

# **Supercritical Fluids and Nanotechnology**

**Opportunities for Multidisciplinary Collaborative Research**

A  
Presentation  
to

Air Force Research Laboratory  
Edwards, CA

**B. Cherhoudi, PhD**

**11 to 12 am**

**Monday, March 3, 2003**

## OBJECTIVES

- A review of opportunities for multidisciplinary research using supercritical fluids (SCF)
- Stimulate further investigations into applications of supercritical fluids
- Stimulate collaborative interdisciplinary works between different groups
- Bring awareness to the importance of supercritical fluid technology and its role in nanotechnology
- Not meant to be a comprehensive analysis of the current state of the science and engineering of supercritical fluids; rather to provide a concise overview of some targeted applications
- Justification for a proposal: Division for Nanoscience and Nanotechnology at AFRL/PRS? to harness tremendous potential of nano world for current and future needs of Air Force. Is it the right time ?

## Table of Contents

- What is nanoscience and nanotechnology
- Significance of nanoscience and nanotechnology
- A classification of nano- science and technology areas
- What is supercritical fluid (SCF)?
- supercritical work at AFRL/PRSA (a brief)
- Supercritical and environmental issues (Green Chemistry)
- Some supercritical applications
- Supercritical and material synthesis
- Some commercial applications of nanoparticles
- Rapid Expansion of Supercritical fluid Solution (RESS) process and nanoparticles
- RESS and polymer materials
- Surfactants and microemulsions (Micelles)
- TiO<sub>2</sub> Synthesis in SCF\_CO<sub>2</sub>
- Nanoparticles in SCF & reverse micelle
- Supercritical fluids and polymers
- Some future trends in nanotechnology
- Future of supercritical fluids in nanotechnology
- Summary and conclusions

## The Message in Brief

- There is an increasing attention on the development of sustainable materials, i.e. **production and transformation technologies, which can ensure quality, reliability, sustainability and cost-effectiveness of materials**. These technologies should allow optimum incorporation into new products, and contribute to the improvement of safety and reliability, realizing that the materials properties and degradation mechanisms have a major impact on society, through safety and environmental considerations.
- The need for high performance materials has forced manufacturers **to rationally design new materials with specified functionality**.
- **Nanotechnology** is one of the key technologies to solve the accompanying problems. Its pivot is **the synthesis of ultra-fine particles with dimensions in the range between a few nm to a few hundred nm**. **Nanoparticles** are of enormous interest and they are in high demand for various applications such as surface treatment, pigments, for nutritional or pharmaceutical use, in cosmetics, and in transparent polymer composites which block efficiently transmittance of UV-light and **polymer composites** for gas transport.
- The nanoparticles can consist of an organic or inorganic core and are ideally covered by an additional layer for stabilization and solubilization. **By careful selection of the size and morphology, as well as the chemical nature of the constituents, nanoparticles can be tailored for a wide range of applications.**



## The Message in Brief

- The drive in electronics, in sensor technology, biotechnology and in many other industry sectors has been towards **smaller and smarter units**.
- Nanotechnology is the latest response to this drive, and **all over the world nanotechnology is examined for its potential role in the future**. The subject of nanotechnology is vast and it may take many years to exploit it fully.
- One area of nanotechnology that has been developing faster than most areas, is *preparation and application of nanoparticles*. They have already shown their usefulness in a number of areas including material engineering, drug design, and localized drug treatment. Smaller and faster sensors with improved selectivity and sensitivity are already based on nanoparticles.
- In general **nanoparticles can be expected to result in superior materials, lighter and better adapted products**.
- A number of methods are available for **production of nanoparticles**. (gas phase condensation, vapor condensation, colloidal wet chemistry, milling processes)
- These methods suffer from low yields and high costs, and from heavy energy consumption during the preparation processes.
- Many nanoparticles can only be produced today using organic solvents and the **complete removal of the solvent from the particles is a serious problem**.
- **Using supercritical fluids as solvent**, it is suggested that cost-effective, efficient, cleaner, and more size- morphology- controlled nanoparticles can be made available.<sup>5</sup>

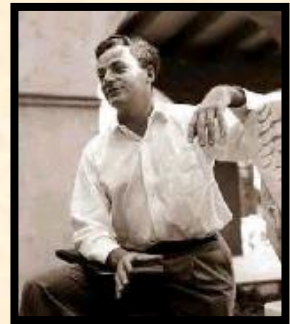
# There's Plenty of Room at THE NANO- WORLD

## There's Plenty of Room at the Bottom

by Richard P. Feynman

Classic talk by Richard Feynman given on  
December 29th 1959

American Physical Society at the California Institute of Technology (Caltech)

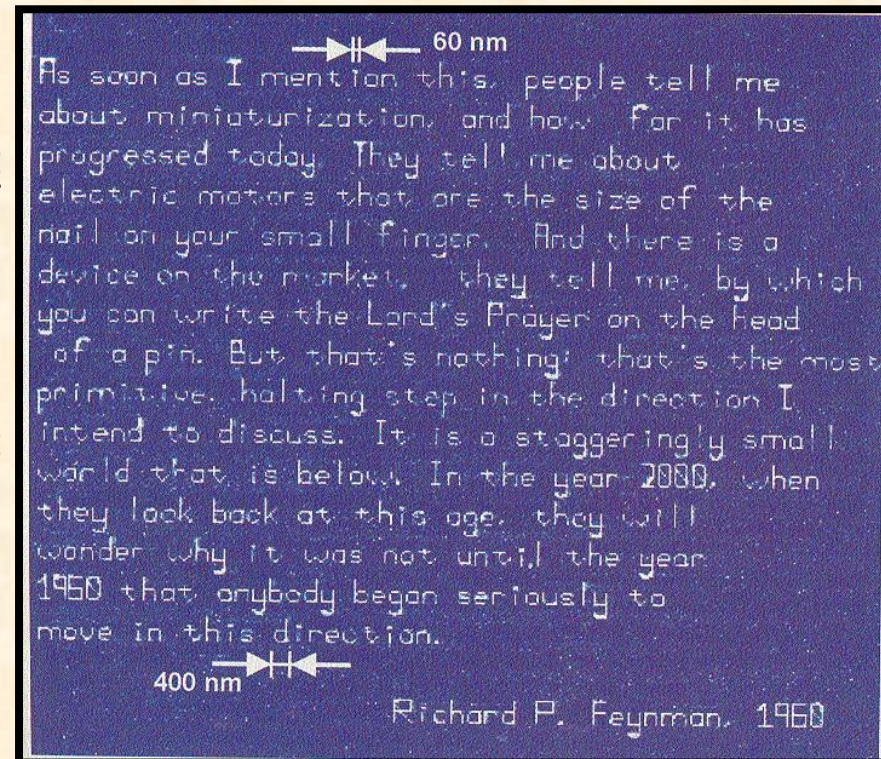


*Why cannot we write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin?*

Let's see what would be involved. The head of a pin is a sixteenth of an inch across. If you magnify it by 25,000 diameters, the area of the head of the pin is then equal to the area of all the pages of the Encyclopaedia Britannica. Therefore, **all it is necessary to do is to reduce in size all the writing in the Encyclopaedia by 25,000 times.** Is that possible? The resolving power of the eye is about 1/120 of an inch---that is roughly the diameter of one of the little dots on the fine half-tone reproductions in the Encyclopaedia. This, when you demagnify it by 25,000 times, is still 80 angstroms in diameter---32 atoms across, in an ordinary metal. **In other words, one of those dots still would contain in its area 1,000 atoms.** So, each dot can easily be adjusted in size as required by the photoengraving, and **there is no question that there is enough room on the head of a pin to put all of the Encyclopaedia Britannica.**

Furthermore, it can be read if it is so written. Let's imagine that it is written in raised letters of metal; that is, where the black is in the Encyclopedia, we have raised letters of metal that are actually 1/25,000 of their ordinary size. **How would we read it?** .....

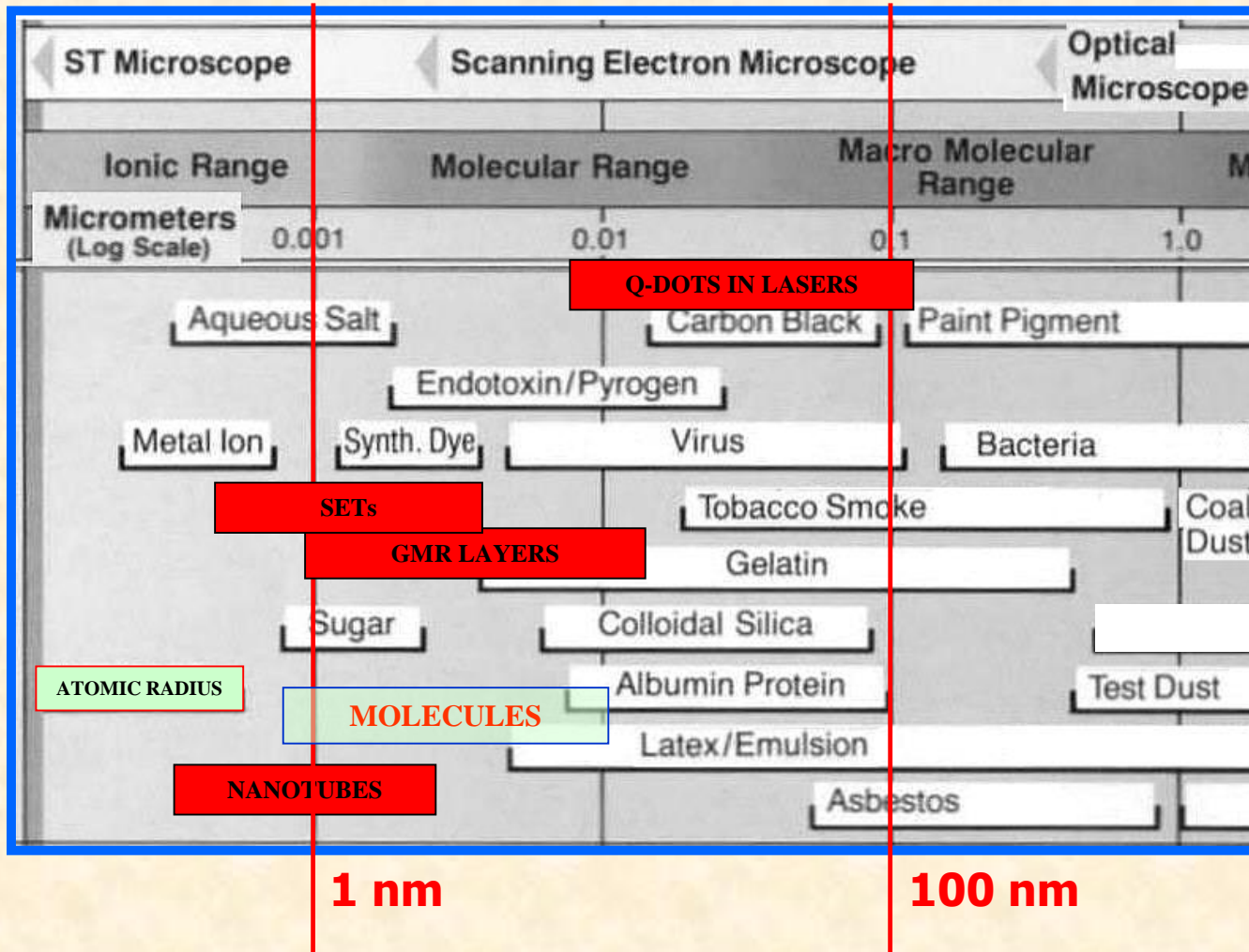
Taking on Feynman's miniaturization challenge, researchers at Northwestern University use an AFM tip to write a paragraph of nanometer-sized letters with a single layer of mercaptohexadecanoic acid on gold surface. Contrast is enhanced by surrounding each letter with a layer of second "ink" – octadecanethiol.





