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Assessing the transferability of common *top-down* and *bottom-up* coarse-grained molecular models for molecular mixtures.

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Supplementary Material

Table S 1 Scaling factors used, and iterations required, for IBI optimisation. The numbers in parenetheses are, respectively, the number of iterations after which only the R-R interaction and pressure were optimised, and the α used for the iterations after this.

x_{oct}	Iterations	α	f
0.0	62	0.1	0.0005
0.2	183	0.4	0.0005
0.3	248	0.3	0.0005
0.5	278	0.35	0.0005
0.7	300 (297)	0.35 (0.15)	0.0005
0.8	266 (271)	0.35 (0.2)	0.0005
1.0	56	0.5	0.001

Table S 2 Scaling factors used, and iterations required, for the MS-IBI optimisation. The numbers in parenetheses are the number of MS-IBI iterations which were carried out, after which pressure correction was applied. For the MS-3c and MS-4c models the same η value was used for each reference concentration, for the MS-2t model, a different η value was used at each temperature.

Model	Iterations	η	f
MS-3c	319 (300)	0.2	0.0004
MS-4c	310 (295)	0.2	0.0004
MS-2t	248	0.7 at 238 K, 0.5 at 378 K	0.0001

Calculation of mixing free energies

Free energies of mixing were calculated using the methodology described by Darvas *et al.*,[1] which is based on the thermodynamic cycle shown in Figure S1. ΔA_{pure} and ΔA_{sol} were calculated from the vaporisation free energies, $\Delta_{\mathrm{vap}}A$ of octane, benzene, and the relevant mixture, as described in Equations 1 and 2. The free energy of mixing of two ideal gases, $\Delta A_{\mathrm{ideal}}$ was calculated analytically using Equation 3. The free energy of mixing, $\Delta_{\mathrm{mix}}A$, was then calculated from Equation 4.

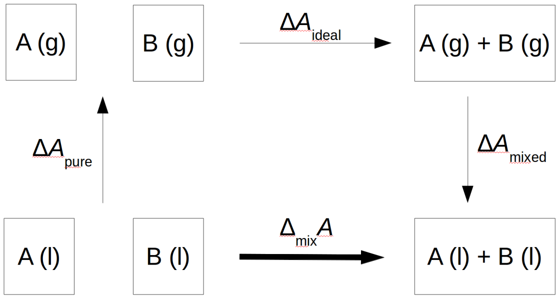

Fig. S 1 Thermodynamic cycle used to calculate ΔA_{mix} for octane and benzene.

$$\Delta A_{\mathrm{pure}} = x_{\mathrm{oct}}\Delta_{\mathrm{vap}}A_{\mathrm{oct}} + x_{\mathrm{ben}}\Delta_{\mathrm{vap}}A_{\mathrm{ben}} \tag{1}$$

$$\Delta A_{\mathrm{mixed}} = -\Delta_{\mathrm{vap}}A_{\mathrm{mixture}} \tag{2}$$

$$\Delta A_{\mathrm{ideal}} = RT\left(x_{\mathrm{oct}}\ln x_{\mathrm{oct}} + x_{\mathrm{ben}}\ln x_{\mathrm{ben}}\right) \tag{3}$$

$$\Delta_{\mathrm{mix}}A = \Delta A_{\mathrm{pure}} + \Delta A_{\mathrm{mixed}} + \Delta A_{\mathrm{ideal}} \tag{4}$$

Vaporisation free energies were calculated in a similar way to solvation free energies. However, instead of decoupling the intermolecular interactions for one molecule, the intermolecular interactions are simultaneously decoupled for all the molecules in the system. The same soft-core parameters and strategies for picking λ points were used as for solvation free energies.

