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

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#### Abstract

The melting behavior of ovalene  $(C_{32}H_{14})$ , hexabenzocoronene  $(C_{42}H_{18})$  and circumcoronene (C<sub>54</sub>H<sub>18</sub>) clusters is analyzed 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 [4, 44, 45], and have been related to questions of the health hazards arising from the combustion products [55], the exploration of the interstellar space [34, 42, 71] 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 [14], 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.



Figure 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).

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 [61], and have been identified in premixed and non-

premixed flames using numerical tools [12, 49, 75] and experimental methods [23, 26]. 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. Although several synthesis methods have been documented for HBC [16, 17, 22, 56], the purity of the sample limits the investigation of phase transformation. The bulk melting points of HBC was suggested to be above 973 K [5, 16, 17, 19, 48], but no exact value has been reported. Compared to HBC itself, the phase transition data of the HBC-derivatives is better documented [30, 36]. 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 point 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 [3, 32, 37, 47, 70].

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) [58], 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 [59]. In particular, Chen and coworkers [14] investigated the size-dependent melting behaviour of homogenous PAH clusters composed of pyrene and coronene, using molecular dynamics with an isotropic potential for the PAH interactions (termed isoPAHAP) [65, 66]. 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, 57, 59] and only a handful of exceptions are known [2, 11, 51]. Molecular dynamics simulations have also been used in the combustion community to improve the understanding of soot inception [15, 21, 54, 69, 73].

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 (Figure 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 [66], and the corresponding atom-centred point-charges were parameterised by a transferable electrostatic model for PAH molecules [64].



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

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 [14, 63–65]. 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. Since the in-plane vibrations of LPAHs are typically frozen due to a high Debye temperature of 2500 K [52], the molecules should be treated as rigid bodies to account for this effect. Recall that the Debye temperature defines the critical temperature at which the degree of freedom "unfreezes" and becomes excitable. However, a previous study indicated that melting is dominated by the excitation of modes governed by the intermolecular interactions of the molecules, with little influence of the intramolecular interactions [1].

We applied the same method as in previous work [14] 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 [14]. Later, a simulated annealing process was applied to rearrange the relaxed configuration by a heating and cooling cycle which took 1.0 ns in total. During this cycle, the lowest temperature for OVA, HBC and CIR was 300 K, 300 K and 500 K, respectively, whilst the highest temperature was 800 K, 900 K and 1000 K, respectively. In the simulated annealing step, the cut-off for the intermolecular interactions was 1.5 nm to reduce the computational cost and

Molecule	e nC <sup>a</sup>	$\mathrm{nH}^b$	C/H	$\mathbf{nR}^{c}$	largest H–H pair	largest C–C pair
					distance (nm)	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

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

<sup>*a*</sup> nC represents the number of Carbon atoms.

<sup>b</sup> nH represents the number of Hydrogen atoms.

 $^{c}$  nR represents the number of aromatic rings.

a coupling parameter of 0.5 ps has been used in velocity rescaling thermostat [8] to control the temperature. The annealed configurations were further equilibrated at a range of temperature conditions for the exploration of their melting behavior, but only the last 1 ns trajectory of equilibration runs is used for statistics and this is consistent with previous work [14]. During the equilibrium step, we applied a larger cut-off, 3 nm, to include most of the non-bonded interactions accurately and the system temperature was controlled every 0.5 ps by a chain of Nosé-Hoover thermostats [67] where 10 Nosé-Hoover thermostats were coupled to improve the ergodicity.

To determine whether a system is equilibrium, the energy profile was monitored during the simulations. As soon as no systematic shift was observed in the intermolecular energy evolution, we considered the system to be in equilibrium. Typically, one equilibration run of 10 ns was sufficient for most of the clusters [14] with a few exceptions. In the latter cases, up to 30% molecules evaporated from the surface during the first equilibration run, for example at 1200 K for CIR<sub>200</sub>. The serious evaporation phenomenon was only observed at temperatures higher than 950 K and 1150 K for HBC and CIR clusters respectively. The reason behind this phenomenon mainly lies in the improper initial configuration and the relatively high temperature. This issue introduces large errors in the intermolecular energy calculations, and to address this, the clusters have been repacked to their original size by adding the PAH stacks cut from the remainder of the cluster and a new batch of equilibration runs were performed.

In all MD simulations the trajectories were computed by integrating the classical equations of motion using the velocity Verlet algorithm [68] and the integration time step was set to 1 fs. All simulations were performed *in vacuo* without periodic boundary conditions using the Gromacs 4.5.4 program [67]. The computational cost of MD simulations in this work is approximately 2 millions CPU-hours in total and this imposes a constraint on the number and size of the PAH molecules that we can consider.

### **3** Results

### **3.1** Particle properties

Fifteen different OVA, HBC, and CIR clusters were considered in this work. The properties of the their final configurations at the respective melting points are summarised in

**Table 2:** Investigated clusters (indices refer to the number of molecules in the cluster), corresponding spherical diameters, densities at the melting point and melting point temperatures.

