

# Theoretical and Computational Chemistry at the University of Edinburgh

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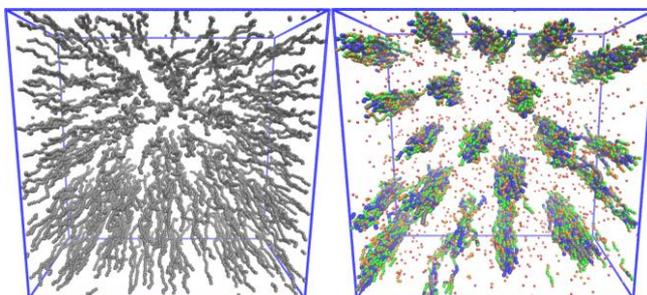
<http://www.molsim.chem.ed.ac.uk/>

In this short introductory talk, I will briefly describe the long history and current status of Chemistry at Edinburgh, and give an overview of our theoretical and computational research. I will summarise ongoing projects on magnetic fluids [1], laser-induced nucleation [2], and soft-matter phenomena such as molecular self-assembly and interfacial adsorption [3]. This will set the scene for presentations by the other members of the Edinburgh team.

[1] **Structure, dynamics, and thermodynamics of ferrofluids**

P. J. Camp

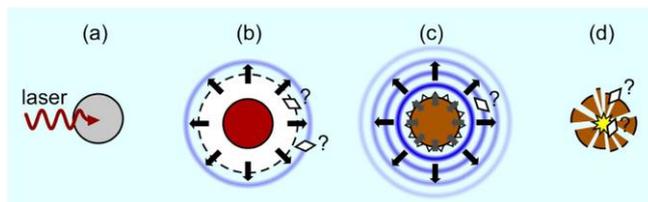
In *Modern Problems of Molecular Physics*, Eds. L. A. Bulavin and A. V. Chalyi, *Springer Proceedings in Physics* **197**, 185-204 (2018)  
doi:10.1007/978-3-319-61109-9



[2] **Non-photochemical laser-induced nucleation**

A. J. Alexander and P. J. Camp

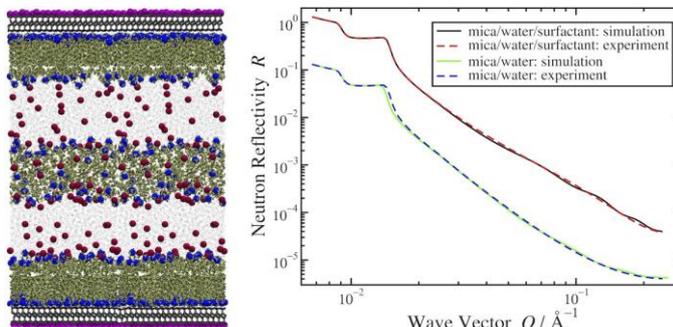
*J. Chem. Phys.* **150**, 040901 (2019)  
doi:10.1063/1.5079328



[3] **Self-assembly and adsorption of cetyltrimethylammonium bromide and didodecyldimethylammonium bromide surfactants at the mica-water interface**

G. Tsagkaropoulou *et al.*

*Soft Matter* **15**, 8402-8411 (2019)  
doi:10.1039/C9SM01464K



# **Molecular simulations of functionalised copolymers in bulk and in confinement: uncovering the role of functional-group distribution**

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Organic additives in oil-based lubricants are used to reduce friction, reduce wear, reduce oxidation, increase performance, improve viscosity index, and even control the way the oil degrades. With such important roles being played by the additives, it is imperative that the physical mechanisms of action are understood, so that better, more efficient lubricants can be developed. This work is focused on atomistic molecular dynamics (MD) simulations of polymeric additives possessing different distributions of polar functional groups (FGs) attached to a polyethylene-polypropylene copolymer backbone.

The functionalised copolymers are immersed in a non-polar solvent, either in bulk or in confinement between parallel iron-oxide walls. The MD simulations reveal that the size of the copolymer – as measured by the radius of gyration or the end to end distance – is very sensitive to the distribution of FGs on the backbone. This is shown to be due to the association of the FGs, and the detailed atomistic interactions responsible for this are elucidated. In addition, predictions of the form factor,  $P(q)$ , can be tested against results from small-angle neutron scattering experiments. Similarly, MD simulations of confined copolymer solutions point towards a link between the functional-group distribution and the adsorption of the copolymers on to the iron-oxide surfaces, particularly the copolymer's lateral spread and normal height, measured through the radius of gyration and mass-density profiles. Some links between these structural properties and the tribological effects of functionalised copolymers are put forward.

## **References:**

1. Apóstolo R. F. G.; Camp P. J.; Cattoz B. N.; Dowding, P. J.; and Schwarz, A. D.; 'Effect of functional-group distribution on the structure of a polymer in non-aqueous solvent'; *Molecular Physics* **2018**; *116*, 2942–2953.
2. Apóstolo R. F. G.; Tsagkaropoulou G.; and Camp, P. J.; 'Molecular adsorption, self-assembly, and friction in lubricants'; *Journal of Molecular Liquids* **2019**; *227*, 606-612.

# **Molecular Simulations of Lubricant Base Oils at High Pressure**

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Lubricants are used widely in industry to reduce the effects of friction and wear. Lubricants for engine applications are typically composed of a base oil and various additives; the rheology of these base oils is very important as the lubricants are exposed to a wide range of pressures and shear rates.

Recent high-pressure experiments at Edinburgh indicate that model base oils – squalane and a poly-alpha-olefin (PAO) mixture – are no longer hydrostatic media above roughly 1 GPa. Diamond-anvil cell measurements show that the hydrostatic limit for these base oils is in the range of 0.74 to 1.24 GPa, as they appear to undergo solidification. X-ray diffraction shows no Bragg peaks, suggesting that a glassy structure, and not a crystalline structure, is formed.

In this work, the structure, dynamics, and thermodynamics of squalane and the PAO mixture were studied using molecular-dynamics (MD) simulations. The equation of state, self-diffusion coefficient, viscosity, and radial distribution functions were calculated over a wide range of pressures, from 0.0001 to 10 GPa. The results show that molecular diffusion is essentially arrested above about 0.1 GPa, which supports the hypothesis that the samples are kinetically trapped in metastable amorphous-solid states. The shear viscosity is immeasurably large at very high pressures, but the coefficient governing its increase from ambient pressure is in good agreement with the available literature data. Subtle changes in the short-range real-space correlations are related to a collapse of the molecular conformations with increasing pressure, while the evolution of the static structure factor shows excellent correlation with the available X-ray diffraction data. Overall, this study shows that these common lubricant base oils solidify and form a glassy structure at around 1 GPa. This could have major implications for the tribological properties of lubricants under the high-pressure, high-shear conditions found in engines.