SUPPLEMENTARY INFORMATION

The Non-Ideality in Thymol+Menthol Type V Deep Eutectic Solvents

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FIGURES

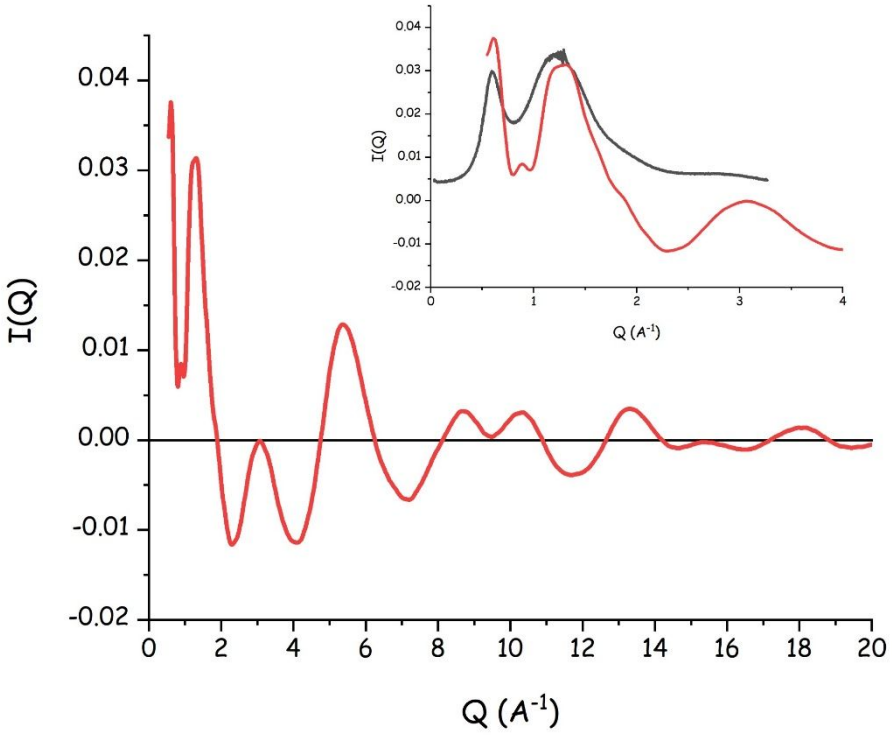

Figure S1. MD-computed X-ray scattering pattern of the 1:1 thymol+menthol mixture. In the inset, this data set (red line) is compared with the experimentally derived pattern (black line), in the accessible Q range. Note that the two data sets are differently normalised, so quantitative agreement is not expected.