In this case, all simulations were run in the *NVT* ensemble, so the results are Helmholtz free energies of mixing. Simulations of pure octane and benzene were carried out at their equilibrium densities, as calculated from *NpT* atomistic simulations. The volumes for each mixture were then calculated from

$$V_{\mathrm{mixture}} = x_{\mathrm{oct}}V_{\mathrm{oct}} + x_{\mathrm{ben}}V_{\mathrm{ben}} \tag{5}$$

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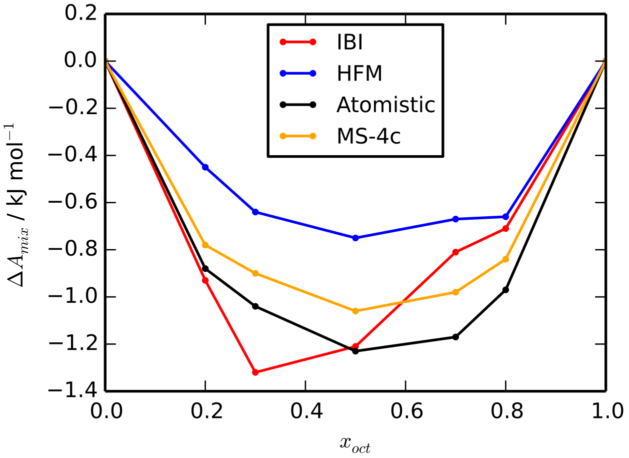

Fig. S 2 Helmholtz free energies of mixing of octane-benzene mixtures, using atomistic, IBI, MS IBI and HFM models.

