MODELLING OF FULLERENE PRODUCTION BY THE ELECTRIC ARC-DISCHARGE METHOD

Seminar

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Outline

Fullerenes

What are fullerenes?

Fullerens are carbon forms that consist of a:

- spherical (buckyballs),
- ellipsoid, or
- cylindrical (buckytubes = nanotubes)

arrangement of carbon atoms.

Unique properties:

- chemical stability
- extreme strength
- can absorb light
- act as superconductors

Possible applications:

- medicine and electronics
- engineering and construction
- composites, paints, coatings
- aluminium, steel

Buckyballs

- Formed of pentagon and hexagon units of carbon
- Form hollow geodesic domes; bonding strains are equally distributed
- Most common: C_{60}

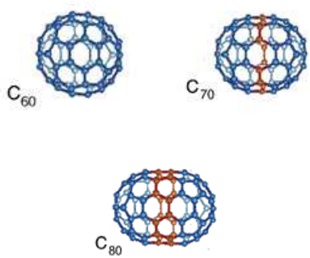

Figure: Buckyballs C_{60}, C_{70} and C_{80} [1].

Single-wall carbon nanotubes (SWNT).

- type: closed, open
- graphene sheet rolled into a tube, caped with half a buckyball
- type: armchair ($m = 1$), zigzag ($n = m$), chirial

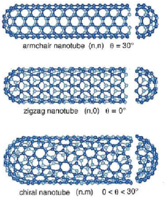

Figure: Single-wall nanotubes [3].

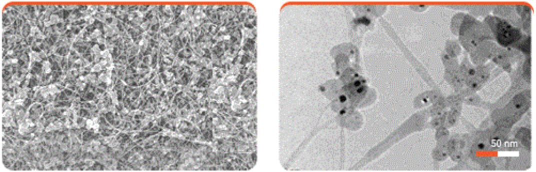

Figure: SEM (left) and TEM (right) images of SWNT bundles [4].

Multi-wall carbon nanotubes (MWNT)

- multiple concentric or rolled graphene sheets
- type: Russian Doll model (concentric cylindres), Parchment model (a single sheet of graphene is rolled around itself)

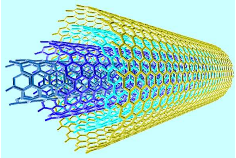

Figure: Multi-wall nanotube [5].

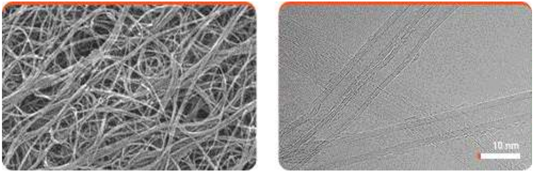

Figure: SEM (left) and TEM (right) images of MWNT bundles [4].

Fullerene production

Production techniques

- Arc-discharge:
  - Arc vaporisation of 2 carbon rods placed a few mm apart.
  - SWNT, MWNT, buckyballs. Short tubes of random sizes in need of purification. The most efficient.
- Laser ablation (vaporisation):
  - Blast graphite with intense laser pulse.
  - Mostly MWNT, SWNT. Long tubes, MWNTs riddled with defects, diameter of SWNTs is controllable.
- Chemical vapour deposition (CVD):
  - A gas of carbon source is injected into an oven where heated substrate is present.
  - SWNT, Long bundles of tubes, good diameter control, few defects, costly.

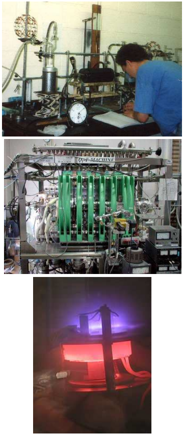

Figure: 1. Arc-discharge apparatus [9]. 2. Laser ablation apparatus [7]. 3. CVD apparatus [8].

