Development of new coarse-grained models for chromonic liquid crystals: insights from *top-down* approaches

Thomas D. Potter, Jos Tasche, Elin L. Barrett, Martin Walker & Mark R. Wilson

Supplementary Information

1. GROMACS topology file containing force field information for the MARTINI TP6EO2M model.

```
; TP6EO2M_GMX.top


[ defaults ]
; nbfunc        comb-rule       gen-pairs       fudgeLJ fudgeQQ
;1               2               yes             0.5     0.8333
1  1

[ atomtypes ]
;name   bond_type     mass     charge   ptype   sigma         epsilon       Amb
 CC       CC          24.00000  0.00000   A      0.0             0.0
 CO       CO          25.00000  0.00000   A      0.0             0.0
 AI       AI          44.00000  0.00000   A      0.0             0.0
 AO       AO          31.00000  0.00000   A      0.0             0.0
 P4   P4       72.00000  0.00000   A      0.0             0.0
 BP4     BP4          72.00000  0.00000   A      0.0             0.0
 POL     POL          24.0      0.000     A 0.0 0.0
 D         D          24.0      0.000     A 0.0 0.0

[ nonbond_params ]
;name name     fubct 4*e*(s^6) 4*e*(s^12)
P4  P4  1  0.21558E-00  0.23238E-02 ; attractive
BP4  BP4  1  0.21558E-00  0.23238E-02 ; attractive
CC       CC  1  0.66375E-01  0.41957E-03 ; 75intermediate, s=0.43
CO       CO  1  0.66375E-01  0.41957E-03 ; 75intermediate, s=0.43
AI       AI  1  0.85338E-01  0.53946E-03 ; 75almost attractive, s=0.43
AO       AO 1  0.85338E-01  0.53946E-03 ; 75almost attractive, s=0.43
P4  BP4  1  0.76824E-00  0.26348E-01 ; supra attractive, s=0.57
P4       CC  1       0.11642E-00     0.12549E-02 ; semi repulsive
P4       CO  1  0.11642E-00     0.12549E-02 ; semi repulsive
P4   AI 1  0.17246E-00  0.18590E-02 ; semi attractive
P4       AO  1       0.17246E-00     0.18590E-02 ; semi attractive
P4      CC  1  0.11642E-00     0.12549E-02 ; semi repulsive
BP4      CO  1  0.11642E-00     0.12549E-02 ; semi repulsive
BP4       AI  1  0.17246E-00     0.18590E-02 ; semi attractive
BP4       AO  1  0.17246E-00     0.18590E-02 ; semi attractive
CC        CO  1  0.66375E-01  0.41957E-03 ; 75intermediate, s=0.43
CC        AI  1  0.58789E-01     0.37162E-03 ; 75almost intermediate, s=0.43
CC        AO  1  0.58789E-01     0.37162E-03 ; 75almost intermediate, s=0.43
CO        AI  1  0.58789E-01     0.37162E-03 ; 75almost intermediate, s=0.43
CO        AO  1  0.58789E-01     0.37162E-03 ; 75almost intermediate, s=0.43
AI        AO 1  0.85338E-01  0.53946E-03 ; 75almost attractive, s=0.43
POL  POL  1  0.17246E-00  0.18590E-02 ; semi attractive
POL   CC     1       0.14336E-00     0.15454E-02 ; intermediate 95%
POL   CO     1       0.14336E-00     0.15454E-02 ; intermediate 95%
POL   AI      1   0.16384E-00     0.17660E-02 ; semi attractive 95%
POL   AO      1   0.16384E-00     0.17660E-02 ; semi attractive 95%
  D     D       1       0.00000E-00     0.00000E-00 ; no LJ interaction
  D    CC       1       0.00000E-00     0.00000E-00 ; no LJ interaction