Mixing free energy results are plotted in Figure S2

References

1 M. Darvas, P. Jedlovszky and G. Jancsó, *J. Phys. Chem. B*, 2009, **113**, 7615–7620.

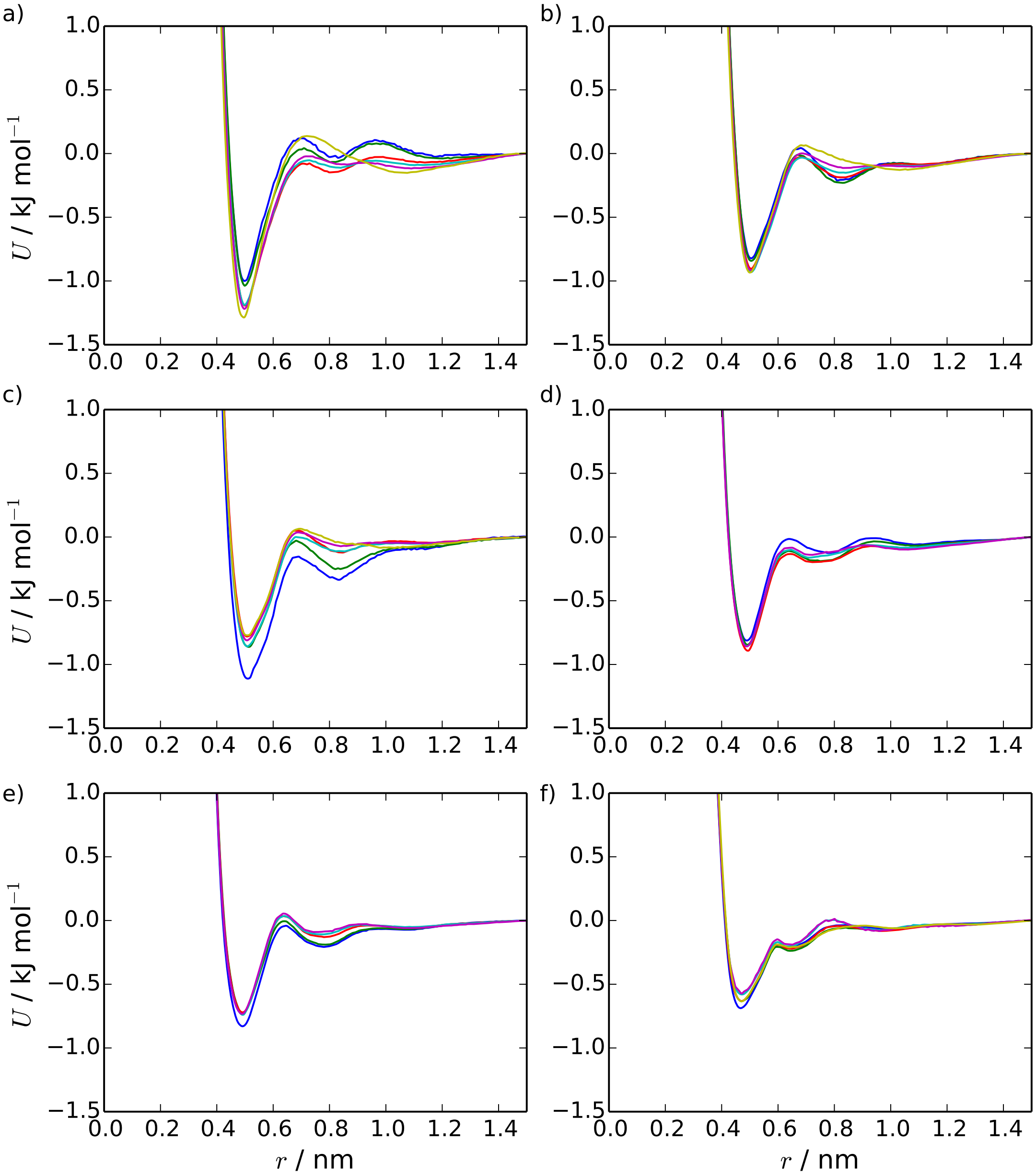

Fig. S 3 Non-bonded potentials parametrised using IBI for the a) A-A, b) A-B, c) B-B, d) A-R, e) B-R, f) R-R interactions. Each potential in each plot parametrised at a different octane concentration: 20% (blue), 30% (green), 50% (red), 70% (cyan) and pure octane or benzene (yellow).

