Advances in Pulsed Laser Deposition of ultra-low density carbon foams

Alessandro Maffini
Department of Energy, Politecnico di Milano, Italy

E-MRS Spring Meeting, Strasbourg
Symposium X : Photon-assisted synthesis and processing of materials in nano-microscale

18/06/2018
Advances in Pulsed Laser Deposition of ultra-low density carbon foams

What do we know of the foam growth process?
How can this process be controlled?
Advances in Pulsed Laser Deposition of ultra-low density carbon foams

What do we mean by C “foam”?

What do we know of the foam growth process? How can this process be controlled?
Advances in Pulsed Laser Deposition of ultra-low density carbon foams

**What** do we mean by C "foam"?

**Why** do we care about foams?

What do we know of the foam growth process? How can this process be controlled?
Advances in Pulsed Laser Deposition of ultra-low density carbon foams

**What** do we mean by C “foam”?

**Why** do we care about foams?

**How to deposit C foams?**

What do we know of the foam growth process?
How can this process be controlled?
What do we mean by “carbon foams”?


Carbon nanofoam

From Wikipedia, the free encyclopedia

Carbon nanofoam is an allotrope of carbon discovered in 1997 by Andrei V. Rode and co-workers at the Australian National University in Canberra.[1] It consists of a cluster-assembly of carbon atoms strung together in a loose three-dimensional web. The material is extremely light, with a density of 2–10 mg/cm³ (0.0012 lb/ft³).[1][2] A gallon of nanofoam weighs about a quarter of an ounce.[3]

Each cluster is about 6 nanometers wide and consists of about 4000 carbon atoms linked in graphite-like sheets that are given negative curvature by the inclusion of heptagons among the regular hexagonal pattern. This is the opposite of what happens in the case of buckminsterfullerenes, in which carbon sheets are given positive curvature by the inclusion of pentagons.

The large-scale structure of carbon nanofoam is similar to that of an aerogel, but with 1% of the density of previously produced carbon aerogels—or only a few times the density of air at sea level. Unlike carbon aerogels, carbon nanofoam is a poor electrical conductor. The nanofoam contains numerous unpaired electrons, which Rode and colleagues propose is due to carbon atoms with only three bonds that are found at topological and bonding defects. This gives rise to what is perhaps carbon nanofoam's most unusual feature: it is attracted to magnets, and below −103 °C can itself be made magnetic.

What do we mean by “carbon foams”?


Carbon nanofoam

From Wikipedia, the free encyclopedia

Carbon nanofoam is an allotrope of carbon discovered in 1997 by Andrei V. Rode and co-workers at the Australian National University in Canberra. It consists of a cluster-assembly of carbon atoms strung together in a loose three-dimensional web. The material is extremely light, with a density of 2–10 mg/cm³ (0.0012 lb/ft³). A gallon of nanofoam weighs about a quarter of an ounce.

Each cluster is about 6 nanometers wide and consists of about 4000 carbon atoms linked in graphite-like sheets that are given negative curvature by the inclusion of heptagons among the regular hexagonal pattern. This is the opposite of what happens in the case of buckminsterfullerenes, in which carbon sheets are given positive curvature by the inclusion of pentagons.

The large-scale structure of carbon nanofoam is similar to that of an aerogel, but with 1% of the density of previously produced carbon aerogels—or only a few times the density of air at sea level. Unlike carbon aerogels, carbon nanofoam is a poor electrical conductor. The high porosity is primarily due to structural forces.Andrej Rode and colleagues propose is due to carbon atoms with negative curvature. Carbon nanofoam can be used in filters, and it is perhaps carbon nanofoam has the potential to be used for producing large cell carbon foams with a high density of cells or large cell carbon foams with a high density of cells.

In this talk, I will refer to “carbon foam” as:

- Disordered, nanoscale structured material
- (almost) pure carbon
- Void fraction ≈ 99% → density ≈ 10 mg/cm³

Why do we care?

Unconventional magnetism in all-carbon nanofoam

A. V. Rode,1,*,† E. G. Gamaly,1 A. G. Christy,2 J. G. Fitz Gerald,3 S. T. Hyde,1 R. G. Elliman,1 B. Luther-Davies,1 A. I. Veinger,4 J. Androulakis,5 and J. Giapintzakis5,6,*,‡

PHYSICAL REVIEW B 70, 054407 (2004)
Why do we care?

