Nucleation and structure of soot particles

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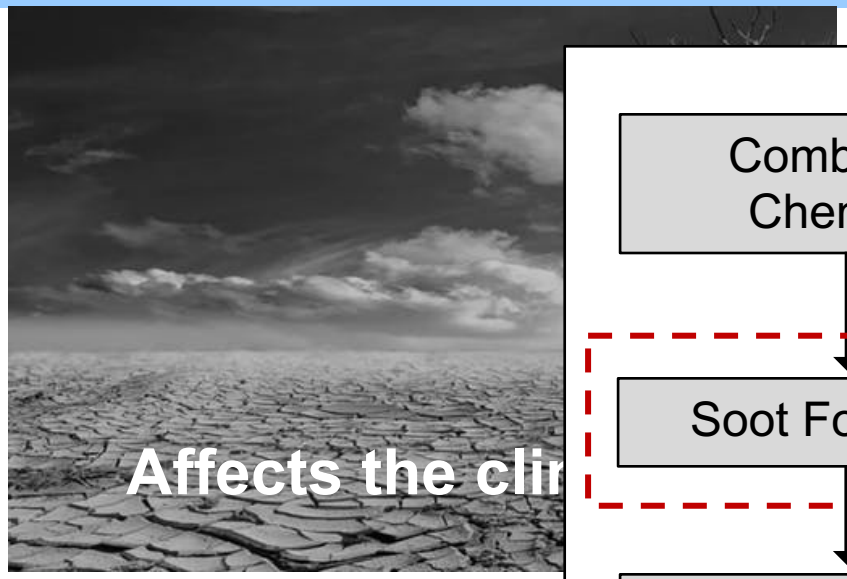
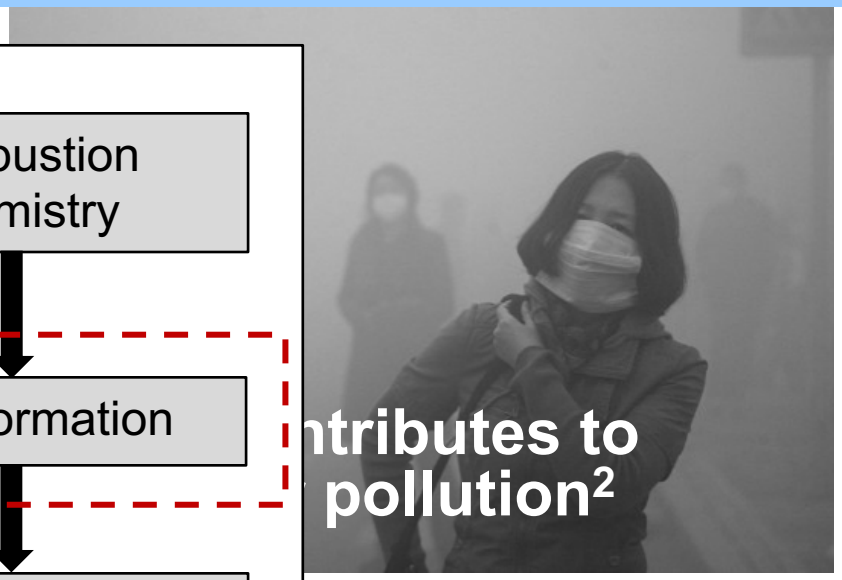
Why study soot?



Affects the cli



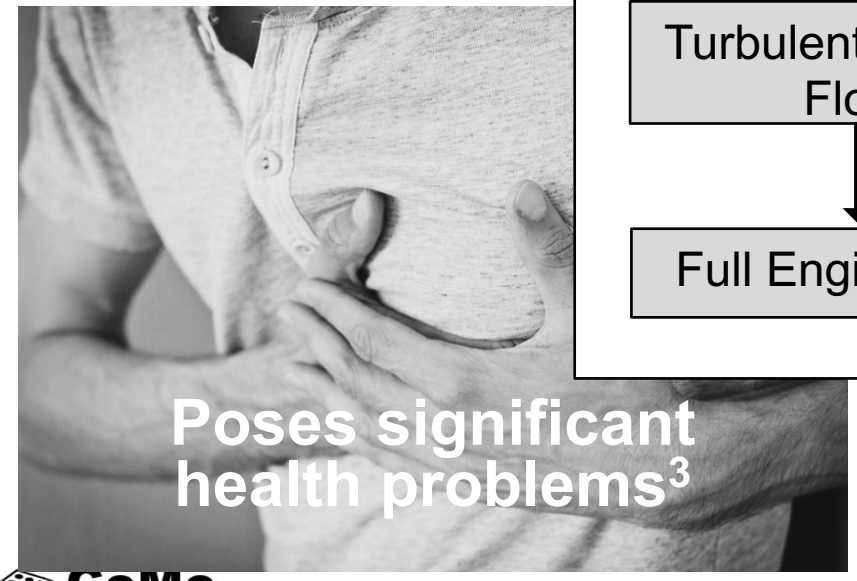
ntributes to pollution[2]