Cluster	Spherical diameter (nm)	Density $(g/cm^{-3})$	Melting point (K)
OVA <sub>50</sub>	3.78	1.17	575
$OVA_{80}$	4.44	1.17	600
$OVA_{100}$	4.75	1.18	615
$OVA_{200}$	5.94	1.19	650
$OVA_{300}$	6.78	1.19	675
$HBC_{50}$	4.11	1.19	810
$HBC_{80}$	4.81	1.19	875
$HBC_{100}$	5.17	1.20	900
$HBC_{200}$	6.49	1.21	975
$HBC_{300}$	7.49	1.23	990
$CIR_{50}$	4.39	1.24	1040
CIR <sub>80</sub>	5.14	1.24	1090
$CIR_{100}$	5.52	1.25	1150
$CIR_{150}$	6.31	1.26	1185
CIR <sub>200</sub>	6.97	1.27	1225

Table 2. The sizes and densities of the clusters were computed by a Monte Carlo integration routine [62]. The spherical diameters were obtained under the assumption of spherical particles and were found linearly related to the number of molecules within a cluster (Figure 6).

To monitor the melting behavior of these clusters, we use the criteria defined previously [14]: intermolecular energy, local and global Lindemann Index and visual inspection of the morphological change. The detailed results can be found in Appendix C. The reduced melting points obtained are plotted in Figure 3 as a function of the inverse cluster diameter. The reduced melting point is defined as the melting point of an individual cluster divided by the melting point of the bulk system. A detailed examination of the melting behavior of OVA, HBC and CIR clusters indicates that their melting mechanisms follow the liquid nucleation and growth theory [40], in which the particles are first observed to melt from the surface and each solid-liquid interface advances towards the centre of the particle afterwards. It follows from this observation that the bulk melting point can be extrapolated using a linear correlation. Following this correlation, the bulk melting point of OVA is well reproduced (Figure 3a). Furthermore, the bulk melting points of HBC and CIR have been obtained by linear extrapolations and were found at 1227 K (Figure 3b) and 1542 K (Figure 3c), respectively.

Experimentally, the bulk melting point of HBC has been predicted to be above 973 K [5, 16, 17, 19] and this rough estimation serves as a lower bound for our prediction. White [72] postulated a linear correlation between molecular properties and normal boiling points at 1 atm for 114 PAH molecules smaller than coronene. Adopting this correlation, the normal boiling point of HBC and CIR was found at 1391.5 K and 1706.3 K respectively. Since the boiling point has to be larger than the melting point at same conditions,



Figure 3: The reduced melting temperature as a function of inverse diameter for the ovalene, hexabenzocoronene and circumcoronene clusters. T<sub>r</sub> is the reduced melting point of an individual cluster (T<sub>cm</sub>/T<sub>bulk</sub>). The solid triangle (▲) indicates the experimentally measured bulk melting points. T<sub>bulk</sub> of ovalene is 770 K [60]. The open triangles (△) or Bulk\* indicate the predicted bulk melting points. Following a linear extrapolation, the predicted bulk melting points are 1227±67 K and 1542±77 K for hexabenzocoronene and circumcoronene, respectively. The configurations of each cluster size at the corresponding melting points are also embedded in the plot with the relative sizes of the clusters preserved. Also included are details about the fitted curves.

the boiling points can be considered as an upper bound for the melting temperature of both the HBC and CIR clusters. Considering both the upper and lower bounds, it is clear

that our predicted values are consistent with current knowledge.

Our methodology for the determination of cluster melting points is subject to two sources of uncertainty. One potential source of error is the finite temperature points for the caloric curves (Figure 7) and the intervals between temperature points introduce minor uncertainties of  $\pm 10-25$  K. The other source of uncertainty lies in the possible superheating of the system [27, 39]. Even though we carried out longer equilibration runs than the common heating and cooling method, the superheating issue cannot be strictly avoided. By definition, the melting point is the temperature at which the solid and the liquid phase coexist. However, for a homogenous system, one always overheats a cluster above its melting point in order to observe the solid-liquid transition due to the lack of a liquid seed. In the superheated region, the system is in a thermodynamically metastable state despite the clusters appearing to be stable within the simulation time and showing the same morphology as in the solid state. A superheated configuration starts to melt when its mechanical instability point is reached and this can introduce up to 20% uncertainty [27]. Note that the introduced uncertainty depends on the cluster size and a larger cluster will result in a larger uncertainty. A careful examination of the ovalene melting curve in this work (Figure 3a) suggests that both the melting points of  $ovalene_{300}$  and  $ovalene_{200}$  suffer from the superheating issue since the predicted values are above the fitted curve. To approximately quantify the introduced uncertainty, we refitted the melting points of ovalene clusters to a linear model and the trendline follows the relationship

$$T_r = 1.0344 - 1.1083/D. \tag{1}$$

From Equation 1, it is obvious that the uncertainty introduced by the superheating issue is 3.44% for ovalene clusters. Assuming the results of HBC and CIR cluster are subject to the same amount of uncertainty, the uncertainty introduced by the superheating issue is 42 K and 52 K for HBC and CIR, respectively. Together with the corresponding uncertainties from finite temperature points for the caloric curves, the total uncertainty in the bulk melting point of HBC and CIR is 67 K and 77 K respectively.

#### **3.2** Estimation of bulk melting point using molecular mass

Soot particles are composed of large numbers of PAHs, but most have not been characterised in detail. The ability to predict the thermodynamic properties of these chemical compounds is essential for future investigations. As no topological information of these compounds is available, the molecular mass serves as a measure to describe such PAHs. The molecular mass has been used to characterise known PAH molecules previously [24, 73].

