Determination of the attractive force, adhesive force, adhesion energy and Hamaker constant of soot particles generated from a premixed methane/oxygen flame by AFM

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Abstract: Atomic force microscopy (AFM) was used to characterize the attractive force, adhesive force and adhesion energy between an AFM probe tip and nanometric soot particle generated by a premixed methane/oxygen flame. Different attractive force distributions were found when increasing the height above burner (HAB), with forces ranging from 1.1–3.5 nN. As the HAB was increased, the average attractive force initially increased, briefly decreased, and then underwent a gradual increase, with a maximum of 2.54 nN observed at HAB = 25 mm. The mean adhesive force was 6.5–7.5 times greater than the mean attractive force at the same HAB, and values were in the range of 13.5–24.5 nN. The adhesion energy was in the range of 2.0–5.6 × 10^{-17} J. The variations observed in the average adhesion energy with increasing HAB were different from those of the average adhesion force, implying that the stretched length of soot particles is an important factor affecting the average adhesion energy. The Hamaker constants of the soot particles generated at different HABs were determined from AFM force-separation curves. The average Hamaker constant exhibited a clear correlation with the graphitization degree of soot particles as obtained from Raman spectroscopy.

Keywords: Soot particle; Atomic force microscopy; Attractive force; Adhesive force; Adhesion energy; Hamaker constant

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1. Introduction

Soot particles are an important pollutant resulting from combustion. Due to their adverse impact on the environment and human health [1,2], soot particles continue to receive much attention in the field of combustion research. Theoretically, soot formation and evolution involves six well-known processes, all of which occur within the span of a few milliseconds: pyrolysis, nucleation, coagulation, surface growth, agglomeration, and oxidation [3]. It is widely accepted that particle coagulation is a significant step leading to soot formation. This phenomenon occurs when one particle collides with another at low speed, following which the particles adhere. Conversely, thermal rebound takes place when the particle velocity exceeds a critical value such that the particles fail to coagulate [4–6]. In the case of small soot particles, the thermal rebound effect can cause the coagulation efficiency to be less than unity. This is because the kinetic energy of particles undergoing Brownian motion may be greater than the adhesion energy resulting from Van der Waals forces, causing the particles to rebound after collision [4,5,7]. In general, the soot coagulation rate depends on various factors, such as temperature, and particle size and surface properties [4,5]. Thus, a study of the surface properties of soot particles is helpful in understanding the particle coagulation mechanism.

Investigations of soot particle surface properties to date have examined the effects of soot nanostructure, primary particle size, surface area, sphericity ratio and surface functional groups [8–14], while few have assessed the force properties of soot particles. Based on the above, the present work employed atomic force microscopy (AFM) to determine the attractive force, adhesive force and adhesion energy of soot particles generated from a premixed methane/oxygen flame.

When measuring the forces between soot particles by AFM, a particle is normally secured to the

probe tip and then brought into contact with another particle on a substrate. However, securing a nano-sized soot particle to the probe tip is extremely difficult and, once this is achieved, precisely positioning the probe tip at the test soot particle is also arduous. For this reason, we performed direct measurements between the probe tip and various soot particles without first securing a particle to the probe tip. The soot particles generated from a premixed methane/oxygen flame were collected on mica substrates using a thermophoretic sampling system. The attractive force, adhesive force and adhesion energy between these soot particles and the bare probe tip were obtained at different heights above burner (HAB) values. In addition, the Hamaker constants of the soot particles were determined based on the curve of the attractive force measured by AFM, and the possibility of a correlation between the Hamaker constant and the degree of soot graphitization was examined.