Arc-discharge cell

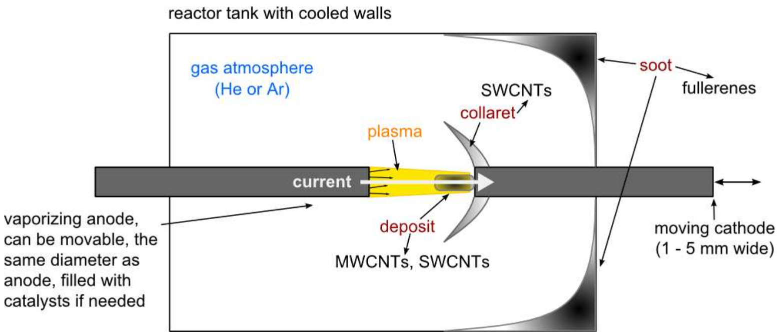

Figure: A scheme of a typical arc discharge reactor chamber and the locations where products are formed (Grlj, 2010).

Models of fullerene growth

Fan (plasma) jet is formed as a consequence of heat and mass transfer.

Review of fullerene modelling:

- Kerstinin, Moravsky (1998): mathematical model combined with kinetics for fullerene formation
- Farhat et al. (2005): mathematical model based on carbon deposition on rotating cathode.
- Bilodeau et al. (1998): 2D model for the analysis of fullerene synthesis.
- Alekseev, Dyuzhev (1999): mathematical model connecting initial jet parameters and fullerene yield.

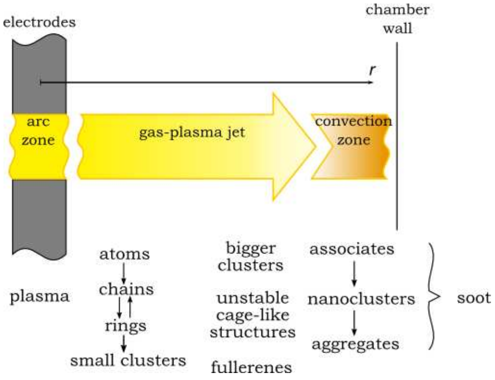

Figure: Fullerene formation scheme in arc discharge (Grlj, 2010).

Physical model

Overview of the general assumptions:

- Steady state.
- Axisymmetric, laminar flow with Re < 10.
- Local thermodynamic equilibrium.

Bilodeau (1998):

- Uniform anode erosion rate over the electrode surface.
- Surface deposition on the cathode is governed by diffusion.
- Energy input in the arc is due to ohmic heating and to the enthalpy flux of electrons.
- 1D electric field.

Farhat (2006):

- Radiation losses are accounted for by the net emission coefficient.
- Temperature dependent fluid properties.

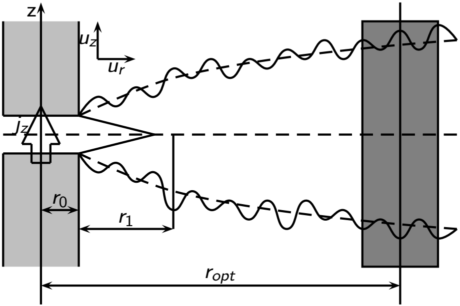

Figure: The sketch of jet fan in arc-discharge reactor.

Continuity equations

Continuity equation - general form:

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{u}) = S_m$$

2D steady state model (Bilodeau, 1998)

$$\vec{\nabla} \cdot (\rho \vec{u}) = S_m$$

Cylindrical coordinates:

$$\frac{\partial \rho}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(\rho r u_r) + \frac{\partial}{\partial z}(\rho u_z) = S_m$$

$$\frac{1}{r}\frac{\partial}{\partial r}(\rho r u_r) + \frac{\partial}{\partial z}(\rho u_z) = 0$$

1D steady state model (Farhat, 2006)

$$\frac{\partial \rho}{\partial t} = -\frac{u_z}{\rho}\frac{\partial \rho}{\partial z} - 2V - \frac{\partial u_z}{\partial z} = 0$$

Momentum equations

Momentum equation - plasma - general form:

$$\frac{D(\rho\vec{u})}{Dt} = -\vec{\nabla}P + \vec{\nabla}^2(2\mu\vec{u}) + \vec{\nabla}\cdot(\mu\vec{\nabla}\times\vec{u}) + \rho\vec{g} + \vec{j}\times\vec{B} + \rho\vec{f}$$

Local thermodynamic equilibrium (L.T.E.)