Combustion Chemistry

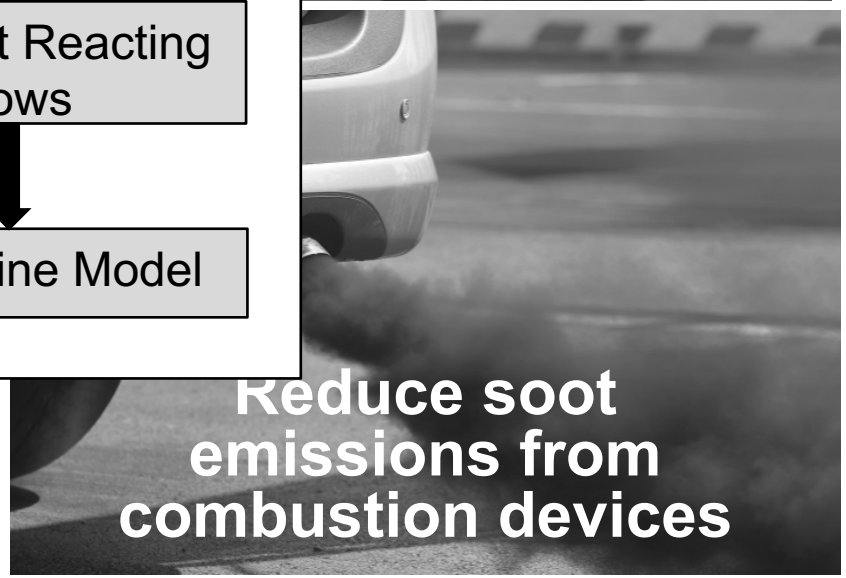
Soot Formation

Turbulent Reacting Flows

Full Engine Model



Poses significant health problems[3]



Reduce soot emissions from combustion devices

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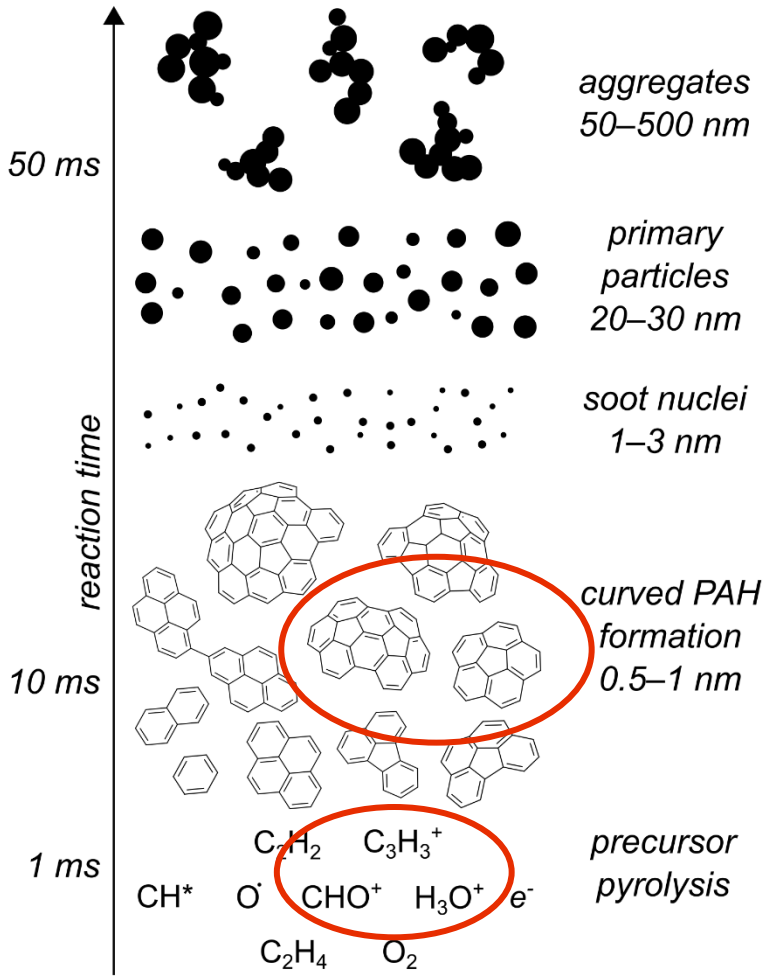
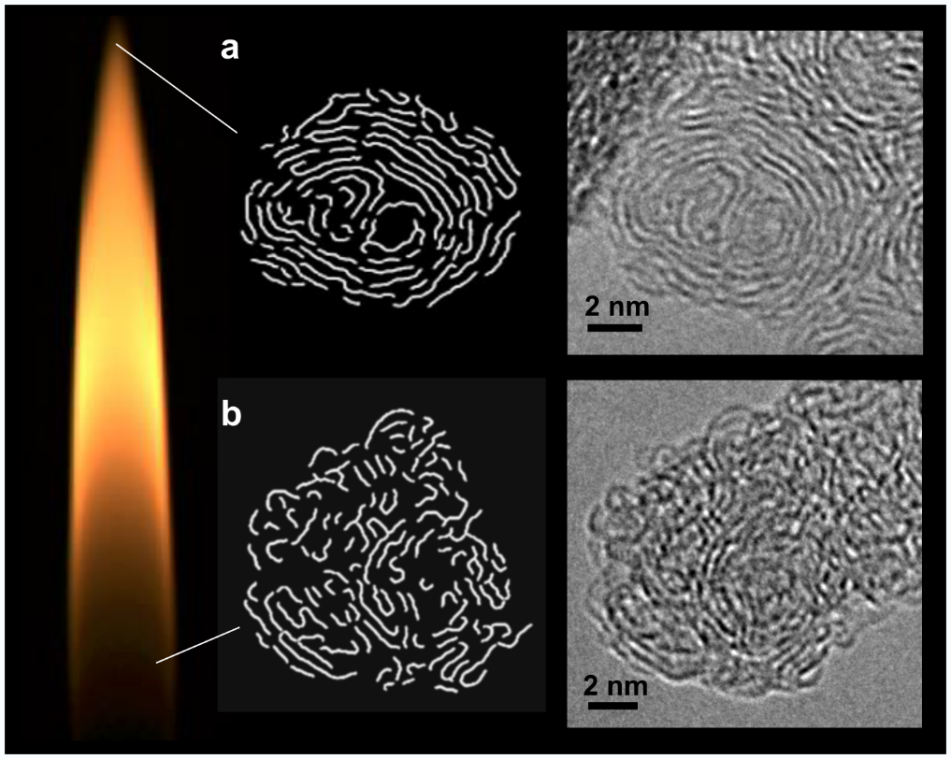
[1]Hansen and Nazarenko, Proc. Natl. Acad. Sci. 101 (2004) [2]Guarnieri and Balmes, The Lancet 383 (2014)
[3]IARC Monographs, 35, (1985)

Soot formation





Driving question:
What role do curved PAHs and ions have in soot nucleation?