2. Materials and methods

2.1. Burner and sampling system

A laminar premixed flame was generated at atmospheric pressure over a 25 mm diameter cooled water sintered bronze McKenna burner (Holthuis & Associates, Sebastopol, USA). The central tube of the burner was used to supply a mixture of methane and oxygen while the concentric porous ring was used to generate a N_2 shield (at a flow rate 30 L/min) that eliminated the interference of the surrounding air on the flame. Three independent mass-flow controllers, each with an accuracy of ±0.02%, were used to adjust the methane, oxygen and shielding gas flows. The fuel/air equivalence ratio in the flame was maintained at 2.4 and the cold gas velocity was kept constant at 6 cm/s. A precision lifting platform (BOCI, Beijing, China) with a positional accuracy of ±0.02 mm was used to adjust the vertical height of the burner. A thermophoretic sampling system based on the thermophoresis principle was employed to sample the flame soot particles. This system incorporated

an advanced linear electric cylinder (FESTO, Germany) that allowed precise and rapid reciprocating motion, with an acceleration and speed of 120 m/s^2 and 3 m/s, respectively. The piston rod was attached to self-closing tweezers (N5, Switzerland) to conveniently fix and detach the mica substrate [15]. A mica substrate with a diameter of 9.9 mm and a carbon supporting film with a diameter of 3 mm were clamped in the tweezers to obtain soot particles at HAB values of 2, 5, 10, 15 and 25 mm. In addition, Teflon filter was used to collect soot samples for Raman analysis using the probe sampling technique. A detailed description of the probe sampling technique has previously been reported in the literature [16]. A customized fast response R-type thermocouple (Pt/Pt-13% Rh with a junction bead diameter of 150 μm) affixed to the electric cylinder was used to measure the flame temperature. After sampling soot particles, the mica substrate and carbon supporting film were stored in a clean culture dish in preparation for the AFM and TEM measurements, and the soot samples on the Teflon filter were scraped to seal in glass bottles for Raman analysis.

2.2. AFM measurements

A silicon rectangular cantilever probe (ContAl, tip radius of 10 nm, BudgetSensors, Bulgaria) with an alumina reflex coating was employed in conjunction with an Agilent 5100 AFM instrument, operating at room temperature and 15% relative humidity. The cantilever spring constant of the probe (k_c) was determined by the thermal noise method [17] to be 0.3427 N m^{-1}. The initial deflection of the probe was –1.0±0.05 V, and the set point was 0 V. The topography of each soot particle deposited on the mica substrate was imaged in the contact mode to locate the particle. Based on the contact mode image, the defined position of the soot particle was selected for the subsequent force analysis (Fig. 1, as indicated by arrows). As the probe approached or retracted from a soot particle, the interactive force between the probe tip and soot particle caused a cantilever deflection,

leading to a shift in the angle of the reflected beam. This shift was detected by the photodiode, resulting in a voltage signal. The degree of cantilever deflection (d) was calculated as $d = \frac{V}{S}$, where V is the signal voltage and S is the photodetector sensitivity as determined based on calibration using freshly cleaved mica as a hard, non-deformable substrate [18]. The associated displacement of the piezoelectric crystal was recorded simultaneously, yielding cantilever deflection versus piezoelectric displacement data. These data were transformed into the force-piezoelectric displacement plot in Fig. 2b based on Hooke's law, $F=k_c \times d$, where F is the interactive force. A force-separation (or force-tip displacement) plot was obtained from Fig. 2b using the scanning probe image processor (S.P.I.P.) software package, as shown in Fig. 2c. From this force-separation curve, we generated the attractive and adhesive forces between the probe tip and soot particle. For each HAB tested, more than 40 particles were selected so as to ensure statistically significant data, and the probe was cleaned in anhydrous ethanol after each sample measurement [19]. Force measurements were repeated at least three times for each particle under the same conditions, and the results were then averaged. The error in the force measurement was determined to be less than 0.02 nN.

2.3. TEM and Raman scattering spectroscopy

Transmission electron microscopy (TEM, Philips Tecnai F20) with a point resolution of 0.248 nm and operating at 200 kV was used to obtain 20,000× images showing the soot morphology. Raman spectra have been recorded by a Renishaw 1000 Raman microscope system using an Ar ion excitation laser with a wavelength of 514.5 nm and 20 mW maximum laser power. Calibration was performed with a silicon wafer by utilizing the first-order phonon band of Si at 520 cm^{-1}. Spectra of soot samples deposited on quartz plates were taken over the range of 2000–900 cm^{-1} with a 50 × magnification objective. An explosion time of 60 s and 5% of the laser beam power were used to

avoid altering or burning the soot sample [20,21]. For each sample, the scanning area was 2 μm in diameter and spectra were recorded at approximately 10 positions. The average of these data was subsequently computed, and an uncertainty of less than 5% was obtained.

