Dust nucleation in very-low pressure plasmas

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Outline

I CONTEXT

II MATERIALS & METHODS

III DUST PARTICLES FORMED IN C₂H₂ PLASMAS

IV DUST PARTICLES FORMED FROM PAHs

V CONCLUSION AND PERSPECTIVE


 Formation of particles

Contreras et al., Laboratory investigations of polycyclic aromatic hydrocarbon formation and destruction in the circumstellar outflows of carbon stars, ApJS (2013)


Couedel et al., Self-excited void instability during dust particle growth in a dusty plasma, PoP (2010)
Formation of particles

NUCLEATION \rightarrow COAGULATION \rightarrow ACCRETION

Contreras et al., Laboratory investigations of polycyclic aromatic hydrocarbon formation and destruction in the circumstellar outflows of carbon stars, ApJS (2013)


Couedel et al., Self-excited void instability during dust particle growth in a dusty plasma, PoP (2010)
Cosmic dusts


![Carbon-rich star diagram](image)

d = $10^{18}$ cm$^3$

d = $10^6$ cm$^3$

d = $10^5 - 10^3$ cm$^3$
Cosmic dusts

Contreras et al., Laboratory investigations of polycyclic aromatic hydrocarbon formation and destruction in the circumstellar outflows of carbon stars, ApJS (2013)
Cosmic dusts

Cosmic dusts

Cosmic dusts

Cosmic dusts

Contreras et al., Laboratory investigations of polycyclic aromatic hydrocarbon formation and destruction in the circumstellar outflows of carbon stars, ApJS (2013)
Cosmic dusts

Nucleation deduced from combustion

Formation of linear polyalkyne

Formation of linear polyalkyne

$$\begin{align*}
2 \text{H} & \longrightarrow \text{C} & \equiv & \text{C} & \longrightarrow \text{H} & \quad \quad \quad \text{H} \quad \text{C} = \text{C} & \equiv & \text{C} & \longrightarrow \text{H} & + \text{H} \\
\text{H} & \longrightarrow \text{C} & \equiv & \text{G} & \longrightarrow \text{H} & + \text{CH} & \quad \quad \quad \text{H} \quad \text{C} = \text{C} & \longrightarrow \text{H} 
\end{align*}$$

Formation of aromatic rings

Formation of linear polyalkyne

\[ 2 \text{H} \rightarrow C\equiv C\rightarrow \text{H} \quad \text{H} \rightarrow C\equiv C\rightarrow \text{H} + \text{CH} \]

Formation of aromatic rings

Hydrogen Abstraction Carbon Addition (HACA)

Nucleation?

PAHs formation / HACA shown in SOOTY FLAMES
Nucleation?

PAHs formation / HACA shown in SOOTY FLAMES

often used
CARBON-RICH STARS

DUSTY PLASMAS
Nucleation?

PAHs formation / HACA shown in **SOOTY FLAMES**

\[ N_n = 5 \times 10^{18} \text{ cm}^{-3} / T = 1000-2000 \text{ K} \]
\[ N_e > 10^{11} \text{ cm}^{-3} / T_e = 0.2 \text{ eV} \]

often used

**CARBON-RICH STARS**

\[ N_n = 5 \times 10^8 \text{ cm}^{-3} / T = 2000-5000 \text{ K} \]
\[ N_e \approx 2 \times 10^2 \text{ cm}^{-3} / T_e = 0.1 \text{ eV} \]

**DUSTY PLASMAS**

\[ N_n = 10^{14}-10^{15} \text{ cm}^{-3} / T = 300 \text{ K} \]
\[ N_e = 10^8-10^9 \text{ cm}^{-3} / T_e = 2-4 \text{ eV} \]
Dust particle growth in plasmas

- In C$_2$H$_2$ dusty plasmas:

  \[ C_2H_2 \rightleftharpoons \text{PAHs} \rightleftharpoons \text{Dust particles} \]

Dust particle growth in plasmas

- In C\textsubscript{2}H\textsubscript{2} dusty plasmas:

\[ \text{C}_2\text{H}_2 \rightarrow \text{PAHs} \rightarrow \text{Dust particles} \]

MODELLING

Dust particle growth in plasmas

• In C$_2$H$_2$ dusty plasmas:

\[ \text{C}_2\text{H}_2 \rightarrow \text{PAHs} \rightarrow \text{Dust particles} \]