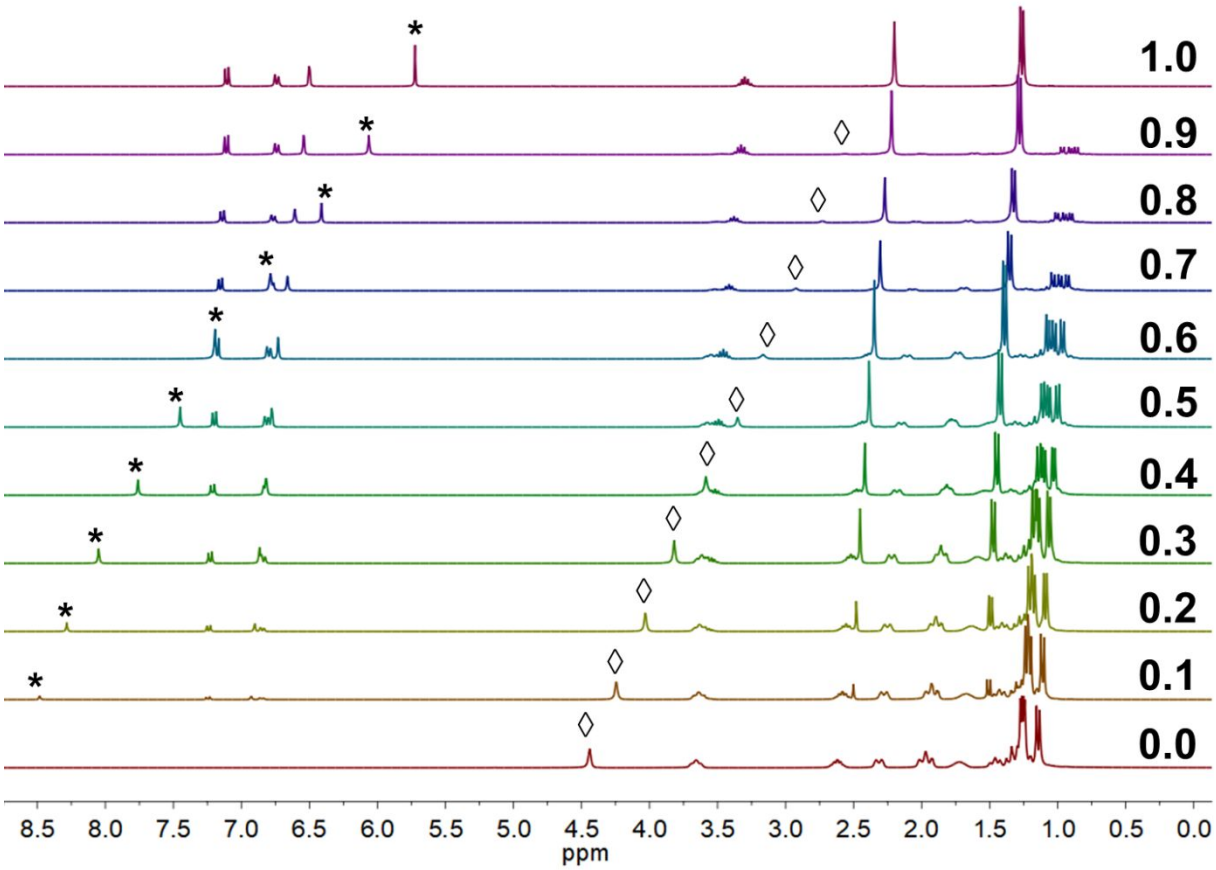

Figure S2. ^{1}H-NMR spectra of the liquid phase of thymol+menthol as a function of thymol molar fraction (x_{thymol}) at T = 328 K (thymol(OH) - *, menthol(OH) - ◊). Pure menthol and thymol are labelled as x_{thymol}= 0.0 and x_{thymol}= 1.0 respectively.

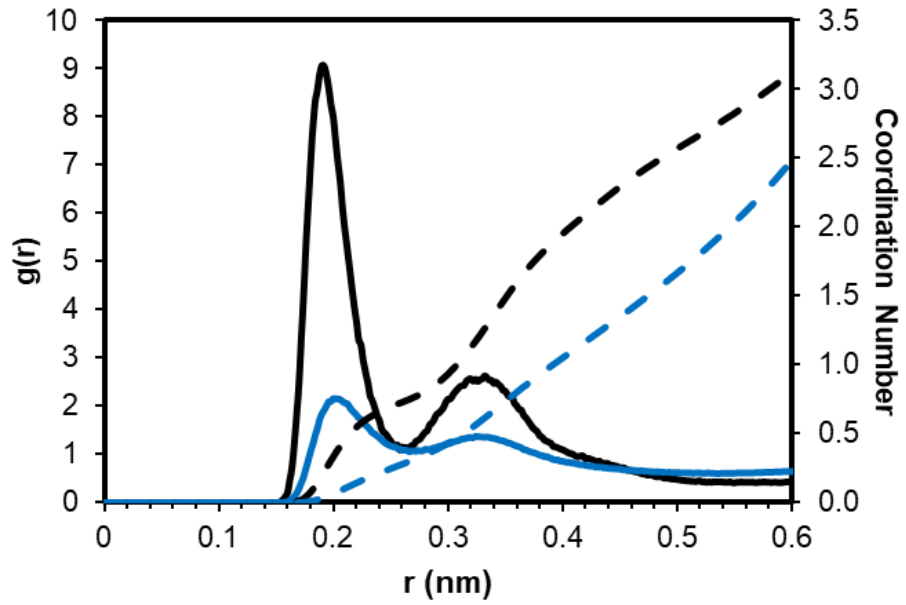

Figure S3. RDF and corresponding coordination numbers of menthol(H)-menthol(O) (black) and thymol(H)-thymol(O) (blue) in their respective pure system at 330 K. System composition corresponds to that of (1) and (5) in **Table S1**.

