Solid–liquid transitions in homogenous ovalene, hexabenzocoronene and circumcoronene clusters: A molecular dynamics study

Dongping Chen [a], Jethro Akroyd [a], Sebastian Mosbach [a], Daniel Opalka [b], Markus Kraft [a,*]

[a] *Department of Chemical Engineering and Biotechnology, University of Cambridge, New Museums Site, Pembroke Street, Cambridge CB2 3RA, UK*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*

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ABSTRACT

The melting behaviour of ovalene ($C_{32}H_{14}$), hexabenzocoronene ($C_{42}H_{18}$) and circumcoronene ($C_{54}H_{18}$) clusters is analysed using molecular dynamics simulations. The evolution of the intermolecular energy and the Lindemann Index is used to determine the cluster melting points. The bulk melting point of each material is estimated by linear extrapolation of the cluster simulation data. The value obtained for ovalene is in good agreement with the phase-transition temperature determined by experiment. We find that the bulk melting point of peri-condensed PAHs is linearly related to their size. The extrapolated hexabenzocoronene and circumcoronene bulk melting points agree with this linear relationship very well. A phase diagram is constructed which classifies the phase of a cluster into three regions: a liquid region, a size-dependent region and a solid region according to the size of the PAHs which build up the cluster. The size-dependent region highlights the range where the phase of a cluster also depends on the cluster size. Due to the similar size and density, a cluster with 50 molecules is considered an analogue for nascent soot particles whilst the bulk system of PAH molecules is seen as an approximation to mature soot particles. A detailed investigation of the phase diagram reveals that the critical size for nascent and mature soot particles in the solid state is $C_{78}H_{22}$ and $C_{54}H_{18}$ at 1500 K respectively.

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1. Introduction

Polycyclic aromatic hydrocarbon (PAH) molecules have attracted intense scrutiny in the scientific community. They have been widely investigated as the building blocks of soot resulting from incomplete combustion of hydrocarbon fuels [44,45,4], and have been related to questions of the health hazards arising from the combustion products [54], the exploration of the interstellar space [71,42,34] and applications of nanotechnology [25,43,74]. An important open question regarding the role of PAHs in the formation and growth of soot is whether PAHs of a given size form stable clusters in a flame environment, and whether they exist as a solid or liquid-like phase. In a previous study [13], homogenous clusters of pyrene and coronene have been investigated using molecular dynamics simulations. It was shown that clusters of these small PAHs cannot survive at flame temperatures, e.g. 1500 K. This suggests that soot particles may be composed of larger PAHs with higher thermal stabilities.

To date, large PAHs (LPAHs), defined for the purpose of this work as PAHs containing eight or more aromatic rings, have received very little attention compared to smaller PAHs. For example, a Google Scholar search on the smallest PAH molecule, "benzene", yielded over two millions hits (April 25th, 2014) whilst the number of hits followed an exponential decay with the increasing size of the PAH molecules (Fig. 1). This illustrates the relative scarcity of the literature about LPAHs compared to small PAHs with only a few aromatic rings.

Historically, the investigation of LPAHs has been hindered by several factors including the difficulty in synthesising them, the large number of isomers for a particular carbon number [46], and a delay in appreciating the environmental significance of these molecules. However, in the combustion literature, peri-condensed PAHs such as ovalene (OVA) and circumcoronene (CIR) have been investigated and shown to be thermodynamically stable as suggested by Stein and Fahr [60], and have been identified in premixed and nonpremixed flames using numerical tools [49,12,75] and experimental methods [26,23]. These molecules are considered to play an important role in nucleation and condensation processes of soot formation [20].

The basic thermodynamic properties of LPAHs, for example the bulk melting point, have not yet been reported in the literature which limits our understanding of these molecules. The main reason still lies in the lack of good techniques for their synthesis.

* Corresponding author.
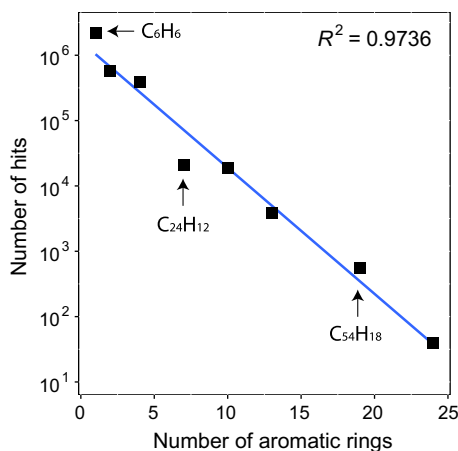 *E-mail address:* mk306@cam.ac.uk (M. Kraft).

Fig. 1. The number of hits on Google Scholar for different PAH molecules as of April 25th, 2014. Note that only the peri-condensed PAH molecules are included. Benzene, coronene and circumcoronene are highlighted. The detailed data is summarised in Table 3 (Appendix A).