Unconventional magnetism in all-carbon nanofoam

A. V. Rode,1,*† E. G. Gamaly,1 A. G. Christy,2 J. G. Fitz Gerald,3 S. T. Hyde,1 R. G. Elliman,1 B. Luther-Davies,1 A. J. Veinger 4† I. Androulakis5 and J. Giapintzakis5,6,*‡

Pore structure engineering for carbon foams as possible bone implant material

Gursel Turgut, Ayhan Eksilioglu, Nagehan Gencay, Emre Gonen, Nezih Hekim, M. F. Yardim, Damlanur Sakiz, Ekrem Ekinci
Why do we care?

Unconventional magnetism in all-carbon nanofoam


Pore structure engineering for carbon foams as possible bone implant materials

Gursel Turgut, Ayhan Eksilioglu, Nezih Hekim, M. F. Yardim, Damlak

Production of thermally conductive carbon foams and their application in automobile transport

V M Samoylov, E A Danilov, E R Galimov, V L Fedyaev, N Ya Galimova, and M A Orlov
Why do we care?

Unconventional magnetism in all-carbon nanofoam

A. V. Rode, 1, 2* E. G. Gamaly, 1 A. G. Christy, 2 J. G. Fitz Gerald, 3 S. T. Hyde, 1 R. G. Elliman, 1 B. Luther-Davies, 1 A. J. Veinger 4 I. Androulakis 5 and J. Giapintzakis 5, 6, 2*


Pore structure engineering for carbon foams as possible bone implant materials

Gursel Turgut, Ayhan Eksilioglu, Nazmi Yildiz, Nezih Hekim, M. F. Yardim, Damlak Turan

Production of thermally conductive carbon foams and their application in automobile transport

IETEM

Graphitic carbon foams as anodes for sodium-ion batteries in glyme-based electrolytes

Jorge Rodríguez-García a, Ignacio Cameán a,*, Alberto Ramos b, Elena Rodríguez a, Ana B. García a
Why do we care?


Unconventional magnetism in all-carbon nanofoam

A. V. Rode,1,*† E. G. Gamaly,1 A. G. Christy,2 J. G. Fitz Gerald,3 S. T. Hyde,1 R. G. Elliman,1 B. Luther-Davies,1 A. J. Veinger4 J. Androulakis5 and J. Giapintzakis5,6,*‡


Pore structure engineering for carbon foams as possible bone implant materials

Gursel Turgut, Ayhan Eksilioglu, Necip Ates, Nezih Hekim, M. F. Yardim, Damla Akinci, Semih Ates

IETEM

Production of thermally conductive carbon foams and their application in automobile transport

https://doi.org/10.1007/s11051-017-4080-7

RESEARCH PAPER

Enhanced specific surface area by hierarchical porous graphene aerogel/carbon foam for supercapacitor

Zhaopeng Xin · Weixin Li · Wei Fang · Xuan He · Lei Zhao · Hui Chen · Wanqiu Zhang · Zhimin Sun
Why do we care?

ERC-2014-CoG No.647554

ENSURE


doi:10.1088/0741-3335/58/3/034019

Development of foam-based layered targets for laser-driven ion beam production

I Prencipe 1,2, A Sgattoni 3,4, D Dellasega 1,5, L Fedeli 3,4, L Cialfi 1, Il Woo Choi 6,7,9, I Jong Kim 6,7,10, K A Janulewicz 6,8, K F Kakolee 6, Hwang Woon Lee 6, Jae Hee Sung 6,7, Seong Ku Lee 6,7, Chang Hee Nam 6,8 and M Passoni 1,5

Enhanced specific surface area by hierarchical porous graphene aerogel/carbon foam for supercapacitor

Zhaopeng Xin · Weixin Li · Wei Fang · Xuan He · Lei Zhao · Hui Chen · Wanqiu Zhang · Zhimin Sun
Carbon foam for laser-plasma ion acceleration

Conventional scheme

- Ultra-short, super-intense laser pulse
- Micrometric thick foil

Advanced target

- ~10 mg/cm³ C foam onto a µm-thick foil

Carbon foam for laser-plasma ion acceleration

Low density C foam

Hot electron cloud

Conventional scheme

Advanced target

- \(\sim 10 \text{ mg/cm}^3\) C foam onto a \(\mu\text{m}\)-thick foil
- Foam enhances laser-plasma coupling

M. Passoni et al. *Phys Rev Acc Beams* 19.6 (2016)
Carbon foam for laser-plasma ion acceleration

Conventional scheme

Advanced target

- ~10 mg/cm³ C foam onto a μm-thick foil
- Foam enhances laser-plasma coupling
- More ions at higher energy

Carbon foam for laser-plasma ion acceleration

- Low density C foam
- Foam enhances laser-plasma coupling
- More ions at higher energy

TARGET IS THE KEY!