Momentum equation - gas - general form:

$$\frac{\partial(\rho\vec{u})}{\partial t} + \vec{\nabla}\cdot(\rho\vec{u}\vec{u}) = -\vec{\nabla}P + \mu\vec{\nabla}^2\vec{u} + \rho\vec{g} + \vec{j}\times\vec{B} + \rho\vec{f}$$

Equation of state - general form:

$$P = \frac{\rho RT}{M}$$

Momentum equations 2

2D model (Bilodeau, 1998)

$$\vec{\nabla} \cdot (\rho \vec{u}\vec{u}) = -\vec{\nabla} P + \mu \vec{\nabla}^2 \vec{u} + \rho \vec{g} + \vec{j} \times \vec{B}$$

Radial momentum:

$$\rho\left(\frac{\partial u_r}{\partial t}+u_r\frac{\partial u_r}{\partial r}+u_z\frac{\partial u_r}{\partial z}\right) = -\frac{\partial P}{\partial r}+\mu\left(\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(ru_r)\right)+\frac{\partial^2 u_r}{\partial z^2}\right)+\rho g_r - j_z B_\theta + \rho f_r$$

Axial momentum:

$$\rho\left(\frac{\partial u_z}{\partial t}+u_r\frac{\partial u_z}{\partial r}+u_z\frac{\partial u_z}{\partial z}\right) = -\frac{\partial P}{\partial z}+\mu\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_z}{\partial r}\right)+\frac{\partial^2 u_z}{\partial z^2}\right)+\rho g_z + j_r B_\theta + \rho f_z$$

1D model (Farhat, 2006)

$$\rho\frac{\partial V}{\partial t} = -\frac{\partial}{\partial z}\left(\mu\frac{\partial V}{\partial z}\right) - \rho u_z\frac{\partial V}{\partial z} - \rho V^2 - \frac{1}{r}\frac{\partial P}{\partial r} = 0$$

Conservation of species

Species conservation equation - general form:

$$\frac{\partial(\rho Y_i)}{\partial t} + \vec{\nabla} \cdot (\rho Y_i \vec{u}) = \vec{\nabla} \cdot (\rho D_i \vec{\nabla} Y_i) + S_{in}$$

2D steady state model (Bilodeau, 1998):

$$\vec{\nabla} \cdot (\rho \vec{u} Y_C) = \vec{\nabla} \cdot (\rho D_C \vec{\nabla} Y_C) + S_{in}$$

1D steady state model (Farhat, 2006):

$$\rho \frac{\partial Y_i}{\partial t} + \frac{\partial(\rho Y_i V_i)}{\partial z} + \rho u \frac{\partial Y_i}{\partial z} = M_i \omega_i$$

Simplification:

$$\rho \frac{\partial Y_i}{\partial t} = M_i \omega_i$$

Conservation of energy

The conservation of energy equation - general form:

$$\frac{D(\rho h)}{Dt} = \vec{\nabla}\cdot(k\vec{\nabla}T) + \frac{\vec{j}^2}{\sigma} + \frac{5}{2}\frac{k_B}{e}\vec{\nabla}\cdot(T\vec{j}) - (k - \rho D_C c_p)\vec{\nabla}(T_C - T_g)\cdot\vec{\nabla}Y_C - Q_{rad} - S_h$$

