# A quantitative study of the clustering of polycyclic aromatic hydrocarbons at high temperatures

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#### Abstract

The clustering of polycyclic aromatic hydrocarbon (PAH) molecules is investigated in the context of soot particle inception and growth using an isotropic potential developed from the benchmark PAHAP potential. This potential is used to estimate equilibrium constants of dimerisation for five representative PAH molecules based on a statistical mechanics model. Molecular dynamics simulations are also performed to study the clustering of homomolecular systems at a range of temperatures. The results from both sets of calculations demonstrate that at flame temperatures pyrene  $(C_{16}H_{10})$  dimerisation cannot be a key step in soot particle formation and that much larger molecules (e.g. circumcoronene, C54H18) are required to form small clusters at flame temperatures. The importance of using accurate descriptions of the intermolecular interactions is demonstrated by comparing results to those calculated with a popular literature potential with an order of magnitude variation in the level of clustering observed. By using an accurate intermolecular potential we are able to show that physical binding of PAH molecules based on van der Waals interactions alone can only be a viable soot inception mechanism if concentrations of large PAH molecules are significantly higher than currently thought.

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### **1** Introduction

Polycyclic aromatic hydrocarbon (PAH) molecules have often been invoked as key intermediates in the chemistry of soot formation and growth. These molecules have been detected in flames and in soot samples [14, 15, 25, 32, 89]. High resolution transmission electron microscopy (HRTEM) images indicate soot particles have a layered carbon structure, which is interpreted as the stacking of large PAH molecules [8, 27, 79]. However, the mechanism through which condensed-phase soot particles form from the gas phase remains poorly understood [82].

In flame environments PAH molecules grow via chemical reaction and detailed mechanisms have been developed to describe this growth [16]. Initially, the transition from gaseous species to condensed-phase particles was thought to be due solely to chemical growth. However, it was found that whilst models based on chemical growth alone could account for observed soot particle concentrations, the mean particle size was underestimated [17]. In addition to chemical growth, it is argued that physical interactions are also significant [9, 16, 17, 82], with the latter being responsible for particle inception via the dimerisation of PAH molecules and further condensation processes which contribute to particle growth. Recent experimental studies using photoionisation mass spectrometry appear to support the presence of stacked PAH molecules as key precursors to nascent soot formation [21, 22].

This hypothesis has also provoked a number of theoretical studies to determine the stability of PAH molecules present in dimers and larger clusters in flame environments [23, 35– 38, 62, 74]. Miller [36] compared the lifetimes of PAH dimers calculated with the characteristic time for chemical growth and concluded that physical binding was only important for PAH molecules larger than 800 amu. However, Schuetz and Frenklach [62] studied collisions between pyrene ( $C_{16}H_{10}$ ) molecules using molecular dynamics (MD) and concluded that the formation of internal free rotors were sufficient to allow dimers to survive long enough to participate in the nucleation process.

The findings of such studies, together with arguments based on experimentally observed number densities of nascent soot particles and gas-phase PAH concentrations have led to soot growth models which consider the dimerisation of molecules as small as pyrene to be the particle inception step [1, 2, 5, 48, 66]. However, this assumption is questionable given their experimental data: the boiling/sublimation points of molecules as large as coronene ( $C_{24}H_{12}$ , 798.2 K [83]) are much lower than typical flame temperatures (approx. 1500 - 2000 K) [82]. Recent experimental work combined with detailed kinetic modelling has confirmed that pyrene dimerisation cannot be the critical particle inception step [58] and that physical dimerisation will only be significant at sizes well beyond that of pyrene. Coronene clusters have also been studied experimentally [60], indicating cluster evaporation at a temperature of  $535 \pm 50 \text{ K}$  — well below flames temperatures. Moreover, recent MD studies [10, 11] of the nucleation of fullerenes and PAH molecules support the need for larger molecule mass and high molecule concentrations for physical interactions to play a significant role in the nucleation process.

The thermal stability of PAH clusters is also of interest in the astrophysics community where PAH molecules have been proposed as carriers of a family of aromatic infrared bands (AIBs) observed in circumstellar envelopes of carbon-rich stars. PAH clusters are thought to make up small carbonaceous grains inside molecular clouds, which are involved in high velocity collisions [56]. These observations have motivated theoretical studies of the physical properties of PAH clusters, such as structure, stability and aggregation [55, 57].

In seeking to model the physical nucleation of PAH molecules it is important to ensure the intermolecular interactions are modelled accurately across the potential energy surface. This is particularly important when studying nucleation processes as nucleation rates are very sensitive to intermolecular binding energies. As shown later, a variation of 40% in the binding energy can lead to an order of magnitude variation in measures of clustering (Figure 9).

Advances in processing power have enabled intermolecular interactions to be studied in PAH molecules up to the size of coronene [28, 29, 50–52] with accurate quantum chemistry methods. Whilst in many cases these studies represent benchmarks in intermolecular interaction energies, they remain impractical for the study of systems of many large molecules. Typically semi-empirical potentials such as the PM3 potential [69] used in Refs. 62, 87 or empirical atom-atom potentials such as the Lennard-Jones (LJ) parameterisation [78] used in Refs. 11, 23, 55, 57 have been used instead. However, these potentials do not necessarily model PAH intermolecular interactions accurately. The PM3 potential is known to often fail to adequately describe dispersion interactions [18, 33] which determine intermolecular binding, whereas the LJ parameterisation has been shown [73, 75] to significantly overestimate the well depths of interactions between small PAH molecules (by as much as 60% against reference SAPT(DFT) calculations in the case of certain coronene dimer conformations).

In recent work we have developed a transferable anisotropic potential for PAH molecules [75, 76] (termed PAHAP) based on only three types of interaction, C–C, C–H and H–H. In the PAHAP potential the short-range exchange-repulsion was modelled using an anisotropic Born-Mayer term and the long-range dispersion was modelled with a damped isotropic  $C_6$  term. Also included was an electrostatic term based on point-charges. The short-range anisotropic term was fitted from high-accuracy short-range interaction energies for dimers calculated using symmetry adapted perturbation theory (SAPT(DFT)) [42–44]. Coefficients for the long-range dispersion term were calculated using the Williams-Stone-Misquitta method [40, 41, 45] and scaled to match dispersion energies calculated using SAPT(DFT). Electrostatic potential-fitted (ESP) point-charges were originally calculated using the Merz-Singh-Kollman scheme [67] which fits the atomic point-charges to the overall molecular electrostatic potential, but recently a transferable electrostatic model based on quadrupole moments has also been developed [76], which allows us to generate charge models for arbitrary PAH molecules.

This new potential was shown to accurately reproduce intermolecular interactions in a variety of dimer conformations for small PAH molecules. In more recent work [73] the accuracy of this potential was assessed by comparison to experiment in the calculation of the second virial coefficients for benzene and the estimation of the exfoliation energy of graphite as well as comparison to independent SAPT(DFT) data for coronene interactions. This potential represents a benchmark transferable potential for PAH interactions which allows detailed study of the underlying potential energy surfaces of PAH clusters [7].

The aim of this article is to study the clustering of PAH molecules using an accurate intermolecular potential. We do this by studying the thermodynamics of homomolecular dimerisation and the molecular dynamics of large homomolecular systems of five representative PAH molecules (Figure 1). These pericondensed molecules are chosen to span a large range of molecular mass and also for their thermodynamic stability at high temperatures [68]. In section 2 we detail the development of the isotopic version of the PAHAP potential for use in standard simulation codes. In section 3 we study the equilibrium thermodynamics of homomolecular PAH dimerisation using a simple model derived from statistical mechanics. In section 4 we report the results of MD simulations using the isoPAHAP potential at a range of temperatures. Included in this section is a study of the collision efficiency of PAH molecules, which is an important parameter in soot models. We conclude by discussing the implications for the role of physical interactions of PAH molecules in flame environments.



**Figure 1:** *PAH* molecules studied: (a) Pyrene  $(C_{16}H_{10})$ , (b) Coronene  $(C_{24}H_{12})$ , (c) Ovalene  $(C_{32}H_{14})$ , (d) Hexabenzocoronene  $(C_{42}H_{18})$ , (e) Circumcoronene  $(C_{54}H_{18})$ 

### **2** Developing an isotropic PAH potential

The PAHAP potential is a benchmark transferable potential for PAH molecules which describes atomic shape anisotropy using angular expansions. However, the angular dependence of this potential is currently not supported by standard MD codes. We have therefore developed an isotropic potential (termed isoPAHAP) based on the PAHAP reference potential suitable for use in these codes.

