4407		
3	1	6	1	125.02	866.8685		
4	3	5	1	118.15	396.9181		

Dihedrals

ai	aj	ak	al	type	gamma	kj (kJ/mol)	n
2	1	3	5	1	180.00	29.617	2
2	1	3	5	1	180.00	-3.071	4
2	1	3	5	1	180.00	0.425	6
2	1	3	5	1	180.00	-0.324	8
6	1	3	5	1	180.00	29.617	2
6	1	3	5	1	180.00	-3.071	4
6	1	3	5	1	180.00	0.425	6
6	1	3	5	1	180.00	-0.324	8
1	2	6	3	2	0.0	452.090	
3	1	4	5	2	0.0	204.912	

Virtual sites

Site	from			funct	theta	d	
7	6	1	2	3	110.901	0.0311	
8	6	1	3	3	110.562	0.0317	

N-methylformamide -TRANS-

Bonds

ai	aj	type	r_{eq} (nm)	kr (kJ/mol nm^2)			
1	2	1	0.1102	302434.840			
1	3	1	0.1343	375239.169			
3	4	1	0.1012	436722.754			
3	5	1	0.1459	273027.620			
1	6	1	0.1239	529302.286			

Angles

ai	aj	ak	type	θ_{eq} (degr)	kθ (kJ/mol rad^2)		
2	1	3	1	113.42	350.8837		
2	1	6	1	121.85	476.7577		
1	3	4	1	117.77	322.8502		
1	3	5	1	123.28	519.2265		
3	1	6	1	124.73	838.9867		
4	3	5	1	118.95	345.2481		

Dihedrals

ai	aj	ak	al	type	gamma	kj (kJ/mol)	n
2	1	3	4	1	180.00	30.004	2
2	1	3	4	1	180.00	-2.684	4
2	1	3	4	1	180.00	0.812	6
2	1	3	4	1	180.00	0.063	8
6	1	3	4	1	180.00	30.004	2
6	1	3	4	1	180.00	-2.684	4
6	1	3	4	1	180.00	0.812	6
6	1	3	4	1	180.00	0.063	8
1	2	6	3	2	0.0	390.754	
3	1	4	5	2	0.0	64.746	

Virtual sites

Site	from			funct	theta	d	
7	6	1	2	3	111.107	0.0313	
8	6	1	3	3	110.827	0.0314	

N,N-dimethylformamide

Bonds

ai	aj	type	r_{eq} (nm)	kr (kJ/mol nm^2)			
1	2	1	0.1102	301726.569			
1	3	1	0.1348	358011.156			
3	4	1	0.1459	229835.248			
3	5	1	0.1458	229835.248			
1	6	1	0.1240	527810.093			

Angles

ai	aj	ak	type	θ_{eq} (degr)	kθ (kJ/mol rad^2)		
2	1	3	1	112.91	300.7422		
2	1	6	1	121.16	356.0927		
1	3	4	1	121.41	408.5675		
1	3	5	1	121.59	408.5675		
3	1	6	1	125.93	832.0239		
4	3	5	1	117.01	647.1233		

Dihedrals

ai	aj	ak	al	type	gamma	kj (kJ/mol)	n
2	1	3	5	1	179.92	18.298	2
2	1	3	5	1	179.92	-3.599	4
2	1	3	5	1	179.92	1.430	6
2	1	3	5	1	179.92	-0.744	8
6	1	3	5	1	179.93	18.298	2
6	1	3	5	1	179.93	-3.599	4
6	1	3	5	1	179.93	1.430	6
6	1	3	5	1	179.93	-0.744	8
1	2	6	3	2	0.0	519.127	
3	1	4	5	2	0.0	279.488	