2D steady state model (Bilodeau, 1998):

$$\vec{\nabla}\cdot(\rho\vec{v}h) = \vec{\nabla}\cdot(k\vec{\nabla}T) + \frac{j_z^2}{\sigma} + \frac{5}{2}\frac{k_B}{e}c_p\vec{j}\cdot\vec{\nabla}T - (k - \rho D_C c_p)\vec{\nabla}(T_C - T_g)\cdot\vec{\nabla}Y_C - Q_{rad} + S_h$$

1D steady state model (Farhat, 2006):

$$\rho c_p\frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right) - \rho c_p u_r\frac{\partial T}{\partial z} - \sum_{i=1}^{n_g}\left(c_{pi}\rho Y_i V_i\frac{\partial T}{\partial r} + \omega_i h_i\right) + S_h - Q_{rad} = 0$$

Boundary and initial conditions

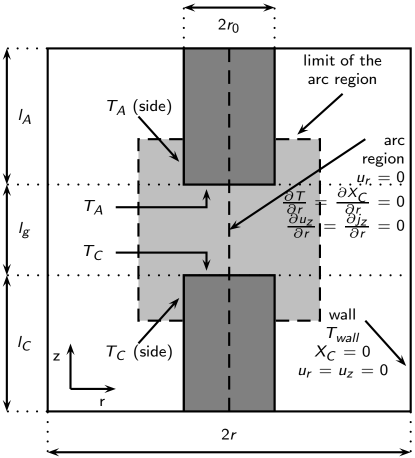

Figure: Boundary and initial conditions (Bilodeau, 1998).

Chemical kinetics model

Kinetic models for fullerene growth:

- intermediate cluster formation
- the pentagon road
- the fullerene road
- the ring road

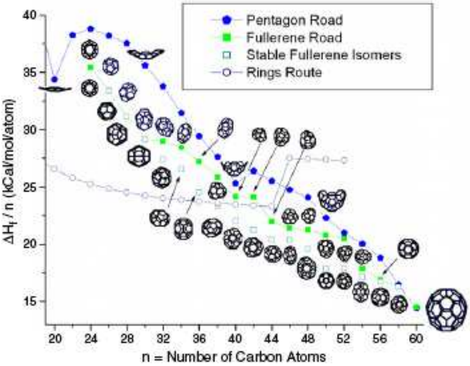

Figure: Comparison of different fullerene growth models [6].

Chemical kinetics model

The fullerene model:

$$k_{1,2r} = A_{1,2r} T^{\beta_{1,2r}} exp\left(- \frac{E_{1,2}r}{RT} \right)$$

$$q_r = k_{1r} \prod_{i=1}^{n_g} C_i^{\nu_{ir}^{'}} - k_{2r} \prod_{i=1}^{n_g} C_i^{\nu_{ir}^{''}}$$

$$\omega_i = \sum_{r=1}^{R} \nu_{ir} q_r = \frac{dC_i}{dt}$$

Chemistry of small clusters

$C + C \leftrightarrow C_2$
$C + C_2 \leftrightarrow C_3$
$C_2 + C_2 \leftrightarrow C_3 + C$

Formation of carbon clusters CC

$C_3 + C \leftrightarrow 0.100CC$
$C_3 + C_2 \leftrightarrow 0.125CC$
$C_3 + C_3 \leftrightarrow 0.150CC$

Growth of carbon clusters CC

$CC + C \leftrightarrow 1.025CC$
$CC + C_2 \rightarrow 1.050CC$
$CC \rightarrow 0.95CC + C$

Formation of fullerene molecules C_{60}^F and C_{70}^F

$CC + C_3 \rightarrow 0.70C_{60}^F$
$CC + C_2 \rightarrow 0.70C_{60}^F$
$CC + C \rightarrow 0.6833333C_{60}^F$

Decay of fullerene molecules C_{60}^F and C_{70}^F

$C_{60F} \rightarrow 1.45CC + C_2$
$C_{70F} \rightarrow 1.70CC + C_2$

Formation of soot nuclei Z and growth of soot

$CC + CC \rightarrow Z$
$Z + C_3 \rightarrow 1.0375Z$
$Z + C_2 \rightarrow 1.025Z$
$Z + C \rightarrow 1.0125Z$