Atom-atom intermolecular potentials approximate the total interaction energy U as a sum over all pairwise atomic interactions between molecules, with each molecule treated as a rigid body:

$$U = \sum_{A} \sum_{A < B} \sum_{a \in A} \sum_{b \in B} U_{ab}(R_{ab}, \Omega_{ab}), \tag{1}$$

where  $U_{ab}(R_{ab}, \Omega_{ab})$  denotes an atom-atom interaction potential. The indices A and B are for molecules, and the indices a and b run over all the atomic sites within each molecule. In general the atom-atom interaction potential depends upon the atom-atom separation,  $R_{ab}$ , and their relative molecular orientation, denoted generically by  $\Omega_{ab}$ . Isotropic potentials arise when orientational dependence is neglected as a simplification assuming that the atoms in a molecule are spherically symmetric.

Tab	le	1:	Parameters	for	isoPA	AHAF	potential potential	in	a.u. <sup>a</sup>
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atom pair	ρ	$\alpha$	$C_6$	
CC	6.0434	1.8783	30.282	
СН	4.9562	1.7560	12.605	
ΗН	4.1195	1.4043	5.2179	

<sup>a</sup> The damping coefficient  $\beta$  and the pre-exponential factor G are taken from Ref. [75] to be 1.6485 a.u. and 0.001 a.u. respectively.

The form of the isoPAHAP potential is given in Eq. 2 and is identical to the original PAHAP potential except that the shape function  $\rho$  is no longer orientation-dependent.

$$U_{ab} = G \exp\left[-\alpha_{ab}(R_{ab} - \rho_{ab})\right] - f_6(R_{ab})\frac{C_{6,\text{iso}}}{R_{ab}^6} + \frac{q_a q_b}{R_{ab}},\tag{2}$$

The first term is the short-range Born-Mayer term multiplied by a constant G, set to 0.001 Hartrees, the second is the damped dispersion term and the third is the point-charge electrostatic term. The dispersion is damped with a Tang-Toennies damping function [72]  $f_6(R_{ab})$  given by

$$f_n(R_{ab}) = 1 - \exp(-\beta R_{ab}) \sum_{k=0}^n \frac{(\beta R_{ab})^k}{k!}$$
(3)

where  $\beta = 1.6485$  a.u., taken from Ref [75]. The dispersion damping has been retained due to the particularly soft repulsive wall given by the PAHAP parameters for the H–H interaction. Without damping the dispersion term it was found the MD code encountered problems associated with the singularity at zero separation. In order to use this potential in standard MD codes we used a tabulated version including tabulated first derivatives which also has the benefit of improving computational performance.

As only three types of atomic interaction are considered in the PAHAP potential (C–C, C–H and H–H) it is possible to fit the isotropic potential parameters by considering the interaction energies of a single homomolecular PAH dimer in a variety of conformations. Using this approach, interaction energies were calculated with the PAHAP potential for 2500 pseudo-random coronene dimer conformations. The monomer geometry and atom-centred point-charges for coronene and the other PAH molecules in Figure 1 were taken from our previous work [76]. The conformations were obtained using the ENERGY-SCAN module in the CAMCASP program [39] and energies were evaluated using the ORIENT program [70]. The ORIENT program was also used to fit the parameters of the isoPAHAP potential by a non-linear optimisation. We used tight harmonic constraints to keep the parameters from deviating too far their original values obtained from the PAHAP potential. The resulting parameters for the isoPAHAP potential are shown in Table 1.

Figure 2 shows scatter plots for the isoPAHAP energies of 2500 pseudo-random dimer conformations for each PAH molecule, plotted against the reference PAHAP energies. Also included are energies calculated using Williams' W99 potential [86] and the LJ parameterisation [78] mentioned in section 1. The isoPAHAP potential matches the PA-HAP energies well with an overall rms deviation of  $0.99 \text{ kJ} \text{ mol}^{-1}$ . This compares to  $4.66 \text{ kJ} \text{ mol}^{-1}$  for the W99 potential and  $61.72 \text{ kJ} \text{ mol}^{-1}$  for the LJ parameterisation. The energetically important stacked conformations are also well predicted by the isoPAHAP

potential. The impressive performance of the W99 potential has been noted before [75], and the relative improvement of isoPAHAP potential is because it has been fitted specifically to PAH interactions and contains a damping function. The W99 potential has been fitted to a much broader range of organic molecules and such transferability inevitably leads to a loss of accuracy relative to potentials with a narrower range of applicability. The LJ parameterisation overestimates well depths and also suffers from an overly repulsive wall, leading to large discrepancies with the PAHAP potential.

The transferability of the isoPAHAP potential to PAH molecules other than coronene is not strictly guaranteed despite the interactions being common to all PAH molecules. This is due to the ratio of the total number of C–C, C–H, H–H interactions differing for each molecule. Thus, fitting parameters to total interaction energies will implicitly include the nontransferable ratio of these interactions. The resulting parameterisation however, is shown to account for the interactions of the other molecules very well and provides a suitably accurate intermolecular potential for the study of the clustering of PAH molecules.

### **3** A thermodynamic model for PAH dimerisation

A simple thermodynamic model for the dimerisation of homomolecular PAH molecules can be constructed using elementary statistical mechanics. The dimerisation considered is  $PAH_i + PAH_i \rightleftharpoons (PAH_i)_2$ , for which, in creating the dimer, six new intermolecular vibrational modes are introduced. As these modes are far weaker than the intramolecular modes, we expect to a good approximation weak coupling between intermolecular and intramolecular modes such that the intramolecular modes in the dimer can be assumed to be unchanged from those in the isolated monomers [58, 82]. We therefore approximate the dimers as rigid bodies.

The change in enthalpy and entropy on dimerisation can be derived from standard expressions for ideal polyatomic gases [34]. The molecular partition function is built from translational, rotational, vibrational, and electronic terms. The rigid-rotor-harmonic-oscillator (RRHO) assumption is employed and the zero-point vibrational energy (ZPVE) is included in the vibrational term. Given these assumptions, the enthalpy of dimerisation is

$$\Delta H = \sum_{i=1}^{6} \left( \frac{1}{2} + \frac{1}{e^{h\nu_i/k_B T} - 1} \right) h\nu_i - 4k_B T - E_{\text{int}},\tag{4}$$

where  $\nu_k$  is the *k*th intermolecular vibrational frequency,  $E_{int}$  is the dimer interaction energy, *h* is Planck's constant,  $k_B$  is the Boltzmann constant and *T* is temperature. The entropy of dimerisation is

$$\frac{\Delta S}{k_B} = \ln \left[ \frac{h^6 p}{\pi^5 (8M)^{3/2} (ek_B T)^4} \frac{\sigma_m^2}{\sigma_d} \frac{(I_{A,d} I_{B,d} I_{C,d})^{1/2}}{I_{A,m} I_{B,m} I_{C,m}} \right] + \sum_{i=1}^6 \left[ \frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T} - 1} - \ln \left(1 - e^{-h\nu_i/k_B T}\right) \right]$$
(5)



**Figure 2:** Total interaction energy scatter plots for each PAH molecule. For each plot 2500 random dimer energies have been calculated with each potential and plotted against the PAHAP energies.

where in addition to quantities already defined,  $I_{k,m}$  and  $I_{k,d}$  are the moments of inertia for monomer and dimer respectively for the kth principal axis of each, M is the monomer mass and  $\sigma_m$  and  $\sigma_d$  are the symmetry numbers for monomer and dimer respectively.

From these expressions the equilibrium constant for reaction,  $K_p$ , can be calculated from the Gibb's free energy

$$K_p = \exp\left(-\frac{\Delta G}{k_B T}\right) = \exp\left(-\frac{\Delta H - T\Delta S}{k_B T}\right) \tag{6}$$

The global minimum dimer conformations with associated interaction energies have been obtained using the isoPAHAP potential with the ORIENT program [70]. ORIENT has also been used to determine the intermolecular normal modes and frequencies based on the approach of Pohorille *et al.* [53] which are shown in Table 2. Symmetry numbers and point groups for monomers and dimers are shown in Table 3.