MODELLING

[Diagram showing chemical reactions]
Dust particle growth in plasmas

- In $\text{C}_2\text{H}_2$ dusty plasmas:

\[ \text{C}_2\text{H}_2 \rightarrow \text{PAHs} \rightarrow \text{Dust particles} \]


EXPERIMENTS
Dust particle growth in plasmas

- In C$_2$H$_2$ dusty plasmas:

\[ \text{C}_2\text{H}_2 \rightarrow \text{PAHs} \rightarrow \text{Dust particles} \]


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**EXPERIMENTS**

**Mass spectrometry**

Descheneaux et al., *Investigations of CH$_4$, C$_2$H$_2$ and C$_2$H$_4$ dusty RF plasmas by means of FTIR absorption spectroscopy and mass spectrometry*, JPD (1999)
Dust particle growth in plasmas

- In C$_2$H$_2$ dusty plasmas:

  \[ \text{C}_2\text{H}_2 \xrightarrow{\text{PAHs}} \text{Dust particles} \]


**EXPERIMENTS**

**Mass spectrometry**

Descheneaux et al., *Investigations of CH$_4$, C$_2$H$_2$ and C$_2$H$_4$ dusty RF plasmas by means of FTIR absorption spectroscopy and mass spectrometry*, JPD (1999)

**Microscopy**

Al Makdessi et al., *Influence of a magnetic field on the formation of carbon dust particles in very low-pressure high-density plasmas*, JPD (2016)

**Very small grains**

PAHs?
No real evidence of PAHs
Dust particle growth in plasmas

- tricky under specific experimental conditions
  for example, with the working pressure
Dust particle growth in plasmas

- tricky under specific experimental conditions
  for example, with the working pressure

At low-pressure
  ➔ probability of recombination <<

Takahashi et al., Solid particle production in fluorocarbon plasmas.
I. Correlation with polymer film deposition, JVSTA (2001)
Dust particle growth in plasmas

- tricky under specific experimental conditions
  for example, with the working pressure

\[ \text{At low-pressure } \Rightarrow \text{ probability of recombination } << \]

However...

Takahashi et al., Solid particle production in fluorocarbon plasmas. I. Correlation with polymer film deposition, JVSTA (2001)

Drenik et al., Trajectories of dust particles in low-pressure magnetized plasma, IEEETPS (2011)
No real evidence of PAHs

What’s happening at really low-pressure?
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ECR plasmas

- static magnetic field
  - electron confinement
  - electron heating
  - \( B=875 \) Gauss \( \leftrightarrow \) microwave \( (2.45 \) GHz)\)

- really-low pressure regime – \( 0.1 \) Pa
ECR plasmas / $\text{C}_2\text{H}_2$

Deposition above the magnets / edges
Ex-situ measurements

Microscopies (SEM / TEM)

Spectroscopies

Astrochemistry Research of Organics with Molecular Analyzer (AROMA)

couples laser desorption/ionization (LDI) techniques
with ion trap mass spectrometry in two steps (L2MS),

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ECR plasmas / C$_2$H$_2$
ECR plasmas / C$_2$H$_2$

10 nm

SEM

TEM

2r$_1$

2r$_2$

5 min

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ECR plasmas / C$_2$H$_2$

10 nm

SEM

TEM

2r$_1$

2r$_2$

isotropic

5 min
→ Growth in the plasma volume
Growth processes?

![Diagram with gas inlet, gas outlet, Langmuir probe, and C2H2]
Growth processes?

Langmuir probe

Gas outlet

C$_2$H$_2$
Growth processes?

Langmuir probe

Gas outlet

C$_2$H$_2$

Positive ions
Growth processes?

Langmuir probe

Gas outlet

C$_2$H$_2$

Positive ions
Growth in the plasma volume

Local growth
Growth in the plasma volume

Local growth

Molecular composition?
AROMA analyses

Normalized intensity

5 min
AROMA analyses

202.07  5 min
191.07
300.10 a.m.u.
AROMA analyses

202.07 \( C_{16}H_{10} \) Pyrene

191.07

300.10 a.m.u. \( C_{24}H_{12} \) Coronene

5 min
AROMA analyses

202.07 $C_{16}H_{10}$

300.10 a.m.u. $C_{24}H_{12}$

Coronene

Normalized intensity

m/z
AROMA analyses

202.07 \( \text{C}_{16}\text{H}_{10} \)