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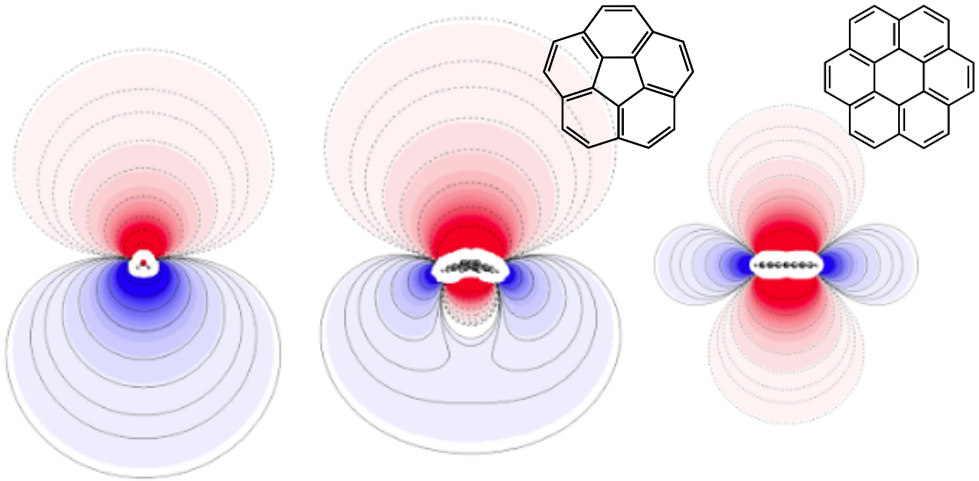
[4]Martin *et al.* J. Phys. Chem. C. (2018)

Dipole moment of curved PAHs



water
1.85 D

corannulene
2.07 D

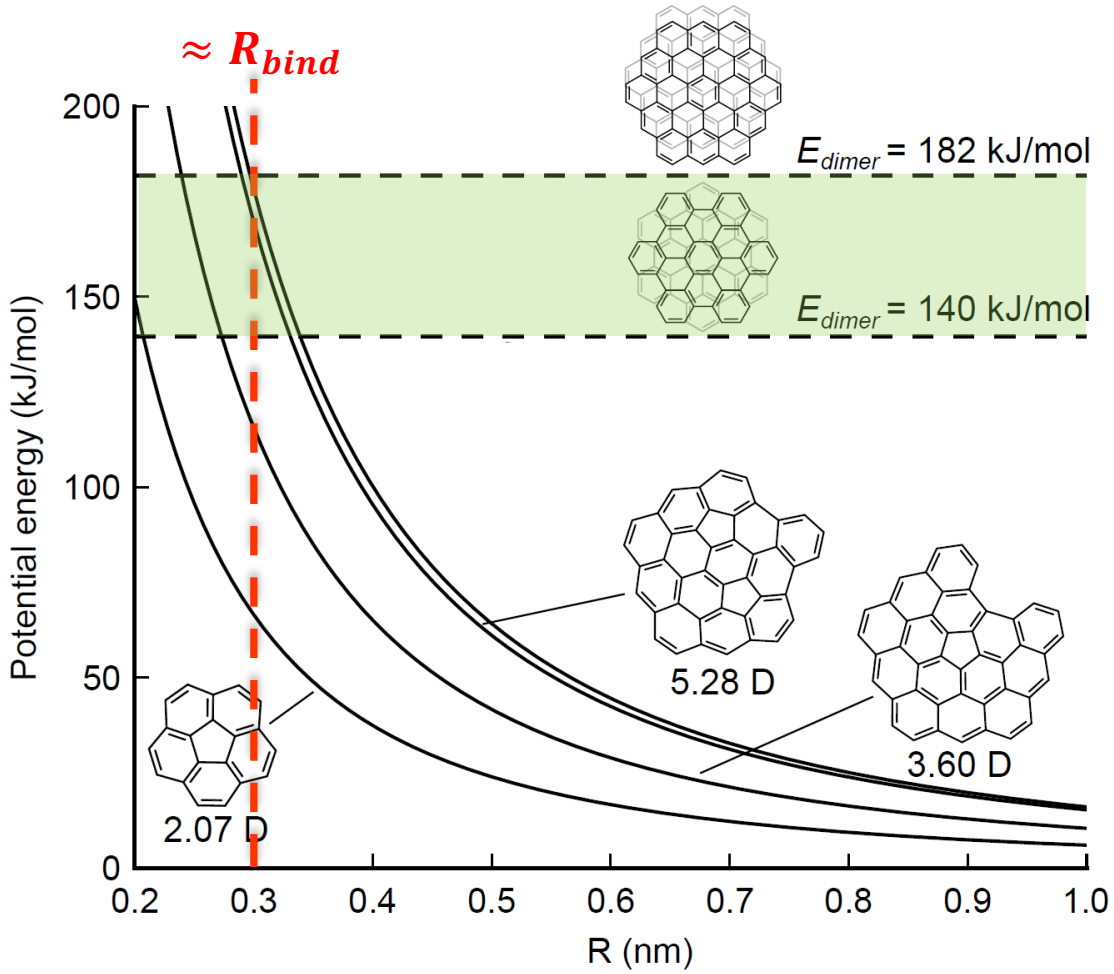
coronene
0 D

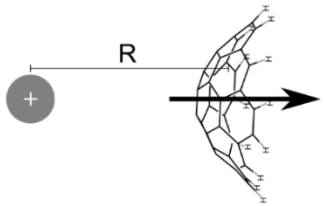
Significant dipole moment is due to the polarisation of π electrons from the concave to convex surface upon straining carbons – flexoelectric effect[5]