# WHAT IS NANO- SCIENCE OR TECHNOLOGY ?

- **Nano:** Between individual atoms/molecules and the macroworld
- **NSF official definition**
  - Deals with materials and systems having the following key properties :



- **Dimension:** At least one dimension from 1 to 100 nanometer (nm)
- **Process:** Designed with methodologies that shows fundamental control over the physical and chemical attributes of molecular-scale structures
- **Building block property:** They can be combined to form larger structures

SET: single-electron transistor  
GMR: Giant magneto resistive  
Q-DOTS: Quantum dots

# SIGNIFICANCE OF NANOSCIENCE & NANOTECHNOLOGY

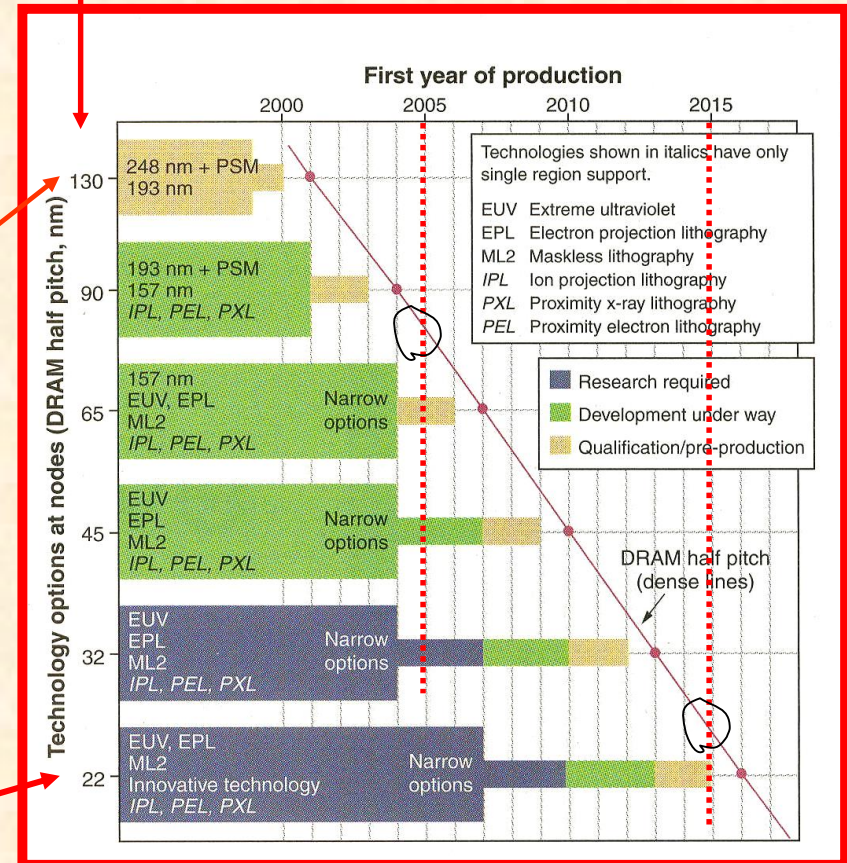
## Material & Microelectronic Industry Connections

- **Materials** and systems built from nanoworld building blocks (i.e. clusters, nanoparticles, nanotubes, nanolayers, etc.) may exhibit superior electrical, chemical, mechanical and optical properties (at least theoretically).
  - Applications: sensors, catalysis, coatings, energy, medical, pharmaceutical, etc.
- **Microelectronics** using photolithography is limited to feature sizes of about 100 nm
- Electronic industry is deeply interested in developing new methods for nanofabrication to maintain its long-term trends of **smaller, faster, and less expensive devices**
- **Nanofabrications:**
  - Extreme UV (10 to 70nm)
  - Electron beam lithography
  - X-ray (0.1 to 10nm)
  - Soft lithography
  - Using Atomic Force Microscopy (AFM) [Dip-pen lithography and Break Junction]
  - **Bottom up** (self-assembly)

### DRAM half pitch, nm [Feature Size]

130 nm

22 nm



Source: International Technology Roadmap of Semiconductors

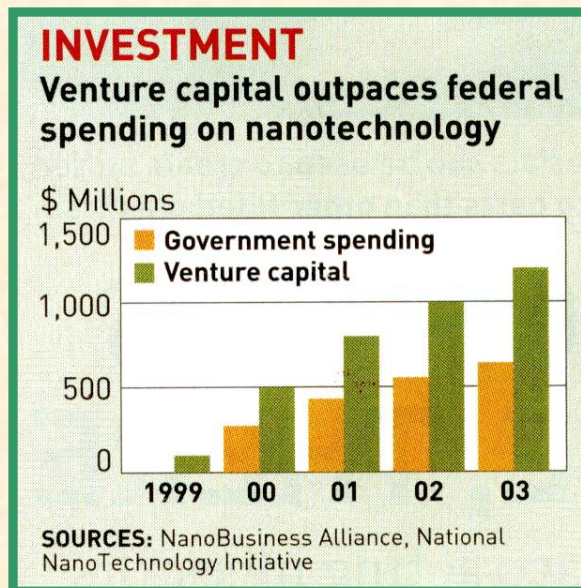
B. Chehroudi, PhD



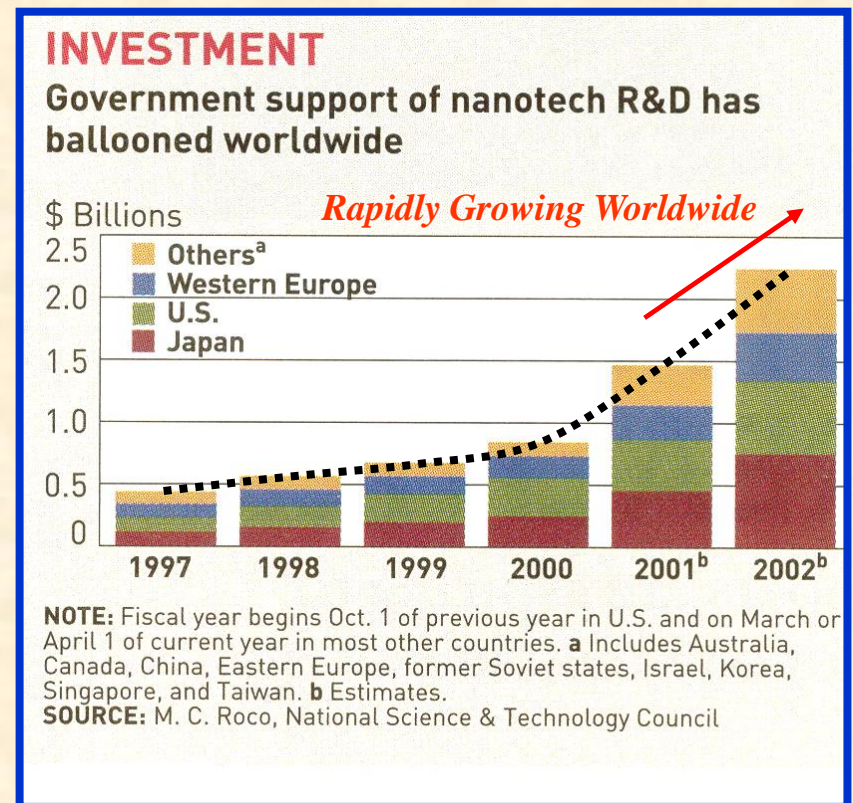
# SIGNIFICANCE OF NANO- SCIENCE & TECHNOLOGY

## Investment and Life Quality Connections

- **The US government:** In just another 10 to 15 years, nanotechnology will impact more than \$1 trillion per year in products and services
- **Nobel Laureate, Richard E. Smalley said:** "It holds the answer, to the extent there are answers, to most of our most pressing material needs in energy, health, communication, transportation, food, water, etc."
- **James Canton, President of the Institute for Global Futures:** "Never has such a comprehensive technology promised to change so much so fast... Inevitably, nanotechnology will give people more time, more value for less cost and provide for a higher quality of existence."



