FOUNDATION FOR
RESEARCH
SCIENCE &
TECHNOLOGY
Tūāpapa Rangahau Pūtaiao

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UNIVERSITY OF
CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

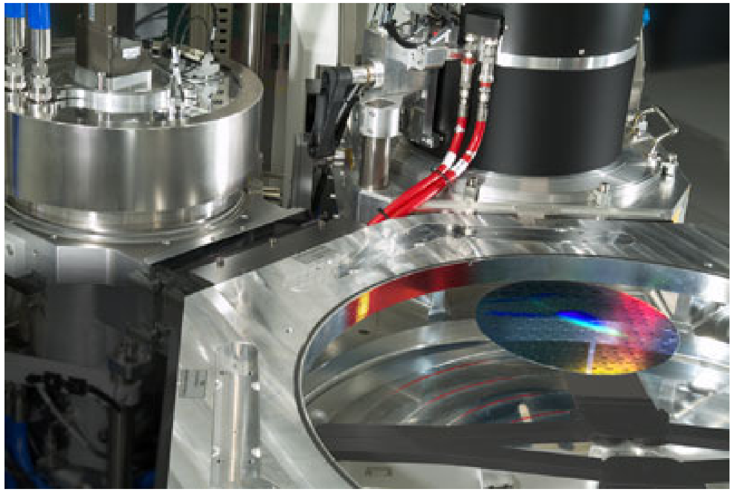
High quality thin film coatings by pulsed pressure CVD

- Contract UOCX0710
- Commenced 1/1/2008, ends 31/12/2010

Conventional CVD
Chemical Vapour Deposition

OPPORTUNITIES

- Thin Film Devices:
  - Solar PV
  - Insulating layers on Semiconductors
  - Piezoceramics
  - Scratch resistant and antireflective coatings on optics
  - Wear resistant coatings on machine tools
- Multi billion $ market for Production Tools



CHALLENGES

- Inefficient, Expensive, Toxic Chemicals
- Uniformity, Quality, Throughput
- Long lead time and high price of equipment are barriers to new products

PP-CVD can meet these challenges and become a transformational product

IF we can design optimised reactors
This requires a modelling capability

Goals of this contract

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PP-CVD
Pulsed- pressure CVD

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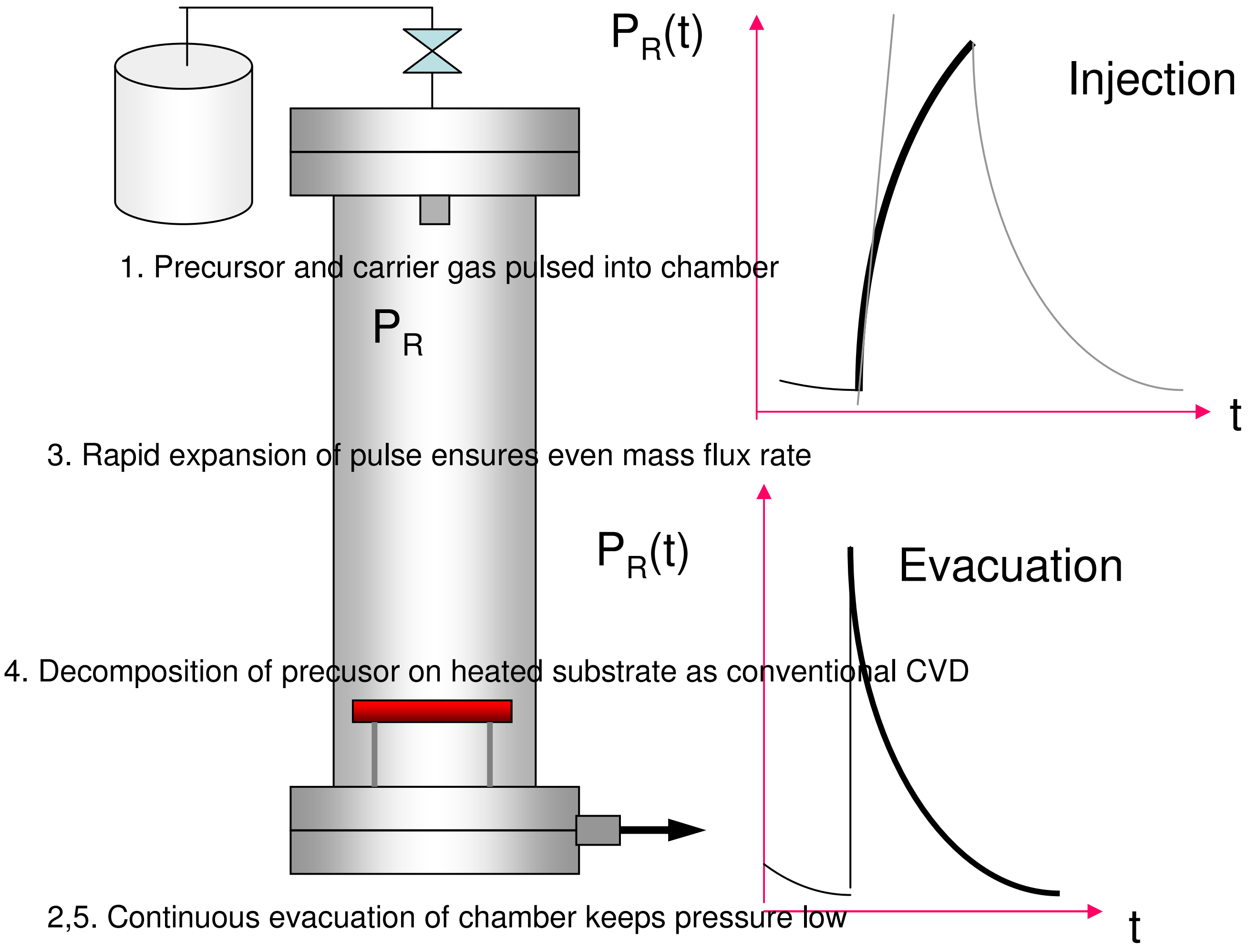
- Rapid expansion
- Mass flux even across chamber
- Films of uniform thickness
- Simple design
- Short lead time
- Successful use in laboratory:
  - Yttria stabilised Zirconia
  - Titanium Dioxide
  - Diamond-like carbon
  - Biocompatible hydroxyapatite
- Estimated cost \$0.1M
- Replace machines currently retailing at \$2M each
- Market at least \$4M/year at entry level

