Electronic Supplementary Information (ESI)

for

Predicting and parameterizing the glass transition temperature of atmospheric organic aerosol components via molecular dynamics simulations

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S1. T_g predictions from MD simulations

Table S1: MD predictions for the T_g of all compounds. Values from the two methods (density and energy of non-bonded potential energy as a function of temperature) implemented to predict T_g and comparison with available experimental data.

Compound	T_g (K) based on density	T_g (K) based on non-bonded potential energy	T_g (K) experimental
1-propanol	118.2 ± 0.4[1]	118.5 ± 6.5[1]	100 ± 7[2]
2-propanol	130.2 ± 0.4[1]	130.9 ± 1[1]	119.4 ± 4[2]
1,2-propanediol	171.2 ± 4.6[1]	180 ± 0.5[1]	170 ± 3[2]
1,3-propanediol	175.9 ± 3.8[1]	178.4 ± 0.3[1]	148 ± 8[2]
1,2,3-propanetriol	216.2 ± 6.5[1]	218.9 ± 5.8[1]	189 ± 7[2]
1-hexanol	149.6 ± 7.1[1]	150.7 ± 0.8[1]	N/A
1,6-hexanediol	242.4 ± 5.7[1]	242.2 ± 7.1[1]	N/A
1,2,6-hexanetriol	258.3 ± 13.4[1]	257.9 ± 9.2[1]	204 ± 6[2]
1-nonanol	167.3 ± 2.2	168.5 ± 0.5	153[2]
1,2-nonanediol	251.6 ± 4.6	248.7 ± 12.1	N/A
1,2,9-nonanetriol	264.4 ± 0.5	266.1 ± 1.6	N/A
1-dodecanol	187.6 ± 1.4	185.3 ± 2.1	N/A
1,2-dodecanediol	259.4 ± 2.3	266.9 ± 1.3	N/A
cyclohexanol	173.5 ± 0.6	173.8 ± 0.6	161[3]
cyclohexanediol	271.4 ± 5.5	273.7 ± 6.1	N/A
cyclohexanetriol	285.8 ± 1.2	286.4 ± 0.8	N/A
cyclononanol	186.3 ± 1.8	190.3 ± 0.35	N/A
Propionic acid	159.6 ± 5.9[1]	160.6 ± 6.2[1]	N/A
Malonic acid	275.3 ± 2[1]	271.7 ± 0.6[1]	N/A
Hexanoic acid	183.2 ± 7.2[1]	183.3 ± 8[1]	N/A
Adipic acid	280.2 ± 12.2[1]	278.8 ± 11.9[1]	N/A
Tricarballylic acid	316.2 ± 1.1[1]	314.2 ± 0.5[1]	N/A
Suberic acid	303.4 ± 3.9[1]	290.5 ± 0.7[1]	N/A
Dimethylsuccinic acid	312.1 ± 3.6[1]	312.3 ± 2.7[1]	N/A