Virtual sites

Site	from			funct	theta	d	
7	6	1	2	3	109.838	0.0311	
8	6	1	3	3	111.215	0.0314	

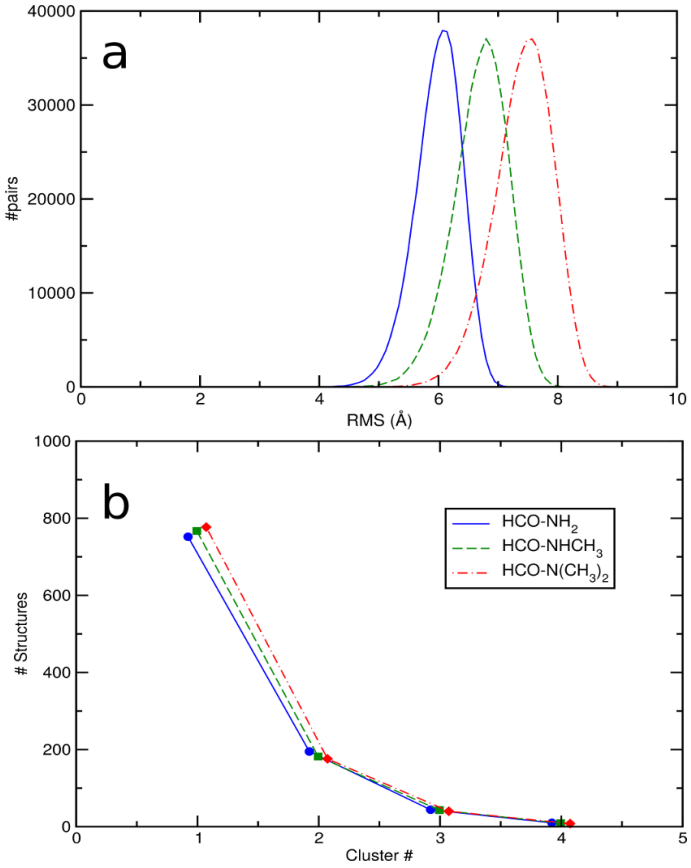

Figure S2: (a) Pair-wise distance histograms obtained from cluster analysis. (b) Clusters sizes.

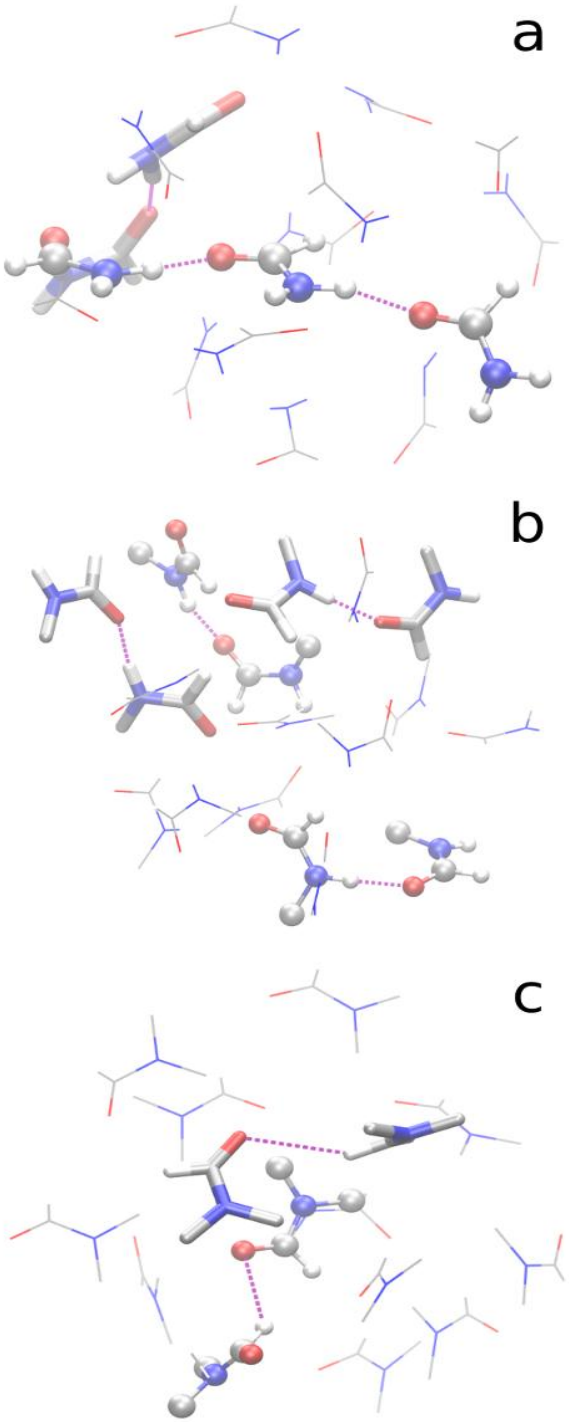

Figure S3: First centroid from cluster analysis of formamide (a), NMF (b) and DMF (c). Licorice or ball and stick representations have been used to selected pairs or triplets of hydrogen bonded (improper bonds for DMF; purple dashed lines) molecules.