- ~10 mg/cm$^3$ C foam onto a μm-thick foil
- Foam enhances laser-plasma coupling
- **More ions at higher energy**

www.ensure.polimi.it
How to produce C foams: Pulsed Laser Deposition (PLD)

Laser Beam
- \( \lambda = 266, 532, 1064 \text{ nm} \)
- Pulse duration = 7ns, energy = 0.1 - 2 J
- Fluence: 0.1 - 20 J/cm\(^2\)
- Max rep. rate = 10 Hz

Background Gas
- Inert (He, Ar..)
- Reactive (O\(_2\))

Target-to-substrate distance

Gas pressure

Laser fluence

“atom by atom” deposition

“Nanoparticle” deposition

Target

Plasma plume

Substrate (almost any kind of substrate)
How to produce carbon foams

$\lambda = 532$ nm
$F = 2.1 \text{ J/cm}^2$
$d_{T-S} = 4.5 \text{ cm}$
How to produce carbon foams

Foam PLD parameters:
- λ = 532 nm
- Ep = 150 mJ
- Fluence 1.6 J/cm²
- 700 Pa of Ar
- Static substrate
- Static target

(... for this talk only!)

Pressure (Pa)
Density (mg/cm³)

Foams
What are “foams” made of?

**Elementary constituents:**
10-20 nm C nanoparticles

**C-C bonding:**
Nearly pure sp² odd-membered rings and few chain-like structures

**Crystalline structure:**
Topologically disordered domains,
Size ~ 2nm

A. Zani et al., Carbon, 56 358 (2013)
Plume expansion and NPs synthesis


PLD plume dynamics & NP production are open research topics!
Plume expansion and NPs synthesis

A sketch of plume dynamics:

1) Adiabatic Expansion
2) Shock wave formation


PLD plume dynamics & NP production are open research topics!
Plume expansion and NPs synthesis

PLD plume dynamics & NP production are open research topics!

**A sketch of plume dynamics:**

1) **Adiabatic Expansion**
2) **Shock wave formation**
3) **Nanoparticle synthesis**

Plume expansion and NPs synthesis

A sketch of plume dynamics:

1) Adiabatic Expansion
2) Shock wave formation
3) Nanoparticle synthesis
4) Nanoparticle aggregation
5) Landing on substrate

Plume expansion and NPs synthesis

A sketch of plume dynamics:
1) Adiabatic Expansion
2) Shock wave formation
3) Nanoparticle synthesis
4) Nanoparticle aggregation
5) Landing on substrate

For the purpose of this talk:
- I won’t discuss SW formation and NP synthesis
- I’ll consider C NPs as “LEGO bricks” to play with

PLD plume dynamics & NP production are open research topics!

Plume expansion and NPs synthesis

A sketch of plume dynamics:
1) Adiabatic Expansion
2) Shock wave formation
3) Nanoparticle synthesis
4) Nanoparticle aggregation
5) Landing on substrate


For the purpose of this talk:
- I won’t discuss SW formation and NP synthesis
- I’ll consider C NPs as “LEGO bricks” to play with

I’ll try to answer these questions:
- What is the NPs aggregation dynamics?
- How aggregation dynamics controls foam properties?
The aim of this talk

1) Adiabatic Expansion
2) Shock wave formation
3) Nanoparticle synthesis
4) Nanoparticle aggregation
5) Landing on substrate


For the purpose of this talk:
- I won’t discuss SW formation and NP synthesis
- I’ll consider C NPs as “LEGO bricks” to play with

I’ll try to answer to these questions:
- What is the NPs aggregation dynamics?
- How aggregation dynamics controls foam properties?
What is said in the literature?

- The **growth of fractal structures** has been observed **since earliest PLD experiments**
- Different **aggregation models** (DLA, DLCCA, RLA,...) in **numeric simulation** of growth
- Diffusion Limited Aggregation on the substrate (**2D-DLA**) is the **most employed**
What is said in the literature?