[5]Martin *et al.* J. Phys. Chem. C 121 (2017)

Interactions with ions

- HRTEM indicates aromatics with 10-20 rings[6]
- Interactions between ions and curved aromatics are strong and long range ($E \propto 1/r^2$)
- Suggests possible soot nucleation mechanism[7]





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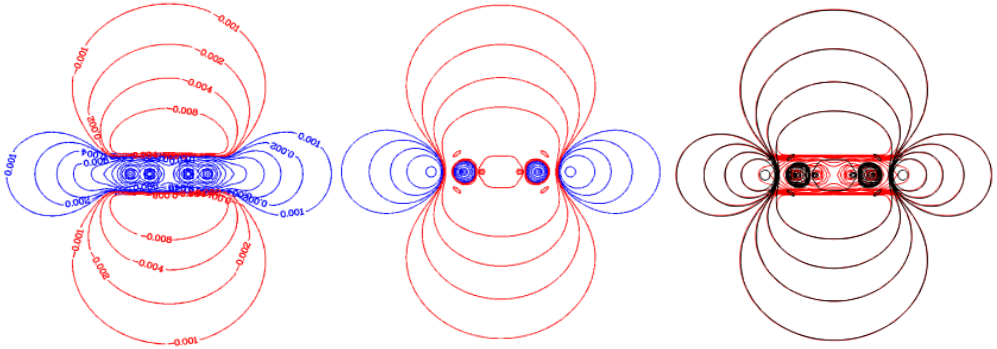
[6]Botero *et al.* Combust. Flame 164 (2016)
[7]Martin *et al.* Proc. Combust. Inst. (2018)

Flexoelectric dipole in MD

Flat PAHs

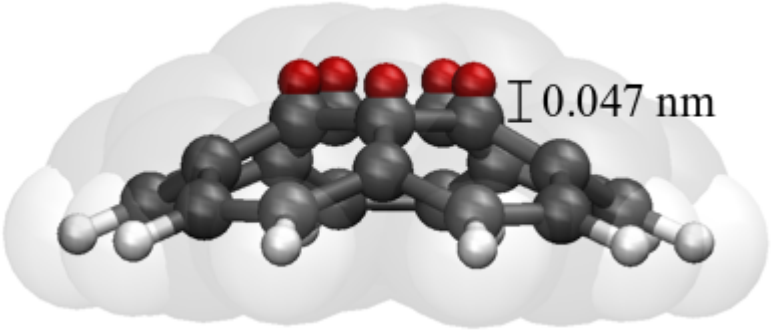
- isoPAHAP: Atom-centred point charges can describe the electrostatics[8]