191.07

300.10 a.m.u. \( \text{C}_{24}\text{H}_{12} \)
AROMA analyses

- $^{15}C_{16}H_{10}$
- Phenanthrene $\rightarrow$ Pyrene

Mass/charge (m/z) values:
- 202.07
- 191.07
- 300.10 a.m.u.
AROMA analyses

Normalized intensity

\[ \text{C}_{15}\text{H}_{11} \]

\[ 191.07 \]

\[ 300.10 \text{ a.m.u.} \]

\[ \text{C}_{16}\text{H}_{10} \]

\[ 202.07 \]

\[ \text{Phenanthrene} \rightarrow \text{Pyrene} \]

one intermediate
$C_xH_y \Rightarrow \text{Double Band Equivalent (DBE)}$

$\text{DBE}(C_xH_y) = x - \frac{y}{2} + 1$
\( C_xH_y \Rightarrow \text{Double Band Equivalent (DBE)} \)

\[
\text{DBE}(C_xH_y) = x - \frac{y}{2} + 1
\]

\( C_{24}H_{12} \quad \text{PAHs} \)

\( C_{16}H_{10} \)
\textbf{C}_x\textbf{H}_y \rightarrow \text{Double Band Equivalent (DBE)}

\[ \text{DBE}(C_xH_y) = x - \frac{y}{2} + 1 \]

- \textbf{C}_{16}\textbf{H}_{10}
- \textbf{C}_{24}\textbf{H}_{12}

PAHs

Carbon addition
Hydrogen abstraction

+ C
+ H
AROMA analyses

94% PAHs + interm.

5 min

Normalized intensity

m/z
Above the magnets

\[ C_2H_2 + e^- \rightarrow C_xH_y^{\circ,+,−} \]
Above the magnets

Nucleation...

$\text{C}_2\text{H}_2 + e^- \rightarrow C_xH_y^{\circ,+,-} \rightarrow \text{PAHs}$

Carbon addition
Hydrogen abstraction
Above the magnets

\[ \text{Carbon addition} \quad \text{Hydrogen abstraction} \]

\[ \text{C}_2\text{H}_2 + e^- \rightarrow \text{C}_x\text{H}_y^{\text{+,+}} \rightarrow \text{PAHs} \rightarrow \text{dust} \rightarrow \text{Deposition} \]
AROMA analyses

94% PAHs + intern.

5 min

672.00 840.00
AROMA analyses

94% PAHs + interm.

Fullerenes

\[ \begin{align*}
C_{56} & \quad 672.00 \\
\ldots & \quad \ldots \\
C_{76} & \quad 840.00
\end{align*} \]

5 min
AROMA analyses

94% PAHs + interm.

Fullerenes

C\textsubscript{56}   ...   C\textsubscript{76}

672.00   840.00
Above the magnets

\[ C_2H_2 + e^- \rightarrow C_{xH_y}^{+,-} \rightarrow \text{PAHs} \rightarrow \text{dust} \rightarrow \text{Deposition} \]

Fullerene growth?
Nucleation of Fullerenes?
Nucleation of Fullerenes?

Arc discharges

Ablation plume
Nucleation of Fullerenes?

Arc discharges

- High electron density / $n_e > 10^{19}$ m^{-3}
- High pressure / $n_{\text{radicals}} > 10^{22}$ m^{-3}
- High temperature / $T > 4000$K

Ablation plume
Nucleation of Fullerenes?

- High electron density / $n_e > 10^{19}$ m$^{-3}$
- High pressure / $n_{\text{radicals}} > 10^{22}$ m$^{-3}$
- High temperature / $T > 4000$K

Obviously far from our conditions...
Formation of Fullerenes?

Heating?
Formation of Fullerenes?

➔ Heating?

Drenik et al., *Trajectories of dust particles in low-pressure magnetized plasma*, IEEETPS (2011)
Formation of Fullerenes?

⇒ Heating?

Rojo et al., Charging and heating processes of dust particles in an electron cyclotron resonance plasma, FSST (2019)

Drenik et al., Trajectories of dust particles in low-pressure magnetized plasma, IEEETPS (2011)
Formation of Fullerenes?

→ Heating?

Rojo et al., Charging and heating processes of dust particles in an electron cyclotron resonance plasma, PSST (2019)

→ T<< to transform PAHs into fullerenes

Drenik et al., Trajectories of dust particles in low-pressure magnetized plasma, IEEETPS (2011)
Formation of Fullerenes?

⇒ Heating?

⇒ Processing of PAHs on dust particles?
Formation of Fullerenes?

- Heating?