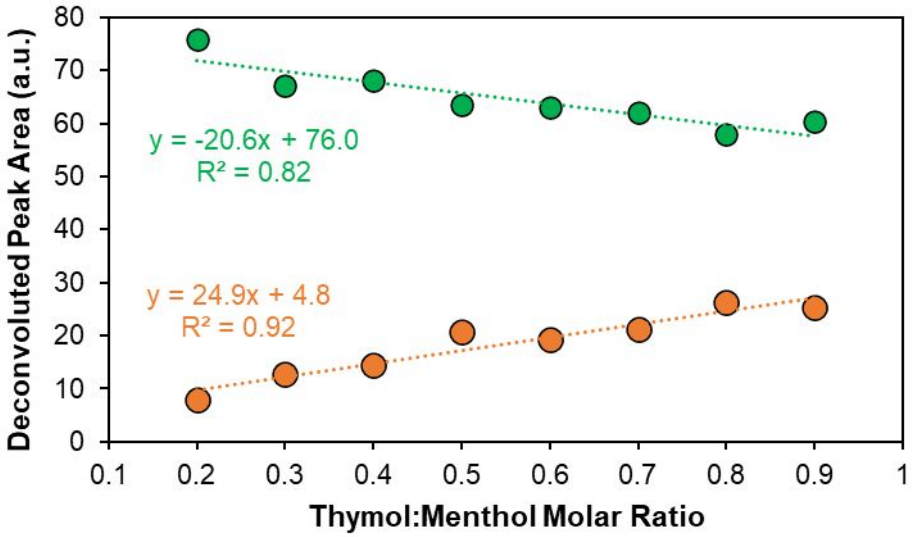

Figure S4. Evolution in the deconvoluted peak area of the γ ν(OH) (orange) and δ ν(OH) (green) bands of Raman spectra of the thymol+menthol eutectic in **Figure 2** of the manuscript as a function of the eutectic molar ratio (T= 293 K).

