Surface properties of heterogeneous polycyclic aromatic hydrocarbon clusters

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The team

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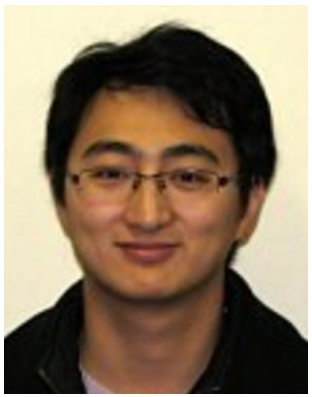

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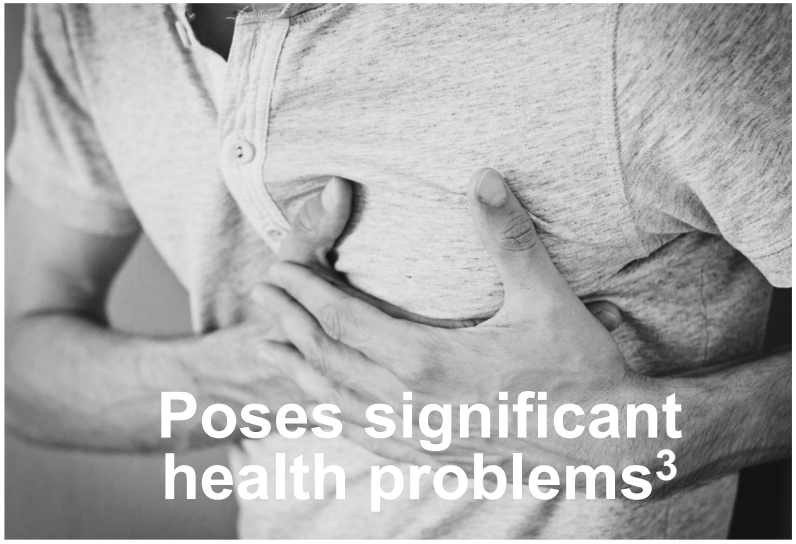
Why study soot?



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[1]Hansen and Nazarenko, Proc. Natl. Acad. Sci. 101 (2004)
[2]Guarnieri and Balmes, The Lancet 383 (2014)
[3]IARC Monographs, 35, (1985)

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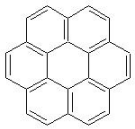
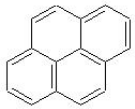
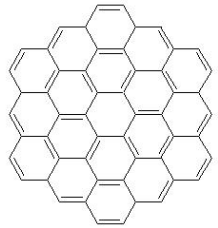
Soot particle model

Detailed atomic studies of soot particles examine clusters containing polycyclic aromatic hydrocarbons (PAHs)

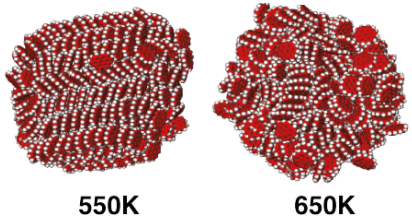






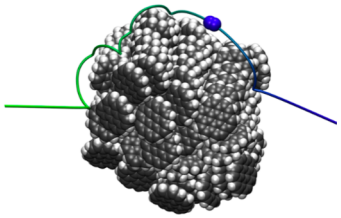
Melting behaviour

Chen, D. et al. Carbon, 67 (2014)



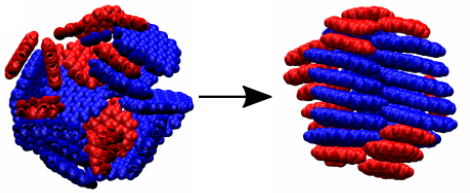
Interactions with gaseous species

Grancic, P. et al. Carbon, 109 (2016)