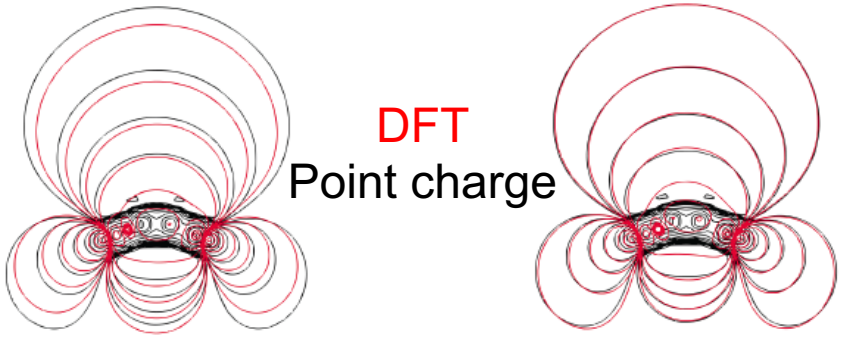


DFT | **Point charge** | **DFT Point charge**

Curved aromatics

- Need virtual atoms (off-site charges) to correctly describe the electrostatics



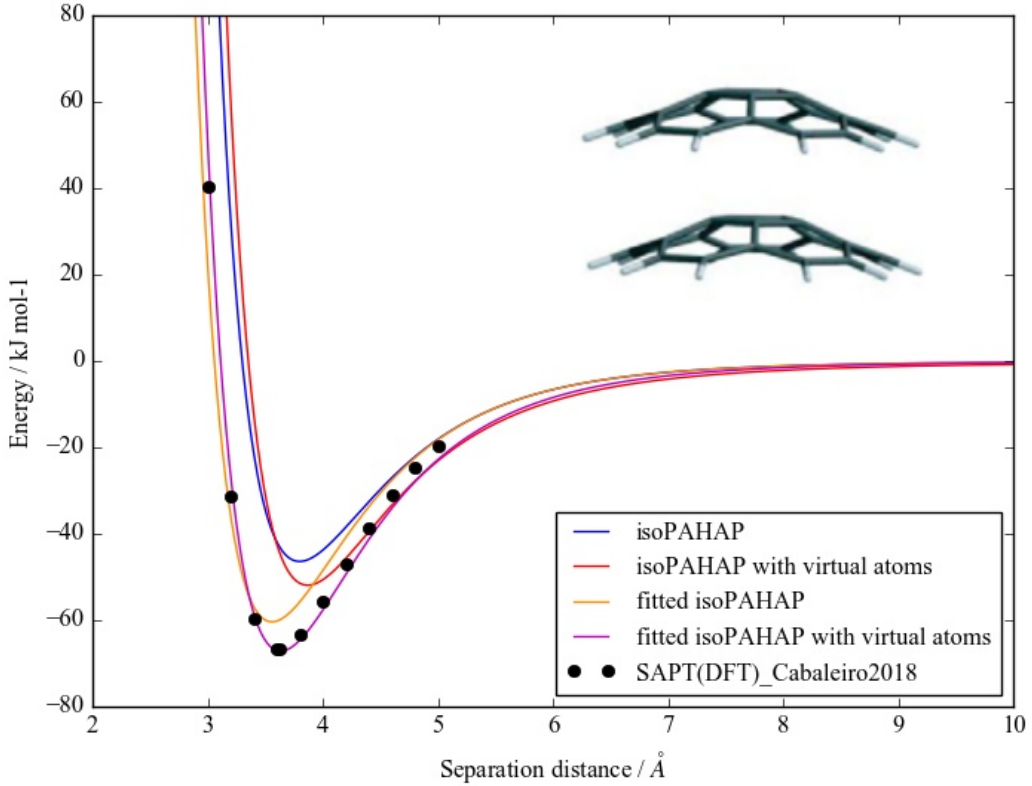


No virtual atoms | With virtual atoms

[8]Totten *et al.* J Chem Theory Comput. 6 (2010)

Fitting the isoPAHAP potential

Interaction energy function of corannulene dimers requires improved isoPAHAP parameters (dispersion, shape function) and virtual atoms



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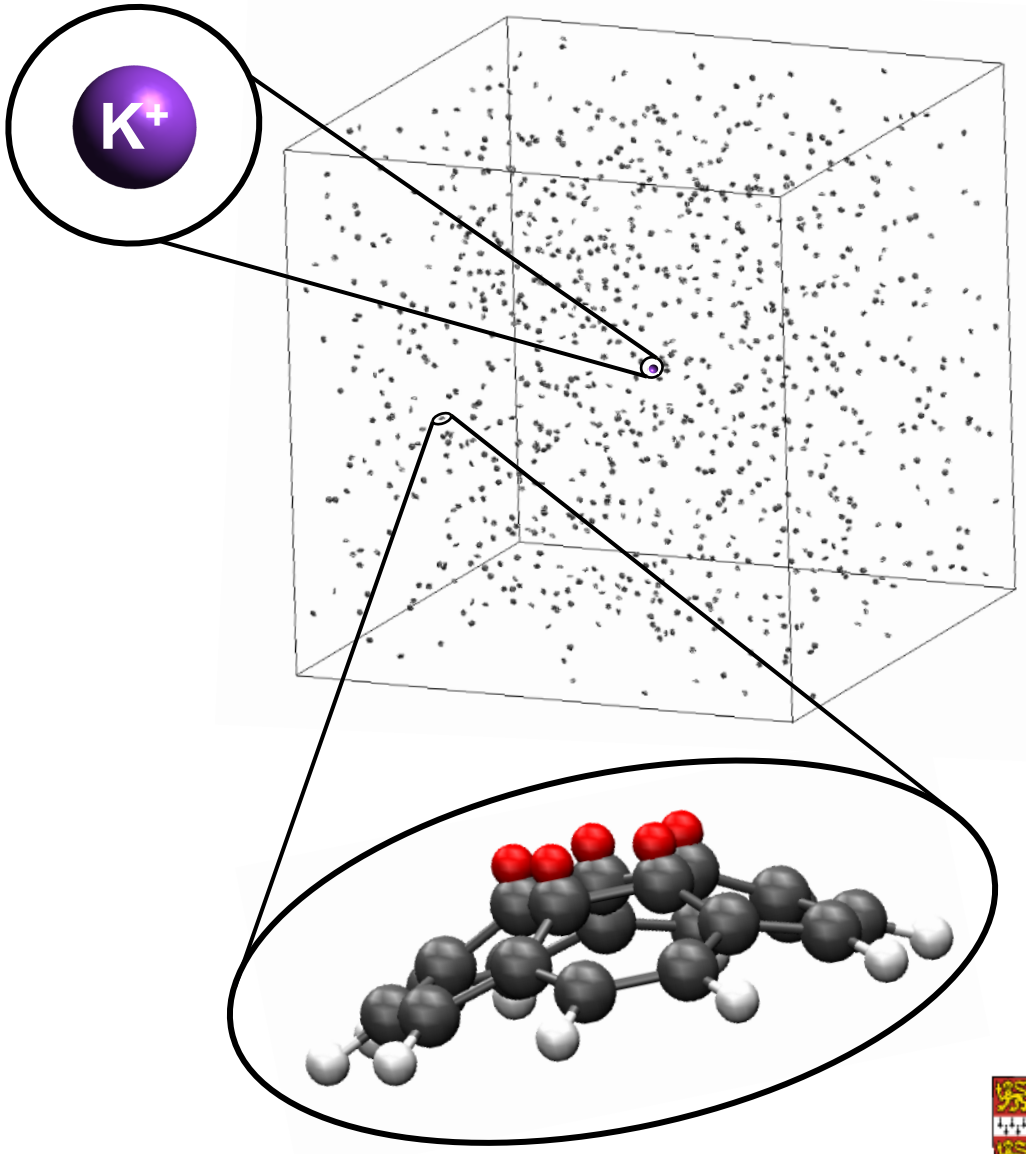
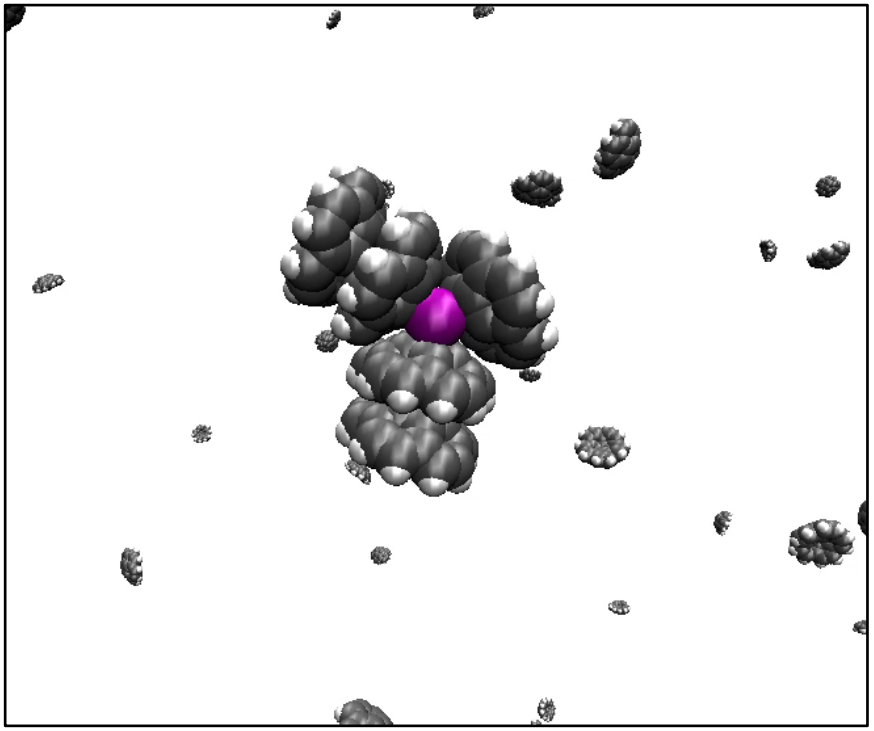
Cabaleiro-Lago *et at.* J. Comput. Chem. 39 (2018)