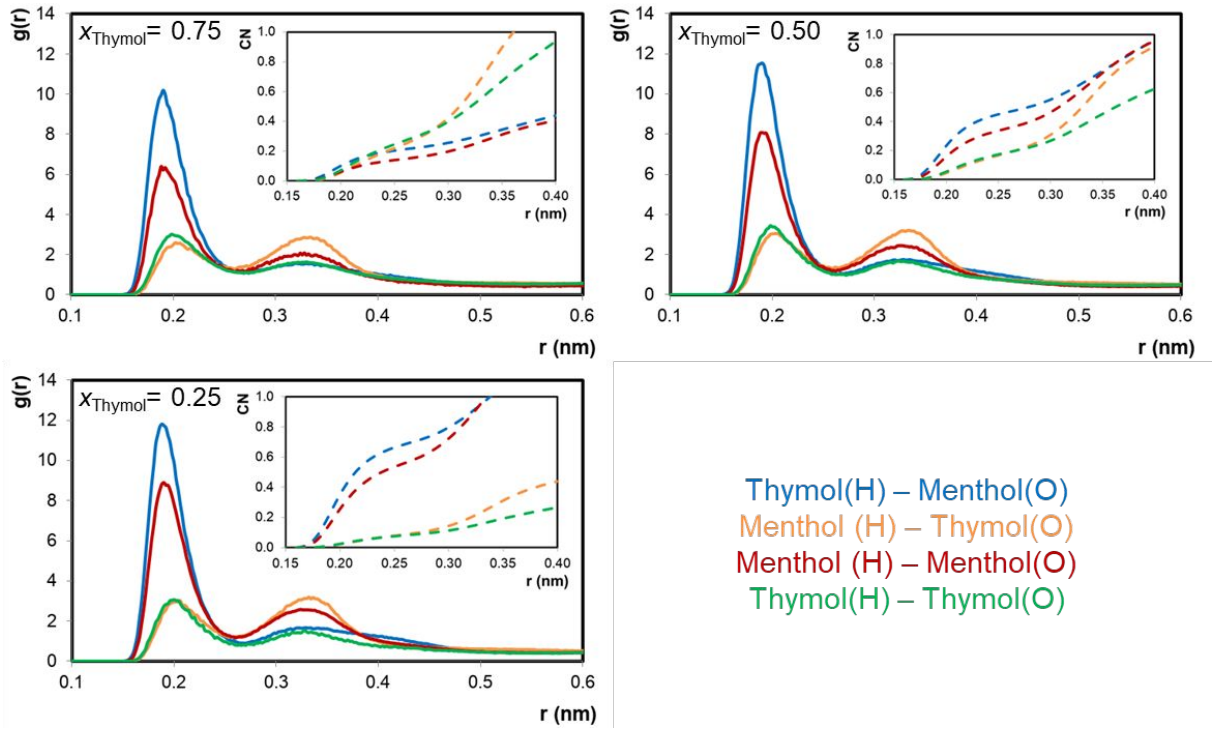

Figure S5. RDF and corresponding coordination numbers of thymol(H)-menthol(O) (blue), menthol(H)-thymol(O) (orange), menthol(H)-menthol(O) (red) and thymol(H)-thymol(O) (green) in the thymol+menthol system at 330 K for various thymol molar fractions (x_{thymol}). System composition corresponds to that of (2) to (4) in **Table S1**.

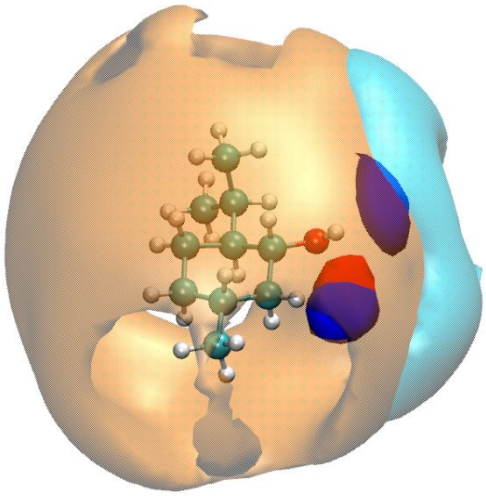

Figure S6. 3D spatial density function (SDF) plot of the 1:1 thymol+menthol system projecting the most probable configurations of the menthol(OH) (blue surface), menthol (full molecule, cyan surface), thymol(OH) (red surface) and thymol (full molecule, orange surface) around the reference menthol molecule. System composition corresponds to that of (3) in **Table S1**.

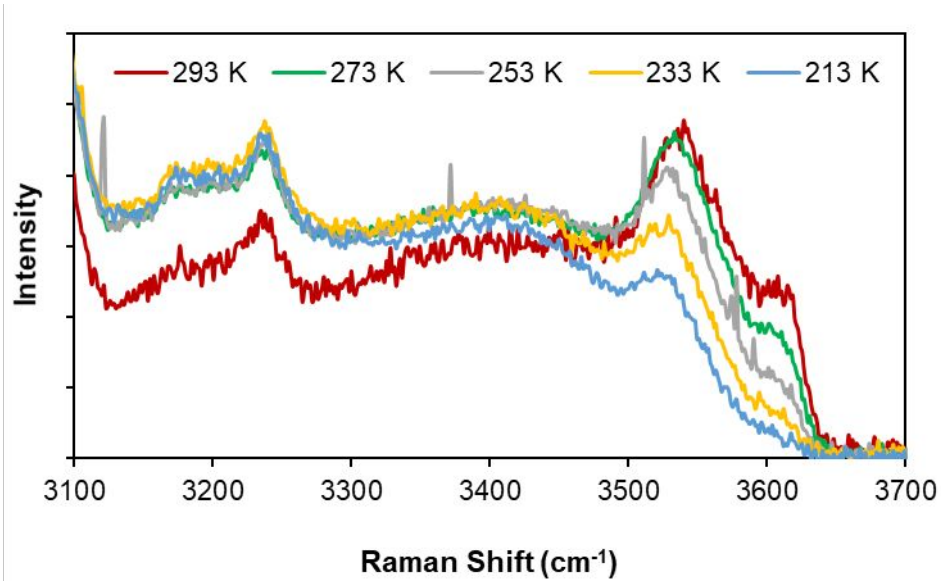

Figure S7. Raman spectra in the ν(OH) stretching region of the liquid thymol+menthol mixture for x_{thymol}=0.5 as a function of temperature.