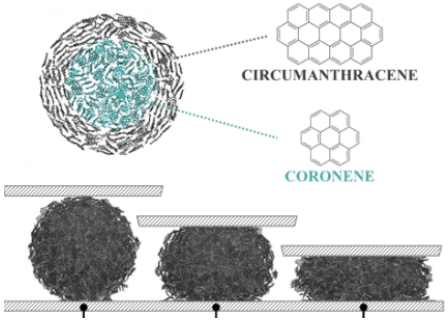
Molecule self-assembly

Bowal, K. et al. Carbon, 143 (2019)



Particle hardness

Pascazio, L. et al. Combust. Flame 219 (2020)



Aim: Use molecular modelling methods to provide a detailed numerical evaluation of soot particle surface properties

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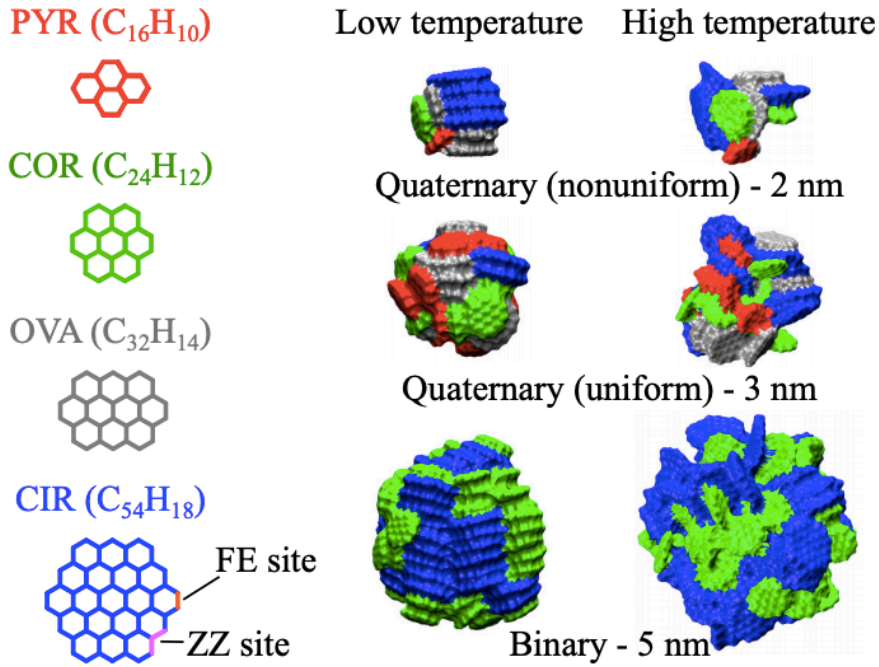
Simulation methods

- Varying particle size, molecule size, molecular ratio
- Replica exchange molecular dynamics to obtain particles across a wide range of temperatures
- Solvent-excluded surface analysis to evaluate the particle surfaces
- Reactive sites: hydrogen atom (H), carbon atom (C), internal carbon atom (IC), edge carbon atom (EC), free-edge site (FE), zig-zag site (ZZ)



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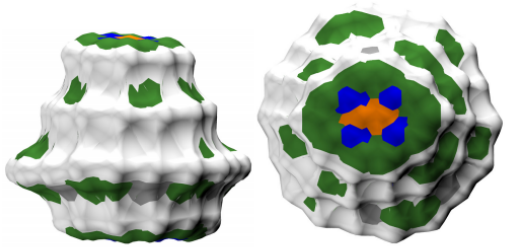
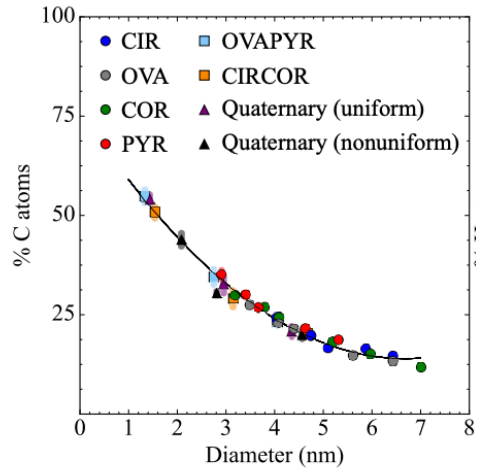
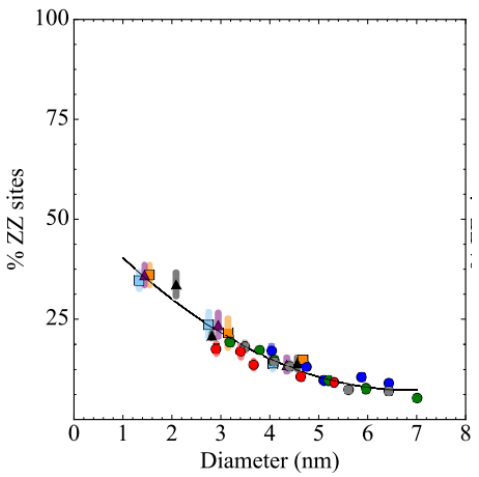
Percent on surface