Curved PAHs and K^+ nucleation

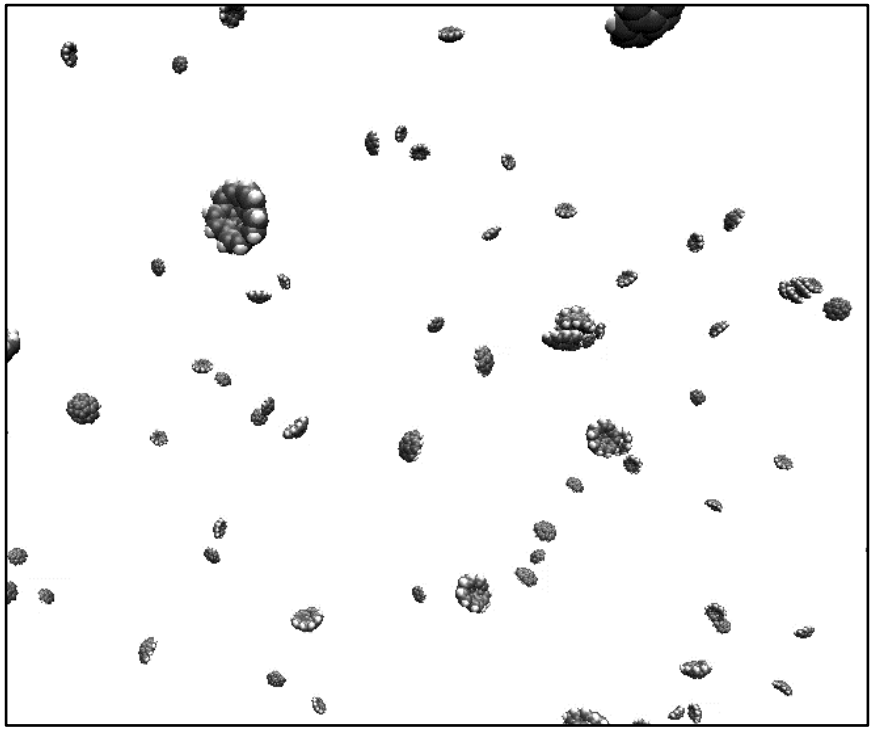
- Large system in molecular dynamics
- New force field: modified isoPAHAP with virtual atoms
- 1000 corannulene molecules
- With and without K^+
- 500, 750, 1000, 1250, 1500 K