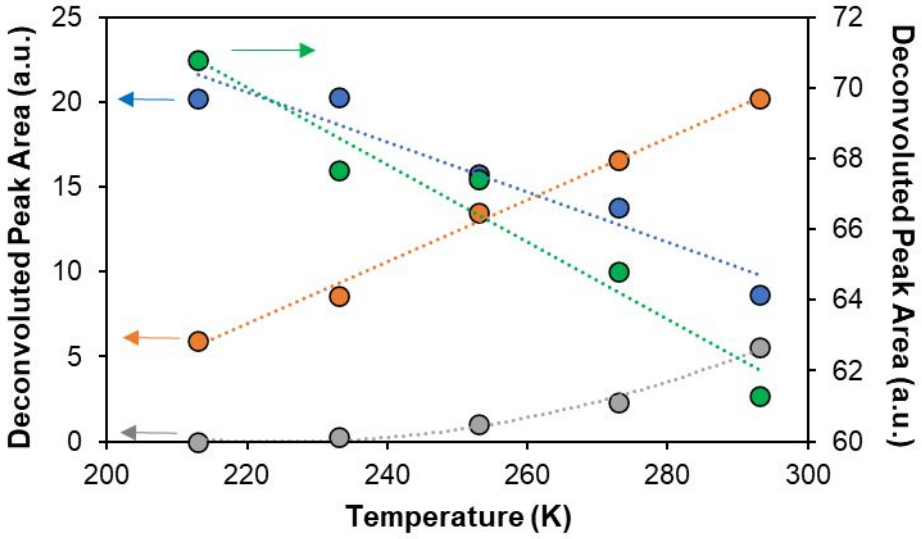

Figure S8. Evolution in the peak area of the various bands in the deconvoluted Raman spectra of the thymol+menthol eutectic in **Figure 4** of the manuscript as a function of temperature (x_{thymol}=0.5). Colour code corresponds to that in **Figure 4** of the manuscript. Lines are drawn to help the eye.