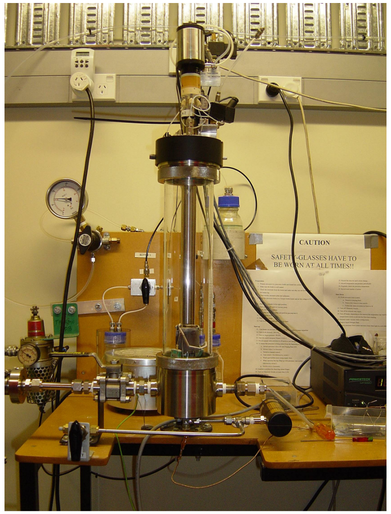


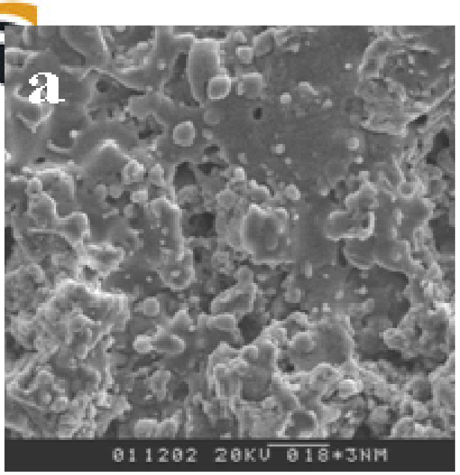
1. Precursor and carrier gas pulsed into chamber

3. Rapid expansion of pulse ensures even mass flux rate

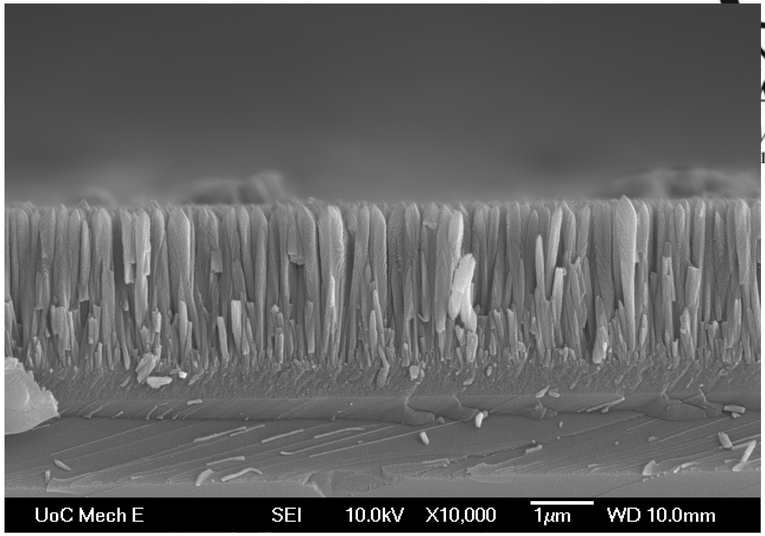
4. Decomposition of precusor on heated substrate as conventional CVD