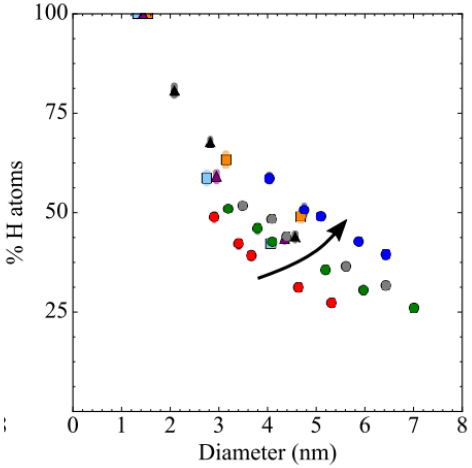
- % of C atoms and ZZ sites on surface not dependent on particle composition
- % of H atoms on surface related to constituent molecule sizes
- % of FE sites on surface dependent on molecular heterogeneity

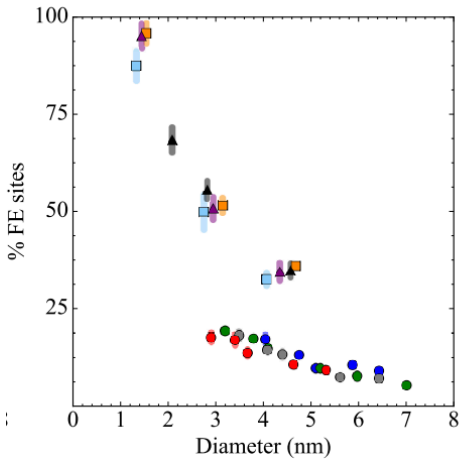


(a) *Side view* (b) *Top view*









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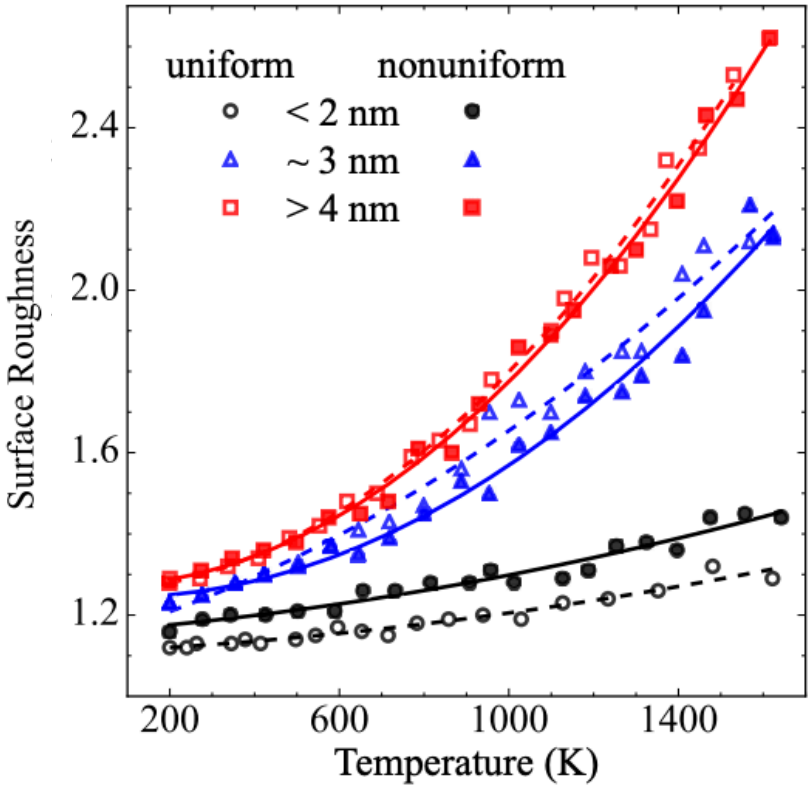
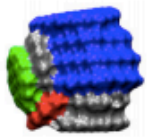
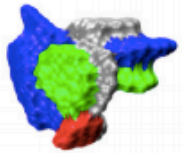
Particle roughness