3. Results and discussion

3.1. Attractive force

The force curve measurements involved two procedures. For each soot sample, a topographical image of the soot particles deposited on the mica substrate was obtained in the contact mode over an area of 1 × 1 μm to locate the particle. Subsequently, force curve measurements were carried out for the selected particle. During the approach phase, the probe tip typically progressed from point A to B, and then underwent a so-called "jump-to-contact" from B to B′, as shown in Fig. 2c. Jump-to-contact occurs when the force gradient of the interaction exceeds the cantilever spring constant [22] and this phenomenon was observed for each soot sample. The value of the attractive force (F_{at}) between the probe tip and soot particle was subsequently calculated based on Hooke's law. In this study, attractive forces were determined for different amounts of soot deposited on the mica substrate at each HAB value by varying the residence time of the substrate in the flame. The measurement results clearly demonstrated that the attractive force is affected only by the properties of the soot particles rather than by the amount of samples collected.

Fig. 3 presents the F_{at} distributions at various HAB values, and demonstrates that the distributions changed along with the HAB. The F_{at} at HAB = 2 mm had a very narrow distribution, with values in the range of 1.1–2.2 nN, while the broadest distribution was observed at HAB = 15 mm, with values in the range of 1.4–3.5 nN. Moreover, upon increasing the HAB from 2 to 5 mm, the F_{at} distribution moved toward higher values, with approximately 64% of F_{at} values above 1.8 nN

at HAB = 2 mm but 87% of F_{at} above this same level at HAB = 5 mm. However, as the HAB was further increased from 5 to 10 mm, the F_{at} distribution shifted toward lower values, with 78% of F_{at} above 1.8 nN at HAB = 10 mm. Upon further increasing the HAB from 10 to 25 mm, the F_{at} exhibited a somewhat broader distribution. This result is attributed to the mixture of nanoparticles and mature soot particles generated at higher HAB values [1,23], which possesses a relatively broad distribution of attractive forces.

The population-averaged attractive force values ($\overline{F_{at}}$) are plotted as a function of HAB in Fig. 4. Here, $\overline{F_{at}}$ is seen to increase with increases in the HAB value from 2 to 25 mm, other than a $\overline{F_{at}}$ decrease on going from HAB = 5 to 10 mm, with a maximum of 2.54 nN observed at HAB = 25 mm. Harris et al. [24] reported that the interactive forces between soot particles primarily result from Van der Waals forces, and these forces can cause an increase at collision rates, thereby promoting the coagulation of soot particles. In Fig. 1, the primary particle diameter in TEM images and equivalent diameter in AFM images were determined using ImageJ and S.P.I.P. software, respectively. For each sample, more than 150 particles were randomly chosen to determine the population-averaged values of primary particle diameters (d_p) and equivalent diameter (d_e). The d_p and d_e of soot particles at different HABs are presented in Table 1. Over the range of experimental flame positions, the d_p values determined by TEM are lower relative to the d_e values determined by AFM. This phenomenon may be attributable to the fact that the partial substance of soot particles is volatilized under vacuum and electron beam conditions in a TEM system [25,26]. In addition, the particles obtained at HAB = 2 and 5 mm are polydisperse, single and transparent, while at HAB = 10 mm, single transparent particles and several chain-like particles coexist. Correspondingly, the $\overline{F_{at}}$ presents a rise-decay trend over the HAB range from 2 to 10 mm. These phenomena suggest that besides attractive force

there are other factors affecting the coagulation of soot particles.

3.2. Adhesive force

During the withdrawal phase, the probe tip typically progresses from C to D and then undergoes a "jump-off-contact" from D to D′ (Fig. 2c). Jump-off-contact occurs when the cantilever elastic constant is larger than the gradient of the tip-sample adhesive force [22]. The adhesive force (F_{ad}) between the probe tip and soot particle can be determined from the cantilever deflection during this jump-off-contact.