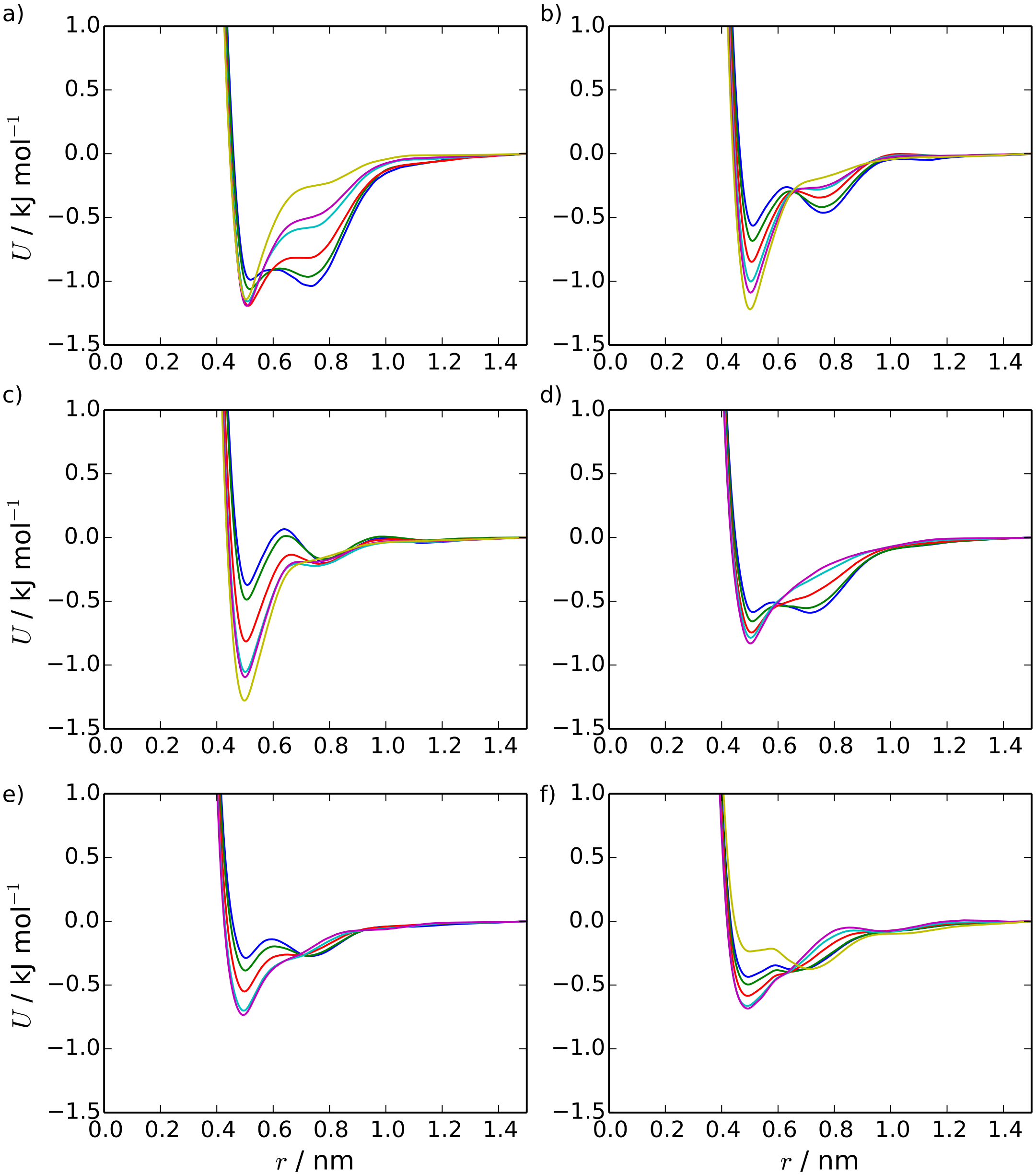

Fig. S 4 Non-bonded potentials parametrised using HFM for the a) A-A, b) A-B, c) B-B, d) A-R, e) B-R, f) R-R interactions. Each potential in each plot parametrised at a different octane concentration: 20% (blue), 30% (green), 50% (red), 70% (cyan) and pure octane or benzene (yellow).