### 3.1 Rigid body interaction energies

Generally, high-symmetry dimer conformations are favoured (Figure 3) by the isoPA-HAP potential and the dimer conformations found for pyrene and coronene match those found using the LJ potential in Ref. 55. The PAHAP potential, however, suggests that the 'shifted graphite' conformation is a lower energy conformation for the coronene dimer than the 'crossed' structure found here [73], in accord with SAPT(DFT) results [50]. The circumcoronene dimer favours the 'graphite' stack over the crossed conformation favoured by the LJ potential [55], although the energy difference between the structures is very small (0.17 kJ mol<sup>-1</sup>). These results suggest that high symmetry can sometimes be an artifact of using an isotropic potential, rather than a genuine preference for the highestsymmetry structures. In all cases, the stacked conformations are favoured over T-shaped dimers, which are the only competitive low-energy minima for smaller PAH molecules [13, 19, 20, 51, 52, 77]. Despite slight differences in the minimum energy conformations depending on the intermolecular potential used, the binding energies between minimum energy conformations differ very little from the PAHAP potential.

### 3.2 Intermolecular vibrations

The intermolecular vibrational modes can generally be separated into two separate groups, the (a) breathing and (b) bending motions being the stiffest, and the (c) shearing and (d) twisting motions the softest. As found with the LJ potential [55] the frequency of the breathing mode grows with increasing PAH mass. The breathing frequency of the circumcoronene dimer is still somewhat below the breathing mode frequency for graphene layers ( $\sim 90 \text{ cm}^{-1}$  [88]).

The increase of the frequencies for larger PAH molecules is due to the stronger interaction per carbon between larger molecules. The repulsion term increases roughly linearly with the number of atoms in a PAH molecule, but because the dispersion interaction acts over longer ranges its contribution increases slightly more rapidly. If the overall interaction scaled exactly linearly with mass, the corresponding force constant would also scale



**Figure 3:** Minimum energy configurations for PAH dimers: (a) Pyrene  $(C_{16}H_{10})$ , (b) Coronene  $(C_{24}H_{12})$ , (c) Ovalene  $(C_{32}H_{14})$ , (d) Hexabenzocoronene  $(C_{42}H_{18})$ , (e) Circumcoronene  $(C_{54}H_{18})$ 

linearly, resulting in the associated frequency remaining constant. However, the effective force constant increases slightly more rapidly than linearly with the mass, which accounts for the increase in the frequency of the breathing mode [55].

The bending mode frequencies are generally slightly lower than those for the breathing modes whilst both the twisting and shearing modes are comparatively soft, which reflects the small corrugation of the molecular planes. Previous work [73] however, highlights that a more pronounced corrugation is actually present and the discrepancy is largely due to an insufficient description of the electrostatic interaction offered by a simple point-charge model. More complex descriptions of the electrostatic interaction, such as distributed multipoles, are required to accurately recover the potential energy surface at positions away from local minima.

### **3.3 Equilibrium constants**

The equilibrium constants for the homomolecular dimerisation (standard state, 1 bar) of the five PAH molecules have been calculated over the temperature range 0 - 2500 K (Figure 4). At high temperatures the harmonic oscillator assumption becomes increasingly inaccurate as anharmonicity becomes important, and the dimer will eventually favour dissociation. A rough measure of the dissociation temperature can be obtained by equating the dimer binding energy  $(-E_{int})$  with the internal energy of the dimer (computed as the sum of translational and rotational degrees of freedom of the constituent molecules in the dimer, 6kT). The transition from solid to dashed line indicates this temperature and serves

Mode (cm <sup>-1</sup> )	★- () () →	$\hat{O}\hat{O}$		↓ () ()†		c) Oc
	(a) breathing	(b) be	nding	(c) she	earing	(d) twisting
(pyrene) <sub>2</sub>	69.97	58.32	56.78	12.46	9.75	7.53
$(coronene)_2$	70.21	66.15	66.15	3.92	3.92	10.27
$(ovalene)_2$	71.55	68.87	65.76	4.58	3.69	8.42
$(hexabenzo coronene)_2$	74.01	67.54	67.54	5.23	5.23	9.03
(circumcoronene) <sub>2</sub>	75.36	70.53	64.81	11.25	7.36	6.45

**Table 2:** Intermolecular frequencies calculated using the isoPAHAP potential

 Table 3: Point groups and rotational symmetry numbers for PAH monomers and dimers

Mologulo	Monomer		Dimer		
WIOICCUIC	Point Group	$\sigma$	Point Group	$\sigma$	
pyrene	$D_{2h}$	4	$C_2$	2	
coronene	$D_{6h}$	12	$D_{6d}$	12	
ovalene	$D_{2h}$	4	$D_2$	4	
hexabenzocoronene	$D_{6h}$	12	$D_{6d}$	12	
circumcoronene	$D_{6h}$	12	$C_{2h}$	2	

to give a rough estimate of the applicability of the model.

For comparison the equilibrium constant calculated for pyrene dimerisation by Sabbah *et al.* [58] is also included which is based on phase space integral treatment of the intermolecular modes. This approach yields a coupled anharmonic prediction of the equilibrium constant, in contrast to our model which assumes harmonic uncoupled intermolecular modes. The minimum energy pyrene dimer conformation predicted by the potential used by Sabbah *et al.* is similar to that predicted by the isoPAHAP potential (Figure 3) and has a similar interaction energy ( $E_{int} = -43.0 \text{ kJ mol}^{-1}$ ). The discrepancy between the models is therefore likely to be mainly due to the lack of anharmonicity in our calculations rather than differences in the potentials, but the model presented here offers an opportunity to get a qualitative grasp of the equilibrium dimerisation of PAH molecules as a function of PAH size.

The general trend shows an expected increase in dimer stability as PAH size increases. The balance between monomer and dimer is reversed (when  $\Delta G = 0$ ) at a temperature of 332 K for pyrene which compares to 401 K reported by Sabbah *et al.* [58]. The corresponding values for coronene, ovalene, hexabenzocoronene and circumcoronene are 591 K, 727 K, 1031 K and 1387 K respectively. These temperatures remain below typical flame temperatures and indicate that even molecules as large as circumcoronene are unlikely to undergo physical dimerisation to a significant degree.

It should be noted, however, that these values are very sensitive to the binding energy. The LJ potential predicts a significantly larger minimum interaction energy for circumcoronene  $(-261.1 \text{ kJ mol}^{-1} \text{ in a } D_6 \text{ twisted conformation})$  which also manifests itself in larger frequencies for the breathing and bending vibrational modes. The increase in the vibrational frequencies acts to lower  $K_p$  and mitigates against the rise caused by the increase in interaction energy, but the combined effect raises the temperature at which  $\Delta G = 0$  to 1815 K. Thus, the LJ potential would predict significant dimerisation at typical flame temperatures (see Figure 9).



**Figure 4:** Equilibrium constants for dimerisation of PAHs as a function of temperature. Transitions from solid to short dashed lines occur at temperature when  $E_{int} = -6kT$ . Below the  $K_p = 1$  ( $\Delta G = 0$ ) line we expect monomers to be more stable.

### 4 Molecular dynamics simulations of PAH clustering

The formation of soot in flames is kinetically controlled and therefore the applicability of models based on equilibrium thermodynamics is limited. In order to assess the stability of PAH clusters in flame-like environments we must consider the dynamic behaviour of molecules as they nucleate into clusters.

Homomolecular systems of the five PAH molecules were simulated using the canonical NVT ensemble with cubical periodic boundary conditions in order to observe the temperature and molecule size dependence on PAH clustering. Each simulation contained 1000 molecules at a concentration of  $2 \times 10^{18}$  cm<sup>-3</sup>. This ensured finite-size effects were negligible [84]. The large number of molecules also ensured robust collision efficiency statistics could be gathered. The Nosé-Hoover thermostatting method [26, 46] was used to maintain a constant temperature with a time constant of 0.05 ps. Five system temperatures

were studied with the highest temperature corresponding to a typical flame temperature: 500 K, 750 K, 1000 K, 1250 K and 1500 K.

As PAH molecules are relatively rigid and possess high intramolecular frequencies, the ability to accommodate collision energy into intramolecular modes is limited and it is the intermolecular modes which will be most important in determining cluster stability. We therefore judge the intermolecular interaction to be most important, warranting the development of the isoPAHAP potential. A tabulated form of the isoPAHAP potential was used to model the intermolecular interactions with a cut-off of 30 Å and a spacing of 0.005 Å, which is sufficient to ensure the interpolation error is negligible. For the intramolecular interactions we follow Ref. 11 by using the aromatic parameters from the OPLS-AA force field [30, 31] for bonds, angles and dihedrals.