2,5. Continuous evacuation of chamber keeps pressure low

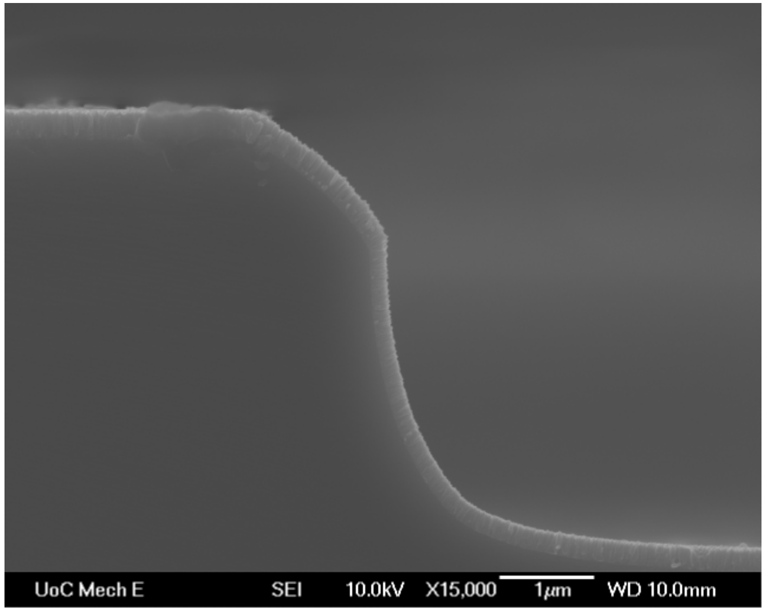




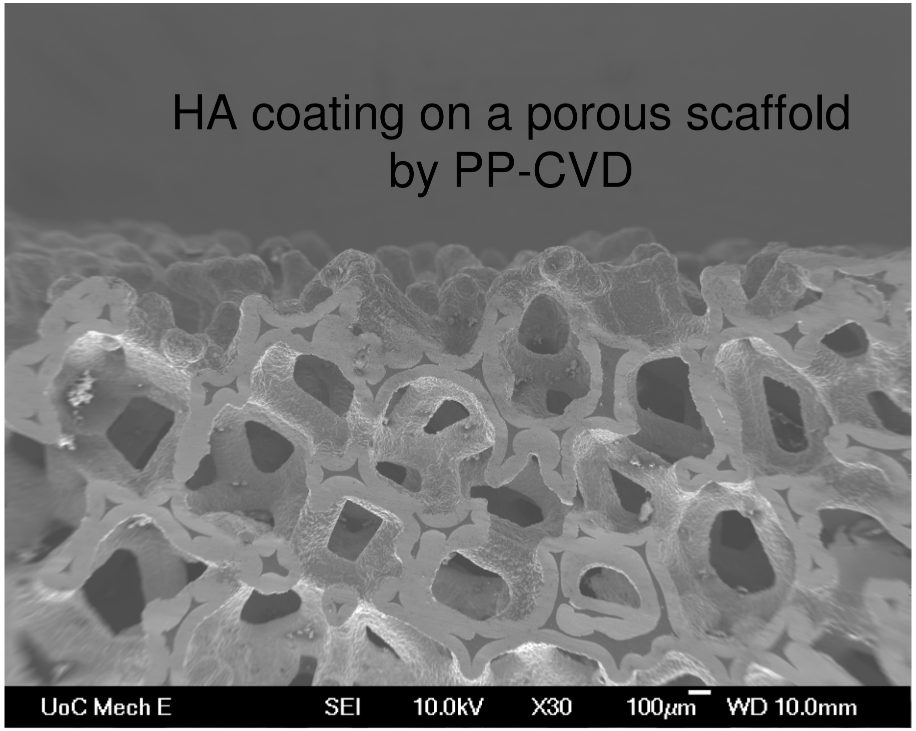
Sol-gel coating



TiO2 coating by *PP-CVD*



TiO$_2$ by PP-CVD



HA coating on a porous scaffold by PP-CVD

Strategic plan

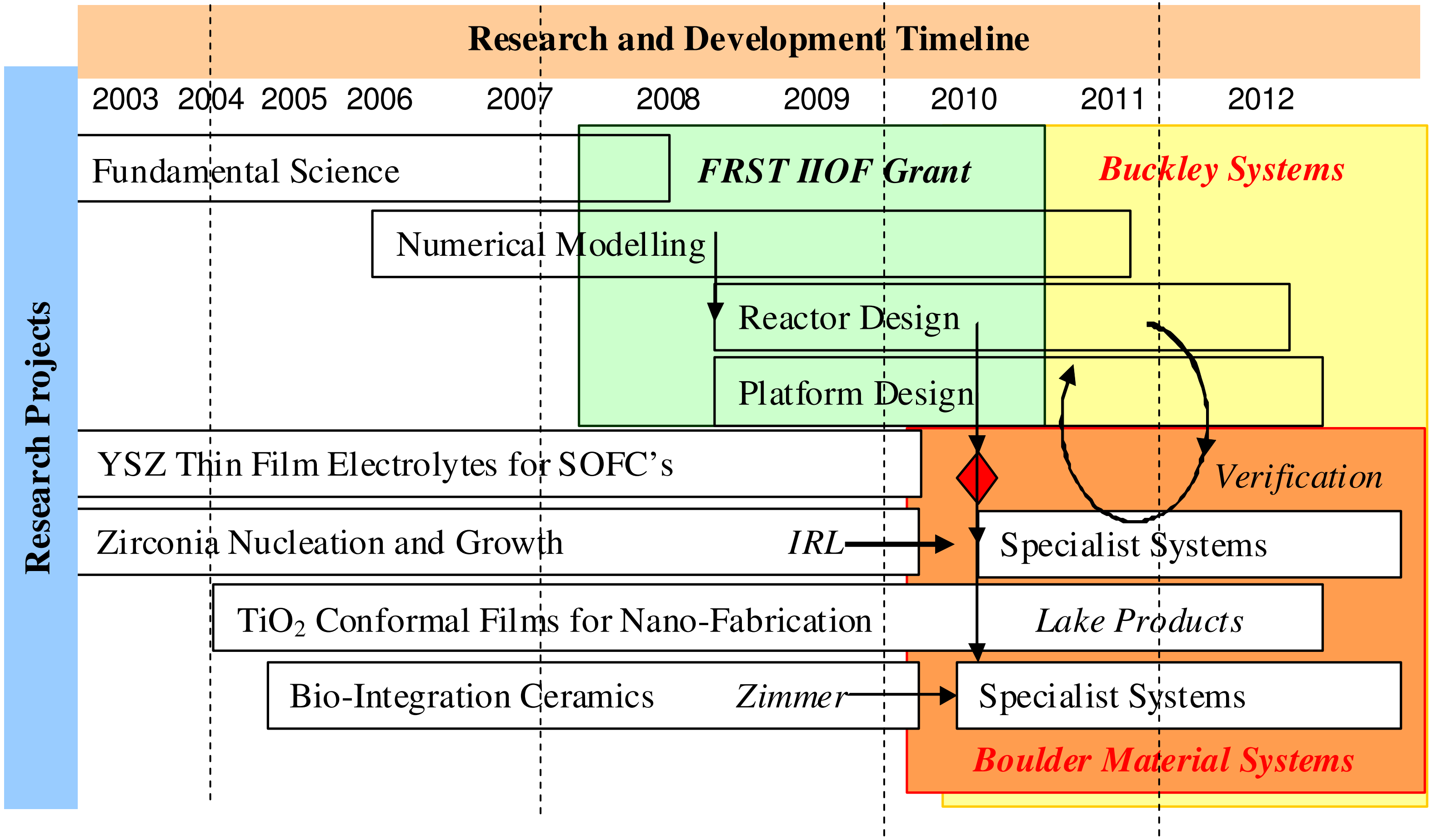
Development of PP-CVD concept

Trial systems and proof of principle

Development of numerical modelling for optimisation

Design and demonstration of systems optimised for production

Sale of systems, development to order for new coating products



Research and Development Timeline

2003 2004 2005 2006 2007 2008 2009 2010 2011 2012

Research Projects

Fundamental Science

FRST IIOF Grant

Buckley Systems

Numerical Modelling

Reactor Design

Platform Design

YSZ Thin Film Electrolytes for SOFC's

Verification

Zirconia Nucleation and Growth *IRL* → Specialist Systems

TiO_2 Conformal Films for Nano-Fabrication *Lake Products*

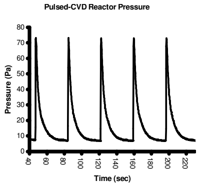
Bio-Integration Ceramics *Zimmer* → Specialist Systems

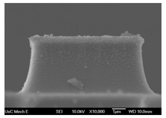
Boulder Material Systems

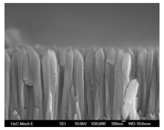
Strategic plan

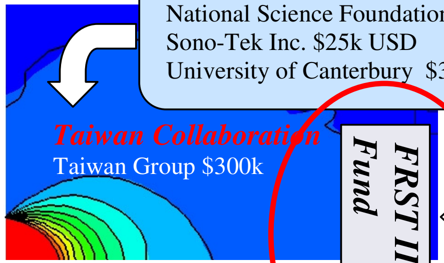
Innovative Concept
National Science Foundation $100k USD
Sono-Tek Inc. $25k USD
University of Canterbury $30k

University of Canterbury









Taiwan Collaboration
Taiwan Group $300k

FRST IIOF Fund

Fundamental Science
Marsden Fund Grant $100k
Marsden Fund Grant $912k

Numerical Modelling
TEC Top Achiever Scholar $98k
RSNZ ISAT Linkages $14k
UC Supercomputer Time $18k

Experimental Facilities
UC Laboratory Build $240k
UC Laboratory Equipment $100k

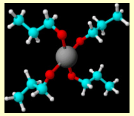
Reactor Design and Build
UC Research Grant $70k
IRL Ltd. $20k
UC Post-Doc $104k

Research-Scale System Design
UC Summer Scholarship Grant $2k
University of Colorado $4k

Boulder Material Systems NZ
UCI3 Innovation Incubator
Canterprise

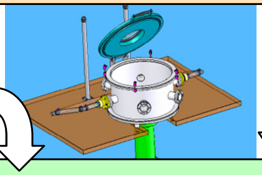
Material Processing - Zirconia
UC Research Scholarship Grant $60k
IRL Ltd. $80k
National Science Foundation $5k

Chemistry Route- BioCeramics
FRST Post Doc $218k
Canterprise (Patent) $2k
Zimmer Inc. $80k