Dimethylhexanedioic acid	297.3 ± 1.7[1]	296.5 ± 1.4[1]	N/A
Cyclobutanedicarboxylic acid	315.9 ± 6.2[1]	309.5 ± 0.6[1]	N/A
Norpinic acid	320.7 ± 0.7[1]	320.4 ± 1[1]	N/A
3-methyl-1,2,3-butanecarboxylic acid	336.7 ± 6.7[1]	351.2 ± 11.1[1]	305 ± 2[4]
Nonanoic acid	195.3 ± 6.9	201.6 ± 0.8	N/A
Azelaic acid	302.1 ± 1.3	303.5± 1.7	N/A
Dodecanoic acid	200 ± 3.4	204.1 ± 1.1	N/A
Dodecanedioic acid	316.3 ± 3.1	295.3 ± .6	N/A
Cyclopentanecarboxylic acid	215.6 ± 1.7	212. ± 12	N/A
Cycloheptanecarboxylic acid	242.4 ± 1.7	243.9 ± 1.2	N/A
2-propanone	112 ± 0.45	108.8 ± 1.9	100[3]
Propanal	105.5 ± 1.8	104.7 ± 0.4	N/A
2-hexanone	133.9 ± 1.4	133.6 ± 0.9	N/A
Hexanal	122.9 ± 0.5	122.6 ± 1.3	N/A
2-Nonanone	165.6 ± 0.3	163.3	N/A
Nonanal	157.2 ± 0.5	152.2 ± 2.4	N/A
Diacetyl	162.6 ± 4.9	155.2 ± 3.3	N/A
Cyclopropanone	118.3 ± 0.8	106.5 ± 0.9	N/A
Cyclohexanone	161.3 ± 2	153.8 ± 1.2	N/A
Cyclononanone	181.3 ± 1	181.6 ± 1.1	N/A
Pyruvic acid	192.6 ± 2.6	192.9 ± 1.9	N/A
5-Oxohexanoic acid	205.3 ± 0.9	204.8 ± 1.1	N/A
6-Oxononanoic acid	225 ± 1.4	227.1 ± 0.2	N/A
Oxomalonic acid	285.7 ± 2.1	286.1 ± 4.2	N/A
2-Oxoadipic acid	294.2 ± 3.4	286.3 ± 0.4	N/A
Lactic acid	213.2 ± 11.8	220.8 ± 2.52	207 ± 18[2]
Tartronic acid	288.4 ± 2.7	288.2 ± 2.9	N/A
Hydroxy acetone	162.4 ± 2.5	163 ± 1	N/A
Dihydroxy acetone	206.3 ± 3	305.9 ± 1.3	N/A
Cis-pinonic acid	255.1 ± 2.2[1]	255 ± 0.9[1]	N/A
Pinonaldehyde	185.1 ± 1.9[1]	184.7 ± 2.2[1]	N/A

S2. Effect of molecular weight and O:C ratio per category of compounds

A) Carbonyls

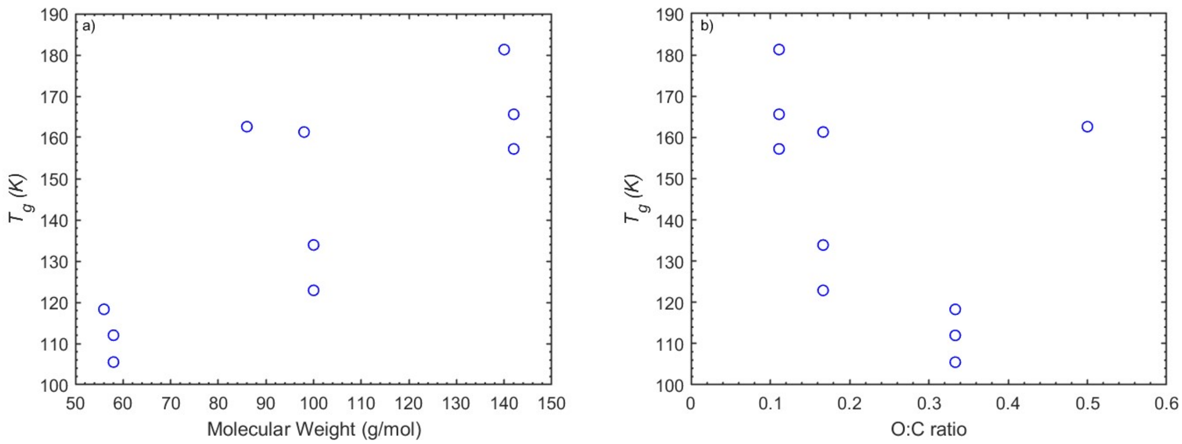

Figure S1: T_g as a function of molecular weight (a) and O:C ratio (b) for the carbonyls.