The initial model - domain scheme

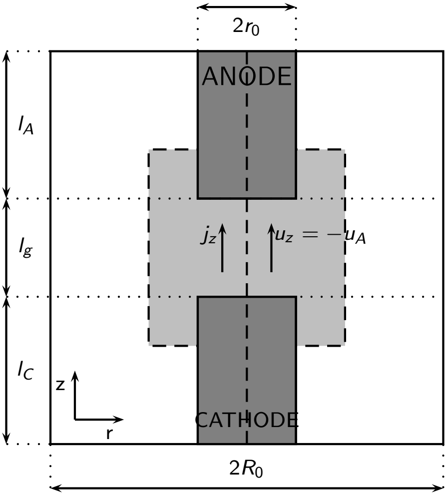

Figure: 1D domain scheme.

The initial model

The initial model is based on 1D Farhat model (Farhat, 2006).

- Continuity eq.:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial z}(\rho u_z) - 2V - \frac{\partial u_z}{\partial z} = 0$$

- Momentum eq.:

$$\rho \frac{\partial u_r}{\partial t} = -\frac{\partial}{\partial z}\left(\mu \frac{\partial u_r}{\partial z}\right) - \rho u_z \frac{\partial u_r}{\partial z} - \frac{\partial p}{\partial r} - j_z B_\theta$$

- Energy eq.:

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(k \frac{\partial T}{\partial z}\right) - \rho c_p u_r \frac{\partial T}{\partial z} - \sum_{i=1}^{n_g}\left(c_{pi} \rho Y_i V_i \frac{\partial T}{\partial r} + \omega_i h_i\right) + \frac{j_z^2}{\sigma} = 0$$

- Species conservation eq.:

$$\rho \frac{\partial Y_i}{\partial t} = M_i \omega_i$$

The initial model - boundary and initial conditions

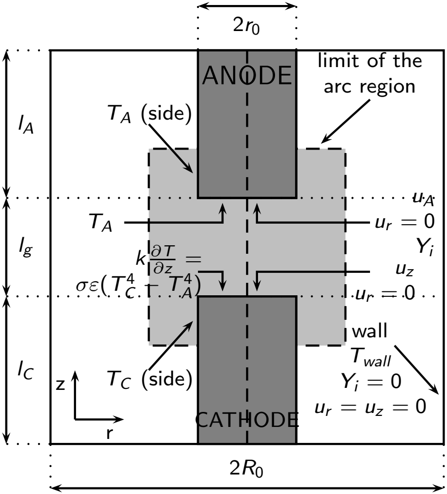

Figure: Boundary and initial conditions for 1D model (Farhat, 2006).

The improved model - domain scheme

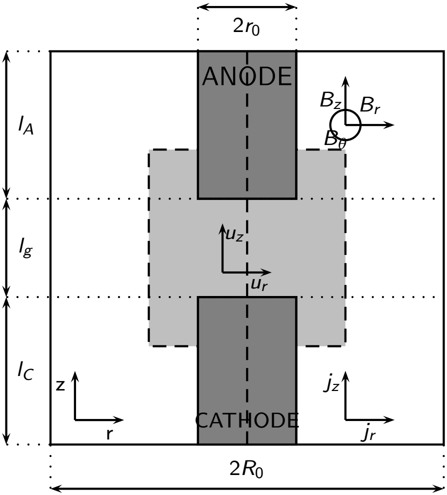

Figure: 2D domain scheme.

Improved model

Initial model is going to be expanded to more dimensions (2D).
Improved model is based on Bilodeau model (Bilodeau, 1998).