- The **growth of fractal structures** has been observed since earliest PLD experiments.
- Different **aggregation models** (DLA, DLCCA, RLA,…) in *numeric simulation* of growth.
- Diffusion Limited Aggregation on the substrate (2D-DLA) is the **most employed**.

The physics in a 2D-DLA model

![Diagram of 2D-DLA model](image)

Diffusive motion ("random walk") of NPs

- Sticking of NP and aggregation
- Diffusion on **substrate** → 2D physics

What is said in the literature?

- The growth of fractal structures has been observed since earliest PLD experiments
- Different aggregation models (DLA, DLCCA, RLA,…) in numeric simulation of growth
- Diffusion Limited Aggregation on the substrate (2D-DLA) is the most employed

The physics in a 2D-DLA model

Diffusive motion ("random walk") of NPs
Sticking of NP and aggregation
Diffusion on substrate → 2D physics


2D-DLA can make accurate predictions…

Experiment

What is said in the literature?

- The growth of fractal structures has been observed since earliest PLD experiments
- Different aggregation models (DLA, DLCCA, RLA,...) in numeric simulation of growth
- Diffusion Limited Aggregation on the substrate (2D-DLA) is the most employed

The physics in a 2D-DLA model

Diffusive motion ("random walk") of NPs
Sticking of NP and aggregation
Diffusion on substrate → 2D physics


2D-DLA can make accurate predictions...


..Is 2D-DLA ok also to describe the growth of C foams?
Is 2D-DLA ok to describe foam growth?

With 2D-DLA, aggregate grow like this:
Is 2D-DLA ok to describe foam growth?

With 2D-DLA, aggregate grow like this:

2D-DLA predicts:

1) Very small aggregates for few shots
2) Aggregate size will increase with increasing shots
Is 2D-DLA ok to describe foam growth?

With 2D-DLA, aggregate grow like this:

2D-DLA predicts:

1) Very small aggregates for few shots
2) Aggregate size will increase with increasing shots

We can test experimentally if 2D-DLA is ok:
1) Few shots: **large**, μm-sized **aggregates** (~ 100s NPs!)
1) Few shots: large, μm-sized aggregates (~ 100s NPs!)

2) Aggregates coalesce
1) Few shots: large, μm-sized aggregates (~ 100s NPs!)

2) Aggregates coalesce but having almost constant size
1) Few shots: large, μm-sized aggregates (~ 100s NPs!)

2) Aggregates coalesce but having almost constant size
1) Few shots: large, \( \mu \text{m} \)-sized aggregates (~ 100s NPs!)

2) Aggregates coalesce but having almost constant size

2D-DLA fails!
Let’s recap...

**What we have learned so far:**

- Aggregation is **not** 2D-DLA
- 3D (i.e. “In flight”) dynamics
- Aggregate average **diameter** $2R$
Let’s recap…

What we have learned so far:
- Aggregation is **not** 2D-DLA
- 3D (i.e. “In flight”) dynamics
- Aggregate average **diameter** $2R$

What is still missing:
- Prediction of aggregate properties: $2R$?
- “in-flight” aggregation dynamics: time-scale $t_{aggr}$?
- Control with **PLD** process parameters?
Let’s recap…

What we have learned so far:

- Aggregation is not 2D-DLA
- 3D (i.e. “In flight”) dynamics
- Aggregate average **diameter** 2R

What is still missing:

- Prediction of aggregate properties: 2R?
- “in-flight” aggregation dynamics: time-scale $t_{aggr}$?
- Control with PLD process parameters?

1st step: 2R as a function of $t_{aggr}$

Smoluchowski coagulation equation (1916)

+ “Diffusion limited” Kernel
+ Assumption of fractal geometry

$$2R(t_{aggr}) = a (t_{aggr})^b$$
Let’s recap…

What we have learned so far:
- Aggregation is **not** 2D-DLA
- 3D (i.e. “In flight”) dynamics
- Aggregate average diameter $2R$

What is still missing:
- Prediction of aggregate properties: $2R$?
- “in-flight” aggregation dynamics: time-scale $t_{aggr}$?
- Control with PLD process parameters?