B) Hydroxyls

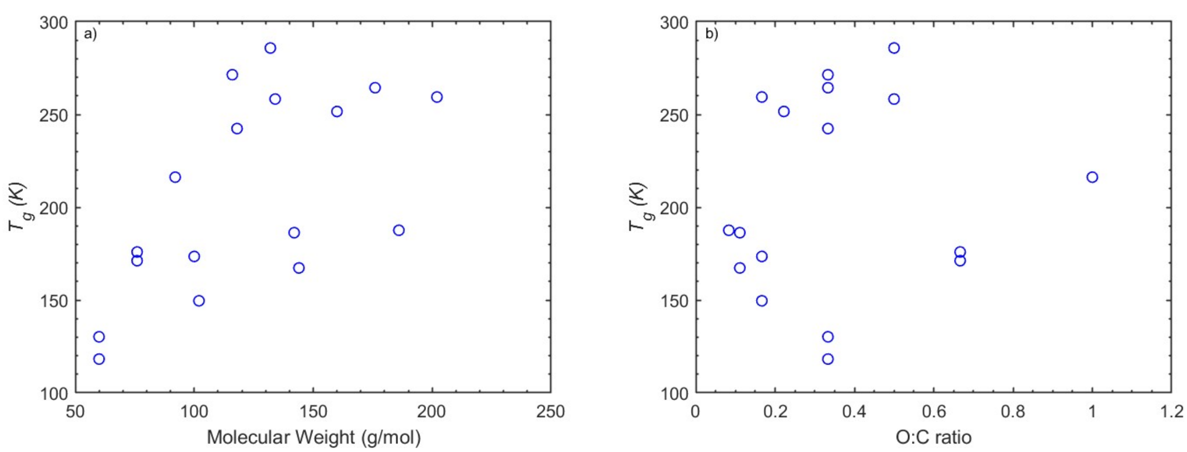

Figure S2: T_g as a function of molecular weight (a) and O:C ratio (b) for the hydroxyls.

C) Carboxyls

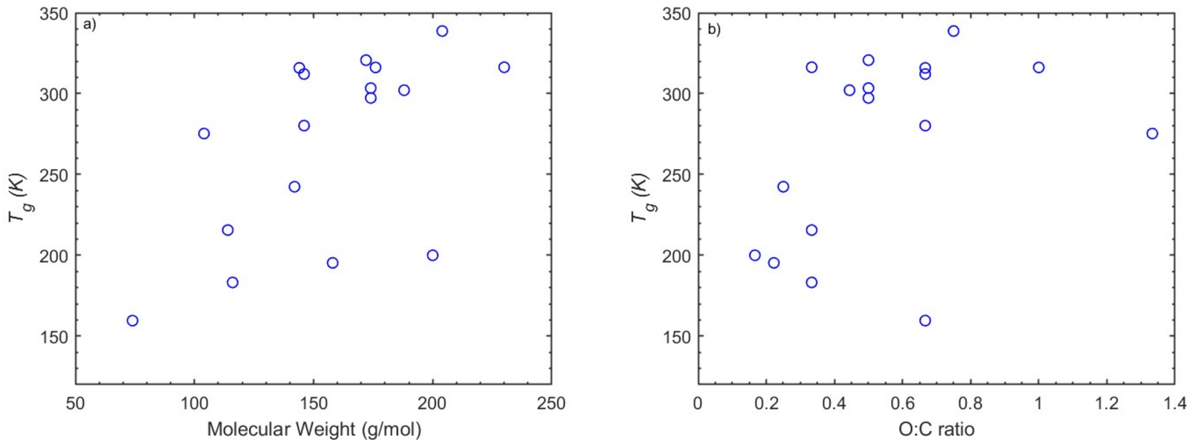

Figure S3: T_g as a function of molecular weight (a) and O:C ratio (b) for the carboxyls.

D) Multifunctionals

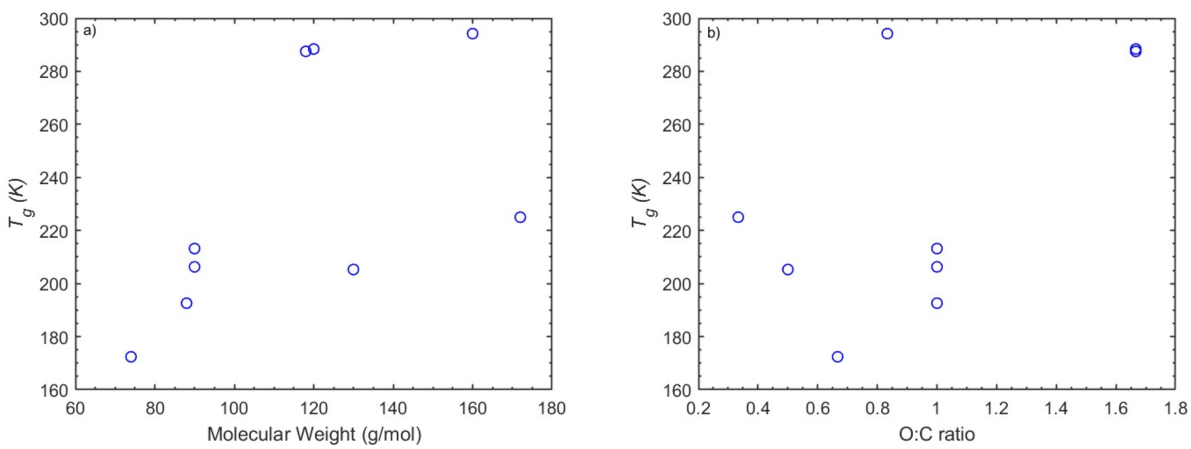

Figure S4: T_g as a function of molecular weight (a) and O:C ratio (b) for the multifunctional compounds.