Molecules were initially randomly located and orientated around the cell and initial velocities were generated from a Maxwell-Boltzmann distribution. The integration time step was set to 1 fs and trajectories were integrated using the velocity Verlet algorithm [71, 80]. All simulations were performed using the GROMACS 4.5.3 [24] program.

#### 4.1 Simulation timescales

One of the problems in MD simulations is relating MD timescales to the timescales of real processes. The nucleation of soot takes place over milliseconds [81] and running MD simulations for such time periods with a suitably small time step would be impractical. However, if it is assumed that collisions between molecules are distributed randomly, such that the occurrence of a collision does not affect the likelihood of subsequent collision, then behaviour seen over real nucleation timescales can be approximated to some extent by observing denser systems over shorter timescales. Following Refs. 10, 11 the characteristic nucleation time in a flame can be related to the simulation nucleation time in a denser system using the argument set out below.

The collision frequency of a molecule A can be expressed from kinetic theory as

$$Z_A = n_A^2 \pi (b_{\text{coll}})^2 \bar{v}_A,\tag{7}$$

where  $n_A$  and  $\bar{v}_A$  are the concentration and average velocity of molecules A in the system, respectively, and  $b_{coll}$  is the collision diameter. The average velocity is given by

$$\bar{v}_A = \sqrt{\frac{8k_BT}{\pi\mu_{AB}}}\tag{8}$$

where  $\mu_{AB}$  is the reduced mass of molecule A and the colliding molecule.

The number of *effective* collisions, leading to cluster formation and growth, will depend on the energies of collision. Since the distribution of energies of a molecular system at equilibrium for a set temperature is independent of the system density, the proportion of effective collisions is also independent of density. The frequency of effective collisions will therefore be given by  $Z \times P(T)$  where P(T) is the probability of sticking and is a function of temperature only. The characteristic timescale for an effective collision  $\Delta t$ , is then given by  $\Delta t = 1/ZP(T)$ . Therefore, given P(T) is density independent, the characteristic timescales and collision frequencies for a flame and MD simulations can be related,

$$\frac{Z_{\rm MD}}{Z_{\rm Flame}} = \frac{\Delta t_{\rm Flame}}{\Delta t_{\rm MD}}.$$
(9)

As the collision diameters and average velocities in MD simulation and flame are equivalent, by virtue of using the same molecules and temperatures, Eqs. 7 and 9 can be combined to give

$$\Delta t_{\rm Flame} = \Delta t_{\rm MD} \left( \frac{n_{\rm MD}}{n_{\rm Flame}} \right)^2.$$
(10)

Using this relationship, a simulation of 1 ns at a density of  $2 \times 10^{18} \text{ cm}^{-3}$ , would correspond to  $\sim 4 \text{ ms}$  in a real flame containing an aromatics concentration of  $1 \times 10^{15} \text{ cm}^{-3}$  [9]. This gives us a plausible way to approach experimental timescales.

However, there are some limitations to this approach. By using inflated system densities we are in effect increasing the supersaturation of the system, which in turn reduces the critical cluster size according to classical nucleation theory [63]. This means that soot nucleation, in the sense of the formation of critical clusters, cannot be studied in this way. The purpose of using high system densities however, is simply to increase the collision frequency, with the goal of observing the onset of clustering and generating statistics on the number of effective collisions, and in this case the approach is valid.

### 4.2 Cluster identification

In studying molecular clustering it is important to define what constitutes a cluster. A simple distance cut-off measured between molecule centres of mass is insufficient as it fails to distinguish between collisions that result in sticking and those that do not in situations where clusters are constantly being formed and destroyed. Therefore we add a further condition that for a pair of molecules to be considered 'bound' they must satisfy the distance cut-off criterion for a critical period of time [90]. The choice of cut-off separation  $r_{\rm crit}$  and time length  $t_{\rm crit}$  are somewhat arbitrary, but have a significant bearing on the number of clusters detected.

Figure 5 shows how the number of clusters found in a single 1 ns trajectory varies when  $r_{\rm crit}$  and  $t_{\rm crit}$  are independently varied. Extremes of molecule size and temperature are shown to indicate the expected variation. Interestingly, larger molecules, such as circumcoronene, show a minimum in the number of clusters detected as a function of  $r_{\rm crit}$  (Figure 5a). At sufficiently low values of  $r_{\rm crit}$  the larger diameters of the molecules result in groups of molecules falling outside  $r_{\rm crit}$  at certain orientations and what should be a single cluster is counted as multiple clusters. This gives rise to an increase in the number of clusters as  $r_{\rm crit}$  decreases.

The effect of temperature on cluster formation is qualitatively different for the two molecules: for pyrene, increasing temperature reduces the number of clusters, whereas for circumcoronene a increase is seen. This can be explained simply as follows. Raising the temperature increases the number of collisions, bringing molecules into closer proximity more often. For larger molecules with stronger intermolecular interactions this results in more



**Figure 5:** The dependence of cluster sizes on cluster definition parameters; (a)  $t_{crit} = 10 ps$ , (b)  $r_{crit} = 15 \text{ Å}$ .

clusters being formed. However, for smaller molecules which have much weaker binding interactions the increased collision energy makes it harder to form new clusters.

Increasing  $t_{\text{crit}}$  results in an expected fall in the number of clusters which flattens at high  $t_{\text{crit}}$ . As we are interested in cluster stability over comparatively long soot nucleation timescales we chose parameter values which suppress the number of clusters detected:  $r_{\text{crit}} = 12 \text{ Å}$  and  $t_{\text{crit}} = 20 \text{ ps}$ .

We have chosen the Nosé-Hoover thermostat in preference to explicitly modelling the bath gas for computational efficiency. However, because this thermostat modifies the temperatures of all molecules uniformly, heat transfer from the interior of clusters, which would naturally be heated by the condensation process, may become unphysical. This is likely to only be significant in large clusters where interior molecules are separated from the gas-phase. PAH clusters tend to adopt stacked or multi-stacked conformations for which this problem will be less significant. Nevertheless, it is important to consider whether the expected frequency of bath gas collisions with a cluster is sufficient to allow redistribution of collision energy within the stability timescale  $t_{crit}$ . Using Eq. 7, the density of a real flame at 1500 K and 1 bar containing a circumcoronene concentration of  $1 \times 10^{15}$  cm<sup>-3</sup>, increased by a factor of  $2 \times 10^3$  for the MD simulations, gives a collision frequency of  $\sim 20 \,\mathrm{ps^{-1}}$  for a nitrogen bath gas. This assumes the collision radius to be the sum of the radii of the two molecules, taken to be 7.5 Å for circumcoronene and 0.55 Å for nitrogen. Thus, a cluster would be expected to undergo  $\sim 4 \times 10^2$  collisions with the bath gas within the stability timescale. This may well be adequate, though a more detailed simulation would be required to confirm this.

#### 4.3 Simulation results

#### 4.3.1 Effect of molecule size

Five trajectories of 1 ns were run for each homomolecular PAH system and the clustering data was averaged over these runs. Figure 6 shows the averaged proportion of bound

molecules and the averaged maximum cluster size as a function of time for each molecule at each temperature. As temperature increases the expected general trend is observed: the proportion of molecules bound and maximum cluster size reduce for all molecules.

Even at 500 K very few pyrene dimers form, which is consistent with the conclusions of Sabbah *et al.* [58], whilst at 1500 K we see significant clustering only with circumcoronene, and even then only relatively small clusters are formed. At low temperatures much larger clusters are formed for both circumcoronene and hexabenzocoronene, although large variations in maximum cluster size were noted between runs. Between 500 K and 750 K there is little difference between the clustering statistics for these two large molecules, whereas both the proportion of bound molecules and maximum cluster size vary significantly for ovalene and coronene.

At low temperatures cluster lifetimes were generally long for larger molecules and some clusters survived the whole period of simulation (Figure 7a). As the temperature increases the maximum lifetimes of clusters tend to decrease and at 1500 K only the circumcoronene system produced clusters which survived for long periods. The averaged maximum cluster sizes are shown in Figure 7b indicating how generally larger clusters are formed for larger PAH molecules and lower temperatures. Interestingly, the maximum size of circumcoronene clusters increases as the temperature is increased from 500 K to 750 K whereas this quantity decreases for the other molecules. This can be understood as follows. The average velocity of circumcoronene molecules (at a given temperature) is lower than that of the smaller molecules due to their larger mass. Thus the collision rate is lower which leads to fewer opportunities for cluster formation and growth. At 500 K the number of collisions and the proportion which successfully bind are almost identical for the two largest molecules leading to similar maximum cluster sizes. At 750 K the number of collisions increases markedly for both molecular systems but circumcoronene has a greater collision efficiency (number of successful collisions/total number of collisions) than hexabenzocoronene. Both effects combine to result in an increase in the circumcoronene maximum cluster size.