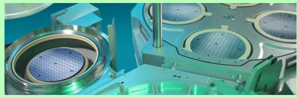
Device Development
Conformal TiO_2 on Nano-Forms
UC Research Scholarship Grant $60k

Industrial Manufacturing Systems
Lake Products TiO_2 Coatings $70k
Microwave and Materials Designs $50k
Zimmer Inc. $750k per tool

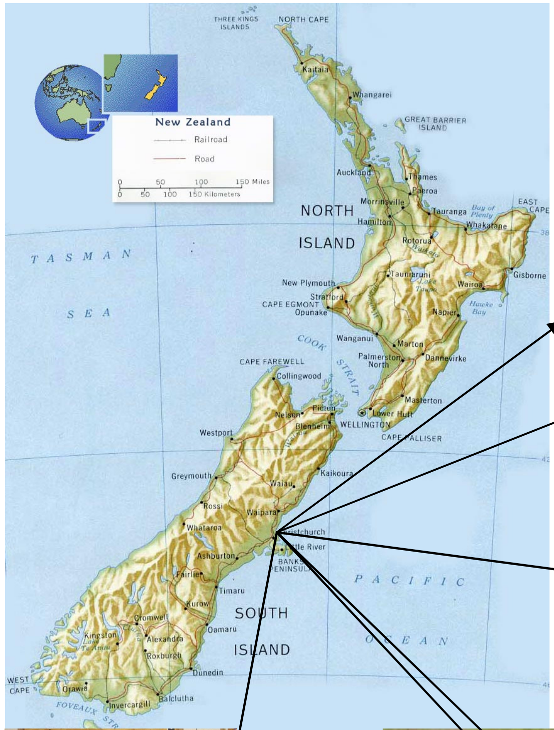


Commercial Platform Design & Development
Buckley Systems Ltd $70k

Commercial PP-CVD Tools Delivered to Market
$4M Sales First 5 Years
Target rapid development for new devices



Key personnel



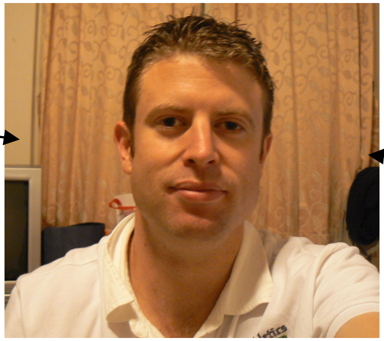
Assoc. Prof. Susan Krumdieck
PP-CVD development

Dr Mark Jermy
Flow field simulation and measurement

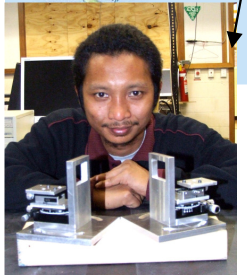
Prof. Jong-Shinn Wu
National Chiao-Tung University
Flow field simulation code development

Dr KC Tseng
National Space Organisation
Flow field simulation code development

Dr Matthew Smith
NCTU and National Centre for High Performance Computing
Flow field simulation code development



Dr Hadley Cave
UC and NCTU
Flow field simulation code development



Mr Zulkhairi Zainol Abidin
Experimental validation of flow field

Mr Lim Chin Wai
Numerical prediction of flow field

A.N. Other
PP-CVD system design

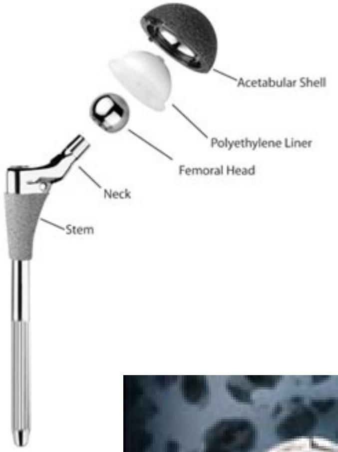
Key relationships

- Buckley Systems *Simon Longdill*
  - Manufacture of final system
    - Current business:
      - precision electromagnets
      - ion beam physics hardware
      - high vacuum equipment
    - *used in the semi-conductor ion implant industry and laboratory research.*
    - Annual turnover is $50 million
    - 150 employees



Future Development

- Breakthrough Products
  - High Temperature Superconductors
    - Industrial Research Ltd
  - Microwave Guides
    - Lake Technology Ltd.
    - Microwave and Materials Designs Pty. Ltd.
  - Bone Implant Bio-Integration Coatings
    - Zimmer, Enztek



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Contract milestones & objectives

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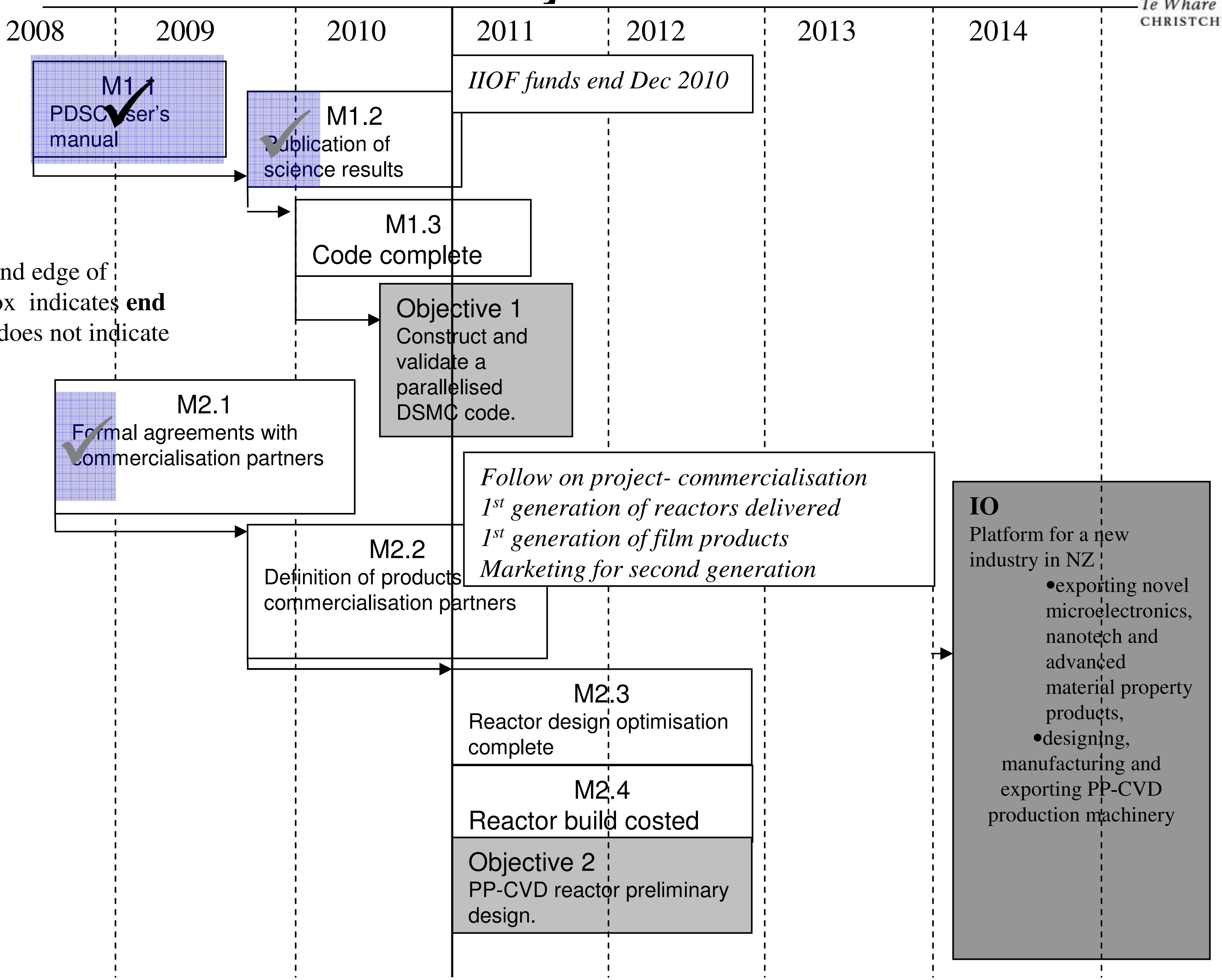