- Continuity eq.:

$$\frac{\partial(\rho)}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(\rho r u_r) + \frac{\partial}{\partial z}(\rho u_z) = S_m$$

- Momentum eq.:

$$\rho\left(\frac{\partial u_r}{\partial t} + u_r\frac{\partial u_r}{\partial r} + u_z\frac{\partial u_r}{\partial z}\right) = -\frac{\partial p}{\partial r} + \mu\left(\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(r u_r)\right) + \frac{\partial^2 u_r}{\partial z^2}\right) + j_z B_\theta$$

$$\rho\left(\frac{\partial u_z}{\partial t} + u_r\frac{\partial u_z}{\partial r} + u_z\frac{\partial u_z}{\partial z}\right) = -\frac{\partial p}{\partial z} + \mu\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_z}{\partial r}\right) + \frac{\partial^2 u_z}{\partial z^2}\right) + \rho g_z + j_r B_\theta$$

- Energy eq.:

$$\frac{\partial(\rho h)}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(r\rho u_r h) + \frac{\partial}{\partial z}(\rho u_z h) = \frac{1}{r}\frac{\partial}{\partial r}\left(rk\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right) + \frac{j_z^2}{\sigma} + \frac{5}{2}\frac{k_b}{e}\left(j_r\frac{\partial T}{\partial r} + j_z\frac{\partial T}{\partial z}\right) -$$

$$-\frac{1}{r}\frac{\partial}{\partial r}(rk - r\rho D_C c_p)(T_C - T_g)\frac{\partial Y_C}{\partial r} - \frac{\partial}{\partial z}(k - \rho D_C c_p)(T_C - T_g)\frac{\partial Y_C}{\partial z}$$

- Species conservation eq.:

$$\rho\frac{\partial Y_C}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(r\rho u_r Y_C) + \frac{\partial}{\partial z}(\rho u_z Y_C) = \frac{1}{r}\frac{\partial}{\partial r}\left(r\rho u_r\frac{\partial Y_C}{\partial r}\right) + \frac{\partial}{\partial z}\left(\rho u_z\frac{\partial Y_C}{\partial z}\right) + S_{in}$$

The improved model - boundary and initial conditions

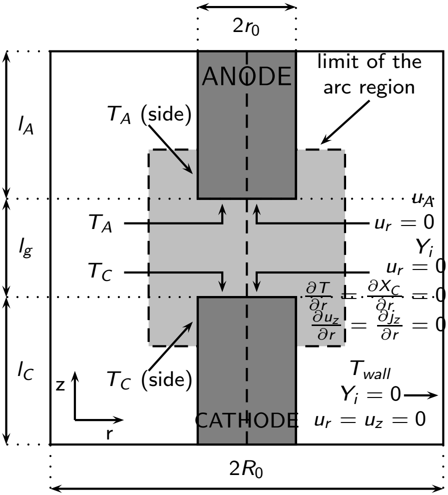

Figure: 2D boundary and initial conditions (Bilodeau, 1998).

Values of reduced input parameters

Input parameters:

constant	label	value
anode diameter	$2r_A$	6 - 7
cathode diameter	$2r_C$	6 - 16 mm
anode length	l_A	15-70 cm
cathode length	l_C	15 -30 cm
reactor length	$l_C + l_A + l_g$	39-100 cm
reactor diameter	$2r$	13.6-30 cm
current	I	60-100 A
pressure	P	100-800 mbar
anode cathode distance	l_g	1-12 mm
anode, cathode tip T	T_A	3300-3800 K
wall temperature	T_w	350 K
mass density of the gas	ρ	$9.24 \cdot 10^{-6} \frac{g}{cm^3}$
carbon mass fraction	n_C	$10^{-4} - 10^{-6}$
initial C mole fraction	N_C	$2.57 \cdot 10^{-4}$
initial C_2 mole fraction	N_{C_2}	0.583
current intensity	j	$3 \cdot 10^6 - 10^7 \frac{A}{m^2}$