Chemical & Engineering News Date: Nov. 2001

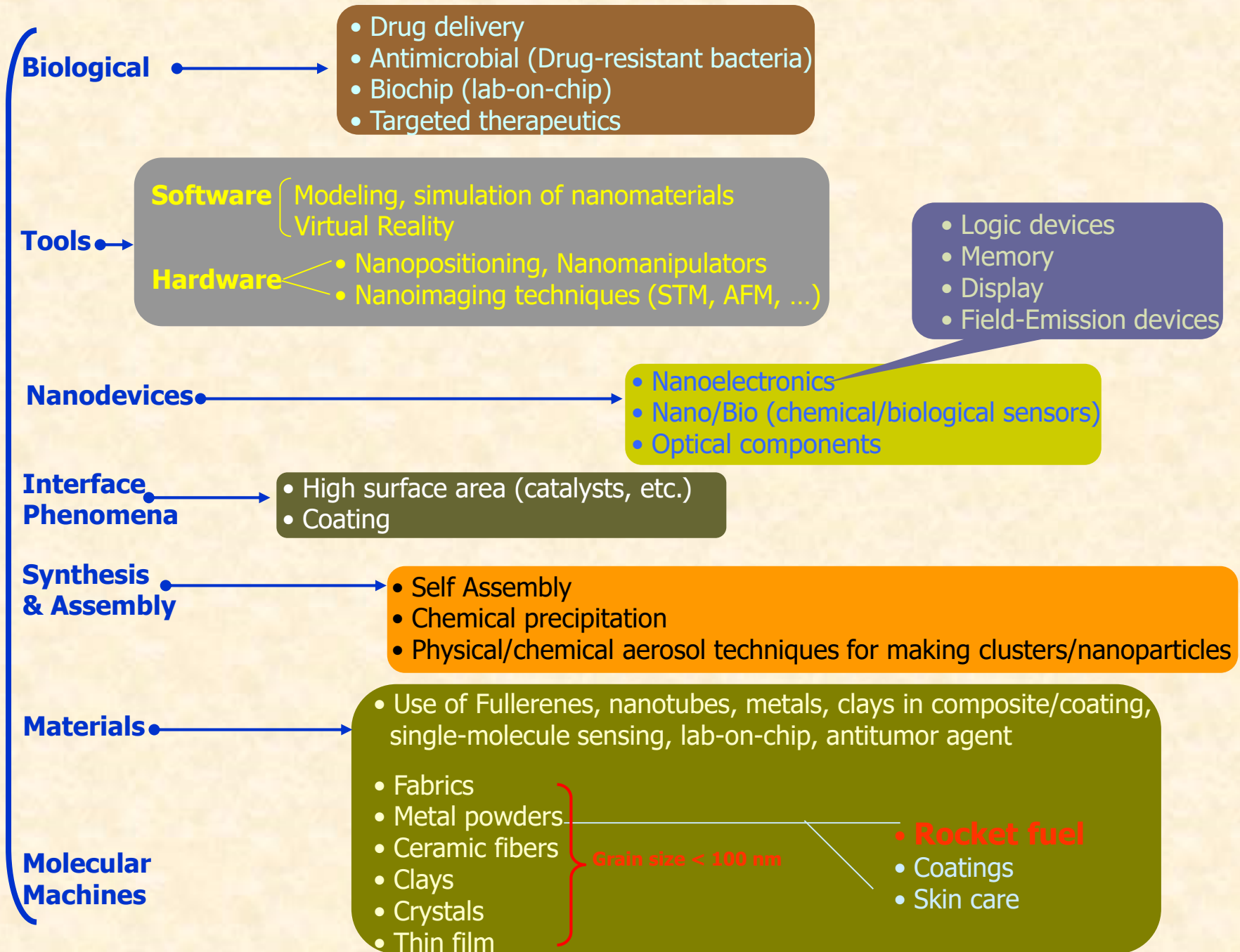


Chemical & Engineering News Date: July 2002

B. Chehroudi, PhD



# A CLASSIFICATION OF NANOTECHNOLOGY AREAS



# AN EXAMPLE OF A NANOTECH PRODUCT APPLICATION

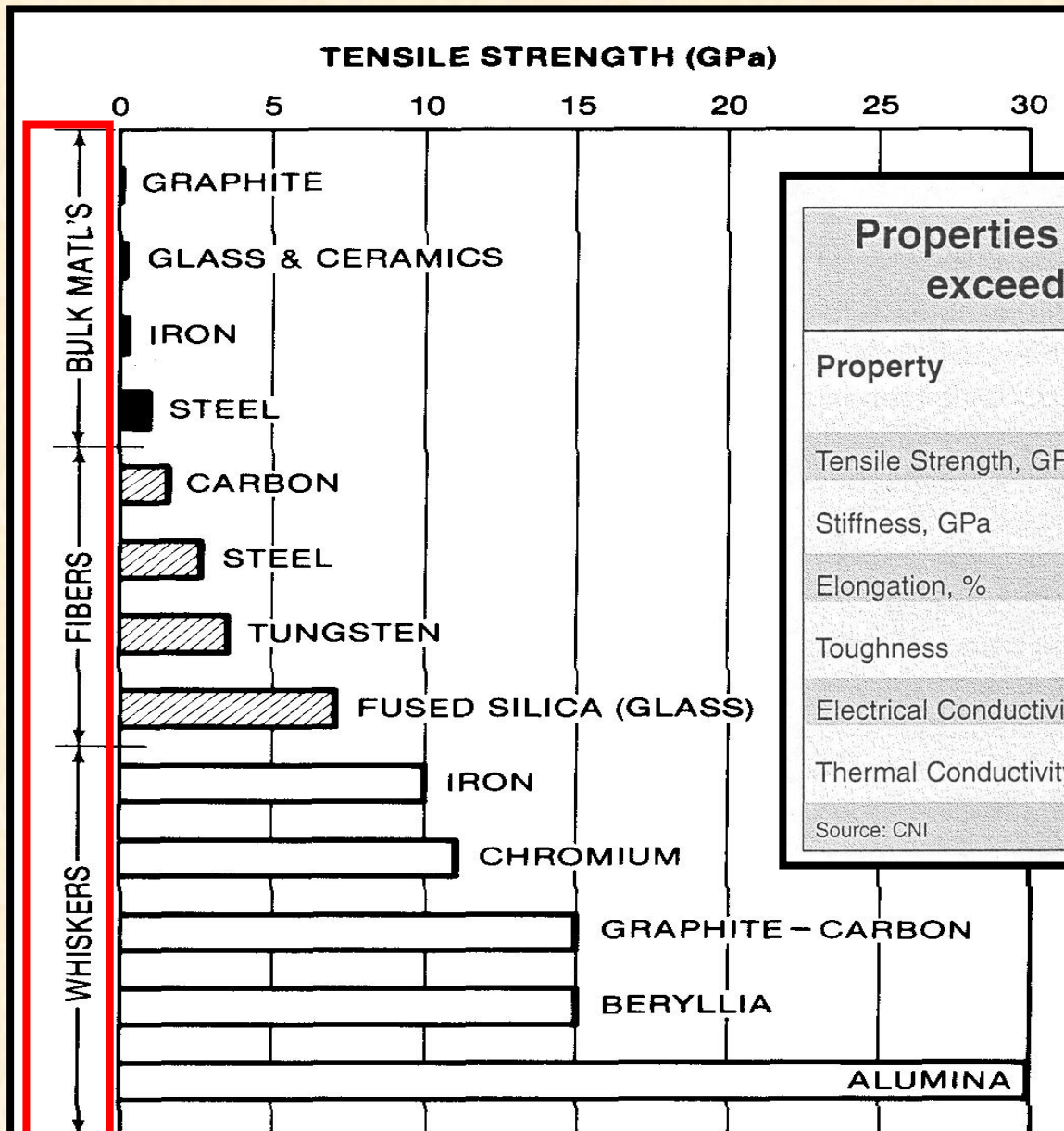
- Hyperion Catalysis: Created Fibril multiwall nanotube (MWNT): 10 to 12 nanometers in dia. And 10 to 15 microns long
- Fibrils produce the same effects as standard carbon fibers at around 1/10 th the loading
- **Everybody is working on single wall nanotube (SWNT).** Leading the work is Carbon Nanotechnologies Inc (founded in 2000 by Richard Smalley, \$500 to \$1000/ gr in 2002, 20-30 g/day production)
- **SWNT:**
  - 0.7 to 2 nm in dia.
  - And have the electrical conductivity of copper.
  - At 4% loading, they provide a compound with thermal conductivity of over 100,000 times that of MWNT
  - They have thermal conductivity of diamond
  - The highest strength, toughness, and stiffness of any molecule.
  - **100 times stronger than steel**
  - **In compounds, they retain or even improve mechanical properties**
- **Other applications:** Conductive compounds, advanced composites, flat-panel displays, lithium ion batteries, high-strength fibers, solar energy convectors, and electronics
- The structures and resulting properties of other fibers are dominated by defects. Thus, the difference between their theoretical and actual properties is huge (a steel wire breaks at about 1% of its theoretical strength)
- CNI can supply the material either in its raw, uncompacted form, or in a form that is purified and similar in size to resin pellets

**Properties of single-wall nanotubes far exceed those of multiwall types**

Property	Single-wall nanotube	<b>STEEL</b>	Multiwall nanotube
Tensile Strength, GPa	100 to 200	<b>1.3</b>	3 to 40
Stiffness, GPa	1400	<b>275 Yield 430 Ultimate</b>	600 to 1000
Elongation, %	20 to 30	<b>20</b>	0.5 to 5.0
Toughness	Tough		Brittle
Electrical Conductivity, S/cm	10,000		<20
Thermal Conductivity, W/m•K	~6000		<2000
Source: CNI			



# AN EXAMPLE OF A NANOTECH PRODUCT APPLICATION



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Source: CNI

**Fig. 7-22.** Tensile strengths of various materials in bulk, fiber, and whisker forms.

## **AN EXAMPLE OF A NANOTECH PRODUCT APPLICATION**

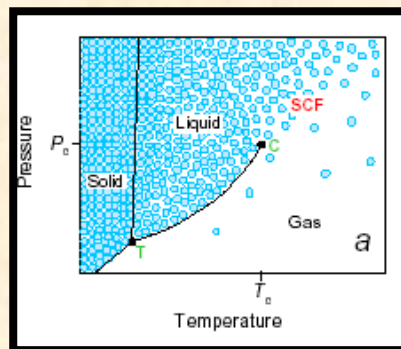
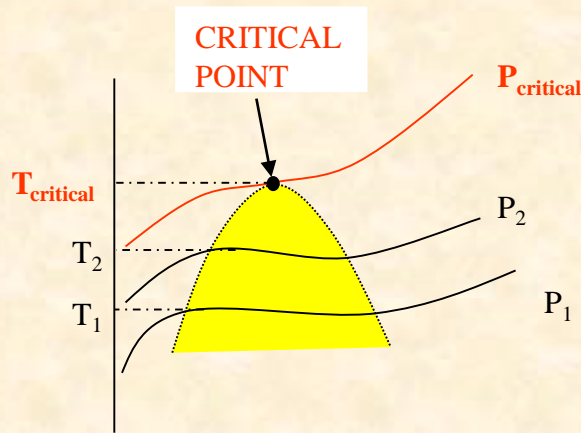
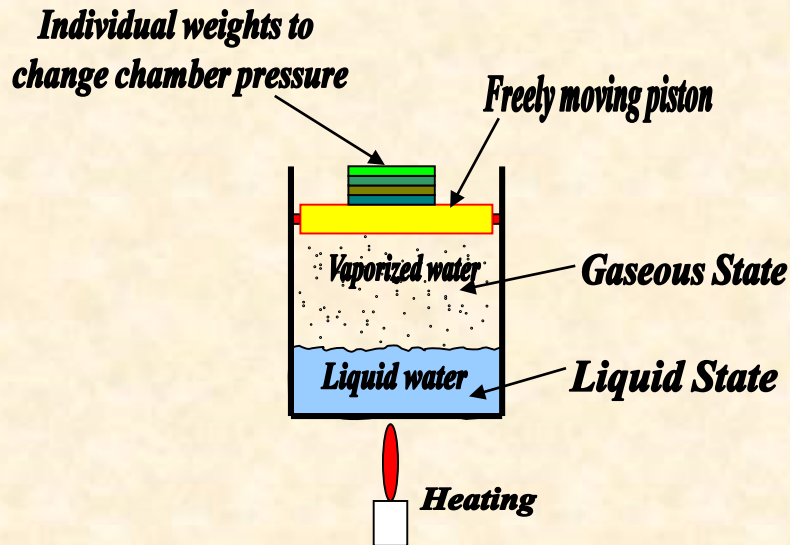
- Carbon nanotubes offer interesting possibilities as support for metal particles
- Such structures can be grown in the form of bundles
- Recent research has demonstrated that Ir nanoparticles deposited into such tube bundles are more effective for decomposition of hydrazine than is Ir supported on a conventional support such as alumina
- This advance is of potential interest for hydrazine-fueled thrusters used on space vehicles
- K. P. De Jong, J. W. Geus, Catal. Rev. Sci. Eng., 42, 481 (2000)