Low temperature



High temperature



- Roughness increases with temperature
- Particle diameter and molecule sizes play a role in roughness
- Molecular composition (binary/quaternary) not very influential

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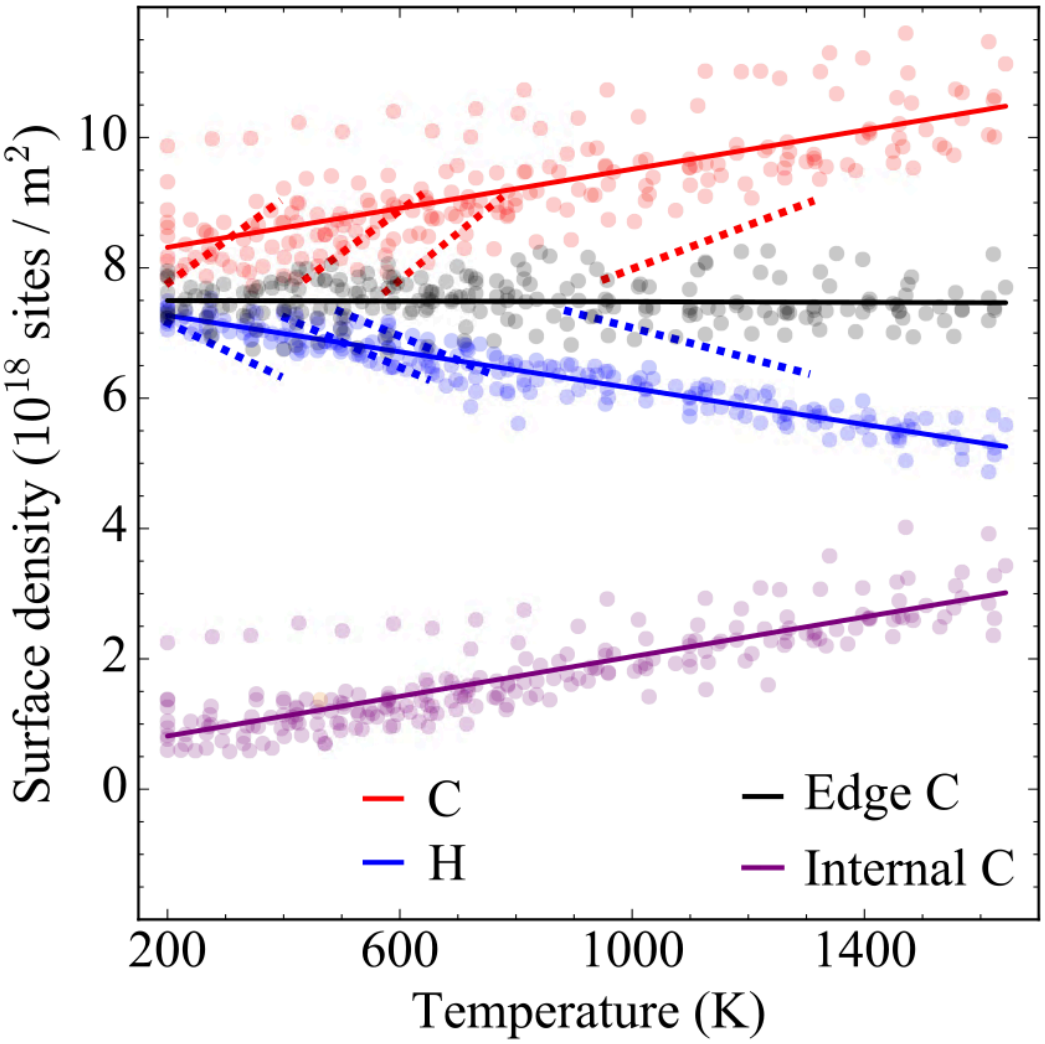
Surface composition