Out of the five homomolecular PAH systems studied, only circumcoronene produces stable clusters at flame temperatures. In Figure 8 we see how the distributions of cluster sizes vary with temperature for the circumcoronene system. At low temperatures an initial rise in dimer concentrations is followed by a decline whilst the number of larger clusters increases. This indicates that there is little barrier to nucleation and subsequent cluster growth. However, at higher temperatures, peaks in dimer concentration are not seen, suggesting either the trajectories are not long enough to capture further growth, or that there is a more significant nucleation barrier precluding growth beyond a certain cluster size [63].

The MD results indicate that large PAH molecules of the order of 50 carbon atoms are required for physical clustering at flame temperatures. However, even at this size it is unclear whether further cluster growth is unhindered or whether the nucleation barrier precludes the formation of larger clusters. It is also unclear to what extent the choice of intermolecular potential affects the degree of clustering.



**Figure 6:** Molecular dynamics results at different temperatures for pyrene (pyr), coronene (cor), ovalene (ova), hexabenzocoronene (hex) and circumcoronene (cir). The upper plots show the percentage of molecules in a bound state and the lower plots show the maximum cluster size for each of the PAH molecules. Standard deviations are indicated by the shaded areas.



**Figure 7:** Molecular dynamics results at different temperatures for pyrene (pyr), coronene (cor), ovalene (ova), hexabenzocoronene (hex) and circumcoronene (cir). (a) maximum lifetimes (averaged lifetimes shown in white bars) and (b) maximum cluster size.

#### 4.3.2 Effect of intermolecular potential and simulation time

In order to investigate influence of simulation time and intermolecular potential single trajectories of 1000 circumcoronene molecules were run for 10 ns with both the isoPAHAP potential and the LJ parameterisation (Figure 9). The proportion of clustered molecules asymptotes after  $\sim 1$  ns with the isoPAHAP potential whereas it takes  $\sim 3$  ns with the LJ potential. However, the value of this quantity differs markedly for the two potentials:  $\sim 15\%$  for the isoPAHAP potential and  $\sim 85\%$  for the LJ potential. Similarly, a large difference is seen in maximum cluster sizes between the isoPAHAP potential, where the cluster size remains between  $\sim 5 - 10$  molecules, and the LJ potential, which produces clusters of up to  $\sim 90$  molecules. The large fluctuations seen for the LJ potential are a consequence of the cluster definition used. Visualising the trajectory showed the formation of large stacks of molecules which bound only loosely to other stacks and therefore did not always lie within the distance cut-off, leading to the rapid fluctuations in maximum cluster size.

The results confirm that choice of potential to model intermolecular interactions is very important. As noted in the thermodynamic analysis (Section 3.3) the LJ potential significantly overbinds the circumcoronene dimer and therefore predicts a much greater concentration of dimers at flame temperatures than the isoPAHAP potential. The same qualitative trends are shown here which suggest that the LJ potential will underestimate the critical size of PAH molecule required for stable cluster formation in flame conditions.

Direct comparison of the MD results with the equilibrium constants is difficult because the clustering seen in the MD results is not restricted to dimerisation, and the equilibrium constant calculations break down at high temperatures. However, at certain temperatures, to a good approximation, only dimers were formed for certain molecules, which allows comparison to the predicted equilibrium dimer concentrations. At 500 K the average pres-



**Figure 8:** Averaged distribution of cluster sizes for circumcoronene at different temperatures.

sure over the five 1 ns pyrene trajectories was 0.215 bar and the average number of dimers in the final 0.1 ns interval was 11.3. This corresponds to an equilibrium constant  $K_p$ , at 1 bar standard pressure, of 0.055 which lies between the value calculated in this work (section 3.3) and the value from Sabbah *et al.* of 0.014 and 0.126 respectively, indicating consistency between the two approaches.



**Figure 9:** Molecular dynamics results for 1000 circumcoronene molecules at 1500 K using the isoPAHAP potential and the LJ parameterisation [78]. The upper plot shows the percentage of molecules in a bound state and the lower plot shows the maximum cluster size for each of the PAH molecules.

### 4.4 Collision efficiency

In the last few years detailed soot models which describe the evolution of soot particles in combustion environments to aid the understanding of the soot formation process with the aim of reducing soot emissions from combustion devices. More recently these models have become much more complex [2, 4, 6, 48, 49, 59, 65], describing several processes, such as gas-phase particle inception, condensation, surface reactions, coagulation and the formation of aggregate structures. The most recent models [59] track individual PAH molecules as they chemically grow and collide to form soot particles. One of the key model quantities, which determines the soot inception and growth rates, is the probability that PAH molecules, or clusters, will stick upon collision. This quantity is termed the *collision efficiency* and is defined as the ratio of successful collisions (*i.e.* collisions which form clusters) to the total number of collisions [12, 54].

The overall collision efficiencies for each homomolecular system, calculated for all collisions regardless of the size of colliding clusters, are shown in Figure 10a. The collision efficiency model developed by Raj *et al.* [54] is also included. This model correlates the collision efficiency to the mass of the smaller collision partner and was obtained by fitting experimental PAH mass spectra obtained from high temperature flames ( $\sim 2000 \text{ K}$ ) to simulated mass spectra obtained using a detailed population balance model.

Direct comparison to the MD results is problematic given that the model proposed by Raj *et al.* defines successful collisions as those in which molecules irreversibly stick to their collision partner. In the MD simulations successful collisions are reversible and therefore the MD collision efficiencies should overestimate the model values. Even so, the MD results indicate that at low flame temperatures ( $\sim 1500 \text{ K}$ ) the collision efficiency should be lower than those suggested by the model, and this supports recent work [58]

which shows that the model significantly overestimates the collision efficiency for pyrene dimerisation.

In Figure 10b we demonstrate a refined collision efficiency model in which the collision efficiency is determined by the temperature and the *reduced mass* of the colliding pair. Correlating the collision efficiency to the reduced mass was chosen pragmatically as it was found to give a better fit than correlating to the combined mass or the smaller mass of the colliding pair.

In order to ensure that a large enough number of collisions had been found to give a reliable collision efficiency, a minimum cut-off was used. This was set to an average of 25 collisions per 1 ns trajectory. From the remaining results the collision efficiency  $C_{\rm E}$  was fitted using a least-squares algorithm based on the reduced mass  $\mu$  of the colliding pair to

$$C_{\rm E} = 1 + \frac{\mu}{a\mu + b} - \frac{1}{a},\tag{11}$$

where a and b are fitting parameters (shown in Table 4) and  $\mu$  is the reduced mass. This functional form was chosen to ensure the correct asymptotic behaviour, *i.e.*  $\lim_{\mu\to\infty} C_{\rm E} = 1$ . Collision efficiencies below 0.01 were ignored to avoid skewing the fit.

At low temperatures this correlation appears to fit the data reasonably well, whereas at higher temperatures the sparsity of data points limits its applicability. The data suggests that at a given temperature there is a critical reduced mass below which the collision efficiency is essentially zero. After this point the collision efficiency will rise but starts to show asymptotic behaviour at larger reduced mass. We anticipate that this correlation will form the basis of new temperature-dependent descriptions of the collision efficiency in soot growth models.



**Figure 10:** Collision efficiencies calculated from MD results for PAHs: (a) the overall collision efficiencies for all collisions as a function of monomer mass for different temperatures, (b) collision efficiency as a function of the reduced mass of the resulting cluster. For comparison (a) contains points calculated using the collision efficiency model reported by Raj et al. [54]

Temperature (K)	Parameters		
	a	b	
500	0.5074	54.13	
750	0.6822	190.0	
1000	0.8032	441.3	
1250	0.8425	714.2	
1500	0.8858	1322	

**Table 4:** Optimised parameters for the collision efficiency model

### **5** Discussion

The aim of this work has been to study the clustering of PAH molecules in the context of soot particle inception. In studying the thermodynamics and molecular dynamics of PAH clustering we have sought to use an accurate description of the intermolecular interactions based on a benchmark PAH potential developed from high-level quantum chemistry calculations.