  D    CO       1       0.00000E-00     0.00000E-00 ; no LJ interaction
  D    AI       1       0.00000E-00     0.00000E-00 ; no LJ interaction
  D    AO       1       0.00000E-00     0.00000E-00 ; no LJ interaction

[ moleculetype ]
;name            nrexcl
TP6EO2M 2

[ atoms ]
;   nr  type  resi  res  atom  cgnr     charge      mass       ; qtot   bond_type
    1    CC     1   MOL    CC    1      ;  -0.02
    2    CC     1   MOL    CC    2      ;  -0.02
    3    CC     1   MOL    CC    3      ;  -0.02
    4    CO     1   MOL    CO    4      ;  0.0801
    5    CO     1   MOL    CO    5      ;  0.0801
    6    CO     1   MOL    CO    6      ;  0.0801
    7    CO     1   MOL    CO    7      ;  0.0801
    8    CO     1   MOL    CO    8      ;  0.0801
    9    CO     1   MOL    CO    9      ;  0.0801
   10    AI     1   MOL    AI    10     ;  0.1407
   11    AI     1   MOL    AI    11     ;  -0.007
   12    AO     1   MOL    AO    12     ;  -0.2038
   13    AI     1   MOL    AI    13     ;  0.1407
   14    AI     1   MOL    AI    14     ;  -0.007
   15    AO     1   MOL    AO    15     ;  -0.2038
   16    AI     1   MOL    AI    16     ;  0.1407
   17    AI     1   MOL    AI    17     ;  -0.007
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   18    AO     1   MOL    AO    18     ;  -0.2038
   19    AI     1   MOL    AI    19     ;  0.1407
   20    AI     1   MOL    AI    20     ;  -0.007
   21    AO     1   MOL    AO    21     ;  -0.2038
   22    AI     1   MOL    AI    22     ;  0.1407
   23    AI     1   MOL    AI    23     ;  -0.007
   24    AO     1   MOL    AO    24     ;  -0.2038
   25    AI     1   MOL    AI    25     ;  0.1407
   26    AI     1   MOL    AI    26     ;  -0.007
   27    AO     1   MOL    AO    27     ;  -0.2038


[ bonds ]
1 2 1 0.212 15000 ;core-core
1 3 1 0.212 15000        ;core-core
2 3 1 0.212 15000        ;core-core
1 4 1 0.212 15000        ;core-core
1 5 1 0.212 15000        ;core-core
2 8 1 0.212 15000        ;core-core
2 9 1 0.212 15000        ;core-core
3 6 1 0.212 15000        ;core-core
3 7 1 0.212 15000        ;core-core
4 5 1 0.212 15000        ;ocore-core
8 9 1 0.212 15000        ;ocore-core
6 7 1 0.212 15000        ;ocore-core
5 9 1 0.424 15000        ;core-adjcore
7 8 1 0.424 15000        ;core-adjcore
4 6 1 0.424 15000        ;core-adjcore

4 10 1 0.276 10000        ;core-arm
10 11 1 0.328 10000  ;arm-arm
11 12 1 0.282  10000  ;arm-arm
5 13 1 0.276 10000        ;core-arm
13 14 1 0.328 10000       ;arm-arm
14 15 1 0.282 10000      ;arm-arm
6 25 1 0.276 10000
25 26 1 0.328 10000
26 27 1 0.282 10000
7 22 1 0.276 10000
22 23 1 0.328 10000
23 24 1 0.282 10000
8 19 1 0.276 10000
19 20 1 0.328 10000
20 21 1 0.282 10000
9 16 1 0.276 10000
16 17 1 0.328 10000
17 18 1 0.282 10000

[angles]
;4 1 2 2 180.0  50
;4 1 3 2 120.0  50
;5 1 2 2 120.0  50
;5 1 3 2 180.0  50
;6 3 1 2 120.0  50
;6 3 2 2 180.0  50
;7 3 1 2 180.0  50
;7 3 2 2 120.0  50
;8 2 1 2 180.0  50
;8 2 3 2 120.0  50
;9 2 1 2 120.0  50
;9 2 3 2 180.0  50

3 7  22 2 180.0  85
7 22  23 2 130.0 85