1\textsuperscript{st} step: $2R$ as a function of $t_{aggr}$

Smoluchowski coagulation equation (1916)
- “Diffusion limited” Kernel
- Assumption of fractal geometry

$$2R(t_{aggr}) = a (t_{aggr})^b$$

2\textsuperscript{nd} step: a model to find $t_{aggr}$
A model (I) to find the aggregation time

- $t=0$ ——— n$^{th}$ laser shot on target ———

Adiabatic expansion

- $t \approx 0$ ——— NPs generation ———

n$^{th}$ Shock wave

- $t=\frac{1}{R \cdot R}$ ——— Aggregate landing ———

- $t=0$ ——— Aggregate landing on target

$\approx n^{th}$ laser shot on target

Aggregate landing

Shock wave

Adiabatic expansion
A model (I) to find the aggregation time

- $t=0 \quad \text{n}^{th} \text{laser shot on target}$

**Adiabatic expansion**

- $t \approx 0 \quad \text{NPs generation}$

**n}^{th} \text{Shock wave**

**Hypotheses (I):**

1) $n}^{th} \text{ shock wave drags aggregates}$

2) Aggregates coalesce during the flight

- $t=1 \quad R \times R$

- $t= \frac{1}{R \times R} \quad (n+1)^{th} \text{laser shot on target}$

**Aggregate landing**
A model (I) to find the aggregation time

- $t=0$ --- $n^{th}$ laser shot on target ---

Adiabatic expansion

- $t \approx 0$ --- NPs generation ---

$n^{th}$ Shock wave

Hypotheses (I):
1) $n^{th}$ shock wave drags aggregates
2) Aggregates coalesce during the flight

$t_{agg} \approx t_{o.f.}$

\[ t = \frac{1}{R \cdot R} \quad (n+1)^{th} \text{ laser shot on target} \]
Let’s recap...

What we have learned so far:
- Aggregation is not 2D-DLA
- 3D (i.e. “in flight”) dynamics
- Aggregate average diameter $2R$

What is still missing:
- Prediction of aggregate properties: $2R$?
- “in-flight” aggregation dynamics: time-scale $t_{aggr}$?
- Control with PLD process parameters?

1\textsuperscript{st} step: $2R$ as a function of $t_{aggr}$

Smoluchowski coagulation equation (1916)
  + “Diffusion limited” Kernel
  + Assumption of fractal geometry

$$2R(t_{aggr}) = a \left(t_{aggr}\right)^b$$

2\textsuperscript{nd} step: a model to find $t_{aggr}$

Hp 1: $n$\textsuperscript{th} shock wave drags aggregates
Hp 2: Aggregates coalesce during the flight

$$t_{aggr} \approx \text{time-of-flight}$$

3\textsuperscript{rd} step: calculating $t.o.f.$
Let’s recap…

What we have learned so far:

- Aggregation is **not** 2D-DLA
- 3D (i.e. “in flight”) dynamics
- Aggregate average **diameter** $2R$

What is still missing:

- Prediction of aggregate properties: $2R$?
- “in-flight” aggregation dynamics: time-scale $t_{aggr}$?
- Control with PLD process parameters?

1st step: $2R$ as a function of $t_{aggr}$

Smoluchowski coagulation equation (1916)
  + “Diffusion limited” Kernel
  + Assumption of fractal geometry

$$2R(t_{aggr}) = a (t_{aggr})^b$$

2nd step: a model to find $t_{aggr}$

Hp 1: $n$th shock wave drags aggregates
Hp 2: Aggregates coalesce during the flight

$$t_{aggr} \approx \text{time-of-flight}$$

3rd step: calculating $t.o.f.$

- Aggregates drag force by Stokes-Einstein eq.
- Fluid velocity by Rankine-Hugoniot eq.

$$t.o.f. \approx \frac{1}{c} \frac{2M}{3(M-1)} d_{TS}$$
Let’s recap...

What we have learned so far:

- Aggregation is **not** 2D-DLA
- 3D (i.e. “**in flight**”) dynamics
- Aggregate average **diameter** 2R

What is still missing:

- Prediction of aggregate properties: 2R?
- “in-flight” aggregation dynamics: time-scale $t_{aggr}$?
- Control with PLD process parameters?

1\textsuperscript{st} step: 2R as a function of $t_{aggr}$

Smoluchowski coagulation equation (1916)
+ “Diffusion limited” Kernel
+ Assumption of fractal geometry

$$2R(t_{aggr}) = a (t_{aggr})^b$$

2\textsuperscript{nd} step: a model to find $t_{aggr}$

Hp 1: $n^{th}$ shock wave drags aggregates
Hp 2: Aggregates coalesce during the flight

$t_{aggr} \approx \text{time-of-flight}$

3\textsuperscript{rd} step: calculating t.o.f.

