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

From nano-seggregation to mesophases: probing the liquid structure of Perfluoroalkylalkanes with ^{129}Xe NMR Spectroscopy.

Pedro Morgado, João Barras and Eduardo J. M. Filipe*

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de
Lisboa, 1049-001 Lisboa, Portugal

Supplementary information

1. Magnetic Susceptibility

The molar magnetic susceptibilities of the studied perfluoroalkylalkanes were measured following the procedure of Hatada and Kitayama,[i] which is an optimized form of the method of Frei and Bernstein.[ii]

The samples of unknown susceptibility were placed inside a glass capillary-sphere microcell (Wilmad 529-A), which consists of a small hollow sphere connected to a cylindrical capillary. This microcell was coaxially placed inside a 10mm NMR tube, with a reference solvent of known susceptibility filling the space around the microcell. ^{1}H and ^{19}F NMR spectra of the samples were then obtained using a broadband 10mm probe and, due to the difference in geometry between the sample in the cylindrical part of the assembly and in the spherical bulb,[iii] the spectra showed two peaks for each resonance. It can be shown that the separation between these peaks is proportional to the difference between the volume susceptibility of the sample χ_s and of the reference solvent χ_r according to

$$\Delta\delta = \frac{4}{3}\pi(\chi_s - \chi_r) \quad (1)$$

In this work, deuterated chloroform (χ_v = -0.738x10^{-6} at 298.15K) was used as a reference solvent, with its deuterium signal used for frequency locking. Both the ^{1}H and ^{19}F spectra were obtained and the average of the separations for all the NMR peaks of each perfluoroalkylalkane was calculated.

The validity and accuracy of the method was verified, using their ^{1}H NMR signals, with two substances of known susceptibility, water and benzene, and the determined susceptibilities reproduced the literature values[i] within experimental uncertainty. The determined molar magnetic susceptibilities are presented in Table 1. Following standard practice, and maintaining consistency with equation 1, the values are presented in units appropriate to the c.g.s. system (should be multiplied by 4π to obtain values for use in SI equations). The combined precision and accuracy of the results are expected to be better than 0.4×10^{-6} cm^3 mol^{-1}. The conversion between molar and volumetric susceptibility of the studied PFAA was done using the density results determined in previous work.[iv,v]

Table S1: Molar magnetic susceptibilities of the perfluoroalkanes studied.

Compound	$-\chi_m/10^{-6}cm^3mol^{-1}$
perfluorobutylpentane	143.1
perfluorobutylhexane	155.2
perfluorobutyloctane	179.1
perfluorohexylhexane	195.1