22 23 24 2 130.0 85
3  6  25 2 180.0 85
6 25  26 2 130.0 85
25 26 27 2 130.0 85
1  4  10 2 180.0 85
4 10  11 2 130.0 85
10 11 12 2 130.0 85
1  5  13 2 180.0 85
5  13 14 2 130.0 85
13 14 15 2 130.0 85
2  8  19 2 180.0 85
8  19 20 2 130.0 85
19 20 21 2 130.0 85
2  9  16 2 180.0 85
9  16 17 2 130.0 85
16 17 18 2 130.0 85

[dihedrals]
;5 1 2 9     2   0.0    20.0
;8 2 3 7     2   0.0    20.0
;6 3 1 4     2   0.0    20.0
;3 7 22 23   2   180.0   5.0
;7 22 23 24  2   180.0   2.5
;3 6 25 26   2   180.0   5.0
;6 25 26 27  2   180.0   2.5
;1 4 10 11   2   180.0   5.0
;4 10 11 12  2   180.0   2.5
;1 5 13 14   2   180.0   5.0
;5 13 14 15  2   180.0   2.5
;2 8 19 20   2   180.0   5.0
;8 19 20 21  2   180.0   2.5
;2 9 16 17   2   180.0   5.0
```

```
;9 16 17 18  2   180.0   2.5

[ dihedrals ] ; impropers
;i      j      k      l    func      eo      ke
; 1      2      3      5     2      0.00     8.0
; 1      2      3      4     2      0.00     8.0
; 2      1      3      9     2      0.00     8.0
; 2      3      1      8     2      0.00     8.0
; 3      2      1      7     2      0.00     8.0
; 3      2      1      6     2      0.00     8.0
; 4      5      3      1     2      0.00     8.0
; 4      5      2      1     2      0.00     8.0
; 8      9      1      2     2      0.00     8.0
; 8      9      3      2     2      0.00     8.0
; 6      7      1      3     2      0.00     8.0
; 6      7      2      3     2      0.00     8.0

[ dihedrals ] ; mark
;  4      1      3      6     2      0.00     30.0
;  5      1      2      9     2      0.00     30.0
;  7      3      2      8     2      0.00     30.0
;   1      2      5      4     2      0.00     30.0
;   1      3      4      5     2      0.00     30.0
;   2      1      8      9     2      0.00     30.0
;   2      3      8      9     2      0.00     30.0
;   3      1      6      7     2      0.00     30.0
;   3      2      6      7     2      0.00     30.0
;  5      1      2      9     2      0.00     30.0
;  7      3      2      8     2      0.00     30.0
;   4      1      3      6     1     180.00     30.0   1
;   5      1      2      9     1     180.00     30.0   1
;   7      3      2      8     1     180.00     30.0   1

   4      1      3      2     1     0.00     30.0   1
   5      1      2      3     1     0.00     30.0   1

   6      3      1      2     1     0.00     30.0   1
   7      3      2      1     1     0.00     30.0   1

   8      2      3      1     1     0.00     30.0   1
   9      2      1      3     1     0.00     30.0   1

;;;;;; POLARIZABLE WATER

[ moleculetype ]
; molname       nrexcl
  W             1

[ atoms ]
;id     type    resnr   residu  atom    cgnr    charge
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[ moleculetype ]
; molname       nrexcl
  AW             1

[ atoms ]
;id     type    resnr   residu  atom    cgnr    charge
 1      BP4      1       AW       AW       1       0

[ system ]
TP6EO2M in water

[ molecules ]
; Compound        nmols
 TP6EO2M          10
 W   3917
 AW           435
```