M1.1 ✓
PDSC User's manual

M1.2 ✓
Publication of science results

M1.3
Code complete

IIOF funds end Dec 2010

Objective 1
Construct and validate a parallelised DSMC code.

Note: left hand edge of milestone box indicates **end date**: width does not indicate duration

M2.1 ✓
Formal agreements with commercialisation partners

M2.2
Definition of products commercialisation partners

Follow on project- commercialisation
1st generation of reactors delivered
1st generation of film products
Marketing for second generation

M2.3
Reactor design optimisation complete

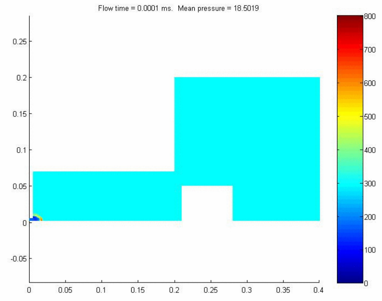
M2.4
Reactor build costed

Objective 2
PP-CVD reactor preliminary design.

IO
Platform for a new industry in NZ
- exporting novel microelectronics, nanotech and advanced material property products,
- designing, manufacturing and exporting PP-CVD production machinery

Development of PDSC (first 24 months)

- Conventional Navier-Stokes solvers (CFD) cannot simulate gas flow in the rarefied regions
- Parallel Direct Simulation Monte Carlo (PDSC)
  - Track individual gas molecules as they travel through the reactor and collide with other gas molecules, walls and substrate
  - Long computational run-times in regions of dense gas
  - Plan to hybridise with a solution scheme which is faster in dense regions
- Quiet Direct Simulation
  - Assume equilibrium: Maxwell-Boltzmann distribution
  - Divide distribution into bins
  - Track motion of collection of molecules in each bin
  - Calculate flow of mass, momentum and energy from cell to cell
- Hybrid
  - Code combining QDS for fast simulation of dense regions and PDSC for rarefied regions

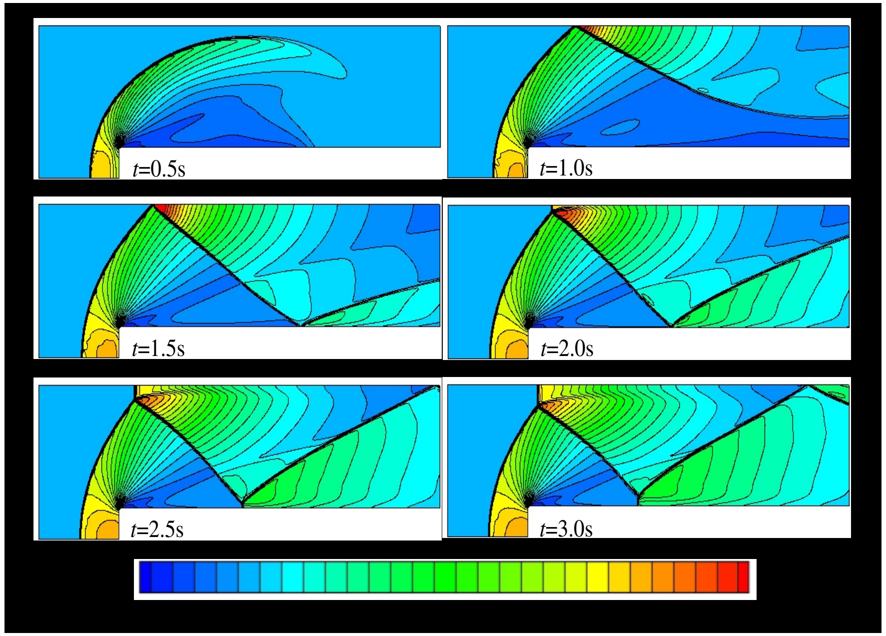


Excellent Progress Exceeds Goals

•**Dense equilibrium**, regions near nozzle and during injection

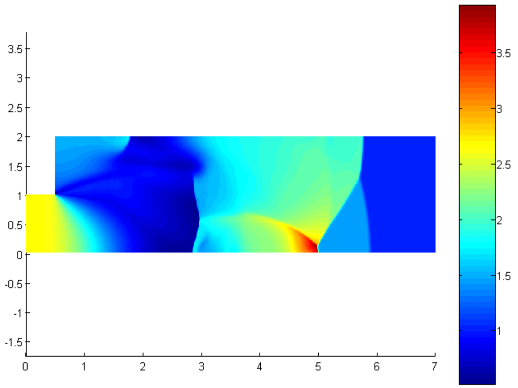
•**Rarefied non equilibrium** regions near substrate and during expansion phase