- Aggregates drag force by Stokes-Einstein eq.
- Fluid velocity by Rankine-Hugoniot eq.

$$t.o.f. \approx \frac{1}{c} \frac{2M}{3(M-1)} d_{TS}$$

4\textsuperscript{th} step: experimental test

$$2R \propto (d_{TS})^b$$

Can be measured!
Can be controlled!
Let’s test the t.o.f. hypothesis...

10 shots, 10 Hz

$d_{ts} = 35 \text{ mm}$

$d_{ts} = 45 \text{ mm}$

$D_{ts} = 55 \text{ mm}$

$D_{ts} = 65 \text{ mm}$
Let’s test the t.o.f. hypothesis...

\[ \Omega = \frac{A}{(d_{TS})^2} \]

- Less coverage because of solid angle reduction
Let’s test the t.o.f. hypothesis...

- Less coverage because of solid angle reduction
- Size almost independent from $d_{ts}$

$$2R \propto (d_{TS})^b$$
Let’s test the t.o.f. hypothesis...

- Less coverage because of solid angle reduction
- **Size almost independent from** $d_{ts}$

$t.o.f.$ hypothesis disproved!!!

![Graph showing total coverage and average diameter vs. target-to-substrate distance](image)

$2R \propto (d_{TS})^b$
Let’s recap...

What we have learned so far:

- Aggregation is not 2D-DLA
- 3D (i.e. “in flight”) dynamics
- Aggregate average diameter 2R

What is still missing:

- Prediction of aggregate properties: 2R?
- “in-flight” aggregation dynamics: time-scale $t_{aggr}$?
- Control with PLD process parameters?

1\textsuperscript{st} step: 2R as a function of $t_{aggr}$

Smoluchowski coagulation equation (1916)

+ “Diffusion limited” Kernel
+ Assumption of fractal geometry

$$2R(t_{aggr}) = a(t_{aggr})^b$$

2\textsuperscript{nd} step: a model to find $t_{aggr}$

1) $t_{aggr} \sim$ time-of-flight

---

POLITECNICO MILANO 1863

55
A model (II) to find the aggregation time

- $t=0$ ———- $n^{th}$ laser shot on target ———-

Adiabatic expansion

- $t \approx 0$ ——— NPs generation ———-

Hypotheses (II):

1) $n^{th}$ SW too quick to drag aggregates

$- t = \frac{1}{R \cdot R} \quad (n+1)^{th}$ laser shot on target
A model (II) to find the aggregation time

1. \( t=0 \) ——— \( n^{th} \) laser shot on target

Adiabatic expansion

2. \( t \approx 0 \) ——— NPs generation

Hypotheses (II):

1) \( n^{th} \) SW too quick to drag aggregates
2) Aggregates coalesce after \( n^{th} \) SW is gone
3) \( (n+1)^{th} \) SW drags aggregates to substrate

3. \( t=\frac{1}{R \cdot R} \) ——— \( (n+1)^{th} \) laser shot on target

(Adiabatic expansion + NPs generation)

\( (n+1)^{th} \) Shock wave
A model (II) to find the aggregation time

- \( t=0 \) ——— n\textsuperscript{th} laser shot on target ———

Adiabatic expansion

- \( t \approx 0 \) ——— NPs generation ———

Hypotheses (II):

1) n\textsuperscript{th} SW too quick to drag aggregates
2) Aggregates coalesce after n\textsuperscript{th} SW is gone
3) (n+1)\textsuperscript{th} SW drags aggregates to substrate

\[ t = \frac{1}{R \cdot R} \] ——— (n+1)\textsuperscript{th} laser shot on target

(Adiabatic expansion + NPs generation)

\[ t = \frac{1}{R \cdot R} + tof \approx \frac{1}{R \cdot R} \] — Aggregate landing

\[ t_{aggr} \approx \frac{1}{R \cdot R} \]
Let’s recap…

What we have learned so far:
- Aggregation is not 2D-DLA
- 3D (i.e. “In flight”) dynamics
- Aggregate average diameter $2R$

What is still missing:
- Prediction of aggregate properties: $2R$?
- “in-flight” aggregation dynamics: time-scale $t_{aggr}$?
- Control with PLD process parameters?