2. SAFT fits to thermodynamic data

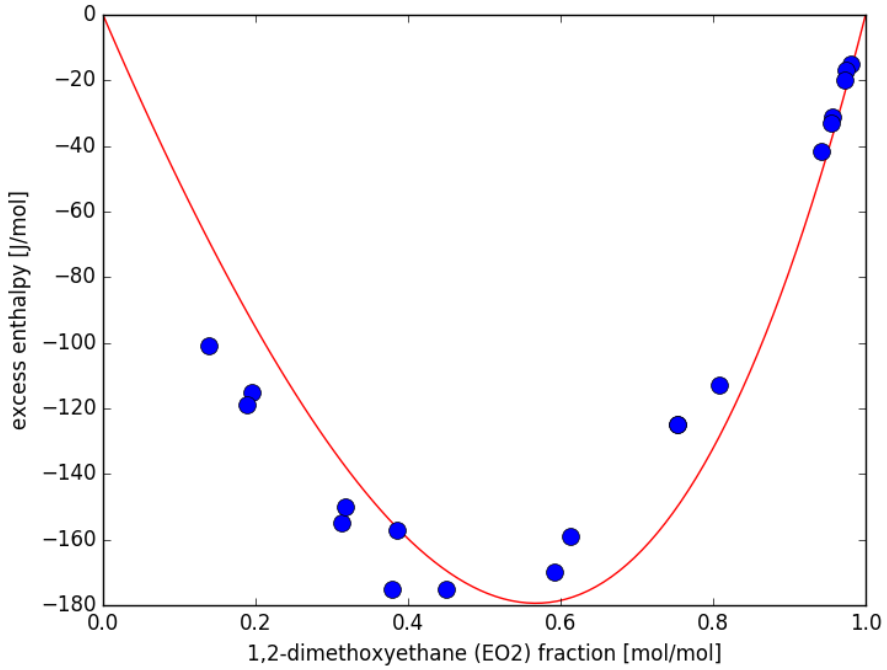

Figure 1. Enthalpies of mixing (excess enthalpies) of 1,2-dimethoxyethane (EO2) and benzene at 298.15 K. The SAFT model (lines) with fitted interaction of $\epsilon_{\mathrm{EO,Ar}} = 323.4$ K to the experimental data (symbols)[1, 2]. Benzene is modelled in the SAFT calculations as a chain, the EO2 model is made of 2 beads fitted to properties of EO4 by Lobanova[3].

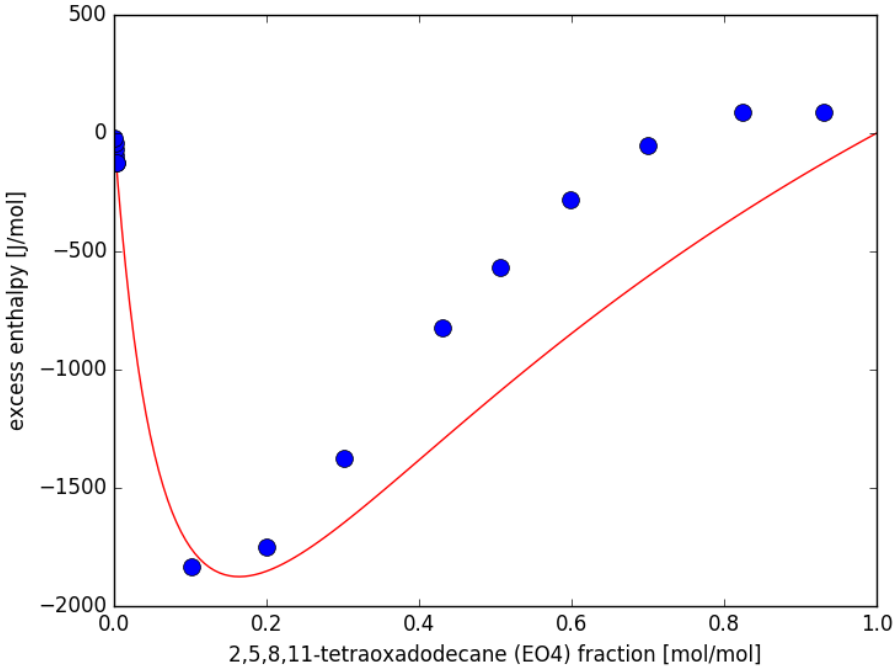

Figure 2. Enthalpies of mixing (excess enthalpies) of 2,5,8,11-tetraoxadodecane (EO4) and water at 298.15 K. The SAFT model (lines) with fitted interaction of $\epsilon_{\mathrm{EO,W}} = 465$ K to the experimental data (symbols)[4, 5].