Values of reduced output parameters

Output parameters:

constant	label	value
anode gas velocity	u_A	$7818 \frac{cm}{s}$
deposition rate		$0.57 - 4.71 \frac{mg}{s}$
electric power dissipation	q	$1.24 \cdot 10^7 \frac{W}{m^2}$
dilution factor at the anode	τ	20
erosion rate	Φ	$1.3 - 25 \cdot 10^{-3} \frac{g}{s}$
estimated electron density	N_e	$3.5 \cdot 10^{15} \frac{1}{cm^3}$
temperature	T	350-17000 K
He number density	n_{He}	$1.4 \cdot 10^{18} \frac{1}{cm^3}$
Ni number density	n_{Ni}	$2.0 \cdot 10^{14} \frac{1}{cm^3}$
Y number density	n_Y	$3.2 \cdot 10^{14} \frac{1}{cm^3}$
growth rate	G	$1 - 1000 \frac{\mu m}{min}$

Qualitative estimation of involved variables

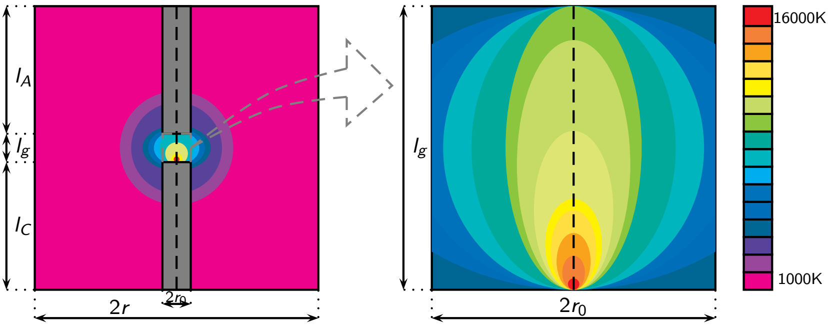

Figure: Estimation of temperature field (Bilodeau, 1998).

Qualitative estimation of involved variables

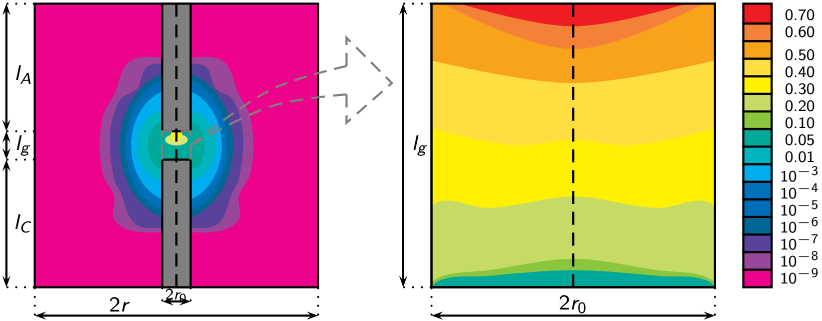

Figure: Estimation of carbon mass fraction field (Bilodeau, 1998).

Qualitative estimation of involved variables

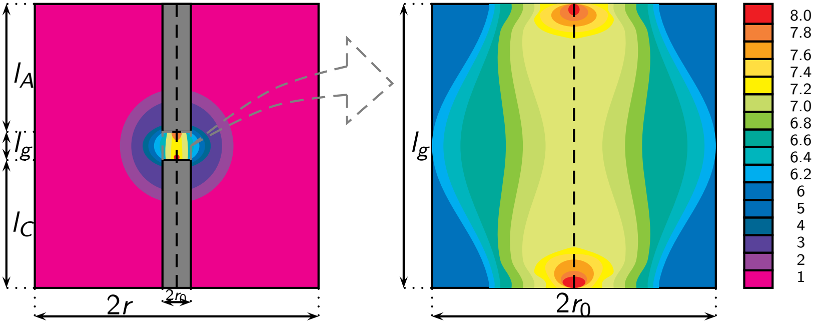

Figure: Estimation of axial current intensity field (Bilodeau, 1998).

