Mixed aromatic clusters: Insights into the core-shell morphology of soot

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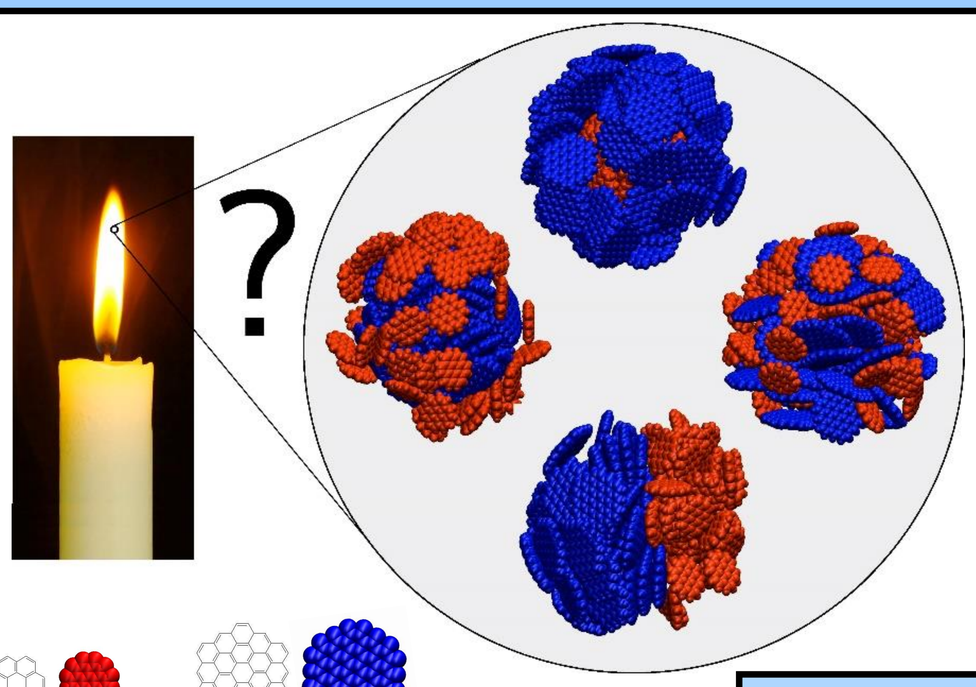
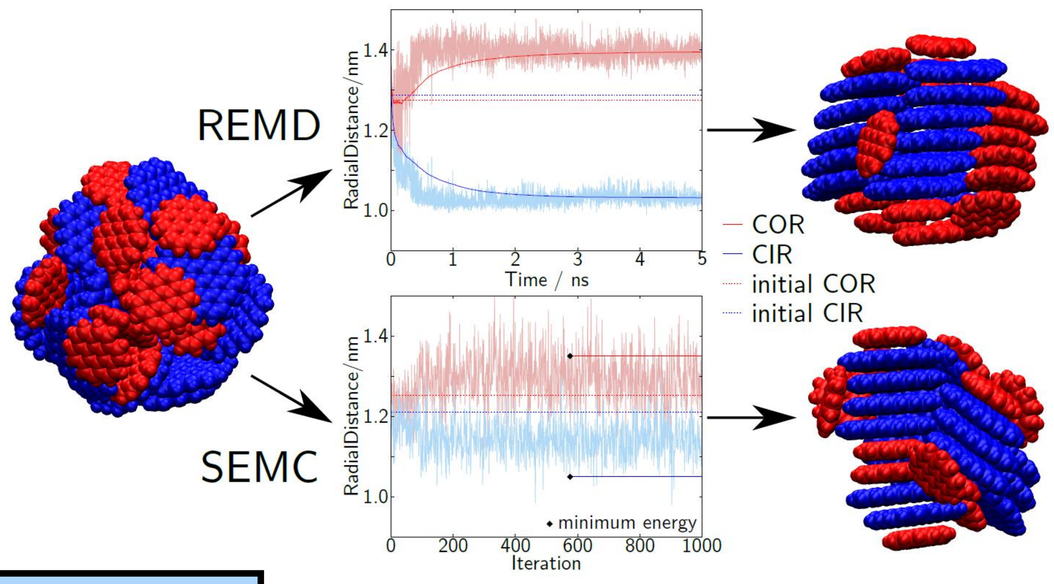