# **AN EXAMPLE OF A NANOTECH PRODUCT APPLICATION**

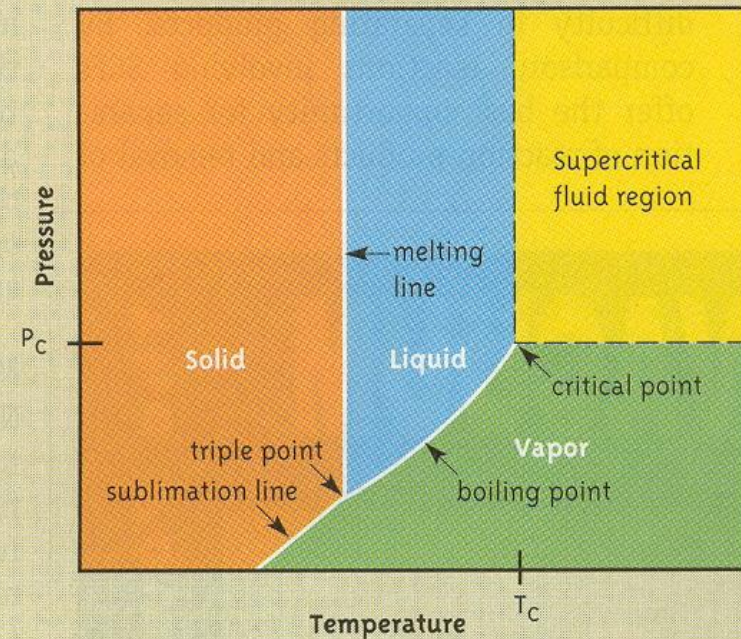
- Carbon nanotube for ignition



# WHAT IS A SUPERCRITICAL FLUID ?



**FIGURE 1: Pressure—temperature phase diagram for a pure substance**

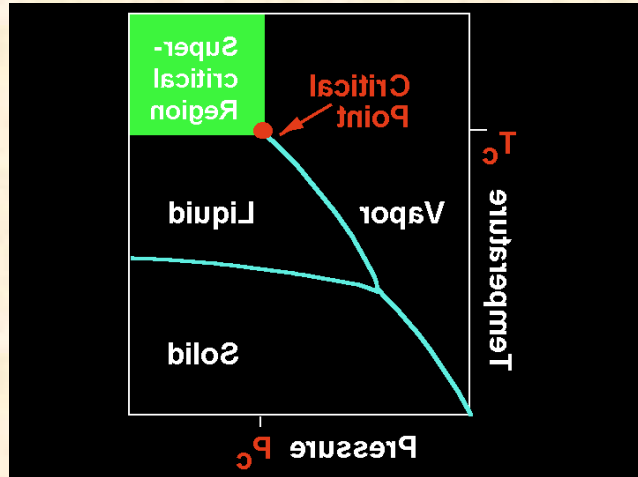


**TABLE 1: Comparison of the critical constants for commonly used fluids**

Fluid	Critical Temperature ( $^{\circ}\text{C}$ )	Critical Pressure (atm)
Carbon dioxide ( $\text{CO}_2$ )	31.1	72.8
Methane ( $\text{CH}_4$ )	-82.1	45.8
Ethane ( $\text{C}_2\text{H}_6$ )	32.3	48.2
Propane ( $\text{C}_3\text{H}_8$ )	96.7	41.9
Argon (Ar)	-122.3	48.0
Nitrous oxide ( $\text{N}_2\text{O}$ )	36.5	72.5
Water ( $\text{H}_2\text{O}$ )	374.1	218.3

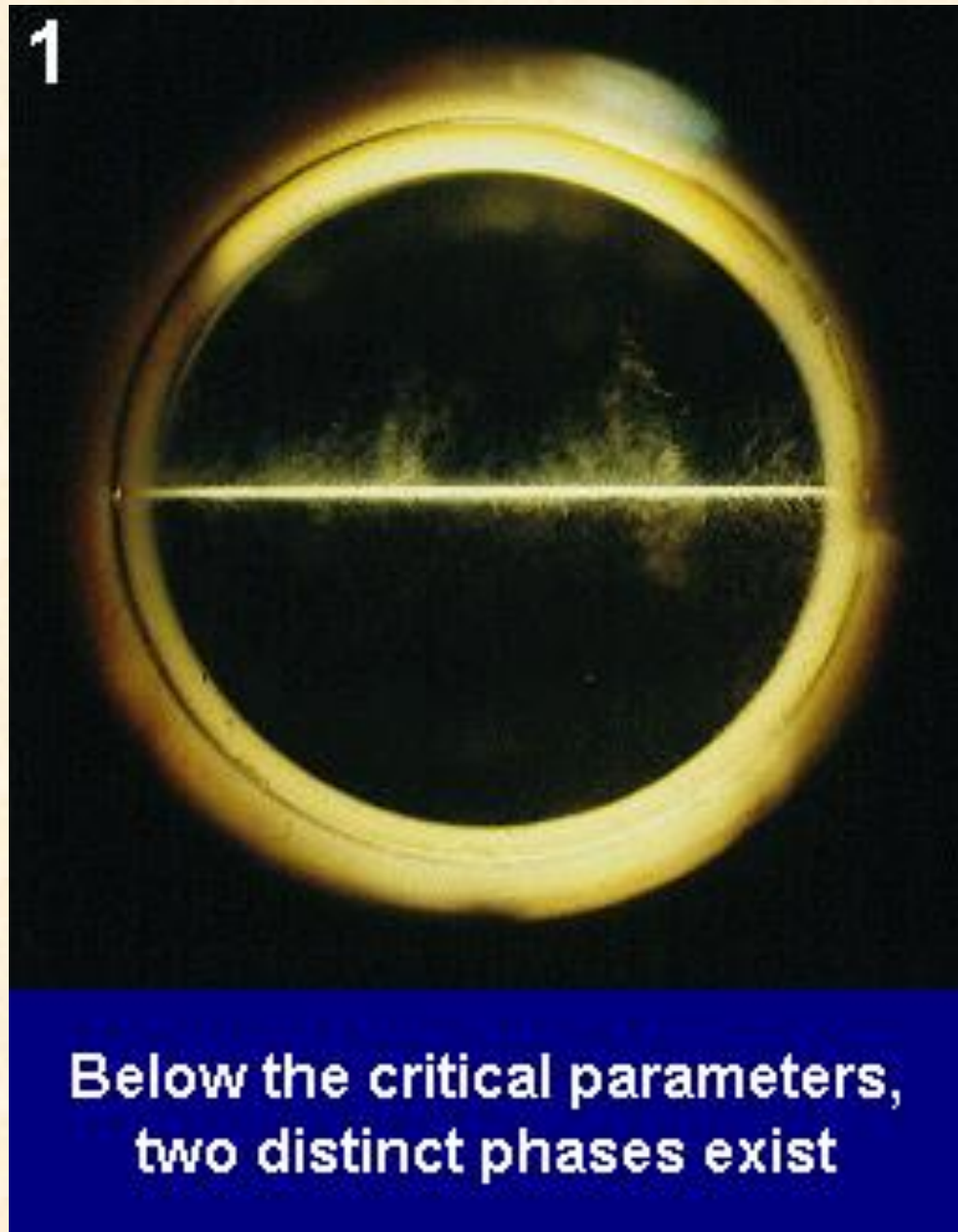


# WHAT IS A SUPERCRITICAL FLUID ?

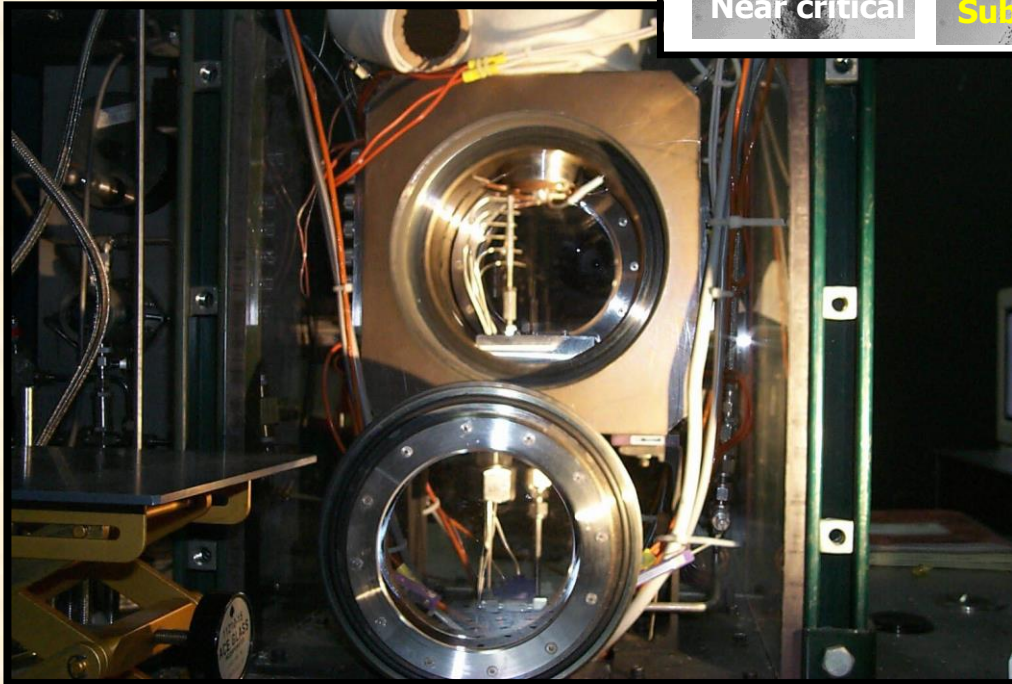
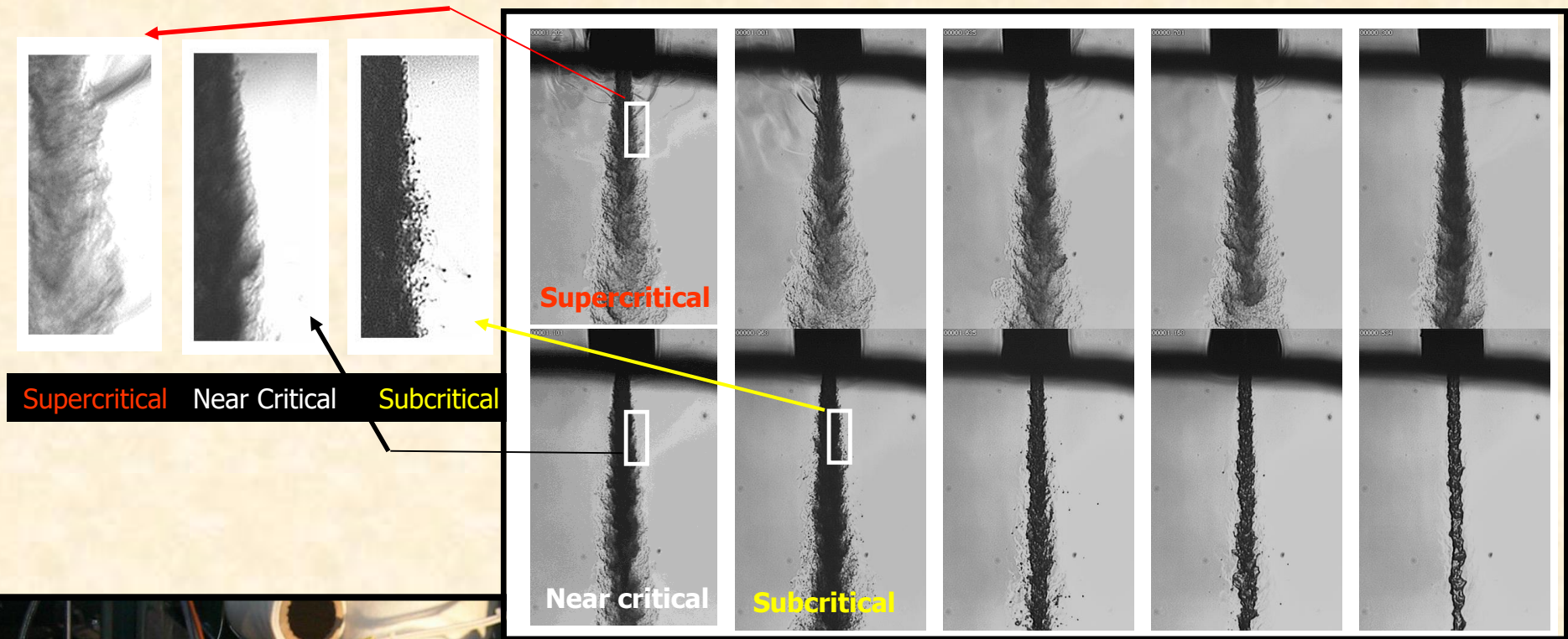