Hypersonic flow over a forward facing cylinder

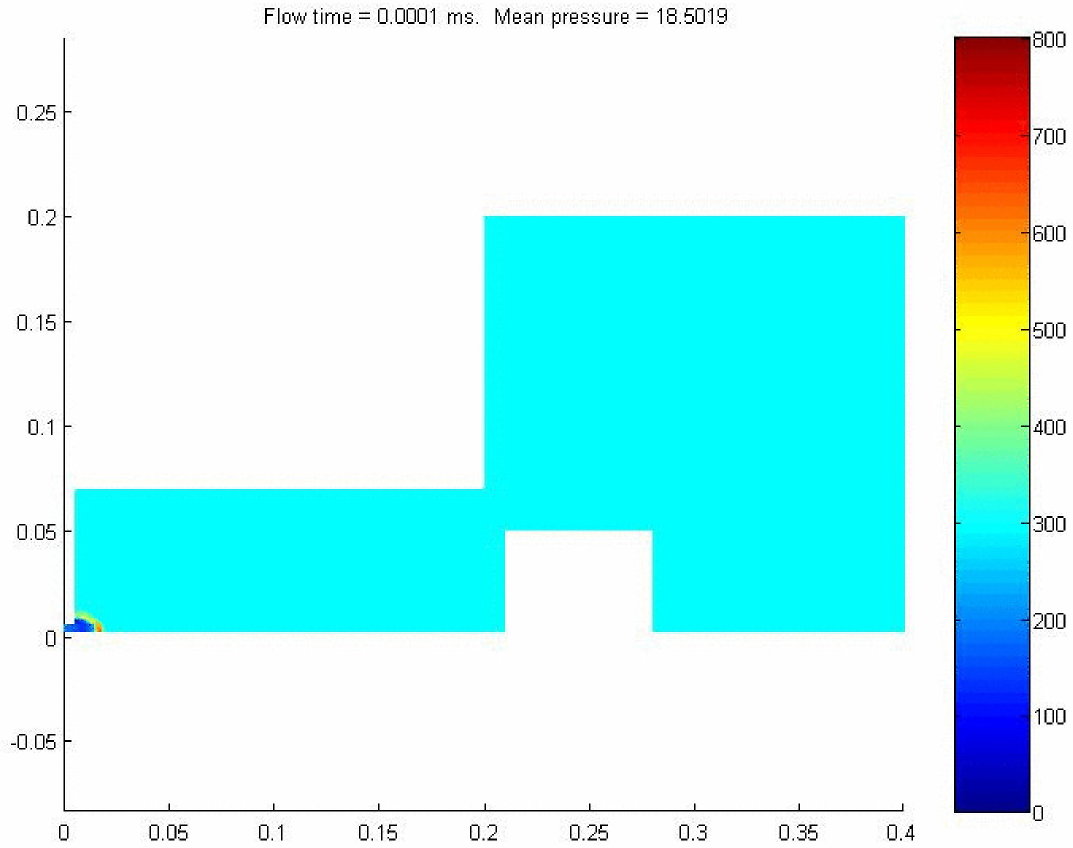


QDS output

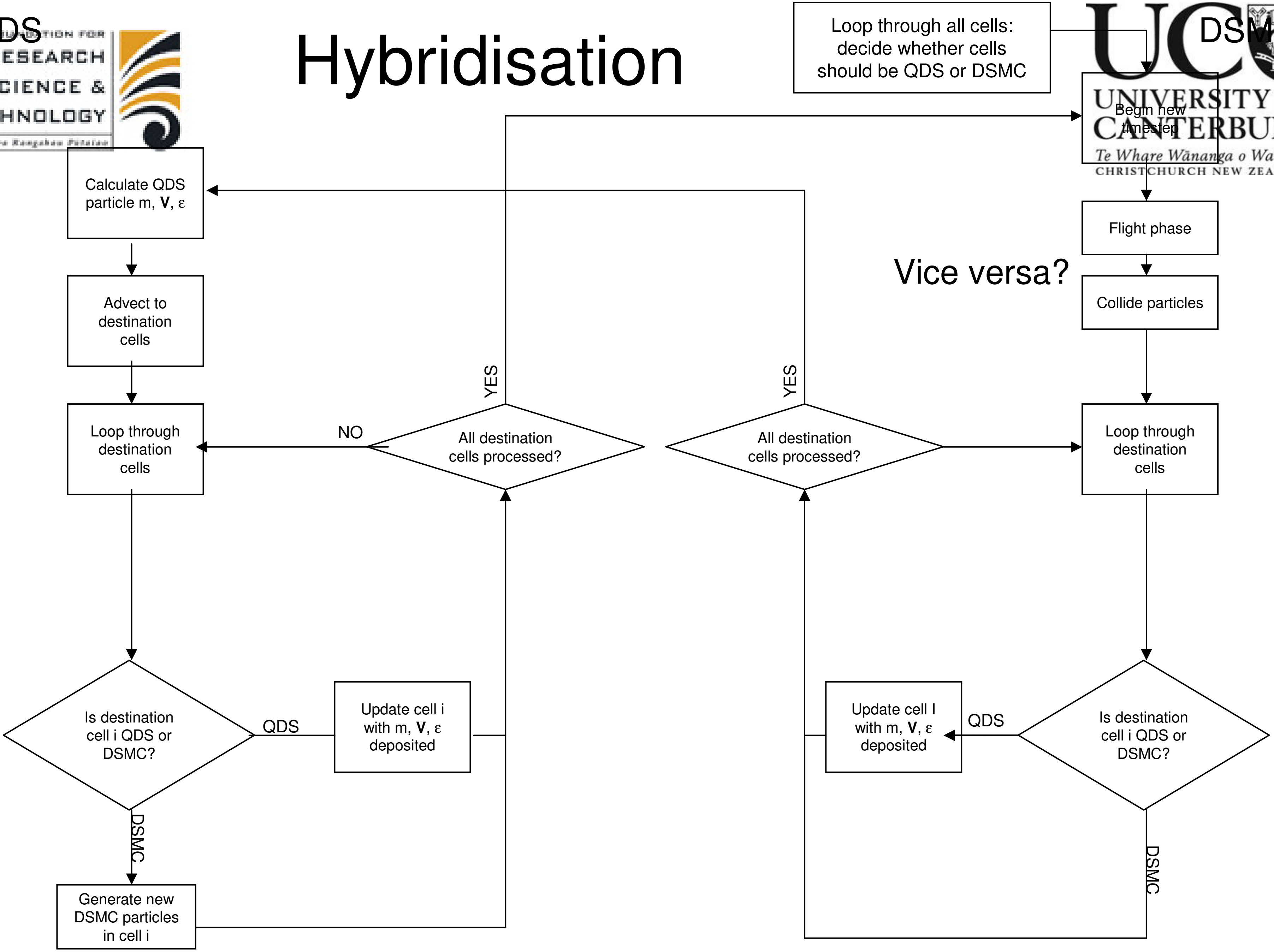
Mach 2.0 shock propagating in a tube with a rapid expansion



New concept reactor: backwards facing substrate



Hybridisation



QDS

DSMC

Loop through all cells: decide whether cells should be QDS or DSMC

Begin new timestep

Flight phase

Collide particles

Loop through destination cells

Is destination cell i QDS or DSMC?

QDS

Update cell I with m, **V**, ε deposited

DSMC

All destination cells processed?