Molecular dynamics simulation videos



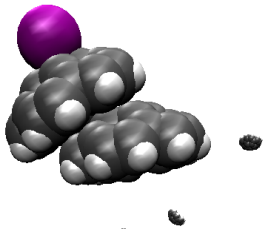
with K+



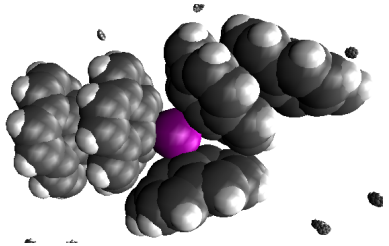
without K+

Molecular dynamics results

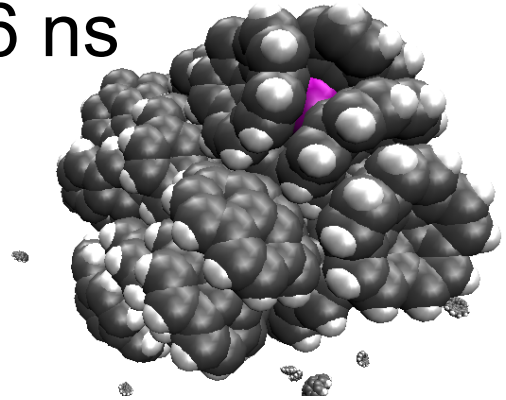
2 ns



3 ns



6 ns

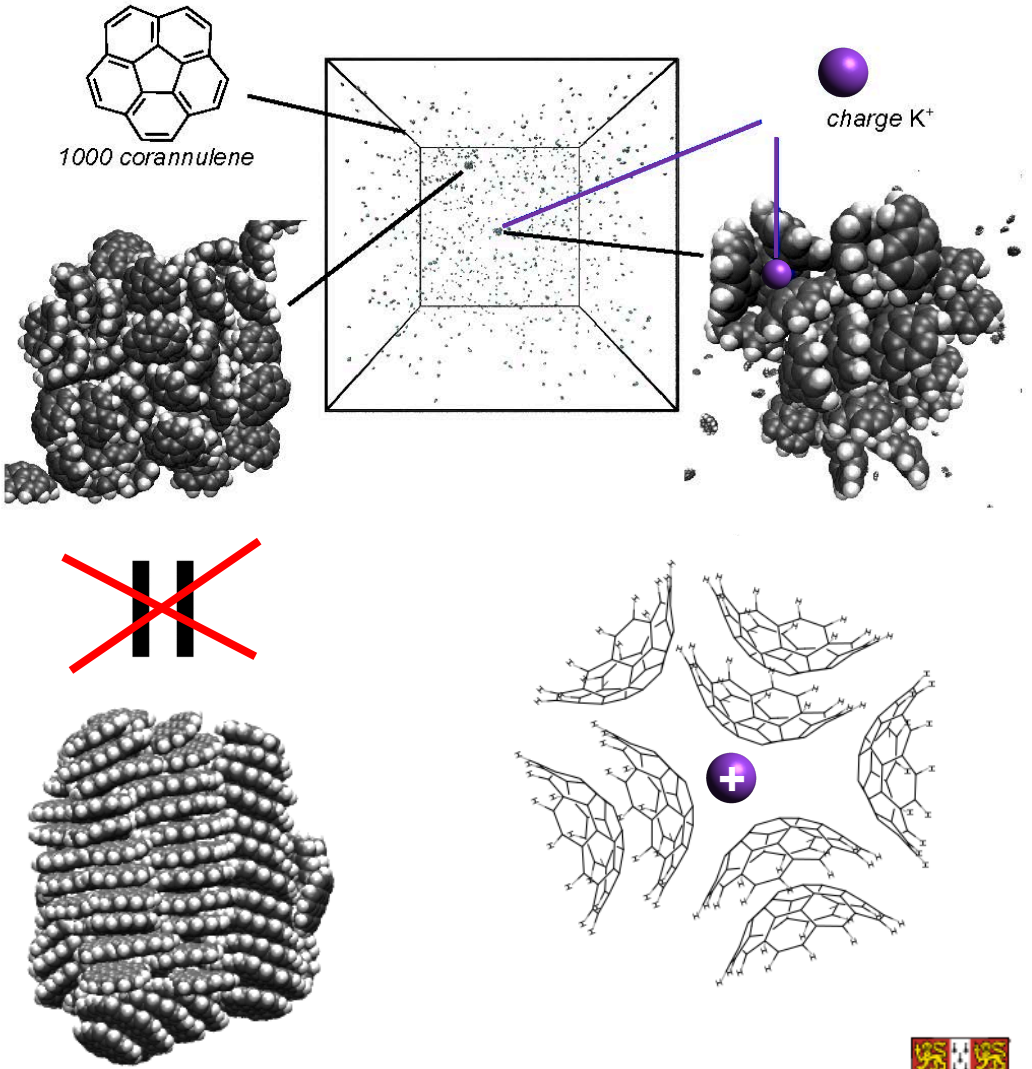


- Clusters formed at 500 and 750 K
- Boiling point is 640 K[9]
- Form spherical-like clusters with small molecular stacks around the ion
- Molecular arrangement maximises electrostatic interactions

[9]Chickos *et at.* J. Chem. Thermodynamics 34 (2002)

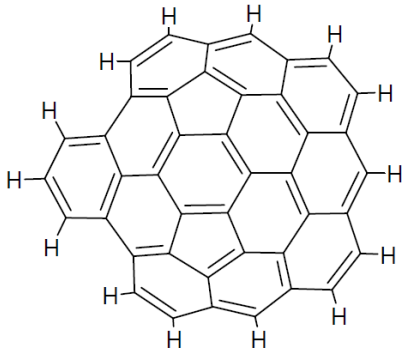
Cluster of curved PAHs

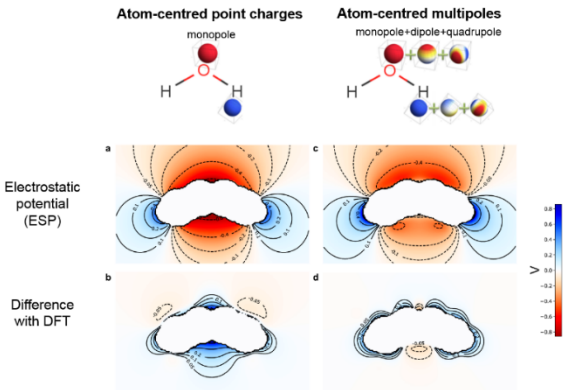
- Morphology different than cluster containing planar aromatics
- Long-range electrostatic interactions play significant role in interactions of curved PAHs

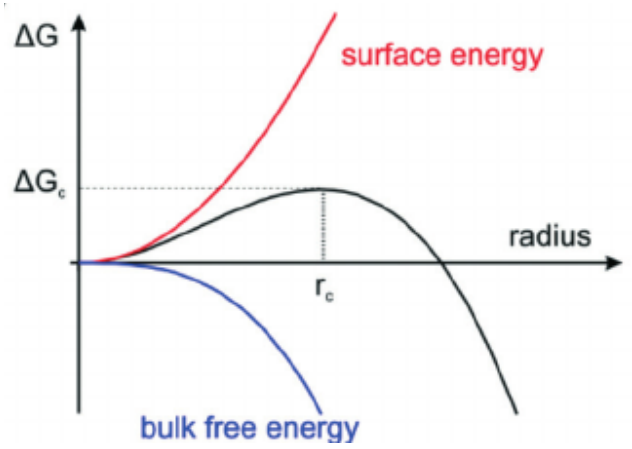


Ongoing / future work

- Extend simulations to larger soot-representative molecule with chemi-ions
- Use advanced MD to determine detailed nucleation properties
- Polarisable molecular dynamics in Tinker-HP