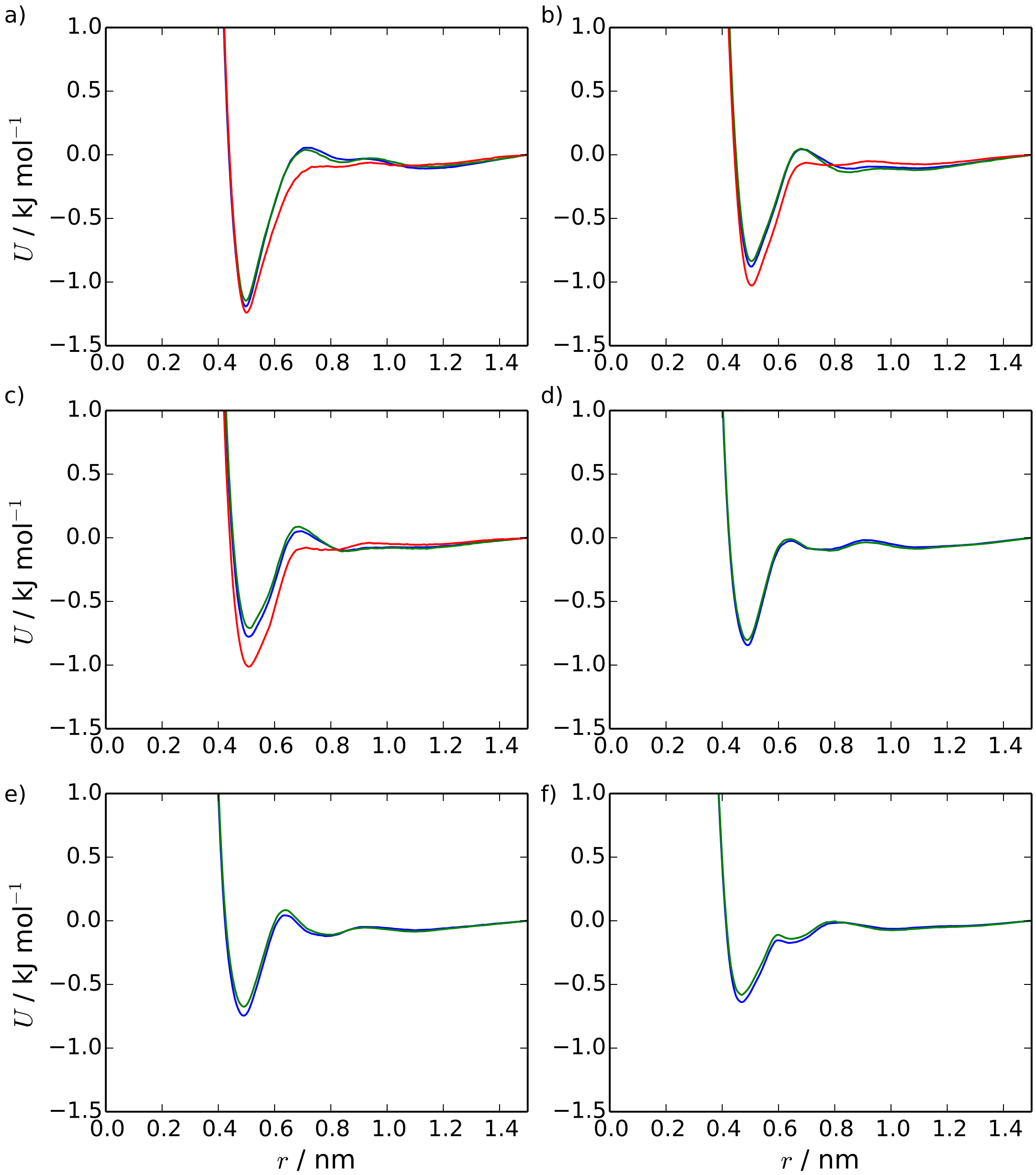

Fig. S 5 Non-bonded potentials parametrised using MS IBI for the a) A-A, b) A-B, c) B-B, d) A-R, e) B-R, f) R-R interactions. Potentials from the MS-3c (blue), MS-4c (green) and MS-2t (red) models.