Supercritical fluid guru: Val Kurkonis (1992):

*"There is no point in doing something in a supercritical fluid just because it's neat. Using the fluids must have some real advantage"*



# SUPERCRITICAL WORK AT AFRL/PRSA (brief)

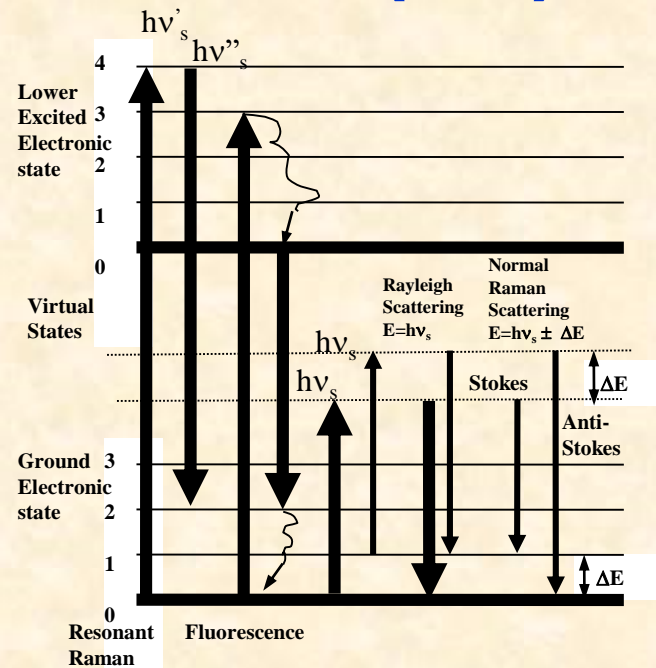
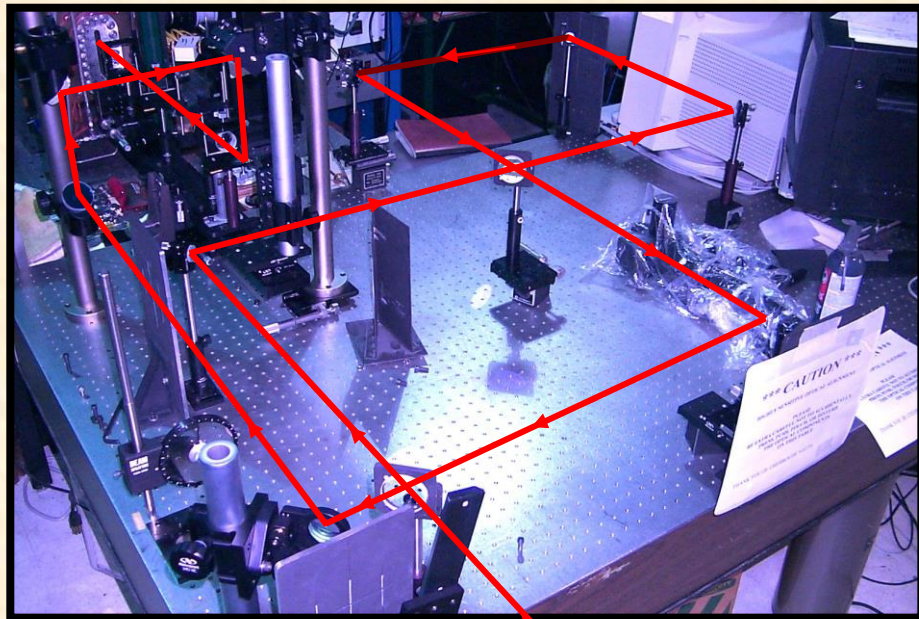


- **SUBCRITICAL CRYOGENIC N<sub>2</sub> JET INJECTED INTO A SUBCRITICAL TO SUPERCRITICAL PRESSURE & TEMPERATURE ENVIRONMENT.**
- **IT SHOWS CHANGES IN APPEARANCE OF THE JET AS AMBIENT PRESSURE REACHED THE CRITICAL POINT AND BEYOND**

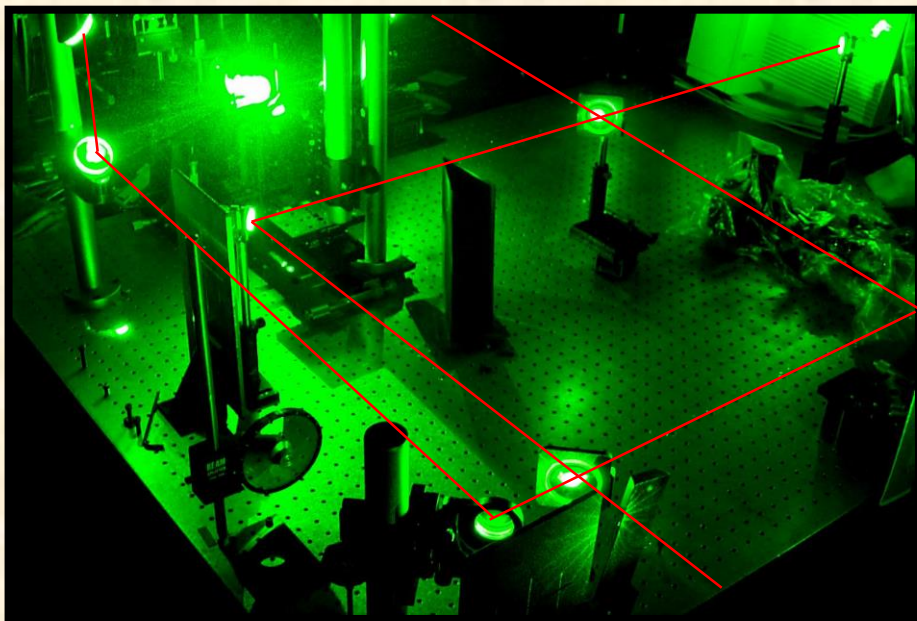
*Chehroudi, et al's research work at AFRL*



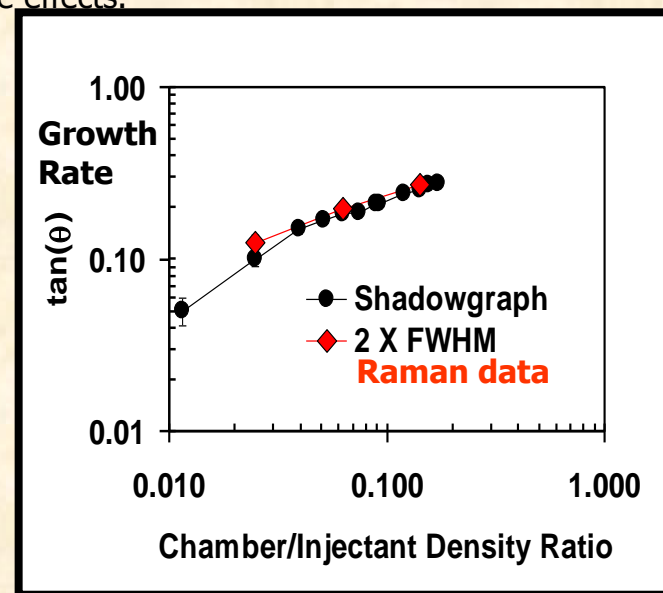
# SUPERCRITICAL WORK AT AFRL/PRSA (brief)



Quantum mechanical description of the Rayleigh, Raman, resonant Raman, and Fluorescence effects.