A linear correlation between bulk melting point and molecular mass for 9 peri-condensed PAHs is reported in Figure 4. This correlation can be used to predict the melting points of other peri-condensed PAHs for which even the chemical structure is unknown. However, the proposed correlation is only valid for peri-condensed PAH molecules. On the one hand, the molecular mass is not a molecular property which can distinguish isomers and consequently, the predicted melting points are the same for all isomers. On the other hand, hydrogen addition processes result in a decrease of the melting point but the proposed



**Figure 4:** The correlation between bulk melting point and molecular mass for 9 pericondensed PAH molecules. The melting point of benzene ( $C_6H_6$ ), naphthalene ( $C_{10}H_8$ ), anthracene ( $C_{14}H_{10}$ ), pyrene ( $C_{16}H_{10}$ ), perylene ( $C_{20}H_{12}$ ), coronene ( $C_{24}H_{12}$ ) and ovalene ( $C_{32}H_{14}$ ) is 278.67 K [35], 353.25 K [53], 491.15 K [53], 424.3 K [28], 553.85 K [9], 710.5 K [60] and 770 K [60], respectively. The bulk melting point of hexabenzocoronene and circumcoronene is predicted at 1227 K and 1542 K from the melting curves in the previous section.

correlation would predict an increasing trend with increasing mass. Therefore, when considering more complex molecules than peri-condensed PAH molecules such as aromaticaliphatic-linked hydrocarbons or peri-condensed aromatics with aliphatic branches, a molecular property containing topological information is a better choice than the molecular mass because the properties of PAHs are a direct function of their topologies. For instance, White [72] found that the normal boiling points and heat of vaporisation are both linearly related to the first-order valence molecular connectivity which is based on the molecular topology and accounts for the chemical nature of a molecule. However, due to the complexity of its estimation, the application of first-order valence molecular connectivity is limited in many circumstances. For peri-condensed PAH molecules, we found that molecular mass is linearly related to the first-order valence molecular connectivity.

#### **3.3** Phase diagram of homogenous PAH clusters using molecular mass

Based on these results and from our previous work [14] we can provide important qualitative insight into the morphology of PAH clusters at flame conditions by extrapolation of the cluster and bulk melting points of peri-condensed PAH molecules. Figure 5 shows a solid-liquid transition diagram (phase diagram) of homogenous peri-condensed PAH clusters in which the phase of one cluster depends on the size of the PAHs within one cluster. Furthermore, the phase diagram is divided into three regions, a liquid region, a size-dependent region and a solid region. Particularly, the size-dependent region defines a region where the phase state of a cluster depends on its size due to the size-dependent melting mechanism [13, 14]. This region is outlined by the melting points of bulk systems (PAH<sub>bulk</sub>) and clusters with 50 molecules (PAH<sub>50</sub>). Specifically, the melting points



Figure 5: Phase diagram of homogenous peri-condensed PAH clusters. The crosses and solid triangles represent the melting points of PAH<sub>200</sub> and PAH<sub>50</sub> clusters composed of pyrene, coronene, ovalene, hexabenzocoronene or circumcoronene molecule whilst the solid squares represent the bulk melting points or PAH<sub>bulk</sub>. The cluster and bulk melting points of both pyrene and coronene are taken from a previous work [14]. Two dashed black lines highlight the fitted curves for melting points of both PAH<sub>50</sub> and PAH<sub>bulk</sub>, and divide the phase diagram into three regions, (i) liquid region (light green), (ii) size-dependent region (light pink) and (iii) solid region (light blue). Also highlighted is the typical flame temperature between 1500 K and 2000 K. Two open diamonds or point A and B suggest the critical size of PAH molecules for PAH<sub>bulk</sub> and PAH<sub>50</sub> at 2000 K respectively. Similarly, two open spheres or point C and D suggest the critical size of PAH molecules for PAH<sub>bulk</sub> and PAH<sub>50</sub> at 1500 K respectively. Four arrows on the x-axis suggest the sizes of the four critical PAHs.

of  $PAH_{50}$  are seen as lower bounds because it is unclear how to determine the phase state of clusters with fewer molecules whilst the melting points of  $PAH_{bulk}$  are considered as upper bounds. In the size-dependent region, the melting points of  $PAH_{200}$  are also reported in Figure 5 and the size of  $PAH_{200}$  is approximately 1.5 times the size of  $PAH_{50}$ (Table 2). From the direct comparison between the melting points of  $PAH_{50}$  and  $PAH_{200}$ we can deduce how the cluster melting point changes with cluster size.

As the interactions between nano-particles are strongly dependent on their physical states (liquid-like coalescence or solid-like fractal growth), the liquid region, size-dependent region and solid region can be also considered as coalescence region, transition region and fractal growth region. In the context of soot particles, we demonstrated the occurrence of a phase change by mass addition using coronene clusters [13] and, in fact, this phenomenon can only occur in the transition region. It should be noted that the fitted melting curve for PAH<sub>bulk</sub> diverges from that of PAH<sub>50</sub> and this suggests that the difference in the cluster melting points of large PAHs is more significant and this temperature window would allow the occurrence of a phase change by mass addition in principle.