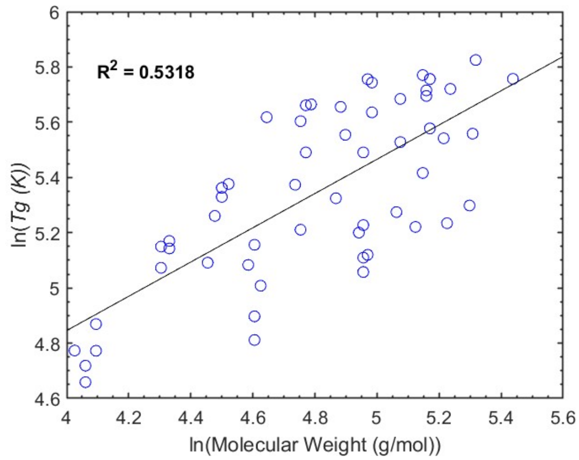

Figure S5: Correlation of the glass transition temperature (T_g) with the molecular weight (M) for the entire dataset. The MD data have been fitted with a power-law of the form $T_g \propto M^a$ as suggested by Novikov and Rössler (2013)[5] and the best fitting has been obtained for α = 0.62.

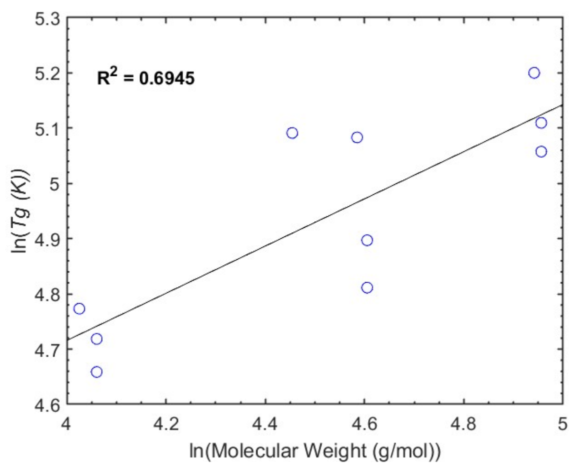

Figure S6: Correlation of the glass transition temperature (T_g) with the molecular weight (M) for the carbonyls. The MD data have been fitted with a power-law of the form $T_g \propto M^a$ as suggested by Novikov and Rössler (2013)[5] and the best fitting has been obtained for α = 0.42.

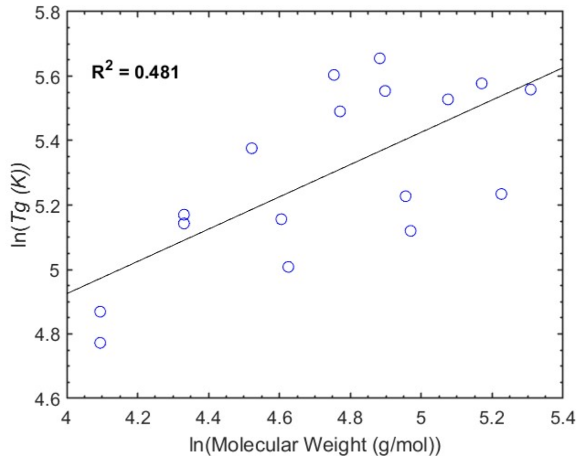

Figure S7: Correlation of the glass transition temperature (T_g) with the molecular weight (M) for the alcohols. The MD data have been fitted with a power-law of the form $T_g \propto M^a$ as suggested by Novikov and Rössler (2013)[5] and the best fitting has been obtained for α = 0.50.