As mentioned in the introduction the rate of clustering is very sensitive to the binding energies of clusters. We have demonstrated this very clearly by the order of magnitude discrepancy seen between the clustering rates calculated with the isoPAHAP potential and the popular LJ parameterisation, which has been used in several studies of PAH clusters [11, 23, 55, 57]. Consequently, it is of paramount importance that we describe the interaction energies between PAH molecules as accurately as we can so as to reduce or remove uncertainties in our results.

Our results strongly suggest that pyrene dimerisation cannot play a significant role in soot particle inception even at low temperatures (500 K). This is in agreement with recent experimental and theoretical work [58]. Nevertheless, in low-temperature regions of the flame (500 - 1000 K), physical nucleation may still be a competitive route for particle inception and growth for molecules larger than pyrene. However, soot particles are known to undergo gas-phase nucleation and grow in the hottest parts of the flame [61, 85]. At 1500 K only circumcoronene was found to dimerise. This suggests that if van der Waals interactions of PAH molecules are solely responsible for particle inception and growth, large PAH molecules must be present in flame environments. This requirement appears to be supported by the PAH mass spectra reported by Happold *et al.* [21, 22] If the multiple peaks observed on the mass spectra are correctly interpreted to represent PAH monomers, dimers and larger clusters, then the clustered monomer masses can be expected to be approx. 500 amu (approx.  $C_{40}$ ), which is in broad agreement with our results.

Accurately determining the concentration of large PAH molecules in flames has proved to be difficult owing to their low concentrations and consequent problems associated with extraction and separation. A rule of thumb often employed for premixed sooting flames is that peak PAH molecule concentration drops by roughly half an order of magnitude with increments of one pericondensed ring [82]. Therefore, in order to account for the observed number densities of particle nuclei  $(10^{11} - 10^{13} \text{ cm}^{-3})$  it is reasoned that inception with PAH molecules such as pyrene or coronene would be needed which have typical mole fractions of  $10^{-5}$  and  $10^{-7}$  respectively. The 10-ring ovalene molecule would have a mole fraction of roughly  $10^{-8}$ , whereas the 19-ring circumcoronene molecule would be expected to have a mole fraction of roughly  $10^{-13}$ , both of which are too small to account for observed soot nuclei concentrations. However, large PAH molecules have been detected both in the gas phase of flames and in nascent soot particles by some researchers, suggesting they are not as rare as thought. Dobbins *et al.* [14] used laser microprobe mass spectroscopy (LMMS) to analyse ethene diffusion flames and found pericondensed PAH molecules as large as 472 amu in precursor soot particles whilst Siegmann *et al.* [64] detected pericondensed PAH molecules up to 600 amu in the gas-phase in dilute methane flames. These authors suggest inclusion of chemical growth mechanisms other than the accepted acetylene addition pathway, and highlight the possibility of reactive dimerisation of PAH molecules.

An alternative solution to this problem is that intermolecular PAH binding is enhanced in flame environments. It has been argued [37] that excited aromatic dimers (termed 'excimers') would be expected to bind much more tightly than dimers held together by van der Waals interactions alone, although the energies quoted for small PAH excimers are almost identical to those calculated with the PAHAP potential. Recently, it has also been argued [82] that certain PAH molecules exist in open-shell singlet ground states, for which there is evidence of localisation of charge in certain peripheral sites, and that this leads to enhanced attractive interactions. However, as yet there is no numerical evidence to support this statement and to accurately probe the intermolecular interactions of large open-shell PAH structures would require considerable computational resources.

This study has focused on the clustering of pericondensed aromatic hydrocarbons (PCAH), however there is also growing evidence of a significant presence of aliphatic functionalities on the surface of nascent soot particles [3, 47]. This suggests the presence of molecules with aromatic and aliphatic content, such as aromatic-aliphatic-linked hydrocarbons (AALH) or pericondensed aromatics with aliphatic branches (PCAB). Recent MD studies have shown that AALH clusters are less stable than PCAH clusters containing molecules of similar mass at flame temperatures [11, 87]. However, PCAB molecules have been shown to cluster at faster rates than PCAH molecules despite having similar collision efficiencies [11]. This may imply that the aliphatic branches present in PCAB molecules act as soft modes which enable the molecule to accommodate more of the collision energy than is possible with PCAH molecules, thus increasing cluster stability. Nevertheless, the collision efficiency seems to be dependent on the pericondensed aromatic content of the molecule, which accounts for the strong  $\pi$  stacking interactions, and this indicates that the size of PCAH remains the key factor for particle inception.

Techniques similar to those we have used in this work could be used to rigourously analyse the proposals outlined above. However if stronger intermolecular interactions or the presence of soft intramolecular vibration modes prove to be insufficient to describe soot nucleation, then it must be concluded that the physical nucleation route can only play a significant role in soot particle inception if concentrations of larger PAH molecules are much higher than currently thought. This requires a mechanism which can account for swift chemical growth of PAH molecules to sizes well beyond pyrene.

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## References

- 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.
- [2] M. Balthasar and M. Kraft. A stochastic approach to solve the particle size distribution function of soot particles in laminar premixed flames. *Combustion and Flame*, 133:289–298, 2003. doi:10.1016/S0010-2180(03)00003-8.
- [3] J. P. Cain, P. L. Gassman, H. Wang, and A. Laskin. Micro-ftir study of soot chemical composition-evidence of aliphatic hydrocarbons on nascent soot surfaces. *Physical Chemistry Chemical Physics*, 12:5206–5218, 2010. doi:10.1039/B924344E.
- [4] M. S. Celnik, R. I. A. Patterson, M. Kraft, and W. Wagner. Coupling a stochastic soot population balance to gas-phase chemistry using operator splitting. *Combustion* and Flame, 148(3):158–176, 2007. doi:10.1016/j.combustflame.2006.10.007.
- [5] M. S. Celnik, A. Raj, R. H. West, R. I. A. Patterson, and M. Kraft. An aromatic site description of soot particles. *Combustion and Flame*, 155(1-2):161–180, 2008. doi:10.1016/j.combustflame.2008.04.011.
- [6] M. S. Celnik, M. Sander, A. Raj, R. H. West, and M. Kraft. Modelling soot formation in a premixed flame using an aromatic-site soot model and an improved oxidation rate. *Proceedings of the Combustion Institute*, 32(1):639–646, 2009. doi:10.1016/j.proci.2008.06.062.
- [7] D. Chakrabarti, T. S. Totton, M. Kraft, and D. Wales. A survey of the potential energy surface for (benzene)<sub>13</sub> cluster. Submitted to Physical Chemistry Chemical Physics.
- [8] H. X. Chen and R. A. Dobbins. Crystallogenesis of particles formed in hydrocarbon combustion. *Combustion Science and Technology*, 159(1):109–128, 2000. doi:10.1080/00102200008935779.
- [9] S. H. Chung and A. Violi. Insights on the nanoparticle formation process in counterflow diffusion flames. *Carbon*, 45(12):2400–2410, 2007. doi:10.1016/j.carbon.2007.07.003.
- [10] S. H. Chung and A. Violi. Nucleation of fullerenes as a model for examining the formation of soot. *The Journal of Chemical Physics*, 132(17):174502, 2010. doi:10.1063/1.3345630.
- [11] S. H. Chung and A. Violi. Peri-condensed aromatics with aliphatic chains as key intermediates for the nucleation of aromatic hydrocarbons. *Proceedings of the Combustion Institute*, 33(1):693–700, 2011. doi:10.1016/j.proci.2010.06.038.