1st step: $2R$ as a function of $t_{aggr}$

Smoluchowski coagulation equation (1916)
  + “Diffusion limited” Kernel
  + Assumption of fractal geometry

$$2R(t_{aggr}) = a (t_{aggr})^b$$

2nd step: a model to find $t_{aggr}$

Hp 1: $n^{th}$ SW too quick to drag aggregates
Hp 2: Aggregates coalesce after $n^{th}$ SW is gone
Hp 3: $(n+1)^{th}$ SW drags aggregates to substrate

$t_{aggr} \approx$ shot-to-shot time

3rd step: experimental test

$$2R \propto \left( \frac{1}{R.R.} \right)^b \equiv (t_{sts})^b$$

Can be measured! Can be controlled!

Can be measured! Can be controlled!
Let’s recap…

### What we have learned so far:
- Aggregation is **not** 2D-DLA
- 3D (i.e. “In flight”) dynamics
- Aggregate average **diameter** $2R$

### What is still missing:
- Prediction of aggregate properties: $2R$?
- “in-flight” aggregation dynamics: time-scale $t_{aggr}$?
- Control with **PLD** process parameters?

#### 1st step: $2R$ as a function of $t_{aggr}$

Smoluchowski coagulation equation (1916)
- “Diffusion limited” Kernel
- Assumption of fractal geometry

$$2R(t_{aggr}) = a \left(t_{aggr}\right)^b$$

#### 2nd step: a model to find $t_{aggr}$

- **Hp 1:** $n^{th}$ SW too quick to drag aggregates
- **Hp 2:** Aggregates coalesce after $n^{th}$ SW is gone
- **Hp 3:** $(n+1)^{th}$ SW drags aggregates to substrate

$$t_{aggr} \approx \text{shot-to-shot time}$$

#### 3rd step: experimental test

$$2R \propto \left(\frac{1}{R \cdot R.}\right)^b \equiv (t_{sts})^b$$

**PLD parameters:**
- 10 shots
- $d_{ts} = 45$ mm
- Shot-to-shot time:
  - 0.1s, 0.2s, 0.5s, 1s, 2s, 5s

**Can be measured!**
**Can be controlled!**
Let’s test the “repetition rate” hypothesis...

- Average size $2R$ significantly affected by shot-to-shot time
Let’s test the “repetition rate” hypothesis...

- Average size $2R$ significantly affected by shot-to-shot time
- **Experimental points nicely fitted by a power law!**

\[ 2R \approx a (t_{sts})^{0.273} \]
Let’s test the “repetition rate” hypothesis...

- Average size $2R$ significantly affected by shot-to-shot time
- Experimental points nicely fitted by a power law!

$2R \approx a(t_{sts})^{0.273}$

R.R. hypothesis confirmed
A summary:

We tried to answer to these questions:

- How NPs aggregate and produce a foam?
- How aggregation dynamics controls foam properties?

In the literature, mostly 2D-DLA

- 2D diffusion-limited aggregation on substrate cannot describe foam growth

A model to describes aggregation dynamics

- Aggregates generated by the n\(^\text{th}\) shot are dragged by (n+1)\(^\text{th}\) shock wave
- Aggregation timescale is given by the shot-to-shot interval
- Aggregates size depends on Rep. Rate and not on d\(_{ts}\)

There’s still work to do

- Why the exponent in 2R scaling law is roughly half than expected?
- Does the model work for other materials and deposition conditions?
- … even in different PLD regimes?
A brand new fs-PLD system

fs-PLD interaction chamber
- PLD mode + Laser processing
- up to 4 targets
- Upstream + downstream pressure control
- Fast substrate heater
- Fully automated software

Coherent Astrella™
- Ti:Shappire, $\lambda=800$ nm
- $E_p > 5$ mJ
- Pulse duration $< 100$ fs
- Peak Power $> 50$ GW
- Rep Rate $= 1000$ Hz
fs-PLD of carbon materials

Compact film

Nanoparticles

Carbon foam

Vacuum

10 Pa Ar

100 Pa Ar

Gas pressure

Argon

Work in progress
Acknowledgment

The “ENSURE” team

M. Passoni  V. Russo  M. Zavelani-Rossi
D. Dellasega  A. Maffini  L. Fedeli  A. Pola
A. Formenti  A. Pazzaglia  F. Mirani

NanoLab Group

….Thank you for your attention!
More info on our website

www.ensure.polimi.it