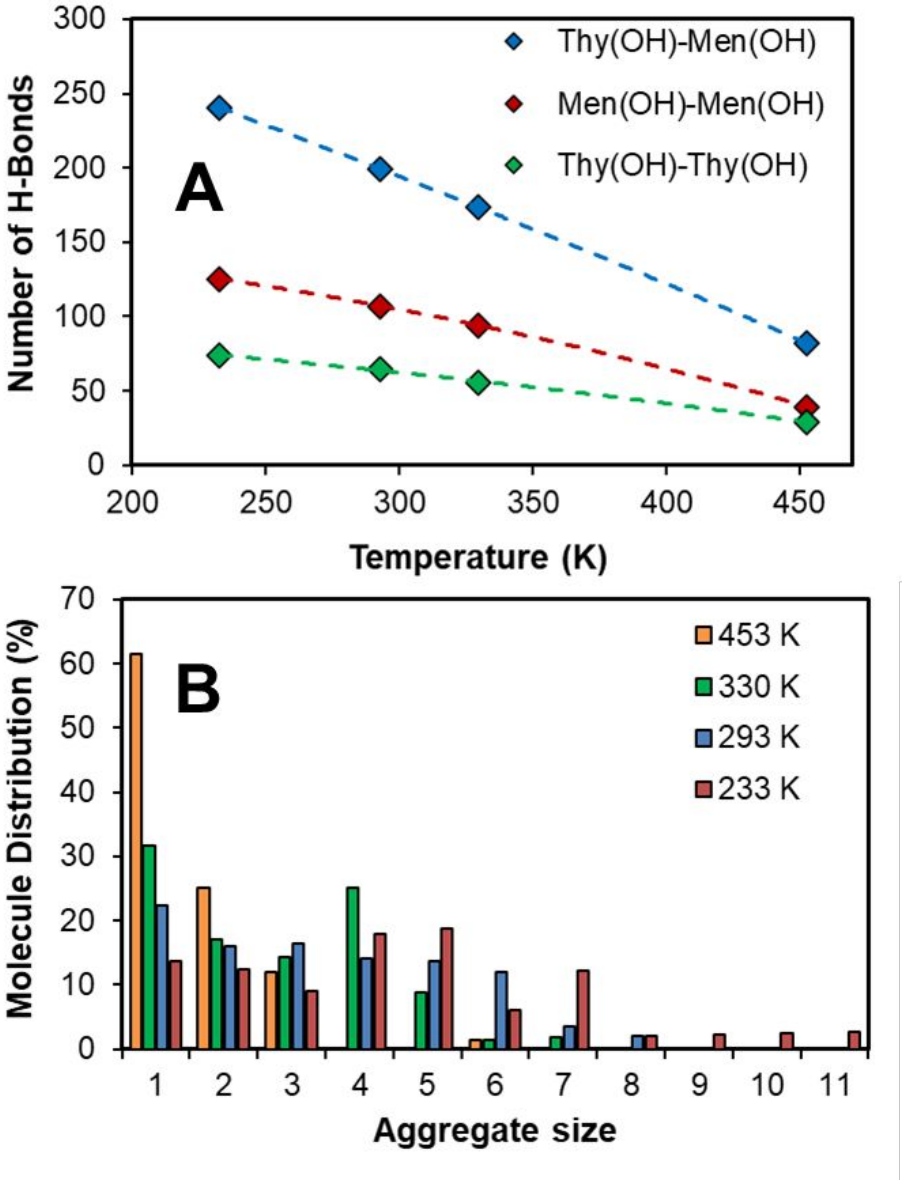

Figure S9. A) Number of H-bonds and B) H-bond cluster population in the MD simulations of the 1:1 thymol+menthol system as a function of temperature (x_{thymol}=0.5, 400 total molecules). H-bonding analysis was performed with bond and angle cut-off values of 0.35 nm and 90^{o} respectively. Aggregate size does not provide information as to the geometry of the H-bonded aggregate, only the number of continuously H-bonded molecules according to the defined geometric criteria. Lines in panel A) are drawn to help the eye. System composition corresponds to that of (3) and (6) to (8) in **Table S1**.

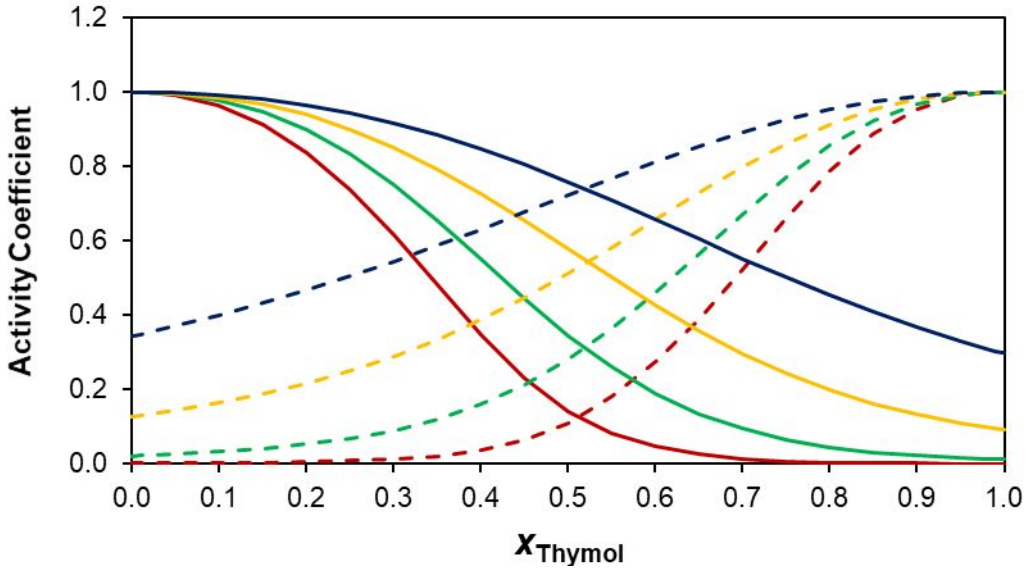

Figure S10. COSMO-RS predicted isothermal activity coefficients of thymol (dashed line) and menthol (full lines) in the thymol+menthol eutectic as a function of x_{thymol} at 223 K (red), 273 K (green), 323 K (yellow) and 373 K (blue).

TABLES

Figure S1. System composition for the all-atom molecular dynamics simulations performed. All systems were simulated in cubic boxes with 400 total molecules. H-bonding analysis was performed with bond and angle cut-off values of 0.35 nm and 90^{o} respectively and averaged over the last 40 ns.

System	x_{thymol}	n(thymol)	n(menthol)	Temperature (K)	Final box volume (nm^3)	Number of hydrogen bonds		
						Thy-Men	Men-Men	Thy-Thy
(1)	0.00	0	400	330	4.90	0.0	381.8	0.0
(2)	0.25	100	300	330	4.87	125.9	221.6	12.0
(3)	0.50	200	200	330	4.84	173.2	94.2	55.9
(4)	0.75	300	100	330	4.83	122.1	20.2	125.5
(5)	1.00	400	0	330	4.81	0.0	0.0	180.9
(6)	0.50	200	200	233	4.73	240.3	125.4	73.8
(7)	0.50	200	200	293	4.80	199.3	107.0	64.5
(8)	0.50	200	200	453	5.09	82.2	39.4	29.0