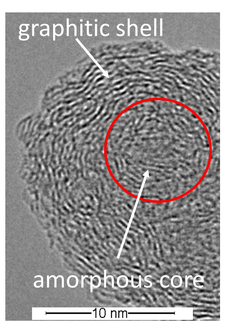
coronene $C_{24}H_{12}$ circumcoronene $C_{54}H_{18}$



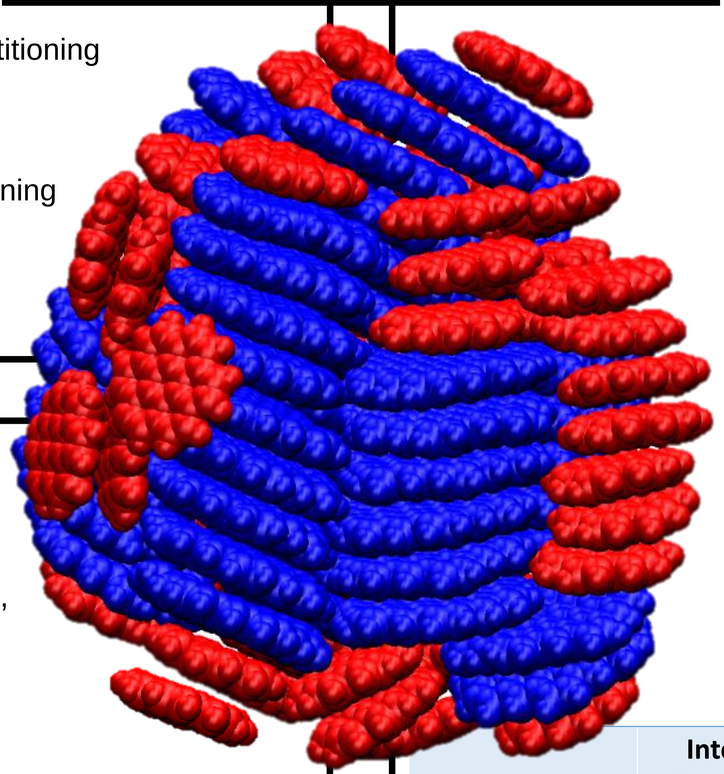
Heterogeneous polycyclic aromatic hydrocarbon clusters are investigated using two independent molecular modelling methods to understand the internal structure of soot particles

1. Introduction

- Polycyclic aromatic hydrocarbons (PAHs) are a key component of soot [1]



- Electron microscopy often shows a partitioning of PAH sizes within soot particles [2]
- Molecular modelling techniques can provide insight into whether this partitioning is due to physical (non-reactive) interactions between PAHs of different sizes



2. Methods

- Evaluate clusters made up of two types of PAHs, containing up to 100 molecules (circumcoronene CIR & coronene COR, ovalene OVA & pyrene PYR)
- Use the isoPAHAP intermolecular potential, parametrised for PAHs [3]

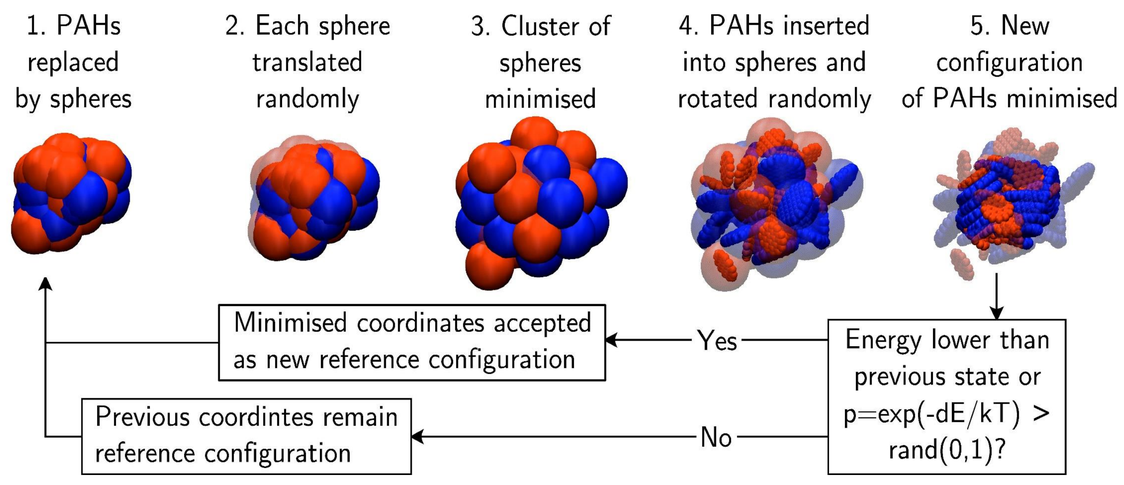
Replica exchange molecule dynamics (REMD)