- [12] A. D'Alessio, A. C. Barone, R. Cau, A. D'Anna, and P. Minutolo. Surface deposition and coagulation efficiency of combustion generated nanoparticles in the size range from 1 to 10 nm. *Proceedings of the Combustion Institute*, 30(2):2595–2603, 2005. doi:10.1016/j.proci.2004.08.267.
- [13] R. A. DiStasio, Jr., G. von Helden, R. P. Steele, and M. Head-Gordon. On the T-shaped structures of the benzene dimer. *Chemical Physics Letters*, 437(4-6):277– 283, 2007. doi:10.1016/j.cplett.2007.02.034.
- [14] R. A. Dobbins, R. A. Fletcher, and H. C. Chang. The evolution of soot precursor particles in a diffusion flame. *Combustion and Flame*, 115(3):285–298, 1998. ISSN 0010-2180. doi:10.1016/S0010-2180(98)00010-8.
- [15] R. A. Dobbins, R. A. Fletcher, B. A. Benner Jr., and S. Hoeft. Polycyclic aromatic hydrocarbons in flames, in diesel fuels, and in diesel emissions. *Combustion and Flame*, 144(4):773–781, 2006. doi:10.1016/j.combustflame.2005.09.008.
- [16] M. Frenklach. Reaction mechanism of soot formation in flames. *Physical Chemistry Chemical Physics*, 4:2028–2037, 2002. doi:10.1039/b110045a.
- [17] M. Frenklach and H. Wang. Detailed modeling of soot particle nucleation and growth. Symposium (International) on Combustion, 23(1):1559–1566, 1991. doi:10.1016/S0082-0784(06)80426-1.
- [18] T. J. Giese, E. C. Sherer, C. J. Cramer, and D. M. York. A semiempirical quantum model for hydrogen-bonded nucleic acid base pairs. *Journal of Chemical Theory* and Computation, 1(6):1275–1285, 2005. doi:10.1021/ct0501021.
- [19] C. Gonzalez and E. C. Lim. A quantum chemistry study of the van der Waals dimers of benzene, naphthalene, and anthracene: Crossed  $(d_{2d})$  and parallel-displaced  $(c_{2h})$  dimers of very similar energies in the linear polyacenes. *Journal of Physics and Chemistry of Solids*, 104(13):2953–2957, 2000. doi:10.1021/jp9936421(74)80240-4.
- [20] S. Grimme. Accurate description of van der Waals complexes by density functional theory including empirical corrections. *Journal of Computational Chemistry*, 25 (12):1463–1473, 2004. doi:10.1002/jcc.20078.
- [21] 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.
- [22] J. Happold, H. H. Grotheer, and M. Aigner. Soot precursors consisting of stacked pericondensed PAHs. In H. Bockhorn, A. D'Anna, A. F. Sarofim, and H. Wang, editors, *Combustion Generated Fine Carbonaceous Particles*, pages 275–285. Karlsruhe University Press, 2007.
- [23] 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.

- [24] B. Hess, C. Kutzner, D. van der Spoel, and E. Lindahl. Gromacs 4: Algorithms for highly efficient, load-balanced, and scalable molecular simulation. *Journal of Chemical Theory and Computation*, 4(3):435–447, 2008. doi:10.1021/ct700301q.
- [25] K. Homann. Formation of large molecules, particulates and ions in premixed hydrocarbon flames; progress and unresolved questions. *Symposium (International) on Combustion*, 20(1):857–870, 1985. doi:10.1016/S0082-0784(85)80575-0.
- [26] W. G. Hoover. Canonical dynamics: Equilibrium phase-space distributions. *Phys. Rev. A*, 31(3):1695–1697, 1985. doi:10.1103/PhysRevA.31.1695.
- [27] T. Ishiguro, Y. Takatori, and K. Akihama. Microstructure of Diesel Soot Particles Probed by Electron Microscopy: First Observation of Inner Core and Outer Shell. *Combustion and Flame*, 108(1-2):231–234, 1997. doi:10.1016/S0010-2180(96)00206-4.
- [28] T. Janowski and P. Pulay. High accuracy benchmark calculations on the benzene dimer potential energy surface. *Chemical Physics Letters*, 447(1-3):27–32, 2007. doi:10.1016/j.cplett.2007.09.003.
- [29] T. Janowski, A. Ford, and P. Pulay. Accurate correlated calculation of the intermolecular potential surface in the coronene dimer. *Molecular Physics*, 108:249–257, 2010. doi:10.1080/00268970903397249.
- [30] W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. *Journal of the American Chemical Society*, 118(45):11225–11236, 1996. doi:10.1021/ja9621760.
- [31] 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.
- [32] Y. Li, L. Zhang, Z. Tian, T. Yuan, J. Wang, B. Yang, and F. Qi. Experimental study of a fuel-rich premixed toluene flame at low pressure. *Energy & Fuels*, 23(3):1473– 1485, 2009. doi:10.1021/ef800902t.
- [33] J. P. McNamara and I. H. Hillier. Semi-empirical molecular orbital methods including dispersion corrections for the accurate prediction of the full range of intermolecular interactions in biomolecules. *Phys. Chem. Chem. Phys.*, 9:2362–2370, 2007. doi:10.1039/B701890H.
- [34] D. A. McQuarrie. *Statistical Mechanics*. HarperCollinsPublishers, New York, 1976.
- [35] J. T. McKinnon and J. B. Howard. The roles of PAH and acetylene in soot nucleation and growth. *Symposium (International) on Combustion*, 24(1):965–971, 1992. doi:10.1016/S0082-0784(06)80114-1.

- [36] J. H. Miller. The kinetics of polynuclear aromatic hydrocarbon agglomeration in flames. *Symposium (International) on Combustion*, 23(1):91–98, 1990. doi:10.1016/S0082-0784(06)80246-8.
- [37] J. H. Miller. Aromatic excimers: evidence for polynuclear aromatic hydrocarbon condensation in flames. *Proceedings of the Combustion Institute*, 30(1):1381–1388, 2005. doi:10.1016/j.proci.2004.08.192.
- [38] J. H. Miller, K. C. Smyth, and W. G. Mallard. Calculations of the dimerization of aromatic hydrocarbons: Implications for soot formation. *Symposium (International)* on Combustion, 20(1):1139–1147, 1985. doi:10.1016/S0082-0784(85)80604-4.
- [39] A. J. Misquitta and A. J. Stone. CamCASP: a program for studying intermolecular interactions and for the calculation of molecular properties in distributed form, 2007. http://www-stone.ch.cam.ac.uk/programs.html.
- [40] A. J. Misquitta and A. J. Stone. Dispersion energies for small organic molecules: first row atoms. *Molecular Physics*, 106(12-13):1631–1643, 2008. doi:10.1080/00268970802258617.
- [41] A. J. Misquitta and A. J. Stone. Accurate induction energies for small organic molecules: 1. Theory. *Journal of Chemical Theory and Computation*, 4(1):7–18, 2008. doi:10.1021/ct700104t.
- [42] A. J. Misquitta and K. Szalewicz. Intermolecular forces from asymptotically corrected density functional description of monomers. *Chemical Physics Letters*, 357 (3-4):301–306, 2002. doi:10.1016/S0009-2614(02)00533-X.
- [43] A. J. Misquitta, B. Jeziorski, and K. Szalewicz. Dispersion energy from densityfunctional theory description of monomers. *Phys. Rev. Lett.*, 91(3):033201, 2003. doi:10.1103/PhysRevLett.91.033201.
- [44] A. J. Misquitta, R. Podeszwa, B. Jeziorski, and K. Szalewicz. Intermolecular potentials based on symmetry-adapted perturbation theory with dispersion energies from time-dependent density-functional calculations. *The Journal of Chemical Physics*, 123(21):214103, 2005. doi:10.1063/1.2135288.
- [45] A. J. Misquitta, A. J. Stone, and S. L. Price. Accurate induction energies for small organic molecules. 2. Development and testing of distributed polarizability models against SAPT(DFT) energies. *Journal of Chemical Theory and Computation*, 4(1): 19–32, 2008. doi:10.1021/ct700105f.
- [46] S. Nosé. A molecular dynamics method for simulations in the canonical ensemble. *Molecular Physics*, 52(2):255–268, 1984. doi:10.1080/00268978400101201.
- [47] B. Öktem, M. P. Tolocka, B. Zhao, H. Wang, and M. V. Johnston. Chemical species associated with the early stage of soot growth in a laminar premixed ethylene-oxygen-argon flame. *Combustion and Flame*, 142(4):364–373, 2005. doi:10.1016/j.combustflame.2005.03.016.