perfluorohexyloctane	214.8

2. Radial distribution functions

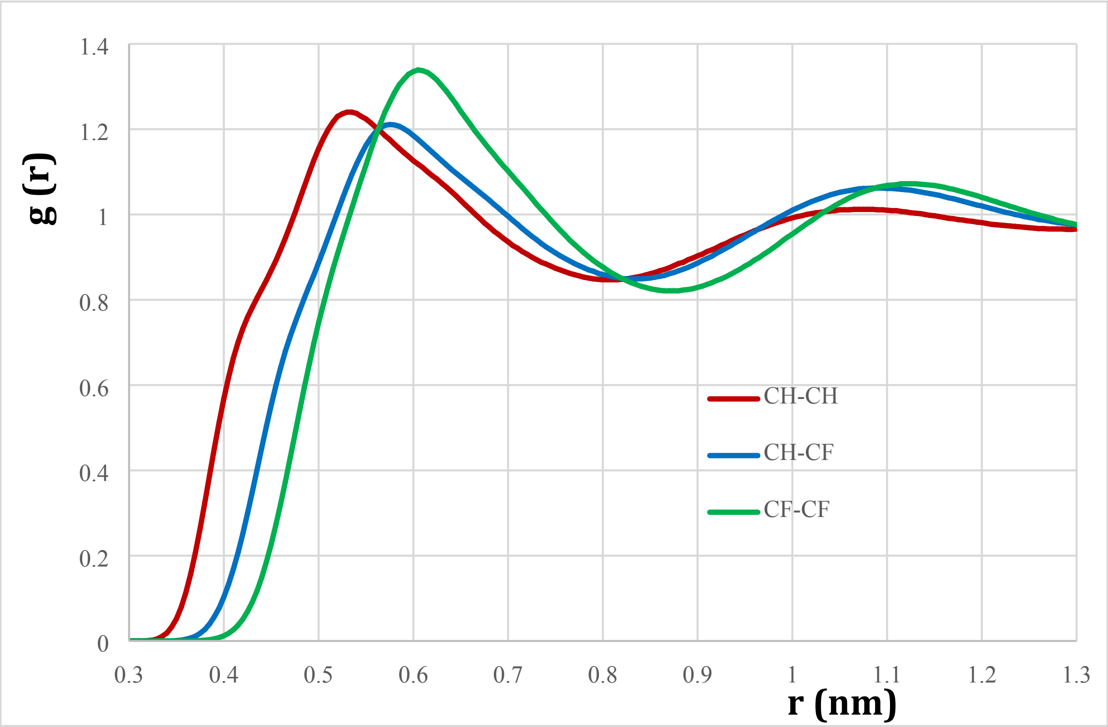

Figure S1. Radial distribution functions between hydrogenated carbons (CH-CH, red), fluorinated carbons (CF-CF, green) and between hydrogenated and fluorinated carbons (CH-CF, blue) for F6H6 at 298K.

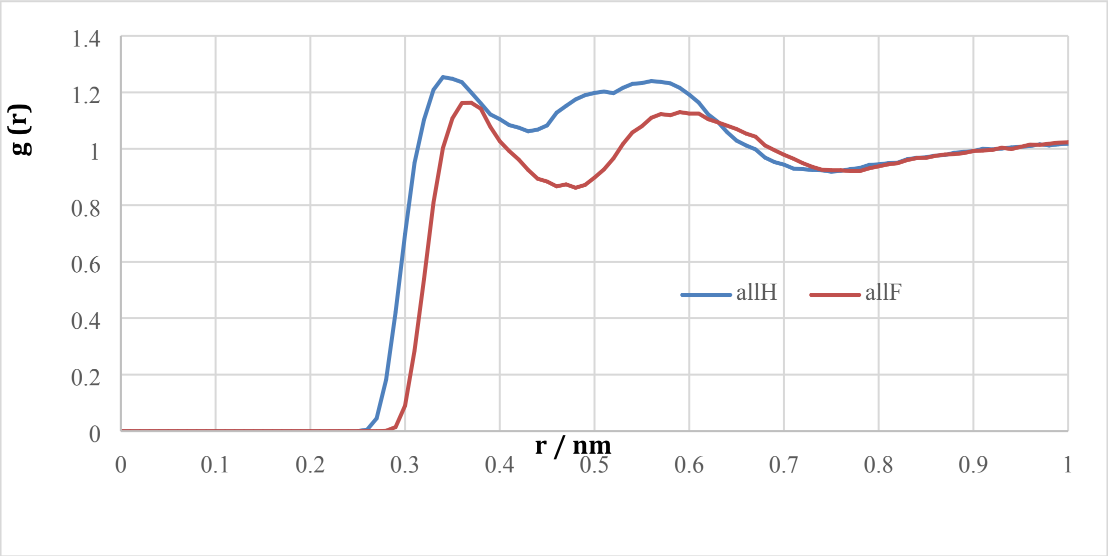

Figure S2. Xenon – hydrogen and xenon – Fluorine radial distribution functions for F6H6 at 298K.