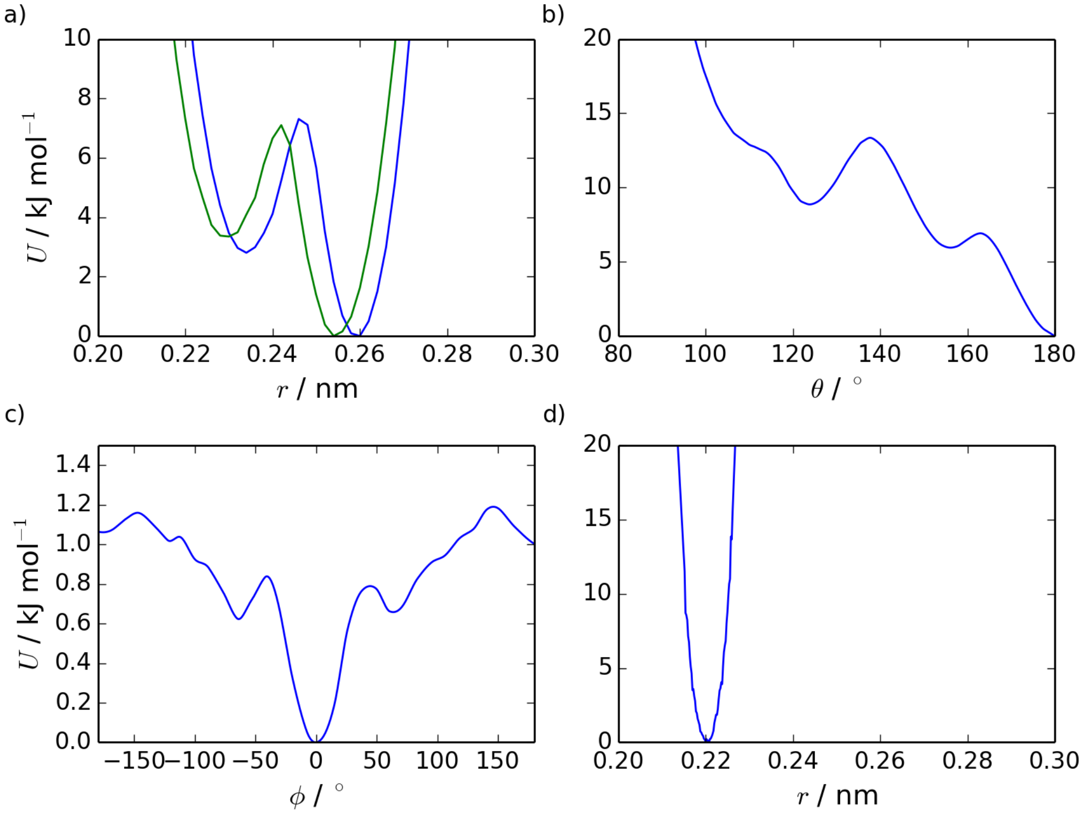

Fig. S 6 Coarse grained bonded potentials from Boltzmann inversion of the pure reference systems at 298 K: a) octane A-B (blue) and B-B (green) bonds, b) octane angle, c) octane dihedral and d) benzene bond (not used in simulations).

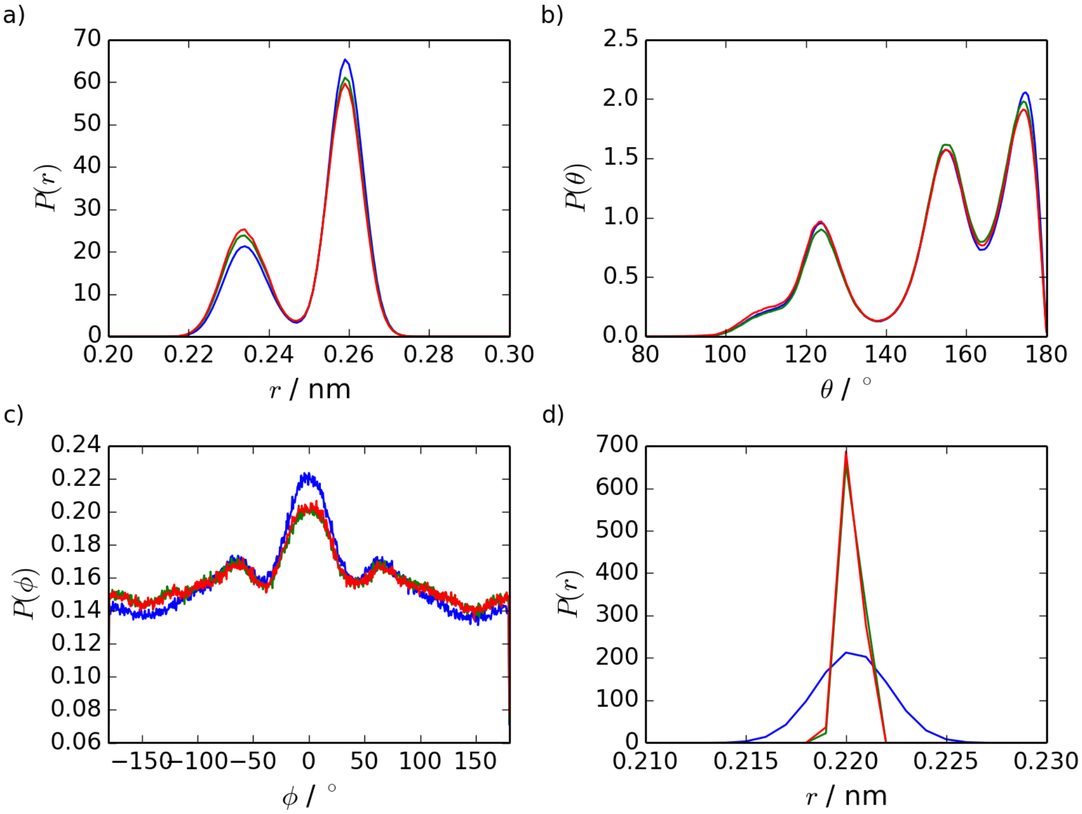

Fig. S 7 Bonded distributions for pure octane and benzene systems from atomistic (blue), IBI (green) and HFM (red) simulations at 298 K. a) octane A-B bond, b) octane angle, c) octane dihedral and d) benzene bond distribution.