- H and C atoms: primarily dependent on temperature, explained by solid-like to liquid-like particle morphology
- EC does not change with temperature – can be described by molecule composition alone

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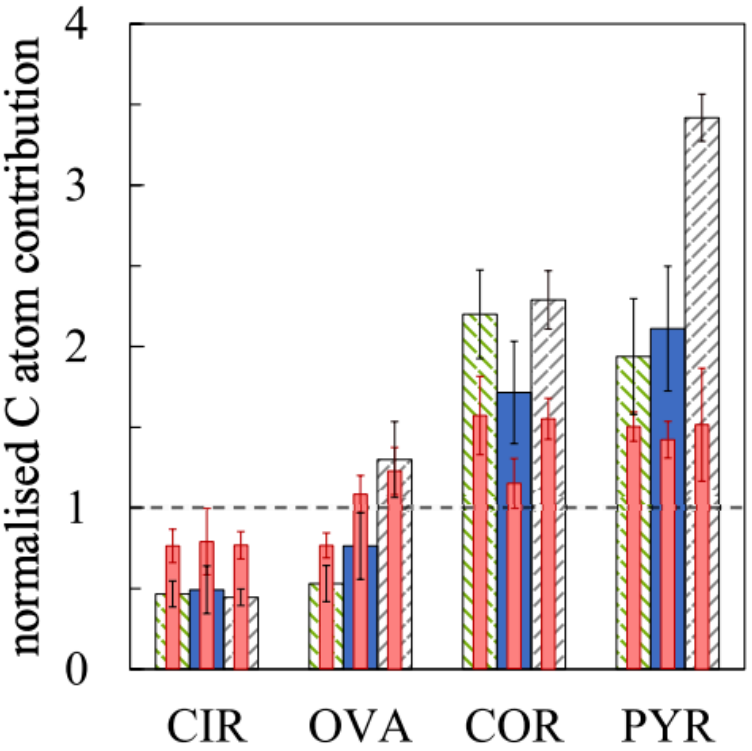
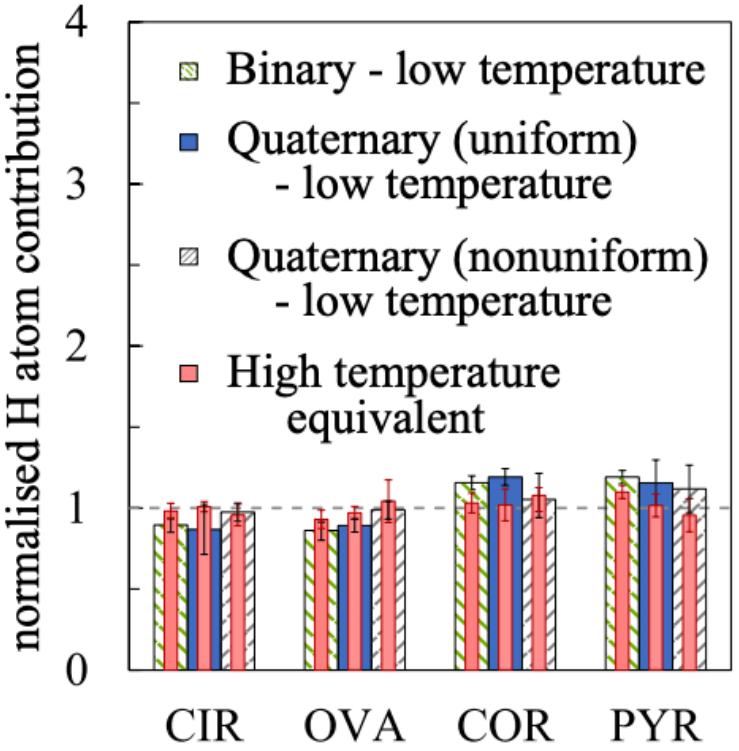
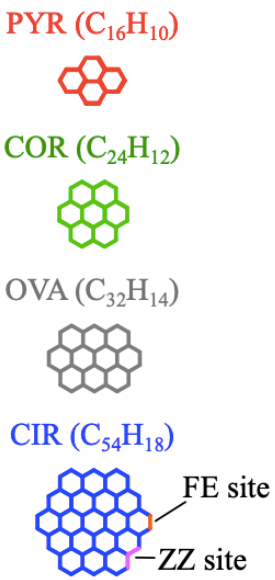
Molecule type contributions