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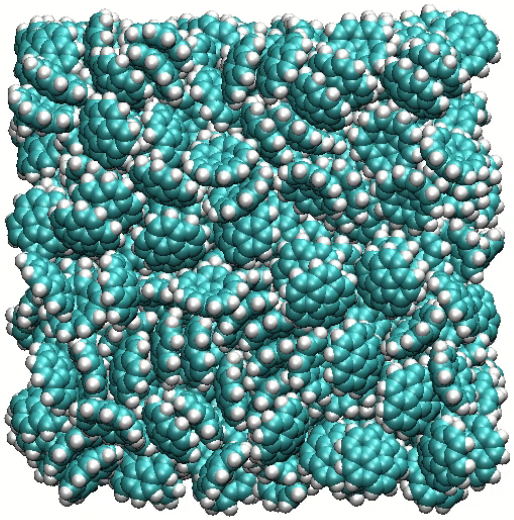
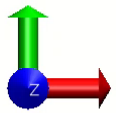
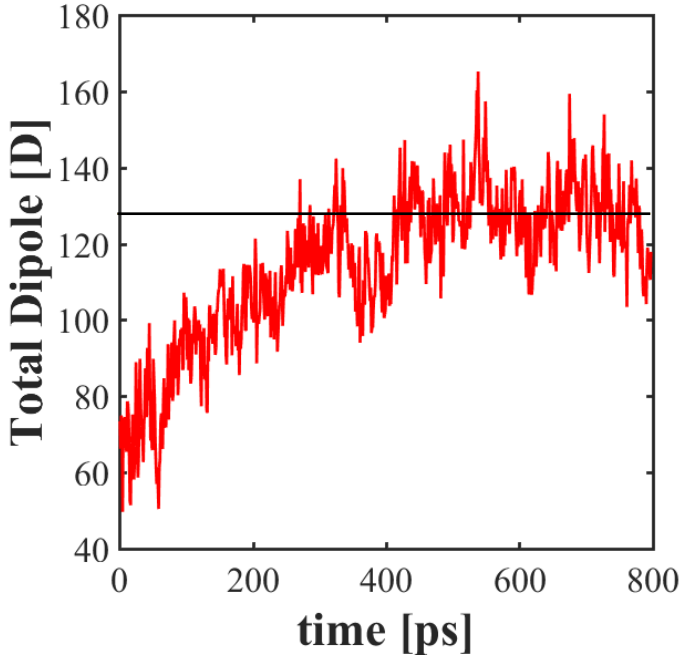
Dielectric constant



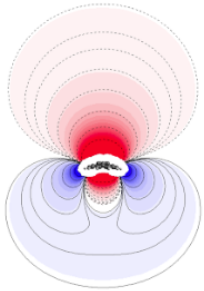




$$\varepsilon = 1 + \frac{4\pi}{3Vk_BT\varepsilon_0}\left(\langle M^2 \rangle - \langle M \rangle^2\right)$$

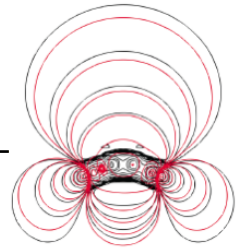
$$\varepsilon \approx 4.3$$

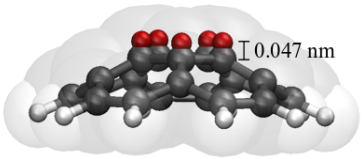
Summary



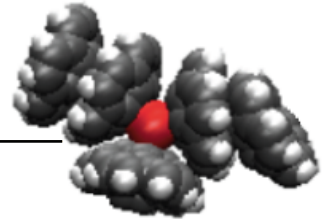
Curved PAHs in soot particles have a significant dipole moment due to the shift of electrons between curved surfaces

Flexoelectric effect cannot be adequately described by an atom-centred charges

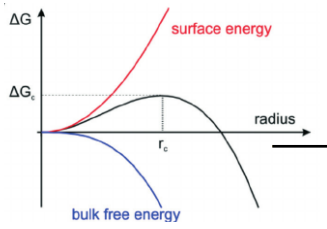




Using off-site point charges and enhanced dispersion interactions allowed description of initial molecular dynamics simulations of large systems



Formation and morphology of cluster around ion showed importance of including enhanced interactions



Work ongoing to determine detailed ion induced classical nucleation model

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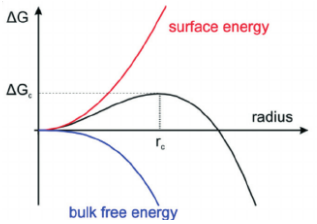
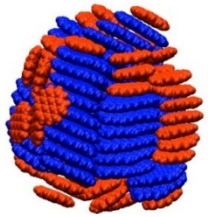
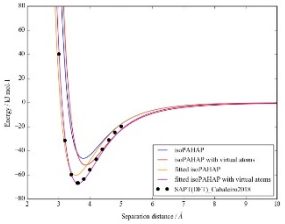
Computer allocation



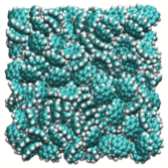


heterogeneous cluster structure

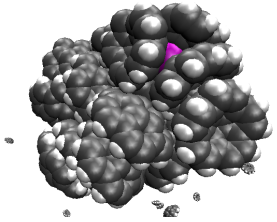
force field development



curved PAH clustering



polarisable force field



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Acknowledgements