Estimated number of equations

Estimated number of equations calculated for a particular point for each time step (without boundary conditions):

- The initial model: 59 (Chemical reactions: $18 \cdot 3$, 5 governing equations)
- The improved model: 61 (Chemical reactions: $18 \cdot 3$, 7 governing equations)

Meshless method and radial basis functions

Meshless method = mesh reduction technique

A numerical simulation algorithm that uses a set of arbitrary nodes to represent the solution of a physical problem.

Radial basis functions (RBF)

General approximation functions of univariate polynomial splines to a multivariate domain.

$$\psi_i(r) = \psi(\vec{p} - \vec{p}_i)$$

Commonly used RBFs:

- Gaussian (GA) $\psi(r) = e^{-(cr)^2}$
- multiquadric (MQ) $\psi(r) = \sqrt{r^2 + c^2}$

General form of an approximation function:

$$\Theta(\vec{p}) = \sum_{i=1}^{N} \alpha_i \psi_i(\vec{p})$$

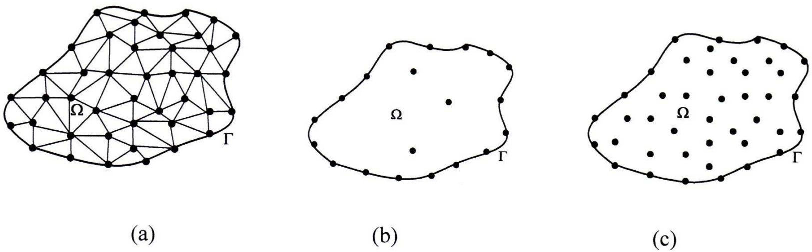

Figure: Irregular domain discretized using (a) 3-noded triangular finite elements, b) boundary element, and (c) arbitrary interior and boundary points using a meshless method [10].

Local radial basis function collocation method

Approximation function:

$$\Theta(\vec{p}) \approx \sum_{i=1}^{N} \alpha_i \psi_i(\vec{p})$$

Collocation condition:

$$\Theta(\vec{p}_i) = \theta_i$$

Linear system of N equations:

$$\mathbf{\Psi}\vec{\alpha} = \vec{\theta}$$

PDE equations:

$$\frac{\partial^i}{\partial p_\iota^i}\Theta(\vec{p}) = \sum_{n=1}^{N} \alpha_n \frac{\partial^i}{\partial p_\iota^i}\Psi_n(\vec{p})$$

Introduction of boundary conditions

- Dirichlet

$$\Theta(\vec{p}) = \Theta_{BC} \quad \rightarrow \quad \Theta(\vec{p}) = \Theta_{BC}$$

- Neuman

$$\frac{\partial}{\partial \vec{n}}\Theta(\vec{p}) = \Theta_{BC} \quad \rightarrow \quad \Theta_{BC} = \sum_{i=1}^{N} \alpha_i \frac{\partial}{\partial \vec{n}}\Psi_i(\vec{p})$$

- Robin

$$\frac{\partial}{\partial \vec{n}}\Theta(\vec{p}) + b\Theta(\vec{p}) = \Theta_{BC} \quad \rightarrow \quad \Theta_{BC} = \sum_{i=1}^{N} \alpha_n \left(a\frac{\partial}{\partial \vec{n}}\Psi_i(\vec{p}) + b\Psi_i(\vec{p}) \right)$$

Conclusions

- Introduction to fullerene production and modelling.
- Presentation of arc - discharge method.
- Formulation of a mathematical model.
- Description of a numerical method.

Future steps:

- Establishment of a minimal model (implement model, solution procedure)
- Comparison with measurements from actual cell

Literature review

More than 150 (154) articles were gathered on the subject of fullerene production and modelling.
A comprehensive review of literature was done and is available at:
https://4pm.cobik.si/projects/tabs/projectPortalTabDefFiles.jsf?list=1&prjId=1118

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