- Surface H atoms: All molecules contribute proportionately
- Surface C atoms: Large molecules contribute less than expected and small molecules contribute more – core-shell structure
- High temperatures move towards expected contributions

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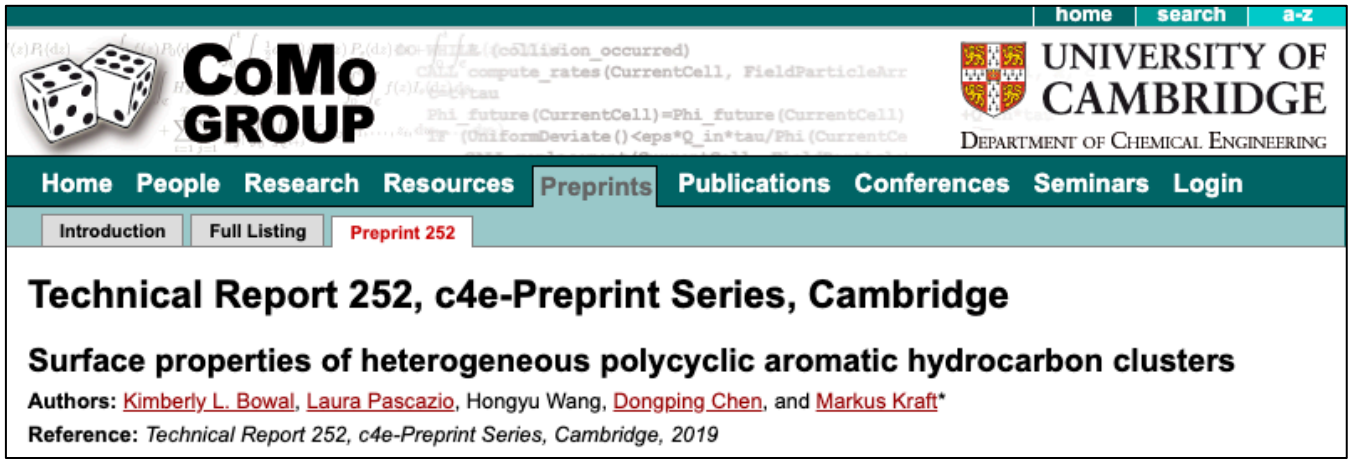
Summary



- Percentage of surface C and ZZ sites depend on particle size. H and FE sites are influenced by molecule size and ratio
- Particle roughness shows that surface area is significantly higher than spherical particle approximations
- Surface density values show us that surface densities of H, IC, and ZZ sites are dependent on temperature, while EC, FE site surface densities can be predicted from average molecule size
- Small molecules contribute more to cluster surface properties than large molecules

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Thank you

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