From a more detailed analysis of the phase diagram in Figure 5 we are able to quantify the critical size of PAHs which can be the building block of solid soot particles at flame condition (1500-2000 K). Because the density and size of nascent soot particles is very similar to that of a  $PAH_{50}$  cluster which is about 4 nm in diameter (Table 2), we can interpret PAH<sub>50</sub> clusters as analogues for nascent soot particles. Similarly, PAH<sub>bulk</sub> can be considered as an approximation to mature soot particles. As highlighted by point D at 1500 K in Figure 5, the critical size of a peri-condensed PAH in a solid nascent soot particle is 938 amu, which corresponds to  $C_{78}H_{22}$  (958 amu). In other words, PAH<sub>50</sub> with peri-condensed PAHs smaller than this critical size would result in a liquid-like configuration and this is consistent with experiments that the existence of liquid-like particles has been demonstrated recently [31, 76]. At 2000 K, the critical size rises up to point B or 1250 amu, and this corresponds to  $C_{102}H_{26}$ . For mature soot particles which appear solidlike at flame conditions, the critical size is highlighted by point A and C at 2000 K and 1500 K, respectively. Specifically, point A corresponds to C<sub>71</sub>H<sub>21</sub> (873 amu) whilst point C corresponds to  $C_{54}H_{18}$  (666 amu). From a thermodynamic point of view, this finding suggests that the size of PAHs within mature soot particles is larger than circumcoronene. This is consistent with previous work which ruled out pyrene dimerisation as a key step in soot inception and larger PAH species, e.g. circumcoronene, have been suggested from the thermal stability of the correspond dimers [66]. Overall, the phase diagram of pericondensed PAH links the phase state of a soot particle and also their morphologies with the thermodynamic nature of its building block. This supports future developments of more accurate particle growth models.

### 4 Conclusions

The melting points of homogenous OVA, HBC and CIR clusters have been estimated from molecular dynamics simulation based on van der Waals and electrostatic interactions alone, using a recently developed methodology. From liquid nucleation and growth theory, the bulk melting point of ovalene was well reproduced and the bulk melting points of HBC and CIR were extrapolated accordingly. Together with previous knowledge of small peri-condensed PAH molecules, a linear correlation between bulk melting point and molecular mass was proposed. More importantly, it was found that the size of the building block dominates the phase state of a nano-particle. The phase state has been examined from a phase diagram which has been constructed using the molecular mass to describe the solid-liquid transition of peri-condensed PAH clusters. This phase diagram can be used to guide the prediction of potential products after the collision of two particles, according to the size and chemical nature of both particles at various temperatures, and in particular, the size-dependent region demonstrates that our previous work regarding to the phase change of coronene clusters by mass addition are valid. Additionally, the morphology of soot particles has been addressed in terms of the particle aging. For nascent soot particles our results suggest that the building block must be as large as  $C_{78}H_{22}$  (29 aromatic rings) for a solid-like structure at 1500 K. The critical size further increases to  $C_{102}H_{26}$  (39 aromatic rings) if the temperature is increased up to 2000 K. In contrast, the critical PAH size within a mature soot particle corresponds to  $C_{54}H_{18}$  (19 aromatic rings) and  $C_{71}H_{21}$ (26 aromatic rings) at 1500 K and 2000 K respectively. These values can be considered as lower bounds of PAH size in mature soot particles at the respective temperatures.

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## **Appendix A: Search criteria on Google Scholar**

Keywords	Number of hits
	on Google Scholar
Benzene	2220000
Naphthalene	580000
Pyrene	394000
Coronene	20800
Ovalene	18600
Hexabenzocoronene	3910
Circumcoronene	550
Circumovalene	40

**Table 3:** The number of hits on Google Scholar for different PAH molecules as of April25th, 2014

## **Appendix B: The spherical diameter of ovalene, hexabenzocoronene and circumcoronene cluster**



**Figure 6:** The spherical diameter of ovalene, hexabenzocoronene and circumcoronene clusters as a function of  $N^{1/3}$  where N is the number of molecules within a cluster. The equations of the straight lines of best fit are shown at the top.

Figure 6 shows linear correlations between the spherical diameter of individual clusters and  $N^{1/3}$  where N is the number of molecules within the cluster. The corresponding  $R^2$  value is 0.9999 for all three cases. These correlations can be used to approximate the size of larger clusters in future work.





Figure 7: Average intermolecular energy per molecule as a function of temperature for different size ovalene, hexabenzocoronene and circumcoronene clusters. The size of the clusters ranges from 50–300 molecules per cluster.

Following a previous methodology [14], intermolecular energy, global and local Lindemann Indices are considered as the criteria to estimate the cluster melting points. The details of these quantities can be found in Ref [14].

The melting point of an individual cluster is defined as the temperature at which shows an energy jump for all OVA, HBC and CIR clusters (Figure 7), and the values are reported on Table 2. Similar to coronene clusters [14], the surface melting is a common pre-melting behaviour of OVA, HBC and CIR clusters at temperature sightly below the melting point (Figure 9, 10 and 11). The thickness of the surface liquid shells are found to increase with the temperature. For example, the thickness of liquid shell on a ovalene<sub>80</sub> increase from 0.7 nm at 500 K to 1.5 nm at 590 K. This surface expansion behavior supports the liquid nucleation and growth theory [40] for OVA, HBC and CIR molecules.



Figure 8: Global Lindemann Index of ovalene, hexabenzocoronene and circumcoronene clusters.



Figure 9: Radial distribution of local Lindemann Index of ovalene clusters, the size of the clusters ranges from 50–300 ovalene molecules per cluster. The error bars are the standard deviations computed from the Lindemann Index of molecules within each shell.