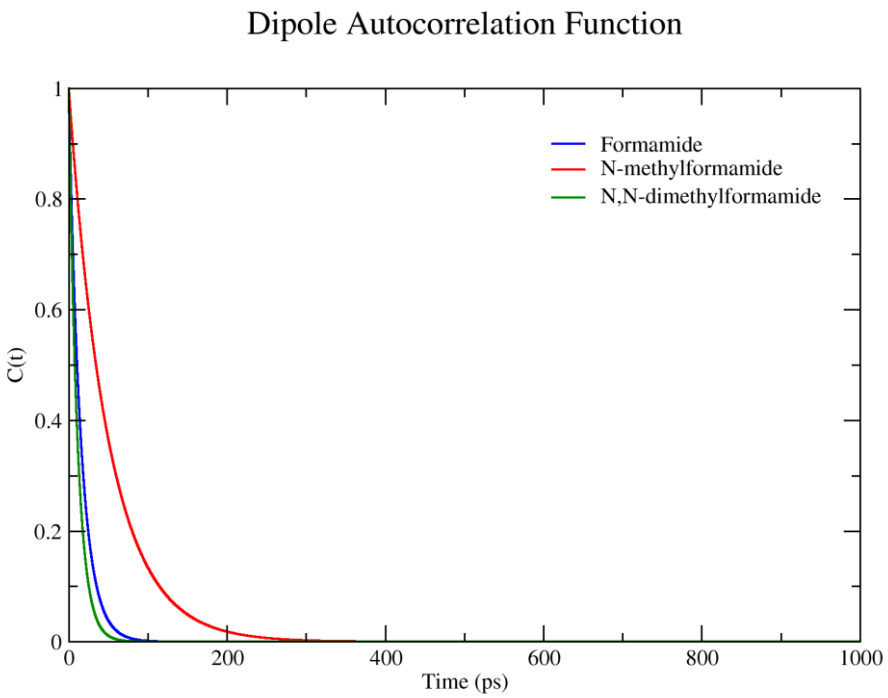

Figure S4: Autocorrelation function of molecular dipole for formamide (blue), N,methylformamide (red) and N,N-dimethylformamide (green).