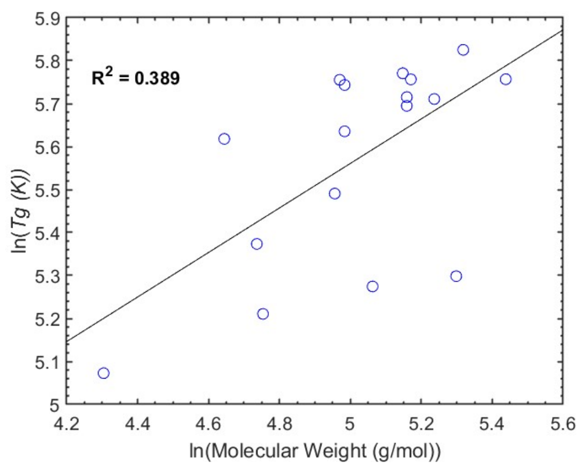

Figure S8: Correlation of the glass transition temperature (T_g) with the molecular weight (M) for the carboxylic acids. The MD data have been fitted with a power-law of the form $T_g \propto M^a$ as suggested by Novikov and Rössler (2013)[5] and the best fitting has been obtained for α = 0.51.

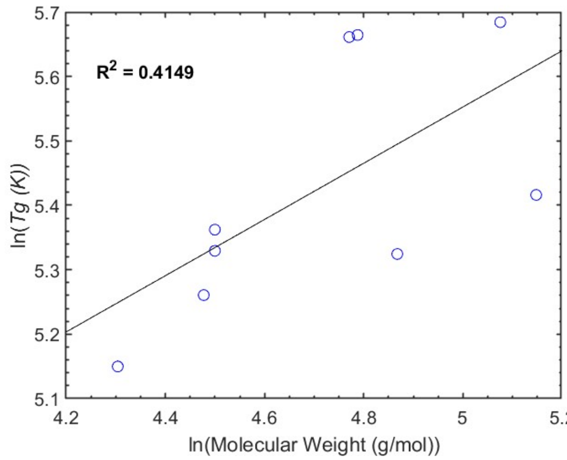

Figure S9: Correlation of the glass transition temperature (T_g) with the molecular weight (M) for the multifunctional organic compounds. The MD data have been fitted with a power-law of the form $T_g \propto M^a$ as suggested by Novikov and Rössler (2013)[5] and the best fitting has been obtained for α = 0.43.

S3. Evaluation of the sensitivity of dataset

To investigate the robustness and sensitivity of our parameterization we examine the variation of the contribution factors. The variation is examined using the leave-one-out scenario, in which we remove all the datapoints once and examine the change in the contribution for each factor considered.

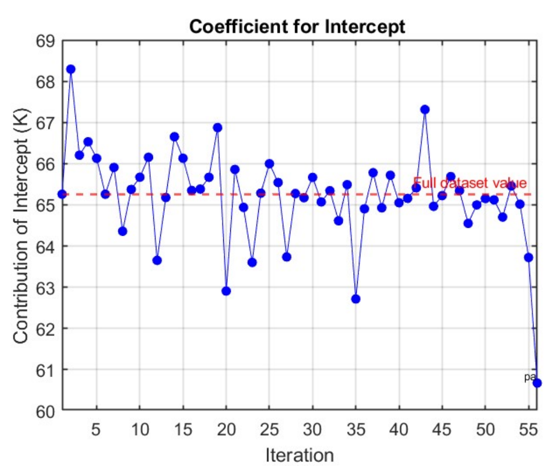

Figure S10: Variation of the intercept's contribution in a leave-one-out scenario with a 5% tolerance threshold. The annotated compounds are those whose removal causes the intercept to deviate by more than 5%.

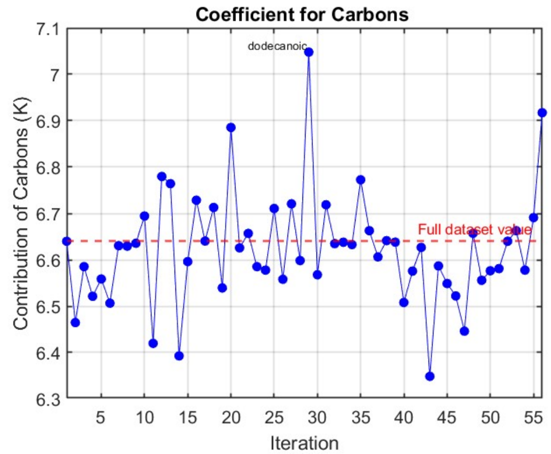

Figure S11: Variation of the intercept's contribution in a leave-one-out scenario with a 5% tolerance threshold. The annotated compounds are those whose removal causes the contribution of carbons to deviate by more than 5%.