Figure 10: Radial distribution of local Lindemann Index of hexabenzocoronene clusters, the size of the clusters ranges from 50–300 hexabenzocoronene molecules per cluster. The error bars are the standard deviations computed from the Lindemann Index of molecules within each shell.



Figure 11: Radial distribution of local Lindemann Index of circumcoronene clusters, the size of the clusters ranges from 50–200 circumcoronene molecules per cluster. The error bars are the standard deviations computed from the Lindemann Index of molecules within each shell.

### References

- P. M. Agrawal, B. M. Rice, and D. L. Thompson. Molecular dynamics study of the melting of nitromethane. *The Journal of Chemical Physics*, 119(18):9617–9627, 2003. doi:10.1063/1.1612915.
- [2] A. Aguado and J. M. López. Anomalous size dependence in the melting temperatures of free sodium clusters: An explanation for the calorimetry experiments. *Physical Review Letter*, 94:233401, 2005. doi:10.1103/PhysRevLett.94.233401.
- [3] D. Andrienko, V. Marcon, and K. Kremer. Atomistic simulation of structure and dynamics of columnar phases of hexabenzocoronene derivatives. *The Journal of Chemical Physics*, 125(12):124902, 2006. doi:10.1063/1.2354156.
- [4] J. Appel, H. Bockhorn, and M. Frenklach. Kinetic modeling of soot formation with detailed chemistry and physics: Laminar premixed flames of C<sub>2</sub> hydrocarbons. *Combustion and Flame*, 121:122–136, 2000. doi:10.1016/S0010-2180(99)00135-2.
- [5] W. Boenigk, M. W. Haenel, and M. Zander. Solid-state carbonization of large polycyclic aromatic hydrocarbons. *Fuel*, 74(2):305–306, 1995. doi:10.1016/0016-2361(95)92671-R.
- [6] S. P. Brown, I. Schnell, J. D. Brand, K. Müllen, and H. W. Spiess. An investigation of  $\pi$ - $\pi$  packing in a columnar hexabenzocoronene by fast magic-angle spinning and double-quantum <sup>1</sup>h solid-state NMR spectroscopy. *Journal of the American Chemical Society*, 121(28):6712–6718, 1999. doi:10.1021/ja990637m.
- [7] P. Buffat and J.-P. Borel. Size effect on the melting temperature of gold particles. *Physical Review A*, 13:2287–2298, 1976. doi:10.1103/PhysRevA.13.2287.
- [8] G. Bussi, D. Donadio, and M. Parrinello. Canonical sampling through velocity rescaling. *The Journal of Chemical Physics*, 126(1):014101, 2007. doi:10.1063/1.2408420.
- [9] F. Casellato, C. Vecchi, A. Girelli, and B. Casu. Differential calorimetric study of polycyclic aromatic hydrocarbons. *Thermochimica Acta*, 6(4):361–368, 1973. doi:10.1016/0040-6031(73)87003-0.
- [10] T. Castro, R. Reifenberger, E. Choi, and R. P. Andres. Size-dependent melting temperature of individual nanometer-sized metallic clusters. *Physical Review B*, 42: 8548–8556, 1990. doi:10.1103/PhysRevB.42.8548.
- [11] S. Chacko, K. Joshi, D. G. Kanhere, and S. A. Blundell. Why do gallium clusters have a higher melting point than the bulk? *Physical Review Letter*, 92:135506, 2004. doi:10.1103/PhysRevLett.92.135506.

- [12] D. Chen, Z. Zainuddin, E. Yapp, J. Akroyd, S. Mosbach, and M. Kraft. A fully coupled simulation of PAH and soot growth with a population balance model. *Proceedings of the Combustion Institute*, 34(1):1827–1835, 2013. doi:10.1016/j.proci.2012.06.089.
- [13] D. Chen, T. Totton, J. Akroyd, S. Mosbach, and M. Kraft. Phase change of polycyclic aromatic hydrocarbon clusters by mass addition. 2013, submitted.
- [14] D. Chen, T. Totton, J. Akroyd, S. Mosbach, and M. Kraft. Size-dependent melting of polycyclic aromatic hydrocarbon nano-clusters: A molecular dynamics study. *Carbon*, 67(0):79–91, 2014. doi:10.1016/j.carbon.2013.09.058.
- [15] D. Chen, J. Akroyd, S. Mosbach, and M. Kraft. Surface reactivity of homogeneous polycyclic aromatic hydrocarbon nano-clusters. 2014, submitted.
- [16] E. Clar and J. Stephen. The synthesis of 1:2, 3:4, 5:6, 7:8, 9:10, 11:12hexabenzocoronene. *Tetrahedron*, 21(2):467–470, 1965. doi:10.1016/S0040-4020(01)82216-X.
- [17] E. Clar, C. T. Ironside, and M. Zander. 28. The electronic interaction between benzenoid rings in condensed aromatic hydrocarbons. 1: 12-2: 3-4: 5-6: 7-8: 9-10: 11-hexabenzocoronene, 1: 2-3: 4-5: 6-10: 11-tetrabenzoanthanthrene, and 4: 5-6 : 7-11: 12-13: 14-tetrabenzoperopyrene. *Journal of the Chemical Society*, pages 142–147, 1959. doi:10.1039/JR9590000142.
- [18] F. Delogu. Structural and energetic properties of unsupported Cu nanoparticles from room temperature to the melting point: Molecular dynamics simulations. *Physical Review B*, 72:205418, 2005. doi:10.1103/PhysRevB.72.205418.
- [19] J. R. Dias. Total resonant sextet benzenoid hydrocarbon isomers and their molecular orbital and thermodynamic characteristics. *Thermochimica Acta*, 122(2):313–337, 1987. doi:10.1016/0040-6031(87)87051-X.
- [20] P. Elvati and A. Violi. Thermodynamics of poly-aromatic hydrocarbon clustering and the effects of substituted aliphatic chains. *Proceedings of the Combustion Institute*, 34(1):1837–1843, 2013. doi:10.1016/j.proci.2012.07.030.
- [21] S. L. Fiedler, S. Izvekov, and A. Violi. The effect of temperature on nanoparticle clustering. *Carbon*, 45(9):1786–1794, 2007. doi:10.1016/j.carbon.2007.05.001.
- [22] R. Goddard, M. W. Haenel, W. C. Herndon, C. Krueger, and M. Zander. Crystallization of large planar polycyclic aromatic hydrocarbons: The molecular and crystal structures of hexabenzo[bc,ef,hi,kl,no,qr]coronene and benzo[1,2,3-bc:4,5,6b'c']dicoronene. *Journal of the American Chemical Society*, 117(1):30–41, 1995. doi:10.1021/ja00106a004.
- [23] J. Happold, H. Grotheer, and M. Aigner. Distinction of gaseous soot precursor molecules and soot precursor particles through photoionization mass spectrometry. *Rapid Communications in Mass Spectrometry*, 21(7):1247–1254, 2007. doi:10.1002/rcm.2955.