Fig. 5 presents the F_{ad} distributions at different HABs. Similar to the trend seen in the F_{at} data in Fig. 3, the F_{ad} values also exhibit different distributions with increasing HAB values. At HAB = 10 mm, a narrow F_{ad} distribution over the range of 15.5–18.0 nN is observed, with a peak at approximately 17 nN, while the particles generated at HAB = 15 mm have a broadened F_{ad} distribution over the range of 14–24.5 nN. For all HABs, the F_{ad} varies within 13.5–24.5 nN. As the HAB increases from 2 to 25 mm, the F_{ad} distribution trends towards higher force values, with about 55% of F_{ad} values above 15.0 nN at HAB = 2 mm, 55% of F_{ad} above 15.5 nN at HAB = 5 mm, 60% of F_{ad} above 16.5 nN at HAB = 10 mm, 70% of F_{ad} above 18.0 nN at HAB = 15 mm and 83% of F_{ad} above 19.5 nN at HAB = 25 mm. These data demonstrate that F_{ad} gradually increases as the soot particles become more mature.

The population-averaged adhesive force values ($\overline{F_{ad}}$) are plotted as a function of HAB in Fig. 6. It is evident that $\overline{F_{ad}}$ gradually increases, from 15.2 to 20.4 nN, with increases in the HAB from 2 to 25 mm. In addition, the $\overline{F_{ad}}$ value is 6.5–7.5 times larger than the $\overline{F_{at}}$ value at the identical HAB. The larger $\overline{F_{ad}}$ values may be attributable to three factors: (1) some adhesive bonds are formed during contact between particles [27], (2) the buckling and wrapping of the soot particle

around the tip during contact increases the contact area and thus increases F_{ad} [28], and (3) force-separation curve hysteresis contributions make $F_{ad} > F_{at}$, even without bonding or deformation [29].

3.3. Adhesion energy

For the probe tip to pull away from the soot particle, the adhesion energy (or the work associated with the adhesive force) must be overcome. The adhesion energy (W_{ad}) can be calculated by integrating the shaded area in Fig. 2c, according to the equation

$$W_{ad} = \int_{z_1}^{z_0} f_{ad} dz, \quad (1)$$

where f_{ad} is the force between the probe tip and soot particle during the withdrawal process, Z_1 is the stretched length at $f_{ad} = 0$, and Z_0 is the stretched length at $f_{ad} = F_{ad}$.

The values of W_{ad} at different HABs calculated according to Eq. (1) are shown in Fig. 7. At HAB = 2, 5 and 10 mm, the W_{ad} values are primarily distributed over the range of 2.0–4.4 × 10^{-17} J, with greater than 81% of W_{ad} values above 2.5 × 10^{-17} J. At HAB = 15 mm, W_{ad} is broadly distributed over the range of 2.7–5.5 × 10^{-17} J. Upon increasing the HAB to 25 mm, the W_{ad} distribution obviously trends toward higher energies, with more than 84% of W_{ad} values above 4.0 × 10^{-17} J.

Fig. 8 shows the population-averaged adhesion energy values ($\overline{W_{ad}}$) as a function of HAB. Upon increasing the HAB from 2 to 5 mm, $\overline{W_{ad}}$ decreases from 3.15 × 10^{-17} to 2.96 × 10^{-17} J. With further increases in the HAB, $\overline{W_{ad}}$ increases to 4.56 × 10^{-17} J at HAB = 25 mm. A close inspection of Figs. 6 and 8 shows that the trends exhibited by the $\overline{F_{ad}}$ and $\overline{W_{ad}}$ data are different, suggesting that the stretched length of the soot particles is also an important factor affecting $\overline{W_{ad}}$. To support this assertion, the average stretched length is also plotted in Fig. 8. It is evident that the stretched length closely correlates with $\overline{W_{ad}}$ because both plots show similar trends as the HAB increases.