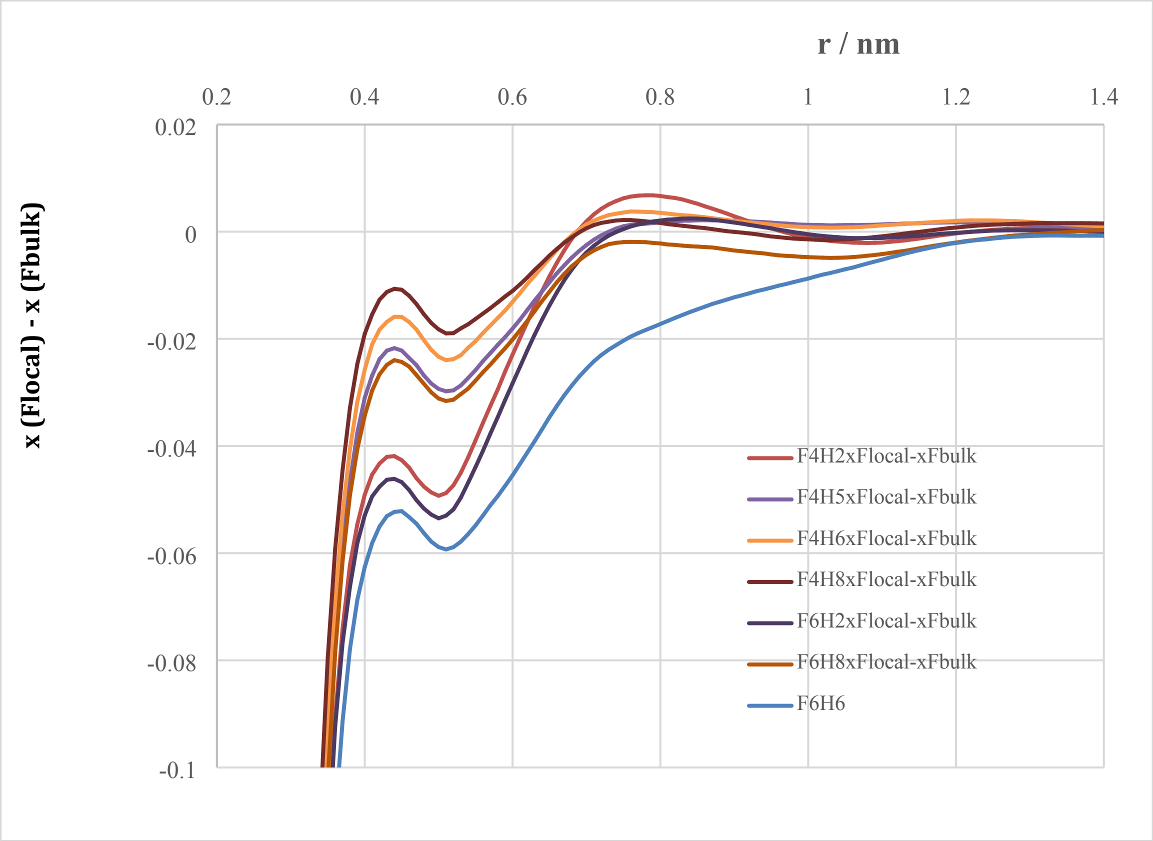

Figure S3. Differences between the local mole fraction of fluorine atoms within the xenon coordination sphere and the bulk mole fraction of fluorine atoms, calculated from the MD simulations.

References

---

[i] Hatada, K., Kitayama, T., *NMR Spectroscopy of Polymers*, Springer, Berlin Heidelberg (2004)

[ii] Frei, K., Bernstein, H.J., *J. Chem. Phys.,* **37**, 1891-1892 (1962)

[iii] Gil, V.M.S., Geraldes, C.F.G.C., *Ressonância Magnética Nuclear - Fundamentos, Métodos e Aplicações*, Fundação Calouste Gulbenkian, Lisboa (1987)

[iv] P. Morgado, H. Zhao, F.J. Blas, C. McCabe, L.P.N. Rebelo, E.J.M. Filipe, Liquid phase behavior of perfluoroalkylalkane surfactants., J. Phys. Chem. B. 111 (2007) 2856–2863. https://doi.org/10.1021/jp063136d.

[v] Morgado, P.; Lewis, J. B.; Laginhas, C. M. C.; Martins, L. F. G.; McCabe, C.; Blas, F. J.; Filipe, E. J. M. Systems Involving Hydrogenated and Fluorinated Chains: Volumetric Properties of Perfluoroalkanes and Perfluoroalkylalkane Surfactants. *J. Phys. Chem. B* **2011**, *115*, 15013–15023.