- [24] J. D. Herdman and J. H. Miller. Intermolecular potential calculations for polynuclear aromatic hydrocarbon clusters. *Journal of Physical Chemistry A*, 112(28):6249– 6256, 2008. doi:10.1021/jp800483h.
- [25] J. P. Hill, W. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii, and T. Aida. Self-assembled hexa-perihexabenzocoronene graphitic nanotube. *Science*, 304(5676):1481–1483, 2004. doi:10.1126/science.1097789.
- [26] K. H. Homann and H. G. Wagner. Some new aspects of the mechanism of carbon formation in premixed flames. *Symposium (International) on Combustion*, 11:371– 379, 1967. doi:10.1016/S0082-0784(67)80161-9.
- [27] Z. H. Jin, P. Gumbsch, K. Lu, and E. Ma. Melting mechanisms at the limit of superheating. *Physical Review Letter*, 87:055703, 2001. doi:10.1103/PhysRevLett.87.055703.
- [28] C. L. Judy, N. M. Pontikos, and W. E. Acree. Solubility of pyrene in binary solvent mixtures containing cyclohexane. *Journal of Chemical & Engineering Data*, 32(1): 60–62, 1987. doi:10.1021/je00047a018.
- [29] G. A. Kaminski, R. A. Friesner, J. Tirado-Rives, and W. L. Jorgensen. Evaluation and reparametrization of the OPLS-AA force field for proteins via comparison with accurate quantum chemical calculations on peptides. *The Journal of Physical Chemistry B*, 105(28):6474–6487, 2001. doi:10.1021/jp003919d.
- [30] M. Kastler, J. Schmidt, W. Pisula, D. Sebastiani, and K. Müllen. From armchair to zigzag peripheries in nanographenes. *Journal of the American Chemical Society*, 128(29):9526–9534, 2006. doi:10.1021/ja062026h.
- [31] M. Kholghy, M. Saffaripour, C. Yip, and M. J. Thomson. The evolution of soot morphology in a laminar coflow diffusion flame of a surrogate for Jet A-1. *Combustion and Flame*, 160(10):2119–2130, 2013. doi:10.1016/j.combustflame.2013.04.008.
- [32] H.-S. Kim, J.-H. Lee, T.-H. Kim, S. Okabe, M. Shibayama, and S.-M. Choi. Phase behavior of hexa-peri-hexabenzocoronene derivative in organic solvent. *The Journal* of Physical Chemistry B, 115(22):7314–7320, 2011. doi:10.1021/jp200882n.
- [33] V. N. Koparde and P. T. Cummings. Sintering of titanium dioxide nanoparticles: A comparison between molecular dynamics and phenomenological modeling. *Journal of Nanoparticle Research*, 10(7):1169–1182, 2008. doi:10.1007/s11051-007-9342-3.
- [34] P. Lavvas, M. Sander, M. Kraft, and H. Imanaka. Surface chemistry and particle shape: Processes for the evolution of aerosols in Titan's atmosphere. *The Astrophysical Journal*, 728:80–91, 2011. doi:10.1088/0004-637X/728/2/80.
- [35] J. Linek, I. Wichterle, and K. N. Marsh. Vapor-liquid equilibria for n-methyl-2pyrrolidone + benzene, +toluene, +heptane, and +methylcyclohexane. *Journal of Chemical & Engineering Data*, 41(6):1212–1218, 1996. doi:10.1021/je9601826.