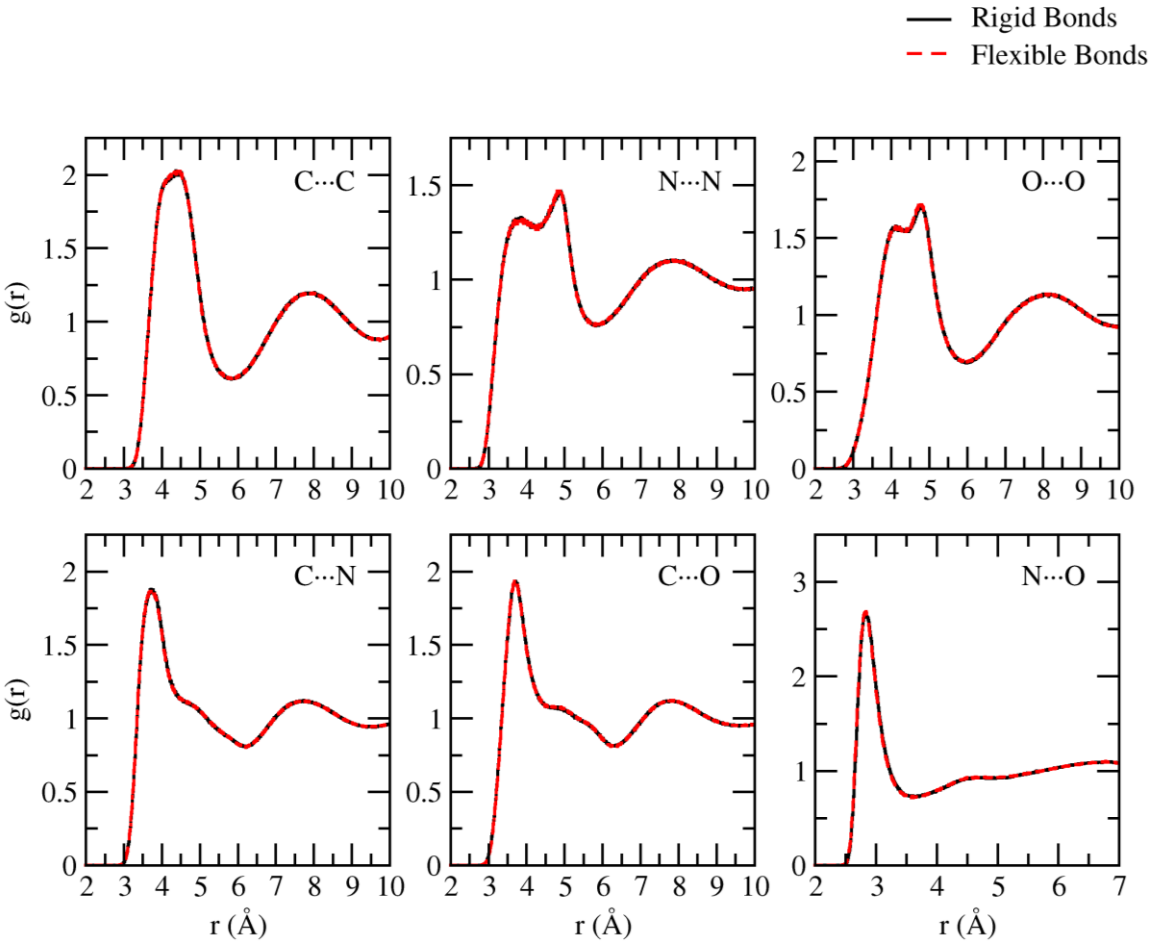

Figure S5: Radial distribution function between chosen atoms in formamide. In dashed red line the results obtained using a flexible bonds model, in full black line a rigid model.

Table S3: The CM5 charges (e) for formamides calculated at the B3LYP/6-31+G(d) level (CM5) and used in the simulations (adjusted) taking into account the water solvent effect by means of C-PCM.

q(e)						
Atom	$HCO\text{-}NH_2$		$HCO\text{-}NHCH_3$ (TRANS)		$HCO\text{-}N(CH_3)_2$	
	CM5	*Adjusted*	*CM5*	*Adjusted*	*CM5*	*Adjusted*
C1	0.191052	0.154584	0.185483	0.149073	0.182184	0.146225
H2	0.131826	0.131826	0.127791	0.127791	0.124605	0.124605
N	-0.566949	-0.566949	-0.430887	-0.430887	-0.298180	-0.298180
H4 (or C4)	0.344993	0.344993	0.345078	0.345078	0.214314	0.214314
H5 (or C5)	0.338973	0.338973	0.211584	0.211584	0.219040	0.219040
O	-0.439895	0.000000	-0.439049	0.000000	-0.441963	0.000000
VS1	0.000000	-0.201714	0.000000	-0.201319	0.000000	-0.203002
VS2	0.000000	-0.201714	0.000000	-0.201319	0.000000	-0.203002

Table S4: Values of O-VS distances (a,b) and C-O-VS (α and β) angles used to generate the position of VS in formamide, N-methylformamide (trans conformers), N,N-dimethylformamide molecules. These values are used to perform simulations of aqueous solutions.

	a (Å)	b (Å)	α (°)	β (°)
$HCO\text{-}NH_2$	0.312	0.316	111.189	110.512
$HCO\text{-}NHCH_3$ (trans)	0.313	0.314	111.092	110.804
$HCO\text{-}N(CH_3)_2$	0.311	0.314	109.863	111.258