**Raman Measurements**



# SUPERCRITICAL WORK AT AFRL/PRSA (brief)

JOURNAL OF PROPULSION AND POWER  
Vol. 19, No. 1, January–February 2003

## Numerical Study of Cryogenic Jets Under Supercritical Conditions

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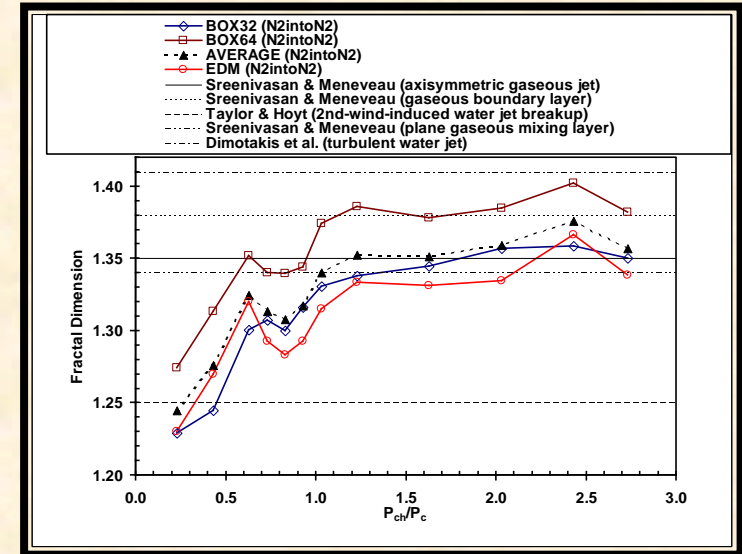
I. Gökalp†

Centre National de la Recherche Scientifique, 45071 Orléans Cedex 2, France  
and

A. R. R. Silva‡

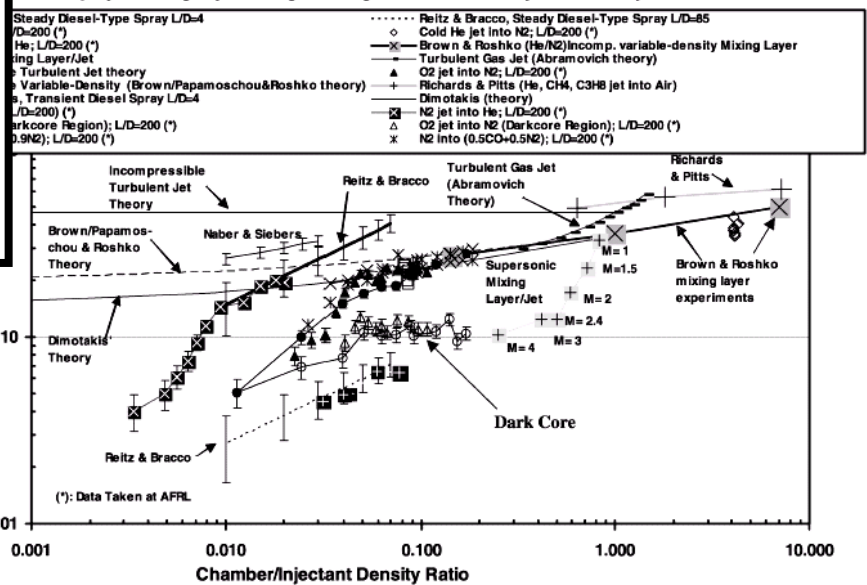
Universidade da Beira Interior, 6201-001 Covilhã, Portugal

The present work is devoted to the study of cryogenic nitrogen jets in sub- and supercritical conditions. A general trend to operate under increasingly higher combustor pressures is observed in rockets, gas turbines, and diesel engines, primarily as a result of enhanced effects on thrust, power, or efficiency. In these conditions the injected fluid(s) can experience ambient pressures exceeding the critical pressure(s) of the propellants, and recent experimental work of Chehroudi et al. showed a quantitative similarity to gas-jet-like behavior (Chehroudi, B., Cohn, R., and Talley, D., "Spray/Gas Behaviour of Cryogenic Fluids under Sub- and Supercritical Conditions," Paper, July 2000; Chehroudi, B., Cohn, R., and Talley, D., "Initial Growth Rate and Visual Characteristics of a Round Jet into a Sub- to Supercritical Environment of Relevance to Rocket, Gas Turbine, and Diesel Engines," AIAA Paper 99-0206, Jan. 1999). This conclusion suggested that it would be expected that the mathematical models and numerical methods used for gaseous flows could also be used for supercritical flows. This paper reports an investigation, exploring this hypothesis, and aims to evaluate the capabilities and limitations of a computational method developed for incompressible but variable density flows when applied to supercritical conditions. The predicted initial jet growth rate was compared with available experimental data for liquid/gaseous jets and mixing layers and showed a good agreement for different supercritical density ratios. For subcritical conditions, when the flow deviates from the gaseous-like behavior, and approaches a more spray-like behavior the incompressible gaseous flow formulation was found inadequate.

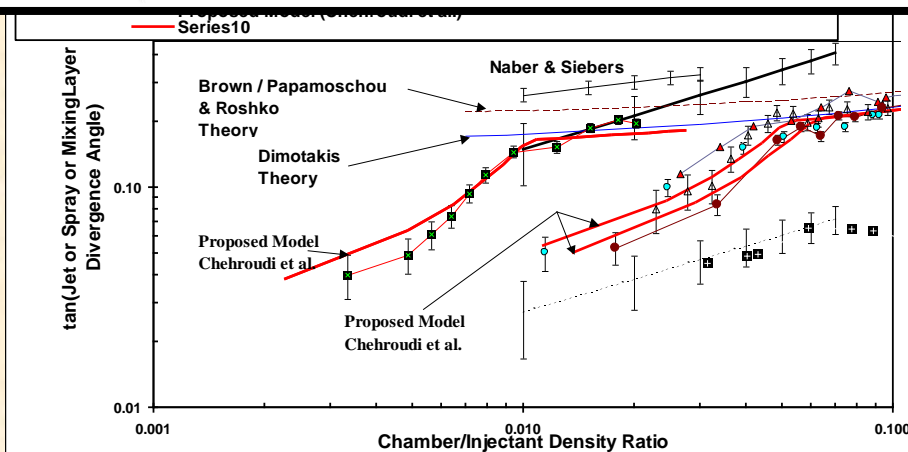


■ Figure shows the FRACTAL DIMENSION  
■ First fractal analysis

### Jet or Spray or Mixing Layer Divergence Angle vs Chamber-to-injectant Density Ratio



■ JET GROWTH RATE MEASUREMENTS AND MODELING.  
■ FIRST QUANTITATIVE ACHIEVEMENT





# **SUPERCRITICAL WORK AT AFRL/PRSA (brief)**

1. Chehroudi, B., Talley, D., and Coy, E., 1999. Initial Growth Rate and Visual Characteristics of a Round Jet into a Sub- to Supercritical Environment of Relevance to Rocket, Gas turbine, and Diesel Engines, 37<sup>th</sup> AIAA Aerospace Science Meeting and Exhibit, AIAA 99-0206, Reno, NV, January 11-14.
2. Chehroudi, B., Talley, D., and Coy, E., 1999. Fluid Jet Injection into Supercritical Condition with Applications to Cryogenic Rocket Engines, 12<sup>th</sup> Annual Conference on Liquid Atomization and Spray Systems, Radisson Hotel City Center, Indianapolis, Indiana, May16-19, 1999.
3. Chehroudi, B., Talley, D., and Coy, E., 1999. Fractal Geometry and Growth Rate of Cryogenic Jets Near Critical Point, AIAA/SAE/ASME/ASEE Joint Propulsion Meeting, AIAA 99-2489, Los Angeles, CA, June 20-24. **(1999 AIAA Best Publication Award, for outstanding and lasting contributions to aeronautical and aerospace sciences)**
4. Chehroudi, B., Talley, D., and Coy, E., 1999. Anatomical Changes of a Cryogenic Jet in Transition to the Thermodynamic Supercritical State, 15<sup>th</sup> Annual Conference on Liquid Atomization and Spray Systems, Toulouse, France, July 5-7.
5. Chehroudi, B., Cohn, R., Talley, D., and Badakhshan, A. 2000. Raman Scattering Measurements in the Initial Region of Sub- and Supercritical Jets, AIAA/SAE/ASME/ASEE Joint Propulsion Meeting, AIAA 2000-3392, Huntsville, AL, 17-19 July.
6. Chehroudi, B., and Talley, D., 2000. Injection into Supercritical Conditions in Cryogenic Liquid Rockets, Fourth International Symposium on Liquid Space Propulsion, LR – Lampoldshausen, Germany. Fourth International Symposium on Liquid Space Propulsion, DLR – Lampoldshausen, Germany, March 13 - 15, 2000.
7. Chehroudi, B., Cohn, R., and Talley, D., 2000. Spray/Gas Behavior of cryogenic Fluids Under Sub- and Supercritical Conditions, Eighth International Conference on Liquid Atomization and Sprays Systems, ICLASS- 2000, Pasadena, California, USA, July 16-20.
8. Chehroudi, B., Cohn, R., and Talley, D., 2001. The Behavior of Cryogenic Shear Layers under Supercritical Conditions, 2<sup>nd</sup> International Symposium on Turbulence and Shear Flow Phenomena, Stockholm, Sweden, 27-29 June, 2001.
9. Chehroudi, B. and Talley, D., 2002. Interaction of Acoustic Waves with a Cryogenic Nitrogen Jet at Sub- and Supercritical Pressures, 40<sup>th</sup> AIAA Aerospace Sciences Meeting & Exhibit, AIAA Paper 2002-0342, Reno, Nevada, 14-17 January.
10. Chehroudi, B., Talley, D., and Coy, E., 2002. Visual Characteristics and Initial Growth Rates of Round cryogenic Jets at Subcritical and Supercritical Pressures, *Physics of Fluids*, Vol. 14, No. 2, February.
11. Chehroudi, B., and Talley, D., 2002. Acoustic Waves and Cryogenic Injection under Supercritical Conditions, 15<sup>th</sup> Annual Conference on Liquid Atomization and Spray Systems, Madison, Wisconsin, 14-17 May.
12. Chehroudi, B., Cohn, R., and Talley, D., 2002. Cryogenic Shear Layers: Experiments and Phenomenological Modeling of the Initial Growth Rate Under Subcritical and Supercritical Conditions, **Invited Paper**, *International Journal of Heat and Fluid Flow*, 23, pp. 554-563.
13. Chehroudi, B., Davis, D., and Talley, D., 2003. Initial Results From A Cryogenic Coaxial Injector In An Acoustic Field. 41st AIAA Aerospace Science Meeting and Exhibit, AIAA 2003-1339, Reno, NV, January 6-9.
14. Chehroudi, B. and Talley, D., 2003. Fractal Geometry of a Cryogenic Nitrogen Round Jet Injected into Sub- and Super-critical Conditions, *Atomization and Sprays*. (Accepted)
15. Chehroudi, B., Cohn, R., Talley, D. and Badakhshan, A., 2003. Spontaneous Raman Scattering Measurements in the Initial Region of a Cryogenic Jet under Sub- and Supercritical Pressures, *AIAA J. of Propulsion and Power*. (to be submitted)
16. ....