Although the adhesion energy values determined in this work are those between a soot particle and the tip rather than between two soot particles, these data can be used to qualitatively evaluate the energy barrier required to prevent particles escaping from one another. In the premixed flame, the motion of soot particle is dominated by Brownian motion, especially for small particles at higher temperatures [5]. If the kinetic energy of a particle originating from Brownian motion exceeds the energy barrier, the particle will bounce off after collision and fail to coagulate. Conversely, if the kinetic energy is lower than the energy barrier, the particles will stick together, resulting in coagulation [6]. In the present study, increasing the HAB from 2 to 5 mm decreased the adhesion energy, indicating a decrease in the energy barrier. However, in addition to the reduction in the primary particle diameter, the combustion temperature increased from 1633 K at HAB = 2 mm to 1673 K at HAB = 5 mm (Fig. 1), which can be attributed to the oxidation reaction being dominant. This combination of increased combustion temperature and reduced primary particle diameter would be expected to intensify the Brownian motion of the soot particles, thus lowering the coagulation rate. Fig. 1 shows that many isolated soot particles were present at HAB = 5 mm, which supports this theory. With further increases in the HAB from 5 to 25 mm, the increase in adhesion energy and primary particle diameter and the decrease in the combustion temperature should improve soot coagulation, and Fig. 1 demonstrates that more aggregate particles are formed as the HAB increases.

3.4. Hamaker constant

The Hamaker constant is a force constant describing the van der Waals forces between two particles or between a particle and a substrate. The attractive force primarily consists of Van der Waals forces (F_{vdW}) along with capillary and electrostatic forces [22]. In the present work, the electrostatic and capillary forces can be considered negligible because the interactions were

determined at minimal separation distances (< 30 nm) during the approach phase in a dry environment (relative humidity < 15%) [30,31]. Consequently, it is assumed that the F_{vdW} is approximately equal to the F_{at} acting between the probe tip and the soot particle during the approach phase [32]. The Hamaker constant is obtained from the curve of the attractive force measured by AFM as the cantilever approaches the soot sample surface, with the expression for F_{vdW} based on the Derjaguin approximation [33,34] being

$$F_{\mathrm{vdW}} \approx F_{at} = -\frac{A \times r_{tip}}{6H^2}, \tag{2}$$

where A, r_{tip} and H are the Hamaker constant for the tip-particle system, the tip radius of curvature (r_{tip}=10 nm) and the tip-particle separation obtained from force-separation curves, respectively. The Hamaker constant for a single soot particle, A_{p}, can be calculated as [35]

$$A_{\mathrm{p}} = \frac{A^2}{A_{tip}} = \frac{\left(-\frac{6H^2 \cdot F_{at}}{r_{tip}} \right)^2}{A_{tip}}, \tag{3}$$

where A_{tip} is the Hamaker constant of silicon, 1.37×10^{-19} J [36].

According to the method suggested by De Falco et al. [31], a freshly cleaved mica substrate was employed as a reference to verify the measurements, and the resulting Hamaker constant was 0.97 ± 0.03×10^{-19} J. This obtained value agrees well with the Hamaker constant of mica substrate reported in the literatures [31], which are of the order of $0.90 \pm 0.03 \times 10^{-19}$ J. The method above was applied to the force-separation curves for each particle assessed, and the average Hamaker constants ($\overline{A_p}$) for soot samples acquired at different HABs were calculated. Fig. 9 shows that the $\overline{A_p}$ values were in the range of 1.98×10^{-19} to 2.58×10^{-19} J. To date, there have been only a limited number of studies that have determined the Hamaker constants of soot particles. De Falco et al. [31] calculated the Hamaker constant of the soot particles produced in fuel-rich ethylene/air laminar premixed flames with

different equivalent ratios to be in the range of 0.95×10^{-19} to 3.5×10^{-19} J. The Hamaker constant and graphitization degree both exhibited an increasing trend with increasing flame equivalent ratios. Lee et al. [37] reported that the Hamaker constant for a highly ordered graphite sample was on the order of $4.7 \pm 0.3 \times 10^{-19}$ J. They concluded that the Hamaker constant of the highly ordered graphite sample represented an upper limit for a perfect graphitized structure and could be considered as a reference during the analysis of mature soot samples. Interestingly, although the Hamaker constants obtained in this study were different from those reported by De Falco et al. [31] and Lee et al. [37], they have the same order of magnitude. This difference is likely due to variations in the origins and synthesis conditions of the soot particles, both of which have important effects on the physico-chemical properties of the particles [9].