Although several synthesis methods have been documented for hexabenzocoronene (HBC) [17,16,22,55], the purity of the sample limits the investigation of phase transformation. The bulk melting points of HBC was suggested to be above 973 K [19,17,48,16,5], but no exact value has been reported. Compared to HBC itself, the phase transition data of the HBC-derivatives is better documented [36,30]. Note that the spread of melting points of HBC-derivatives due to impurities is seen in the work of Brown et al. [6]. The bulk melting points of PAHs with more than 15 aromatic rings, have not been reported because no synthesis routes are yet available at all. Most of the current research relating to LPAHs was performed using numerical methods at different scales [32,3,37,70,47].

In the last decade, the rapid development of computing resources and numerical methods made it possible to accurately reproduce the bulk thermodynamic properties for different systems. Using molecular dynamics methods and a well-tuned potential function, the bulk melting points of nitromethane [1], silicon carbide (SiC) [57], Pd, Pt [50] and Cu [18] have been reproduced. These successful studies encouraged researchers to apply such numerical methods to investigate the melting point of systems that cannot be prepared by current laboratory experiments [58]. In particular, Chen and coworkers [13] investigated the size-dependent melting behaviour of homogenous PAH clusters composed of either pyrene or coronene using molecular dynamics with an isotropic potential for the PAH interactions (termed isoPAHAP) [64,65]. It was shown that the PAH clusters underwent a liquid nucleation and growth melting mechanism, such that the bulk melting points of pyrene and coronene could be estimated by a linear extrapolation of the melting point data for the individual clusters. This provides a numerical method that exploits the size-dependence of the melting point to estimate the bulk melting point by extrapolating from the calculated melting points of different sized clusters. The size-dependence of the melting point is a well-established phenomenon and has been observed for various systems [7,10,33,39,41,58,56] and only a handful of exceptions are known [51,11,2]. Molecular dynamics simulations have also been used in the combustion community to improve the understanding of soot inception by considering Van der Waals and electrostatic forces alone [53,21,68,73,15]. Recently, a few recent studies showed that enhanced binding forces, for instance the chemical bonds formed between PAHs, may also play an important role in soot formation [69,76].

In this work, the size-dependent melting behaviour of different sized homogenous clusters of ovalene (OVA), hexabenzocoronene

(HBC) and circumcoronene (CIR) are investigated using conventional molecular dynamics (MD) simulations with the isoPAHAP potential. The intermolecular energy, the local and global Lindemann indices are used to identify the melting point of each cluster. The bulk melting point of HBC and CIR is predicted by extrapolating from melting points of the individual clusters. We estimate the bulk melting point of peri-condensed PAHs as a function of the PAH mass by extrapolating from the known or computed bulk melting points of PAHs ranging in size from benzene to circumcoronene. Finally, a phase diagram of peri-condensed PAH clusters is constructed to describe the phase state of the clusters as a function of their composition and size, with the aim of identifying the conditions under which clusters of PAHs can exist in a flame environment.

2. Computational method

The current work investigates the melting behaviour of a number of homogenous LPAH clusters, P_N. In what follows, N denotes the number of molecules and varies from 50 to 300. P represents OVA, HBC or CIR (Fig. 2). The detailed intramolecular properties of OVA, HBC and CIR molecules are shown in Table 1. The monomer geometry of OVA, HBC and CIR molecules was obtained from a previous study [65], and the corresponding atom-centred point-charges were parameterised by a transferable electrostatic model for PAH molecules [63].

The MD simulations in this work use the previously developed isotropic potential (termed isoPAHAP) to describe the intermolecular interactions between C–C, C–H and H–H. The details of this potential have been published elsewhere [13,62,64,63]. The molecular structure of LPAHs is assumed to be flexible and the intramolecular interactions have been determined using the aromatic parameters from the OPLS-AA force field [29] for bonds, angles, dihedral and improper dihedral angles.

We applied the same method as in previous work [13] to obtain the equilibrated configurations of PAH clusters from scratch, including initial packing, two-stage energy minimisation, simulated annealing and long equilibrium run. The monomer molecules were initially packed together to create a random cluster-like configuration by PACKMOL [38]. A two-stage energy minimisation was performed to relax the configuration [13]. Later, a simulated
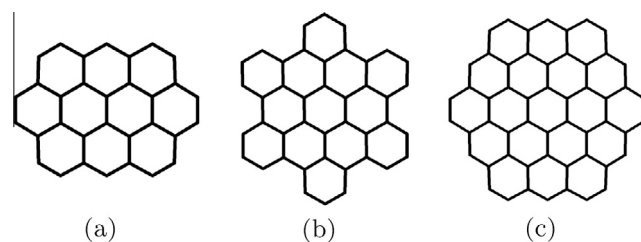

Fig. 2. PAH molecules in this study: (a) Ovalene ($C_{32}H_{14}$). (b) Hexabenzocoronene ($C_{42}H_{18}$). (c) Circumcoronene ($C_{54}H_{18}$).

Table 1
Detailed intramolecular properties of OVA, HBC and CIR molecules.

Molecule	nC[a]	nH[b]	C/H	nR[c]	Largest H–H pair distance (nm)	Largest C–C pair distance (nm)
OVA	32	14	2.286	10	1.196	0.991
HBC	42	18	2.333	13	1.355	1.137
CIR	54	18	3.0	19	1.441	1.239

[a] nC represents the number of carbon atoms.
[b] nH represents the number of hydrogen atoms.
[c] nR represents the number of aromatic rings.