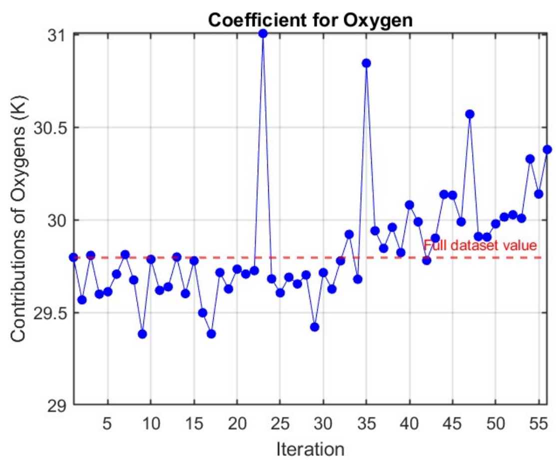

Figure S12: Variation of the intercept's contribution in a leave-one-out scenario with a 5% tolerance threshold. The annotated compounds are those whose removal causes the contribution of oxygens to deviate by more than 5%.

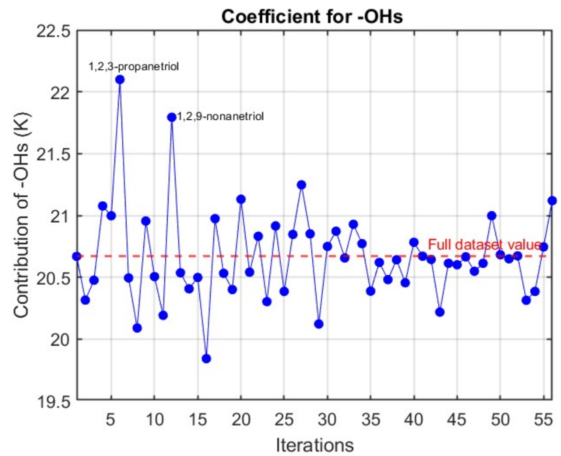

Figure S13: Variation of the intercept's contribution in a leave-one-out scenario with a 5% tolerance threshold. The annotated compounds are those whose removal causes the contribution of hydroxyls to deviate by more than 5%.

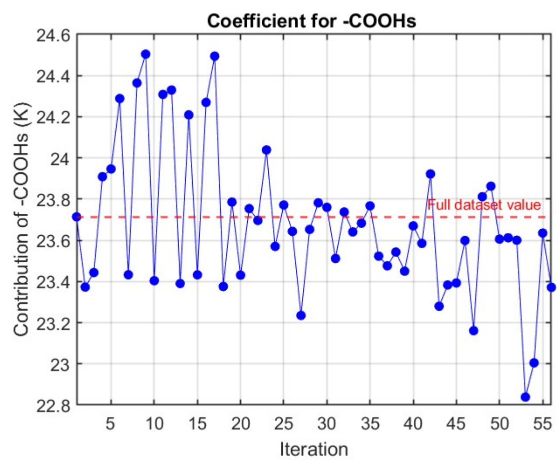

Figure S14: Variation of the intercept's contribution in a leave-one-out scenario with a 5% tolerance threshold. The annotated compounds are those whose removal causes the contribution of caboxyls to deviate by more than 5%.

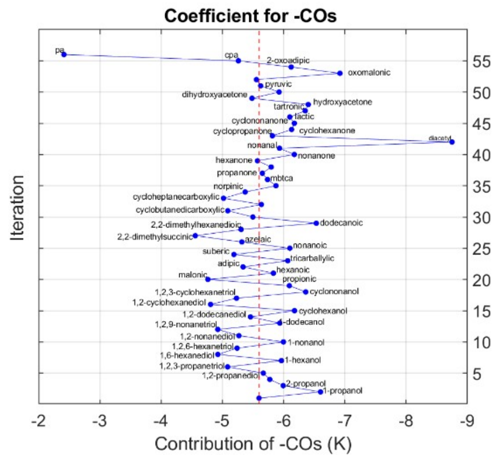

Figure S15: Variation of the intercept's contribution in a leave-one-out scenario with a 5% tolerance threshold. The annotated compounds are those whose removal causes the contribution of carbonyls to deviate by more than 5%.