YES

Calculate QDS particle m, **V**, ε

Advect to destination cells

Loop through destination cells

Is destination cell i QDS or DSMC?

QDS

Update cell i with m, **V**, ε deposited

DSMC

Generate new DSMC particles in cell i

All destination cells processed?

NO

YES

Vice versa?

Potential spinoff

- Fast, robust computer modelling of flow

CFD
Finite element solution of the Navier-Stokes equations
Unstructured mesh for complex bodies
Long meshing time
Numerical instability
Viscosity included

QDS
Finite volume calculation of flux from kinetic theory
Structured mesh with cut-cells for all bodies
Rapid meshing
Stable
Rapid solution time
Requires correct treatment of viscosity

Application to Marsden Fund February 2009

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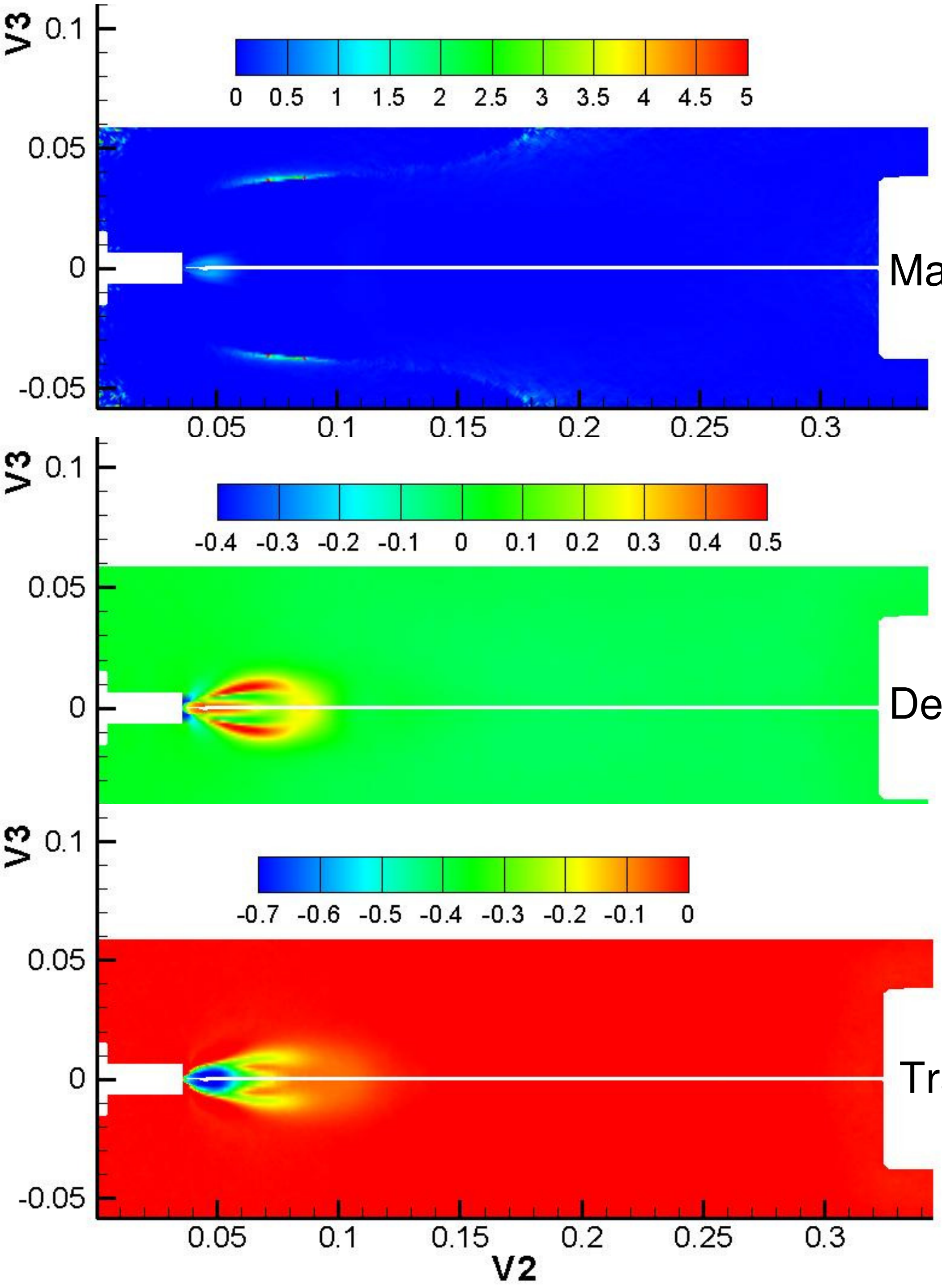
Development of Precursor Collision Models (first 18 months, in parallel with code development)



Mach number

Density

Translational temperature

Potential spinoff- liquid injection PP-CVD

- Liquid precursors
  - Less toxic
  - Easier to handle

Modelling droplet transport in rarefied gas flow

- Continuity Equation:

$$\frac{dm}{dt} = \sum \dot{m}_{in} - \sum \dot{m}_{out} \longrightarrow \frac{dm}{dt} = 4\pi r^2 S_A \left(\frac{M}{2\pi \overline{R}}\right)^{\frac{1}{2}} \left[\frac{P}{T^{\frac{1}{2}}} - \frac{SP_{gas}}{T_{gas}^{\frac{1}{2}}}\right]$$

- Momentum Equation:

$$\frac{\partial \underline{p}_{drop}}{\partial t} = \underline{F}_{gas-drop}$$

$$\underline{F}_{gas-drop} = \frac{\partial \underline{p}_{drop}}{\partial t} = S_A \dot{N}_{coll\ gas-drop} \overline{\underline{p}_{gas}} \longrightarrow \rho_{liquid} \frac{\partial \vec{V}}{\partial t} = S_A \dot{N}_{coll\ gas-drop} \rho_{gas} \vec{V}_{gas}$$