# **SOME APPLICATIONS OF SUPERCRITICAL FLUIDS (SCF)**

<b>Supercritical Fluid Technologies:</b>	<b>Application Examples:</b>
Analytical SF Extraction - has proven to be especially useful for production quality control (QC) when a 20-30 min. SF method is replacing a 6-12 hour soxhlet extraction	Fat Analysis for Food Labeling for Snack Foods; Analysis of
Analytical Capillary SCFC	Hydrocarbon and Simulated Distillation
Analytical Packed Column SCFC	Separation of Enantiomers of Propranolol
Benchtop Sample Preparation Extraction	Soil Extraction for PAHs and Pesticides
Pilot/Pharmaceutical SCF Extraction	Delipidization of Collagen
Prep/Production SCFC	EPA/DHA Concentration & Purification
Production-Scale SCF Extraction	Defatting Cocoa, Lecithin, Nuts, Grain, Etc.
SCF Polymer Fractionation	Fractionation of Polymethylmethacrylate
Counter-Current Column SCF Extraction	Deterpenation of Citrus Peel Oils
Activated Carbon/Adsorbent Regeneration	Bleaching Clay Regeneration
SCWO & Hydrothermal Processing	Hazardous Organic Waste Treatment
SCF Micronizing (RESS)	Precipitated Finely Divided Insulin Solids
SCF Aerosols	Coatings for Drugs & Drug Delivery
Gas Anti Solvent Recrystallization (GAS)	Microcrystallization of $\beta$ -Carotene
SCF Impregnation & Coatings	Production of Microcellular Foam Foods
SCF Cleaning	Tobacco Fluffing & SF Textile Dyeing
SCF Drying	Microelectronics, Polymer & Dry Cleaning
SCF Medium Enhanced Rate Reactions	Aerogel Drying and Document Preservation
SCF Enhanced Enzymatic Hydrolysis	Hydrogenation of Vegetable Oils
SCFX Extrusion	Pretreatment for Hydrolysis of Cellulose

# SUPERCritical AND ENVIRONMENTAL ISSUES

- In USA: Millions of tons of pollutants/year. **WHAT TO DO ?**
  - **End-product environmental monitoring** of existing industrial processes
  - **New industrial processing methods** that support pollution prevention at the source
    - Financial benefits (less \$ for environmental remediation)
    - Other benefits
- US\_EPA: **Green Chemistry Program**
  - Pollution prevention Act of 1990 created to focus on “**source reduction**” of **pollutants** (instead of waste management and pollution control)
  - **Benign-by-design principle** in design, manufacturing, and use of chemicals and chemical processing
  - In 1992:
    - US\_EPA Office of Pollution Prevention and Toxics (OPPT) (formed in 1977) plus NSF jointly funded **Worldwide Green Chemistry Research**
- Much of the **recent funding** by OPPT/NSF goes **to exploit the unique properties of SUPERCritical FLUIDS (SCF)** as an alternative to traditional solvents
- Federal Resource Conservation & Recovery Act (RCRA)
  - Industries using organic solvents must comply with strict regulations regarding
    - On-site storage
    - Recycling
    - Disposal
    - Off-site waste transport
- RCRA & Federal Clear Air Act (CAA) : Suppress soil, air, and water pollution **due to excessive solvent evaporation or improper disposal**



### ■ SCF TECHNOLOGY

- Versatile solvent
- No carcinogenic properties
- No degradation of environment (green)
- .....

### ■ Near critical point:

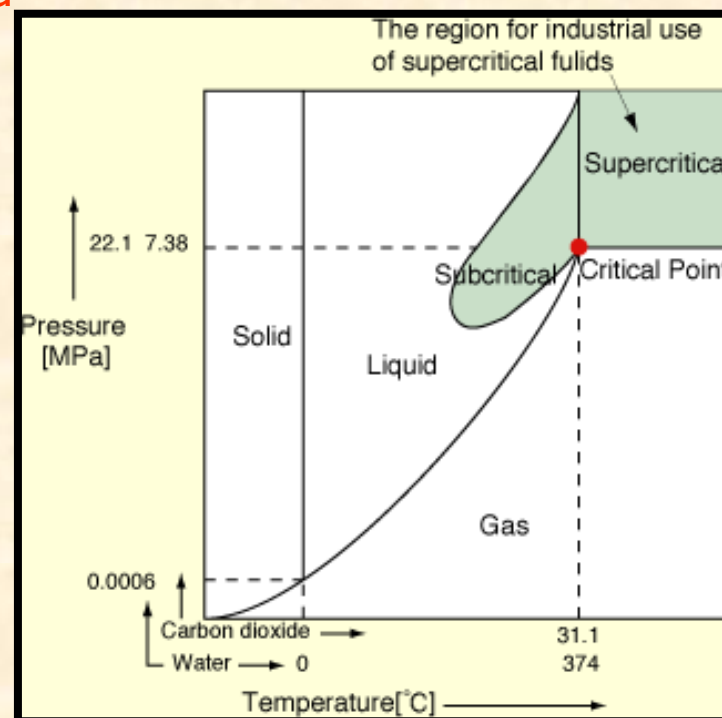
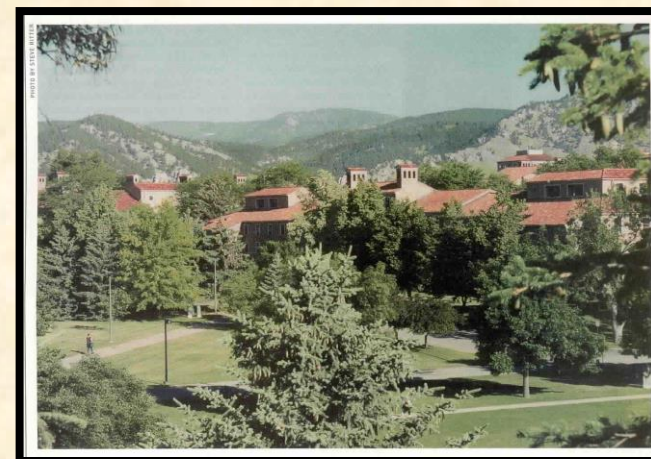
- A very small changes in P or T → Significant changes in (Diffusivity, Density, Solubility) → Useful for synthesis applications: reaction condition (selectivity, rates, pathways) may be sensitively manipulated

### ■ SCF\_CO2 :

- Inexpensive
- No threat to environment (green)
- No threat to human health

### ■ Other applications of SCF:

- Extraction/chromatography
- Inorganic and organic synthesis
- Catalysis
- Material processing
- Dry cleaning
- ...



## SOME SUPERCRITICAL APPLICATIONS (brief)

- SCF Discovered 100 years ago
- In 1970s used to **decaffeinate coffee**
- Since 1970:
  - Extract analysis from variety of complex compounds by manipulation of system pressure and temperature
  - **Problem with conventional methods** (Soxhlet and vacuum extractions):
    - More complex
    - Time/energy intensive
    - Tendency to generate crude extracts
    - Tendency to permanently remove volatile components
- DeSimone et al. → Surfactant design → used for **"solvent free" dry-cleaning application**
- SCF:
  - **Removing PCBs** and other organics from water and soil
  - To **extract metal contaminants**: A chelating agent is commonly added to the fluid, with the soluble metal complex being removed from SCF following system depressurization.
- **Limitations of the SCF\_CO2**:
  - Only capable of dissolving **NONPOLAR** organic-based solute
    - But, addition of small amount of cosolvent such as acetone → significantly improve the solubility of relatively polar solute
  - Recently, solubility of ionic compounds (aqueous metal salts) was enhanced through:
    - **Reverse micelle formation using Fluorinated surfactants** (More Later)

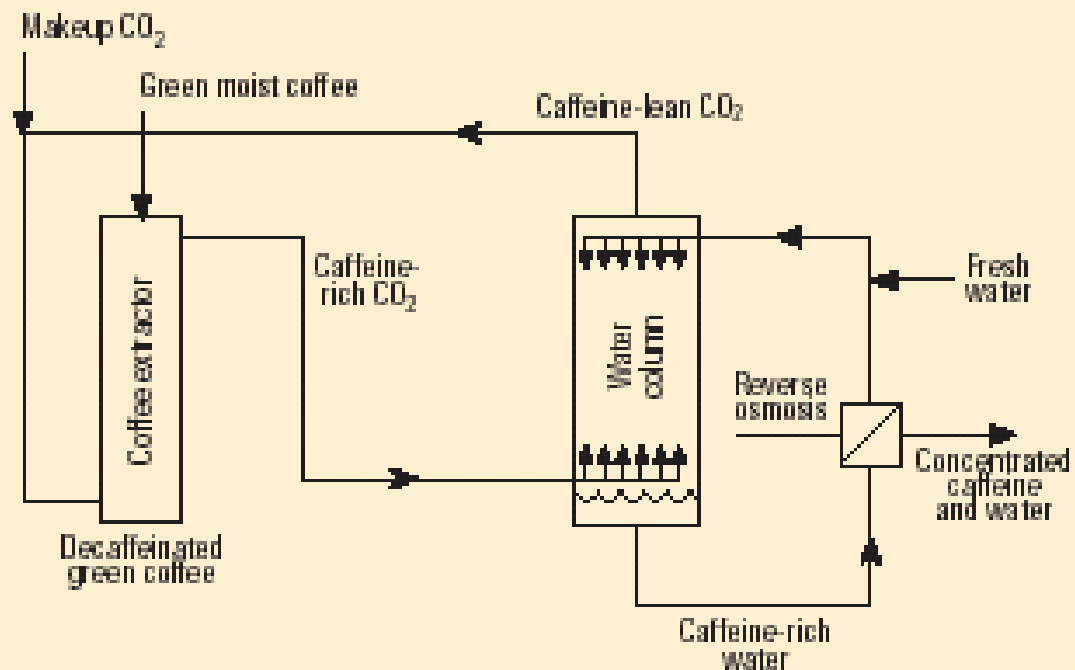


## SOME SUPERCRITICAL APPLICATIONS (brief)

### Decaffeination of Coffee using Supercritical Fluid CO<sub>2</sub>

#### Process schematic for coffee decaffeination using CO<sub>2</sub>

One example of product recovery without a high pressure drop is liquid-liquid extraction against water. The CO<sub>2</sub>-based coffee decaffeination process uses a water-CO<sub>2</sub> extraction to recover the caffeine. Decaffeination is environmentally problematic with typical organic solvents, yet benign with CO<sub>2</sub>.



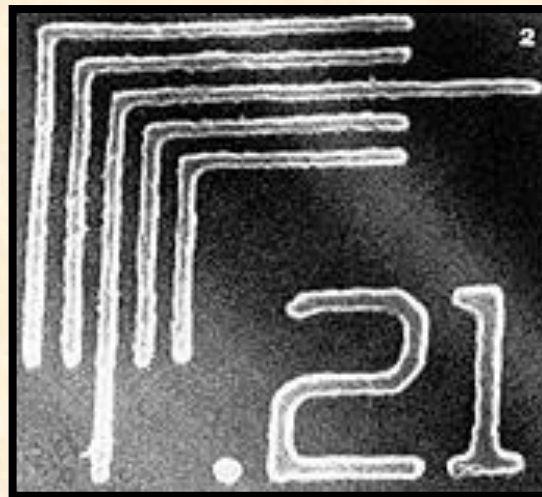
Source: Adapted with permission from Reference (7) in sidebar.