- [48] R. I. A. Patterson and M. Kraft. Models for the aggregate structure of soot particles. *Combustion and Flame*, 151:160–172, 2007. doi:10.1016/j.combustflame.2007.04.012.
- [49] R. I. A. Patterson, J. Singh, M. Balthasar, M. Kraft, and W. Wagner. Extending stochastic soot simulation to higher pressures. *Combustion and Flame*, 145(3):638– 642, 2006. doi:10.1016/j.combustflame.2006.02.005.
- [50] R. Podeszwa. Interactions of graphene sheets deduced from properties of polycyclic aromatic hydrocarbons. *The Journal of Chemical Physics*, 132(4):044704, 2010. doi:10.1063/1.3300064.
- [51] R. Podeszwa and K. Szalewicz. Physical origins of interactions in dimers of polycyclic aromatic hydrocarbons. *Physical Chemistry Chemical Physics*, 10(19):2735– 2746, 2008. doi:10.1039/b719725j.
- [52] R. Podeszwa, R. Bukowski, and K. Szalewicz. Potential energy surface for the benzene dimer and perturbational analysis of  $\pi$ - $\pi$  interactions. *The Journal of Physical Chemistry A*, 110(34):10345–10354, 2006. doi:10.1021/jp0640950.
- [53] A. Pohorille, L. R. Pratt, R. A. LaViolette, M. A. Wilson, and R. D. MacElroy. Comparison of the structure of harmonic aqueous glasses and liquid water. *The Journal of Chemical Physics*, 87(10):6070–6077, 1987. doi:10.1063/1.453481.
- [54] 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.
- [55] M. Rapacioli, F. Calvo, F. Spiegelman, C. Joblin, and D. J. Wales. Stacked clusters of polycyclic aromatic hydrocarbon molecules. *Journal of Physical Chemistry A*, 109(11):2487–2497, 2005. doi:10.1021/jp046745z.
- [56] M. Rapacioli, C. Joblin, and P. Boissel. Spectroscopy of polycyclic aromatic hydrocarbons and very small grains in photodissociation regions. *Astronomy & Astrophysics*, 429(1):193–204, 2005. doi:10.1051/0004-6361:20041247.
- [57] M. Rapacioli, F. Calvo, C. Joblin, P. Parneix, D. Toublanc, and F. Spiegelman. Formation and destruction of polycyclic aromatic hydrocarbon clusters in the interstellar medium. *Astronomy & Astrophysics*, 460(2):519–531, 2006. doi:10.1051/0004-6361:20065412.
- [58] H. Sabbah, L. Biennier, S. J. Klippenstein, I. R. Sims, and B. R. Rowe. Exploring the role of PAHs in the formation of soot: Pyrene dimerization. *The Journal of Physical Chemistry Letters*, 1(19):2962–2967, 2010. doi:10.1021/jz101033t.
- [59] 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.

- [60] 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.
- [61] S. Schraml, S. Dankers, K. Bader, S. Will, and A. Leipertz. Soot temperature measurements and implications for time-resolved laser-induced incandescence (TIRE-LII). *Combustion and Flame*, 120(4):439–450, 2000. doi:10.1016/S0010-2180(99)00117-0.
- [62] 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.
- [63] R. P. Sear. Nucleation: theory and applications to protein solutions and colloidal suspensions. *Journal of Physics: Condensed Matter*, 19(3):033101, 2007. doi:10.1088/0953-8984/19/3/033101.
- [64] K. Siegmann, H. Hepp, and K. Sattler. Reactive dimerization: A new PAH growth mechanism in flames. *Combustion Science and Technology*, 109(1-6):165–181, 1995. doi:10.1080/00102209508951900.
- [65] J. Singh, M. Balthasar, M. Kraft, and W. Wagner. Stochastic modelling of soot particle size and age distribution in laminar premixed flames. *Proceedings of the Combustion Institute*, 30:1457–1465, 2005. doi:10.1016/j.proci.2004.08.120.
- [66] J. Singh, R. I. A. Patterson, M. Kraft, and H. Wang. Numerical simulation and sensitivity analysis of detailed soot particle size distribution in laminar premixed ethylene flames. *Combustion and Flame*, 145:117–127, 2006. doi:10.1016/j.combustflame.2005.11.003.
- [67] U. C. Singh and P. A. Kollman. An approach to computing electrostatic charges for molecules. *Journal of Computational Chemistry*, 5(2):129–145, 1984. doi:10.1002/jcc.540050204.
- [68] 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.
- [69] J. J. P. Stewart. Optimization of parameters for semiempirical methods I. Method. *Journal of Computational Chemistry*, 10(2):209–220, 1989. doi:10.1002/jcc.540100208.
- [70] A. J. Stone, A. Dullweber, O. Engkvist, E. Fraschini, M. P. Hodges, A. W. Meredith, D. R. Nutt, P. L. A. Popelier, and D. J. Wales. ORIENT: a program for studying interactions between molecules, version 4.6, University of Cambridge, 2002. http://www-stone.ch.cam.ac.uk/programs.html.
- [71] W. C. Swope, H. C. Andersen, P. H. Berens, and K. R. Wilson. A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters. *The Journal of Chemical Physics*, 76(1):637–649, 1982. doi:10.1063/1.442716.

- [72] K. T. Tang and J. P. Toennies. An improved simple model for the van der waals potential based on universal damping functions for the dispersion coefficients. *The Journal of Chemical Physics*, 80(8):3726–3741, 1984. doi:10.1063/1.447150.
- [73] T. S. Totton, A. J. Misquitta, and M. Kraft. Assessing the PAHAP potential with application to the exfoliation energy of graphite. Submitted to The Journal of Physical Chemistry A.
- [74] T. S. Totton, D. Chakrabarti, A. J. Misquitta, 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.
- [75] 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.
- [76] 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.
- [77] S. Tsuzuki, K. Honda, T. Uchimaru, and M. Mikami. High-level *ab initio* computations of structures and interaction energies of naphthalene dimers: Origin of attraction and its directionality. *The Journal of Chemical Physics*, 120(2):647–659, 2004. doi:10.1080/00268970110089432.
- [78] B. W. van de Waal. Calculated ground-state structures of 13-molecule clusters of carbon dioxide, methane, benzene, cyclohexane, and napthalene. *Journal of Chemical Physics*, 79(8):3948–3961, 1983. doi:10.1063/1.446263.
- [79] R. L. Vander Wal, A. Yezerets, N. W. Currier, D. H. Kim, and C. M. Wang. HRTEM Study of diesel soot collected from diesel particulate filters. *Carbon*, 45:70–77, 2007. doi:10.1016/j.carbon.2006.08.005.
- [80] L. Verlet. Computer "experiments" on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules. *Phys. Rev.*, 159(1):98, 1967. doi:10.1103/PhysRev.159.98.
- [81] H. G. Wagner. Soot formation in combustion. Symposium (International) on Combustion, 17(1):3–19, 1979. doi:10.1016/S0082-0784(79)80005-3.
- [82] H. Wang. Formation of nascent soot and other condensed-phase materials in flames. *Proceedings of the Combustion Institute*, 33(1):41–67, 2011. doi:10.1016/j.proci.2010.09.009.
- [83] R. Weast and J. Grasselli. *Handbook of data on organic compounds*. Number v. 2. CRC Press, 2nd edition, 1989.
- [84] J. Wedekind, D. Reguera, and R. Strey. Finite-size effects in simulations of nucleation. *The Journal of Chemical Physics*, 125(21):214505, 2006. doi:10.1063/1.2402167.

- [85] M. Weikl, T. Seeger, M. Wendler, R. Sommer, F. Beyrau, and A. Leipertz. Validation experiments for spatially resolved one-dimensional emission spectroscopy temperature measurements by dual-pump cars in a sooting flame. *Proceedings of the Combustion Institute*, 32(1):745–752, 2009. doi:10.1016/j.proci.2008.07.019.
- [86] D. E. Williams. Improved intermolecular force field for crystalline oxohydrocarbons including O–H...O hydrogen bonding. *Journal of Computational Chemistry*, 22(1): 1–20, 2001. doi:10.1002/1096-987X(20010115)22:1;1::AID-JCC2;,3.0.CO;2-6.
- [87] D. Wong, R. Whitesides, C. A. Schuetz, and M. Frenklach. Molecular dynamics simulations of PAH dimerization. In H. Bockhorn, A. D'Anna, A. F. Sarofim, and H. Wang, editors, *Combustion Generated Fine Carbonaceous Particles*, pages 245– 255. Karlsruhe University Press, 2007.
- [88] J. Yan, W. Y. Ruan, and M. Y. Chou. Phonon dispersions and vibrational properties of monolayer, bilayer, and trilayer graphene: Density-functional perturbation theory. *Phys. Rev. B*, 77(12):125401, 2008. doi:10.1103/PhysRevB.77.125401.
- [89] B. Yang, Y. Li, L. Wei, C. Huang, J. Wang, Z. Tian, R. Yang, L. Sheng, Y. Zhang, and F. Qi. An experimental study of the premixed benzene/oxygen/argon flame with tunable synchrotron photoionization. *Proceedings of the Combustion Institute*, 31 (1):555–563, 2007. doi:10.1016/j.proci.2006.07.171.
- [90] K. Yasuoka and M. Matsumoto. Molecular dynamics of homogeneous nucleation in the vapor phase. I. Lennard-Jones fluid. *The Journal of Chemical Physics*, 109(19): 8451–8462, 1998. doi:10.1063/1.477509.