- [36] C. Y. Liu, A. Fechtenkötter, M. D. Watson, K. Müllen, and A. J. Bard. Room temperature discotic liquid crystalline thin films of hexa-peri-hexabenzocoronene: Synthesis and optoelectronic properties. *Chemistry of Materials*, 15(1):124–130, 2003. doi:10.1021/cm020701q.
- [37] V. Marcon, T. Vehoff, J. Kirkpatrick, C. Jeong, D. Y. Yoon, K. Kremer, and D. Andrienko. Columnar mesophases of hexabenzocoronene derivatives. I. Phase transitions. *The Journal of Chemical Physics*, 129(9):094505, 2008. doi:10.1063/1.2969763.
- [38] L. Martínez, R. Andrade, E. G. Birgin, and J. M. Martínez. Packmol: A package for building initial configurations for molecular dynamics simulations. *Journal of Computational Chemistry*, 30(13):2157–2164, 2009. doi:10.1002/jcc.21224.
- [39] Q. Mei and K. Lu. Melting and superheating of crystalline solids: From bulk to nanocrystals. *Progress in Materials Science*, 52(8):1175–1262, 2007. doi:10.1016/j.pmatsci.2007.01.001.
- [40] K. K. Nanda. Size-dependent melting of nanoparticles: Hundred years of thermodynamic model. *Pramana*, 72(4):617–628, 2009. doi:10.1007/s12043-009-0055-2.
- [41] E. C. Neyts and A. Bogaerts. Numerical study of the size-dependent melting mechanisms of Nickel nanoclusters. *The Journal of Physical Chemistry C*, 113(7):2771– 2776, 2009. doi:10.1021/jp8058992.
- [42] F. Pauzat. Computational ir spectroscopy for pahs: from the early years to the present status. *EAS Publications Series*, 46:75–93, 2011. doi:10.1051/eas/1146008.
- [43] W. Pisula, A. Menon, M. Stepputat, I. Lieberwirth, U. Kolb, A. Tracz, H. Sirringhaus, T. Pakula, and K. Müllen. A zone-casting technique for device fabrication of field-effect transistors based on discotic hexa-peri-hexabenzocoronene. *Advanced Materials*, 17(6):684–689, 2005. doi:10.1002/adma.200401171.
- [44] A. Raj, M. S. Celnik, R. Shirley, M. Sander, R. I. A. Patterson, R. H. West, and M. Kraft. A statistical approach to develop a detailed soot growth model using PAH characteristics. *Combustion and Flame*, 156(4):896–913, 2009. doi:10.1016/j.combustflame.2009.01.005.
- [45] A. Raj, M. Sander, V. Janardhanan, and M. Kraft. A study on the coagulation of polycyclic aromatic hydrocarbon clusters to determine their collision efficiency. *Combustion and Flame*, 157(3):523–534, 2010. doi:10.1016/j.combustflame.2009.10.003.
- [46] M. Randić and S. El-Basil. Graph theoretical analysis of large benzenoid hydrocarbons. *Journal of Molecular Structure (Theochem)*, 304(3):233–245, 1994. doi:10.1016/0166-1280(94)80020-0.
- [47] A. Ricca, C. W. Bauschlicher, and L. Allamandola. Protonated polycyclic aromatic hydrocarbons revisited. *The Astrophysical Journal*, 727:128–133, 2011.

- [48] J. M. Robertson and J. Trotter. 248. crystal-structure studies of polynuclear hydrocarbons. part vi. 1,12:2,3:4,5:6,7:8,9:10,11-hexabenzocoronene. *Journal of Chemical Society*, pages 1280–1284, 1961. doi:10.1039/JR9610001280.
- [49] M. Sander, R. I. Patterson, A. Braumann, A. Raj, and M. Kraft. Developing the PAH-PP soot particle model using process informatics and uncertainty propagation. *Proceedings of the Combustion Institute*, 33(1):675–683, 2011. doi:10.1016/j.proci.2010.06.156.
- [50] S. K. R. S. Sankaranarayanan, V. R. Bhethanabotla, and B. Joseph. Molecular dynamics simulation study of the melting of Pd-Pt nanoclusters. *Physical Review B*, 71:195415, 2005. doi:10.1103/PhysRevB.71.195415.
- [51] M. Schmidt, R. Kusche, and H. Haberland. Irregular variations in the melting point of size-selected atomic clusters. *Nature*, 393(6682):238–240, 1998. doi:10.1038/30415.
- [52] M. Schmidt, A. Masson, and C. Bréchignac. Coronene cluster experiments: Stability and thermodynamics. *International Journal of Mass Spectrometry*, 252(2):173–179, 2006. doi:10.1016/j.ijms.2005.10.015.
- [53] W. J. Schmitt and R. C. Reid. Solubility of monofunctional organic solids in chemically diverse supercritical fluids. *Journal of Chemical & Engineering Data*, 31(2): 204–212, 1986. doi:10.1021/je00044a021.
- [54] C. A. Schuetz and M. Frenklach. Nucleation of soot: Molecular dynamics simulations of pyrene dimerization. *Proceedings of the Combustion Institute*, 29(2): 2307–2314, 2002. doi:10.1016/S1540-7489(02)80281-4.
- [55] R. F. Service. Study fingers soot as a major player in global warming. *Science*, 319 (5871):1745, 2008. doi:10.1126/science.319.5871.1745.
- [56] H. Seyler, B. Purushothaman, D. J. Jones, A. B. Holmes, and W. W. H. Wong. Hexaperi-hexabenzocoronene in organic electronics. *Pure and Applied Chemistry*, 84(4): 1047–1067, 2012. doi:10.1351/PAC-CON-11-09-24.
- [57] Y. Shibuta and T. Suzuki. A molecular dynamics study of the phase transition in bcc metal nanoparticles. *The Journal of chemical physics*, 129(14):144102, 2008. doi:10.1063/1.2991435.
- [58] F. Shimojo, I. Ebbsjö, R. K. Kalia, A. Nakano, J. P. Rino, and P. Vashishta. Molecular dynamics simulation of structural transformation in silicon carbide under pressure. *Physical Review Letter*, 84:3338–3341, 2000. doi:10.1103/PhysRevLett.84.3338.
- [59] Q. Shu, Y. Yang, Y. T. Zhai, D. Y. Sun, H. J. Xiang, and X. G. Gong. Size-dependent melting behavior of iron nanoparticles by replica exchange molecular dynamics. *Nanoscale*, 4:6307–6311, 2012. doi:10.1039/C2NR30853C.
- [60] G. Smith. Phase behavior of some condensed polycyclic aromatics. *Molecular Crystals and Liquid Crystals*, 64(1):15–17, 1980. doi:10.1080/01406568008072649.