- Calculates the movement of atoms over 5 ns starting from non-equilibrium configurations
- Many isothermal systems simulated in parallel are able to exchange atomic coordinates to find low energy configurations

Sphere Encapsulated Monte Carlo method (SEMC)

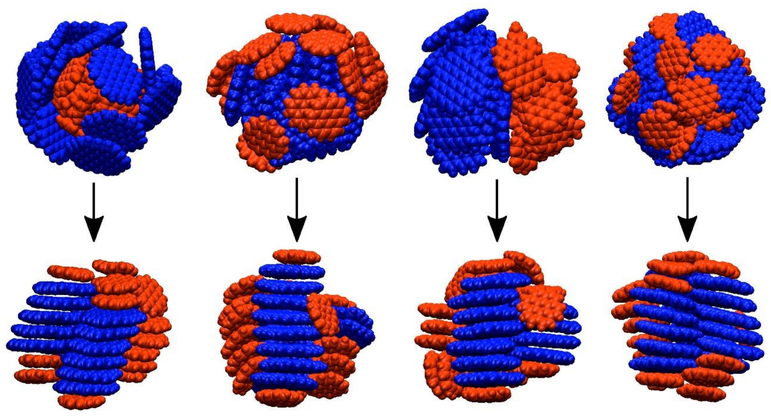
- Novel method developed here to extend the basin-hopping Monte Carlo minimisation method for use with heterogeneous aromatic clusters
- 1000 iterations repeated to search for lowest energy cluster configuration

One iteration of the SEMC

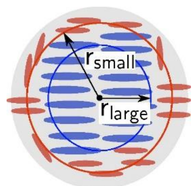


3. Results

- Stable clusters show stacked PAHs in core-shell structure, with larger PAHs in the core, regardless of initial configuration
- Difference in melting points and increased stability of homogeneous stacks causes this phase separation



- Cluster energies and average molecule type radial distances (r) show good agreement between REMD and SEMC



PAH Cluster	Intermolecular Energy (kJ/kmol)		r_{large} / r_{small} (nm)		CPU kilohours	
	REMD	SEMC	REMD	SEMC	REMD	SEMC
$CIR_{16}COR_{16}$	-4.87	-4.61	1.02 / 1.42	1.05 / 1.35	5.3	0.4
$CIR_{50}COR_{50}$	-15.8	-15.9	1.57 / 2.11	1.76 / 1.86	56.2	13.2
$OVA_{16}PYR_{16}$	-2.95	-2.90	0.89 / 1.23	0.97 / 1.07	1.8	0.2
$OVA_{50}PYR_{50}$	-10.9	-9.32	1.38 / 1.74	1.55 / 1.49	23.0	2.0

4. Conclusions

- First simulations of soot-sized heterogeneous PAH clusters
- Sphere Encapsulated MC method developed and applied to large PAH clusters
- Stable clusters consist of stacked PAHs in a core-shell structure, with larger PAHs found closer to the cluster core and smaller PAHs located on the cluster surface – shown by REMD and SEMC methods independently
- Provides insight into structure of nascent soot particles

References

1. Wang, H. (2011). *Proceedings of the Combustion Institute*, *33*, 41-67
2. Alfè *et al.* (2009). *Proceedings of the Combustion Institute*, *32*, 697-704
3. Totton, T. S., Misquitta, A. J., & Kraft, M. (2010). *J. Chem. Theory Comput.* *6*, 683-695

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