- Processing of PAHs on dust particles?

In TEM
Above the magnets

\[ C_2H_2 + e^- \rightarrow C_xH_y^{\circ,+,\cdot} \rightarrow \text{PAHs} \rightarrow \text{dust} \rightarrow \text{Deposition} \]

Processing?
Nucleation in ECR plasmas

- in our conditions

\[ \text{C}_2\text{H}_2 \leftrightarrow \text{PAHs up to} \]

Carbon addition
Hydrogen abstraction
Nucleation in ECR plasmas

- in our conditions

\[ \text{C}_2\text{H}_2 \leftrightarrow \text{PAHs up to } \begin{array}{c}
\text{Carbon addition} \\
\text{Hydrogen abstraction}
\end{array} \leftrightarrow \text{Dust particles} \]
Nucleation in ECR plasmas

• in our conditions

\[
\begin{align*}
C_2H_2 & \quad \rightarrow \quad \text{PAHs up to} \quad \rightarrow \quad \text{Dust particles} \\
\text{Carbon addition} & \quad \text{Hydrogen abstraction} \\
\text{?} & \quad \rightarrow \quad \text{Dust particles}
\end{align*}
\]
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I. CONTEXT

II. MATERIALS & METHODS

III. DUST PARTICLES FORMED IN C$_2$H$_2$ PLASMAS

IV. DUST PARTICLES FORMED FROM PAHs

V. CONCLUSION AND PERSPECTIVE
Plasmas seeded with PAHs
Plasmas seeded with PAHs

Anthracene
Perylene
Benzoperylene
Coronene
Plasmas seeded with PAHs

Anthracene
Perylene
Benzoperylene
Coronene

really larger than in C$_2$H$_2$ ECR plasmas
AROMA analyses
AROMA analyses

![Graph showing intensity vs. m/z for Fullerenes and PAHs processing]
AROMA analyses

Intensity (arb. units)

m/z

Fullerenes
PAHs processing
AROMA analyses

Carbon clusters

Fullerenes
PAHs processing
$C_2H_2 \rightarrow$ PAHs up to \[ \begin{array}{c} \text{Carbon addition} \\ \text{Hydrogen abstraction} \end{array} \] \[ \rightarrow \text{Dust particles} \]
$\text{C}_2\text{H}_2 \leftrightarrow \text{PAHs up to } \text{PAHs up to }$

Carbon addition

Hydrogen abstraction

\[ \text{Dust particles} \]

\[ \text{Dust particles} \]
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IV. DUST PARTICLES FORMED FROM PAHs

V. CONCLUSION
\[ C_2H_2 + e^- \rightarrow C_xH_y^{\circ,+,+} \rightarrow \text{PAHs} \rightarrow \text{dust} \rightarrow \text{Deposition} \]
Nucleation in $\text{C}_2\text{H}_2$ ECR plasmas involve the formation of PAHs

Through similar Hydrogen abstraction Carbon addition pathways as described in combustion
Nucleation in C$_2$H$_2$ ECR plasmas involve the formation of PAHs through similar Hydrogen abstraction Carbon addition pathways as described in combustion.

PAHs further stack into dust particles.
Nucleation in $\text{C}_2\text{H}_2$ ECR plasmas involve the formation of PAHs

Through similar Hydrogen abstraction Carbon addition pathways as described in combustion

PAHs further stack into dust particles

However, a lot of other mechanisms are also involved (thermal heating, electron bombardment, etc.)
C_2H_2 \rightarrow \text{PAHs up to } \begin{array}{c}
\text{\includegraphics[width=1cm]{PAH.png}}
\end{array} \\
\text{Carbon addition} \\
\text{Hydrogen abstraction} \\
\begin{array}{c}
\text{\includegraphics[width=1cm]{PAH.png}}
\end{array} \\
\rightarrow \text{Dust particles} \\
\begin{array}{c}
\text{\includegraphics[width=1cm]{PAH.png}}
\end{array} \\
\rightarrow \text{Dust particles}

\begin{array}{c}
\text{PROCESSING}
\end{array}

\begin{array}{c}
\not\rightarrow
\end{array}
Carbon addition

Hydrogen abstraction

$C_2H_2 \rightarrow \text{PAHs up to } \begin{array} \text{PAH structure} \end{array} \rightarrow \text{Dust particles}$

$\Leftrightarrow$ Dust particles

+ $H_2$

R. Clergeroux - CAP DPP Symposium - June 2020
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