- [61] S. E. Stein and A. Fahr. High-temperature stabilities of hydrocarbons. *The Journal of Physical Chemistry*, 89(17):3714–3725, 1985. doi:10.1021/j100263a027.
- [62] T. S. Totton, D. Chakrabarti, A. J. Misquitta, M. Sander, D. J. Wales, and M. Kraft. Modelling the internal structure of nascent soot particles. *Combustion and Flame*, 157(5):909–914, 2010. doi:10.1016/j.combustflame.2009.11.013.
- [63] T. S. Totton, A. J. Misquitta, and M. Kraft. A first principles development of a general anisotropic potential for polycyclic aromatic hydrocarbons. *Journal of Chemical Theory and Computation*, 6(3):683–695, 2010. doi:10.1021/ct9004883.
- [64] T. S. Totton, A. J. Misquitta, and M. Kraft. A transferable electrostatic model for intermolecular interactions between polycyclic aromatic hydrocarbons. *Chemical Physics Letters*, 510(1-3):154–160, 2011. doi:10.1016/j.cplett.2011.05.021.
- [65] T. S. Totton, A. J. Misquitta, and M. Kraft. Assessing the PAHAP potential with application to the exfoliation energy of graphite. *The Journal of Physical Chemistry A*, 115(46):13684–3693, 2011. doi:10.1021/jp208088s.
- [66] T. S. Totton, A. J. Misquitta, and M. Kraft. A quantitative study of the clustering of polycyclic aromatic hydrocarbons at high temperatures. *Physical Chemistry Chemical Physics*, 14:4081–4094, 2012. doi:10.1039/C2CP23008A.
- [67] D. Van Der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, and H. J. C. Berendsen. Gromacs: Fast, flexible, and free. *Journal of Computational Chemistry*, 26(16):1701–1718, 2005. doi:10.1002/jcc.20291.
- [68] L. Verlet. Computer "experiments" on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules. *Physical Review*, 159(1):98, 1967. doi:10.1103/PhysRev.159.98.
- [69] A. Violi. Modeling of soot particle inception in aromatic and aliphatic premixed flames. *Combustion and Flame*, 139:279–287, 2004. doi:10.1016/j.combustflame.2004.08.013.
- [70] H. Wang and M. Frenklach. Transport properties of polycyclic aromatic hydrocarbons for flame modeling. *Combustion and Flame*, 96(1-2):163–170, 1994. doi:10.1016/0010-2180(94)90167-8.
- [71] J. L. Weisman, T. J. Lee, F. Salama, and M. Head-Gordon. Time-dependent density functional theory calculations of large compact polycyclic aromatic hydrocarbon cations: Implications for the diffuse interstellar bands. *The Astrophysical Journal*, 587:256–261, 2003. doi:10.1086/368103.
- [72] C. M. White. Prediction of the boiling point, heat of vaporization, and vapor pressure at various temperatures for polycyclic aromatic hydrocarbons. *Journal of Chemical* & Engineering Data, 31(2):198–203, 1986. doi:10.1021/je00044a020.

- [73] D. Wong, R. Whitesides, C. Schuetz, and M. Frenklach. *Molecular dynamics simulations of PAH dimerization*, pages 245–255. Proceedings of an International Workshop held in Villa Orlandi, Anacapri, May 13-16, 2007. Editor: H. Bockhorn, A. D'Anna, A. F. Sarofim and H. Wang. Karlsruhe University Press.
- [74] J. Wu, M. D. Watson, L. Zhang, Z. Wang, and K. Müllen. Hexakis(4-iodophenyl)peri-hexabenzocoronene - A versatile building block for highly ordered discotic liquid crystalline materials. *Journal of the American Chemical Society*, 126(1):177– 186, 2004. doi:10.1021/ja037519q.
- [75] E. K. Y. Yapp, J. Akroyd, S. Mosbach, A. A. Knobel, A. J. Smith, D. Chen, E. M. Webster, H. J. Miller, and M. Kraft. Numerical simulation of the evolution of soot precursor particles in a laminar ethylene diffusion flame. *submitted*, 2014.
- [76] B. Zhao, K. Uchikawa, and H. Wang. A comparative study of nanoparticles in premixed flames by scanning mobility particle sizer, small angle neutron scattering, and transmission electron microscopy. *Proceedings of the Combustion Institute*, 31 (1):851–860, 2007. doi:10.1016/j.proci.2006.08.064.