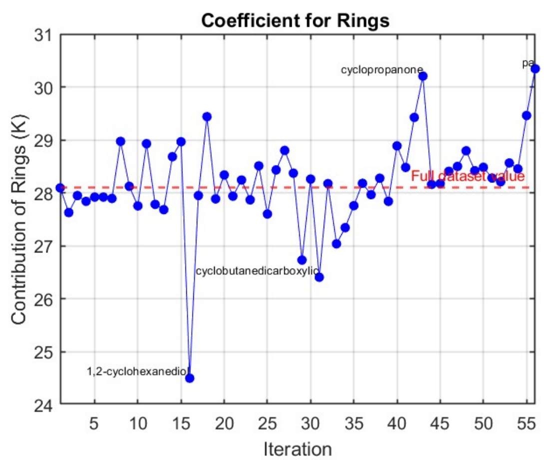

Figure S16: Variation of the intercept's contribution in a leave-one-out scenario with a 5% tolerance threshold. The annotated compounds are those whose removal causes the contribution of rings to deviate by more than 5%.

S4. Estimating the Glass Transition Temperature using the VFT equation

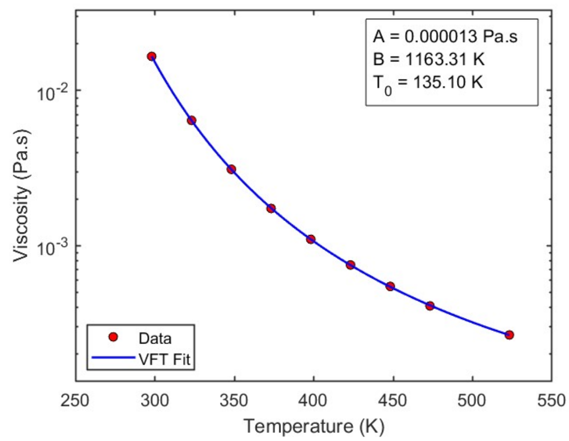

Figure S17: Indirect estimation of the T_g of 1-dodecanol by fitting the viscosity data of Fu et al.[6] with the VFT equation, Eq. (2) in the main text.

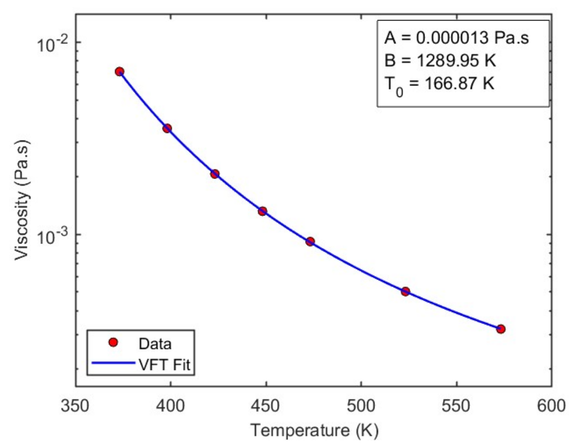

Figure S18: Indirect estimation of the T_g of 1,12-dodecanediol by fitting the viscosity data of Fu et al.[6] with the VFT equation, Eq. (2) in the main text.

S5. Comparison with other parameterizations

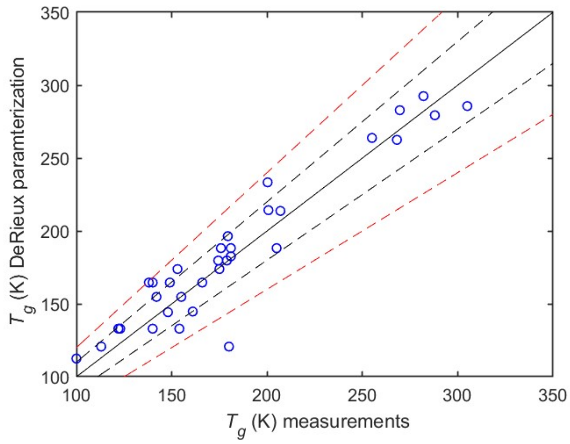

Figure S19: Comparison of the DeRieux et al.[7] parametrization against measurements. The solid line is the 1:1 curve while the dashed black line indicates the ±10%, and the dashed red line represents the ±20% deviations from 1:1.

References

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