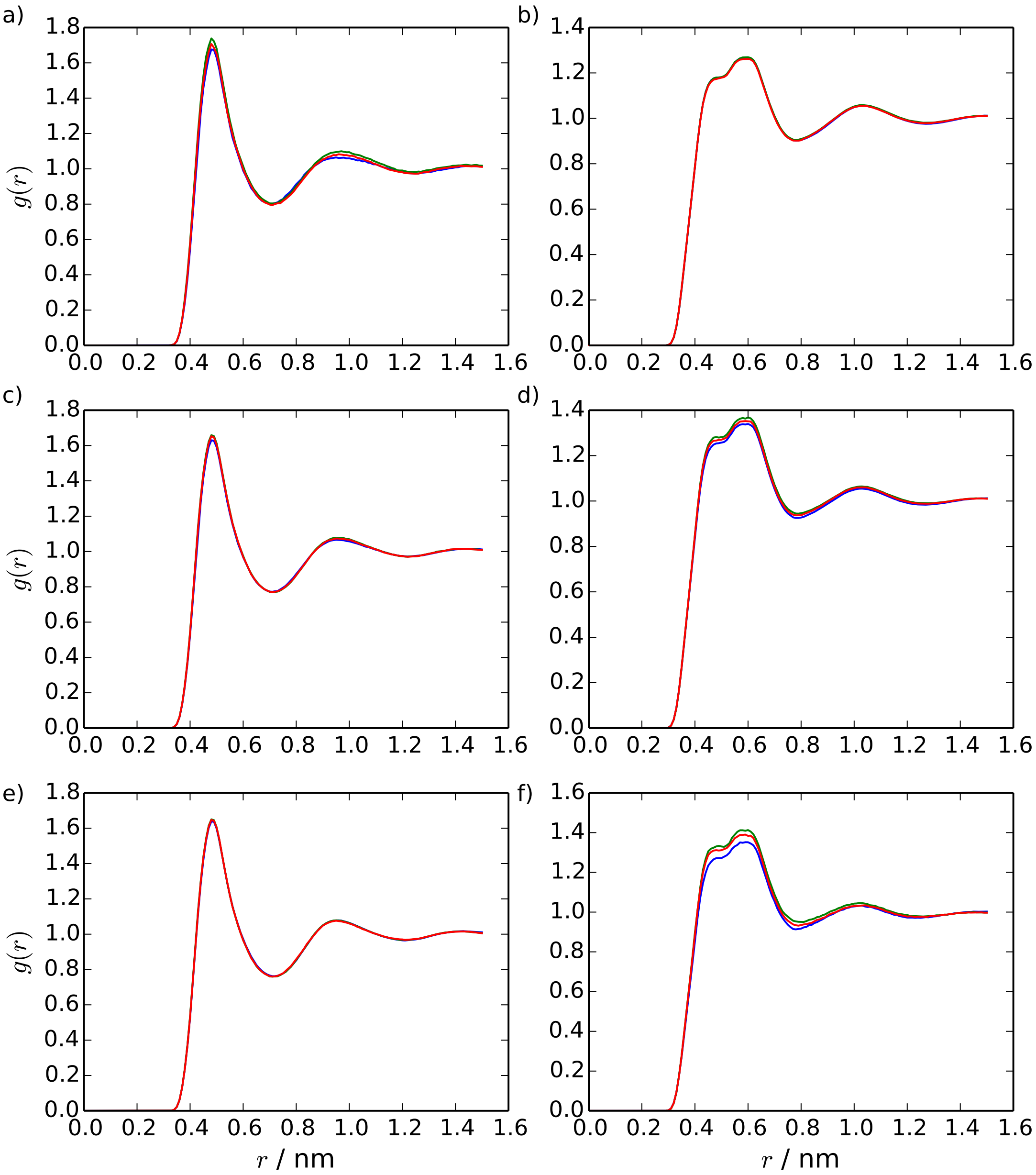

Fig. S 8 Non-bonded distributions from simulations of the MS-3c (green) and MS-4c (red) models, compared to atomistic simulation results (blue). The plots show: a) A-A at 20% octane, b) R-R at 20%, c) A-A at 50%, d) R-R at 50%, e) A-A at 80%, f) R-R at 80%.