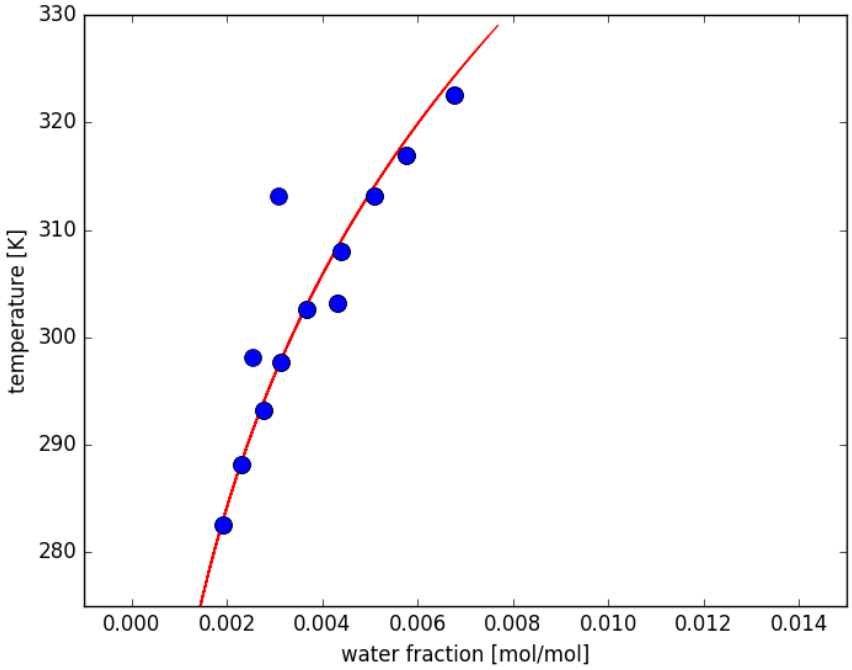

Figure 3. Solubility limit of water in benzene. The experimental data was measured at 1 bar, the SAFT calculations were performed at 5 bar to keep the water model from boiling, which does not significantly influence the solubility. The SAFT model (lines) are with a fitted interaction of $\epsilon_{\mathrm{Ar,W}} = 195$ K to the experimental data (symbols)[6–8].

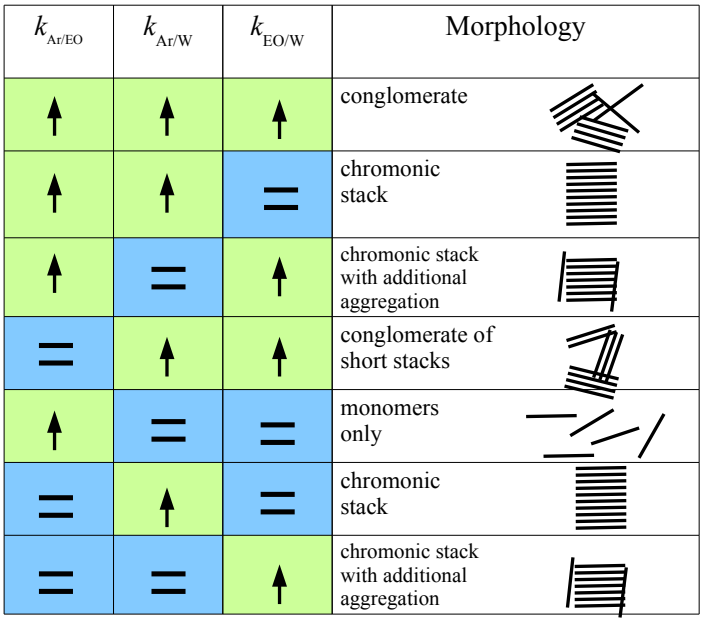

Figure 4. The influence of unfavourable cross-interactions on chromonic stacking. Results are shown for the final revised SAFT model with the same bond lengths as used in the MARTINI model. Up arrows indicate interactions that are less favourable than mixing rules with $k_{ij} = 0.2$. Equals signs indicate $k_{ij} = 0$. For the case where pure combining rules are used ($k_{ij} = 0$ for all cross-interactions), only monomers and transcient self-assembled dimers are seen.

References

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