To probe the correlation between the Hamaker constant and the graphitization degree, Raman scattering spectroscopy was used to characterize the graphitization degree of the soot particles. In Raman spectra, the G peak is related to a C–C stretching motion along the longitudinal axis of the graphitic plane, while the D peak originates from the breakdown of the selection rules for graphene atoms in the breathing vibrational mode, with an intensity that depends on the level of disorder of the graphitic structure [38]. The D to G peak area ratio (I_D/I_G) is directly related to the size and defects in the basal plane of the graphene layers and is frequently used to estimate the graphitization degree of soot [38,39]. That is, a low value of I_D/I_G is representative of a high graphitization degree. Figs. 9 and 10 demonstrate that there was a positive correlation between the Hamaker constant and the graphitization degree of the soot particles. The particles generated at HAB = 2 mm had much lower $\overline{A_p}$ values and lower graphitization degree than those acquired at HAB = 5 mm. As the HAB was increased further, from 5 to 10 mm, the $\overline{A_p}$ and graphitization degree both decreased. Over the

HAB range of 10−25 mm, the increase in $\overline{A_p}$ coincided with an increase in the graphitization degree. Similar findings were reported by De Falco et al. [31], who determined that an increase in the Hamaker constant accompanied a continuous increase in the graphitization degree of soot particles associated with increasing the size of the aromatic domains and/or the three-dimensional internal ordering.

4. Conclusions

The attractive force, adhesive force, and adhesion energy between soot particles and the probe tip were investigated by AFM. Different attractive and adhesive force distributions were observed with an increase in the HAB. At a low HAB value of 2 mm, the attractive force showed a narrow distribution, while a broader distribution was evident at a moderate HAB of 15 mm. The average attractive force first increased then briefly dropped before undergoing a gradual increase as the HAB increased, with a maximum of 2.54 nN at HAB = 25 mm. A narrow adhesive force distribution was observed at a HAB of 10 mm, while a broad distribution was found at a HAB of 15 mm. The average adhesive force gradually increased with increasing HAB values, remaining in the range of 15.2–20.4 nN. The adhesion energy values were within the range of 2.0–5.6 × 10^{-17} J for all HABs investigated. The stretched length of soot particles is an important factor affecting the average adhesion energy, because the characteristic shape of average adhesion forces is different from that of average adhesion energy as the HAB increased.

Assuming that van der Walls forces primarily contribute to the attractive force, the attractive force values determined experimentally were used to calculate the Hamaker constants for the soot particles. As the HAB value was raised, the average Hamaker constant decreased after an initial increase and then slowly increased again. A positive correlation was identified between the average

Hamaker constant and the graphitization degree obtained from Raman spectroscopy.

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Figure captions

Fig. 1. TEM (left) and AFM (right) images of soot particles acquired at different HAB values.

Fig. 2. (a) Schematic illustration of the force measurement apparatus, (b) the interactive force between the soot particle and probe tip as a function of the piezoelectric crystal position, and (c) the interactive force between the soot particle and probe tip as a function of separation.

Fig. 3. Distributions of the attractive force (F_{at}) between soot particles and probe tip at various HAB values.

Fig. 4. Average attractive force ($\overline{F_{at}}$) between soot particles and probe tip as a function of the HAB. The error bars indicate the standard error.

Fig. 5. Distributions of the adhesive force (F_{ad}) between soot particles and probe tip at various HAB values.

Fig. 6. Average adhesive force ($\overline{F_{ad}}$) between soot particles and probe tip as a function of the HAB. The error bars indicate the standard error.

Fig. 7. Distributions of the adhesion energy (W_{ad}) between soot particles and probe tip at various HAB values.

Fig. 8. Average adhesion energy ($\overline{W_{ad}}$) between soot particles and probe tip, and the stretched length of soot particles, as functions of the HAB. The error bars indicate the standard error.

Fig. 9. Average Hamaker constant ($\overline{A_p}$) for soot particles as a function of the HAB. The error bars indicate the standard error.

Fig. 10. I_D/I_G ratio as a function of the HAB. The error bars indicate the standard error.