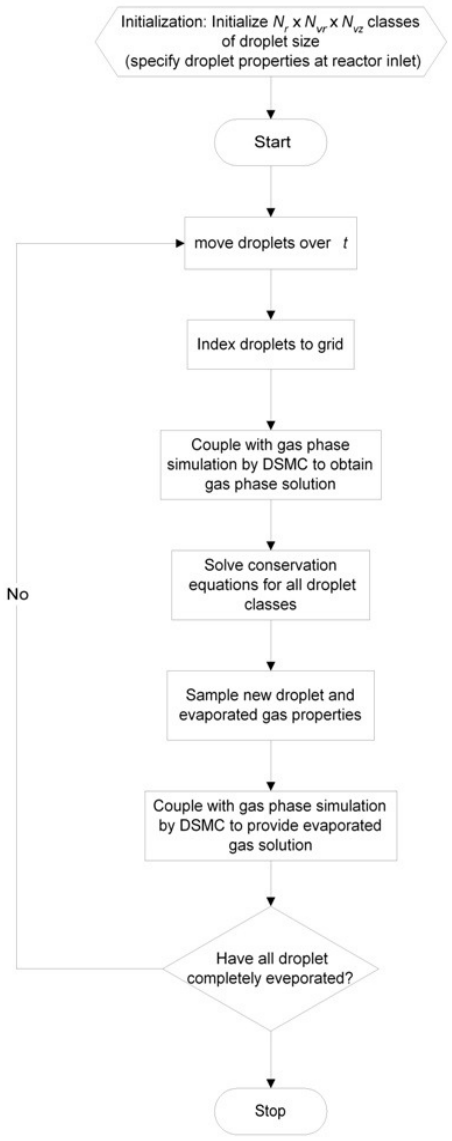
- Energy Equation:

$$\dot{E}_{rad} + \dot{E}_{condense} - \dot{E}_{evap} = \frac{dU}{dt}$$

$$\varepsilon\sigma 4\pi r^2 (T_{sur}^4 - T^4) + S_A \dot{N}_{coll\ gas-drop} h_{vap}(T) - \frac{dm}{dt}\left[h_{vap}(T) - h_{liq}(T)\right] = \rho_{liquid} \frac{4}{3}\pi r^3 c_p \frac{\partial T}{\partial t}$$

$$\frac{\partial T}{\partial t} = \frac{3}{4\rho_{liquid}\pi r^3 c_p}\left[\varepsilon\sigma 4\pi r^2 (T_{sur}^4 - T^4) + S_A \dot{N}_{coll\ gas-drop} h_{vap}(T) - \frac{dm}{dt}\left[h_{vap}(T) - h_{liq}(T)\right]\right]$$

Lagrangian Approach



Initialization: Initialize $N_r \times N_{vr} \times N_{vz}$ classes of droplet size (specify droplet properties at reactor inlet)

Start

move droplets over t

Index droplets to grid

Couple with gas phase simulation by DSMC to obtain gas phase solution

Solve conservation equations for all droplet classes

Sample new droplet and evaporated gas properties

Couple with gas phase simulation by DSMC to provide evaporated gas solution

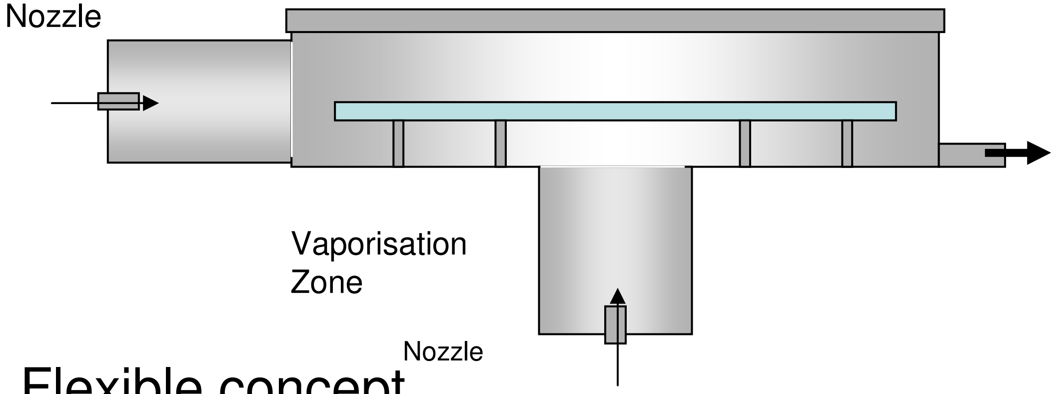
Have all droplet completely eveporated?

No

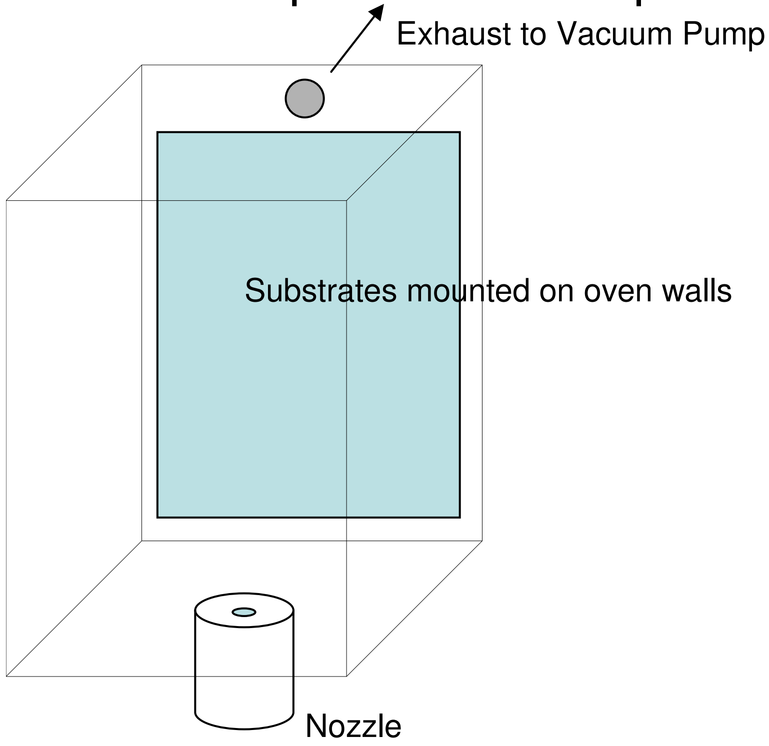
Stop

New Reactor Configurations

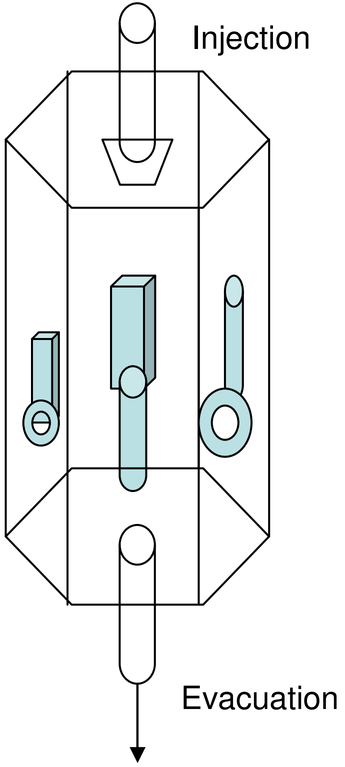
Minimum volume concept



Free expansion concept



Flexible concept



Inverted oven concept:
radiant heater in centre of cold
walled chamber