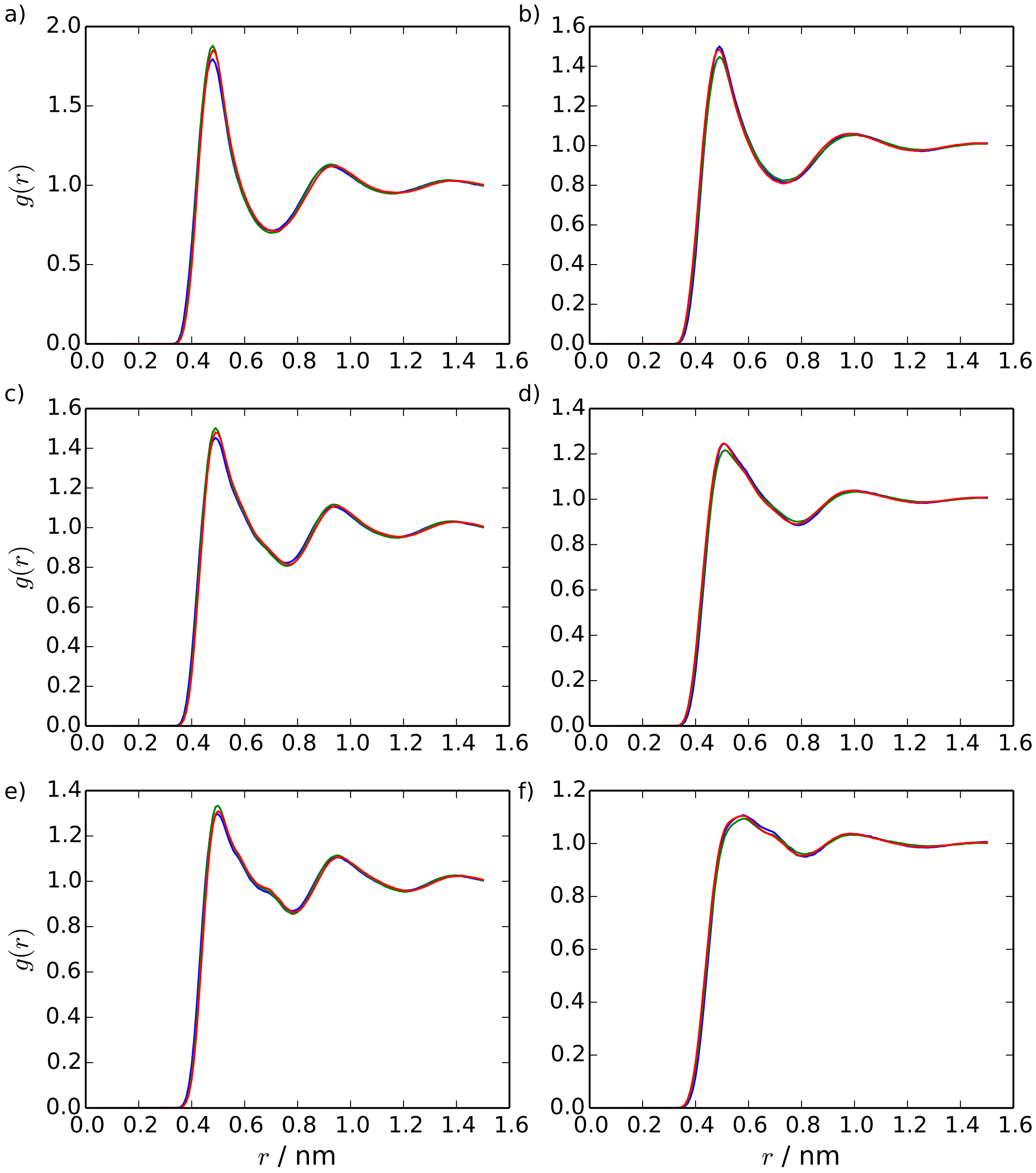

Fig. S 9 Non-bonded distributions from simulations of the MS-2t model simulated at: constant-NVT and the correct atomistic density (green), constant-NPT and 1 bar pressure (red); and the atomistic model (blue). The plots show: a) A-A at 238 K, b) A-A at 378 K, c) A-B at 238 K, d) A-B at 378 K, e) B-B at 238 K, f) B-B at 378 K.