# AN INTERESTING SUPERCRITICAL APPLICATION (LITHOGRAPHY)

## ■ Application of SCF in Lithography

- Another process that can benefit from low solvent viscosity is lithography. **Supercritical fluids tend to have much lower viscosities than liquid solvents.** At Cornell University USA, Ober has developed diblock **co-polymer resists for 193 nm wavelength lithography using SCF\_CO<sub>2</sub> as the developing solvent.** Using this method, lithographic resolutions as low as 200 nm can be achieved (see figure), as a result, in part, of the interfacial segregation behavior exhibited by the block copolymers resists. The Cornell team believes that **SCF\_CO<sub>2</sub> development could play a key role in the fabrication of high aspect ratio features because of the absence of surface tension forces.**
- Ober's research focuses on image development using supercritical CO<sub>2</sub>. In fact, the viscosity of CO<sub>2</sub> is also low in the liquid state. It has extremely low surface tension and surface energy, lower than even many fluorocarbons, **which gives the solvent remarkable wetting properties.** Using this fact, *Carbonell and DeSimone* at the *NSF Centre for Environmentally Responsive Solvents and Processes*, **have developed techniques for spin coating polymer resists onto silicon wafers directly from liquid CO<sub>2</sub>.**
- A combination of these two technologies could result in **a completely new photolithographic process** that uses no organic or aqueous solvents whatsoever, either in the coating or developing steps.

Electron image of a 193nm wavelength photolithographic image developed using **supercritical CO<sub>2</sub>.**

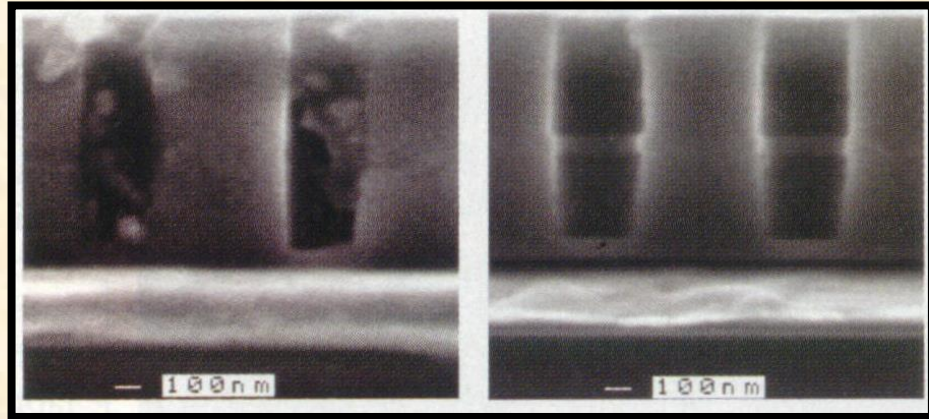


# MORE ON SUPERCRITICAL APPLICATIONS IN LITHOGRAPHY

- As porous low-dielectric materials are starting to be used and chip architectures become ever smaller (width below 130 nm for new generation of ICs), **the surface tension of water no longer will allow it to be readily removed from pores or to penetrate smaller spaces.**
- The smaller architectures also do not have sufficient mechanical integrity to withstand processing with high-surface-tension liquids
- **International Sematech**, a research consortium formed by the semiconductor industry to help set standards, demonstrate new technology development, and solve common problems, **has targeted supercritical CO2 as one enabling process to get around the water problem**
- Very low surface tension and gaslike viscosity of the **SCF allow removal of photoresist masks as well as post-etching and other treatment residues from small structures using fewer chemicals and without the need of water** (This target has the entire semiconductor industry- chip makers, companies that provide machines for fabricating chips, and industrial gas suppliers- working on developing solutions)
- One of these solutions is SCORR (**Supercritical CO2 Resist Remover**), a process originally at LANL and has been automated by SC Fluids with its Arroyo System. SC Fluids has teamed with Air Products & Chemicals, ATMI, and IBM to complete the development of Arroyo. Air Products & IBM are currently testing the Arroyo system, and the first commercial units are expected to be in operation in 2003
- Eventually, all water- and solvent- based processing and polymer deposition, chemical mechanical planarization, lithography, and cleaning – could be carried out by dry processing using CO2 ( Joseph DeSimone)
- The **NSF** Science & Technology Center for Environmentally Responsible Solvents & Processes, **is building a demonstration facility for the “dry fab of the future” on NC State’s campus.**
- DeSimone is working to develop CO2-processible photoresists, copper-oxidizing and –chelating agents, and other compounds to optimize dry processing

## **SUPERCLEAN**

Supercritical CO2 technology developed by DeSimone’s group in conjunction with Micell Technologies provides a water-free method to clean each residues during chip fabrication





# NANOMETER POWDERS

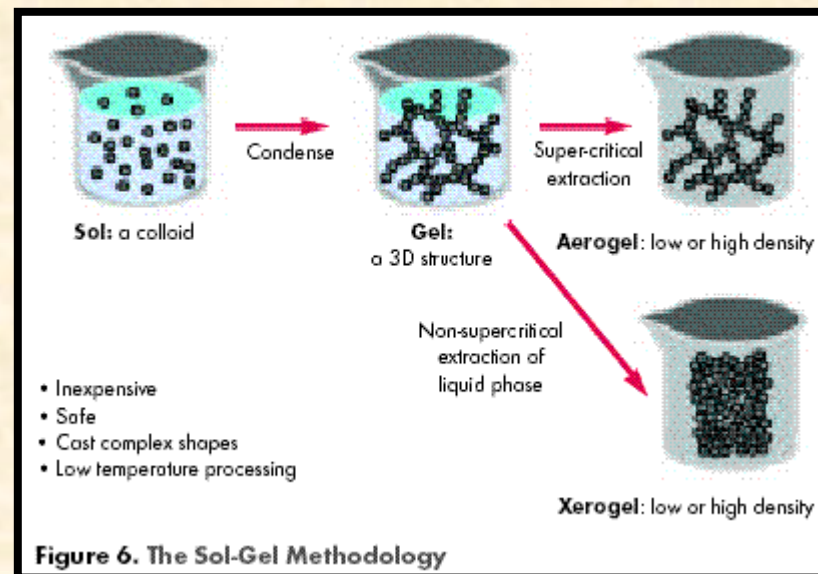
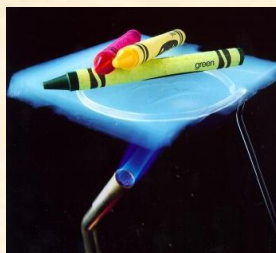
## ■ Nanometer metal powders

- Burn rate modifiers in propellants (Sol-gel, supercritical/nanoparticle)
- Burn rate modifier as components in fuel air explosive
- Burn rate modification in energetic structural materials
- High-intensity explosives
- Powders of some transition metals and their alloys are used in:

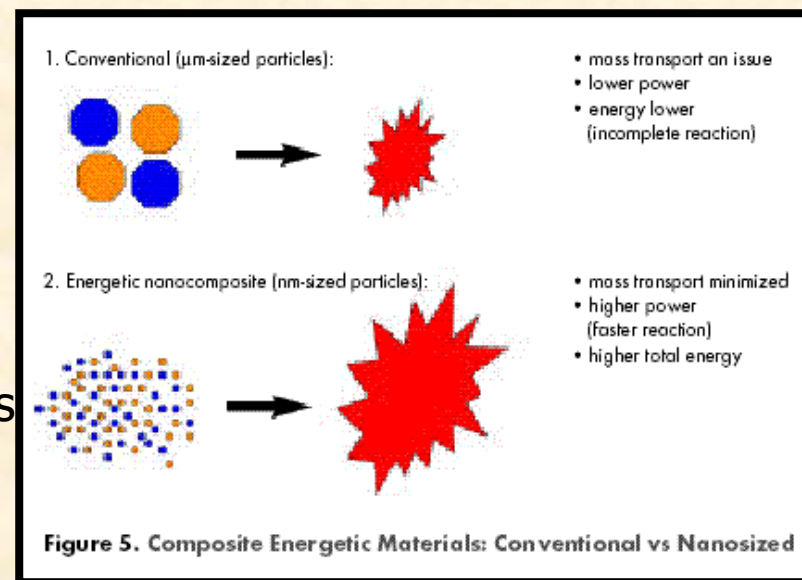
- Thin film technology:
  - Production of conductive pastes for hybrid integrated circuitry
  - Metallization of multilayer ceramic (MLC) capacitors

## ■ Other applications of nanoparticles:

- Advanced catalyst
- Pharmaceuticals
- Pesticides
- Optical barriers
- Semiconductor crystallites
- Enhancing bulk material mechanical properties
- Lubricants
- .....



- **Sol-gel chemistry:** Reaction of chemicals in solution to produce nano-sized primary particles ("sol"), which can be linked to form a 3-D solid network, a "gel", with the remaining solution residing within open pores.
- Solution chemistry determines the resulting nanostructure and composition, which in turn determines the material properties
- Controlled evaporation of the liquid phase results in a dense porous solid (xerogel), while **SUPERCritical extraction eliminates the surface tension of the retreating liquid phase, producing highly porous "aerogels"**.



# SUPERCritical AND Material Synthesis (Nanoparticles, a brief)

■ Metal powder production manufacturing (see below) gives nonuniform size distribution that require milling of the agglomerated powders:

- Powder mixing / calcination
- Metal-organic decomposition from nonaqueous solution
- Precipitation from aqueous solution of metal salts
- .....

■ Nanoparticle production using Supercritical Fluids (SCF)

- In past two years:
  - SCF was used as medium for nanoparticle growth
    - Dissolve a component in SCF → Particles are isolated by **Rapid Expansion of Supercritical Solution (RESS)** → dissolved components are deposited as extremely fine particles
  - Another method: Uses **microemulsion**
    - (Aqueous metal salt + reducing agent +surfactant) added to SCF → The nanoparticles are deposited by RESS → Particles are shown to be free of atomic incorporation and extremely homogeneous in size (VERY IMPORTANT)

■ SCF and thin-film technology:

- **Chemical vapor deposition (CVD) used SCF for growth of thin films:**
  - Supercritical fluid transport CVD (SFT-CVD) allows relatively nonvolatile precursors to be introduced into the deposition chamber as they are soluble in SCF
  - **Traditional thermal CVD uses ONLY volatile precursors**
  - Complex films as BaTiO<sub>3</sub> & YBCO have been successfully deposited using SFT\_CVD by dissolving stoichiometric amount of metal β-diketonate precursors within the SCF. **Using traditional CVD to do this is very complex because more than one solid or liquid precursors must often be used each possessing unique solubility**



# SUPERCRITICAL AND Material Synthesis (Nanoparticles, a brief)

## ■ Safety issues

- High pressure ! Unappealing
  - This problem has been circumvented by use of flow reactors analogous to those reported by [Poliakoff research group](#) at the University of Nottingham
- **Flow reactors** also offset the problem created by altering the critical temperature of the fluid by dissolution of solute; that is, with **batch reactors**, the critical temperature of the reaction mixture change significantly as the reaction proceeds.
- Also, if one uses autoclave, it is typically small to reduce the danger associated with large volume at high pressures

# A COMMERCIAL APPLICATION OF NANOPARTICLES

- Enhancing gas-barrier properties in resins such as **nylon**
- Can be employed as a cost-effective means of **increasing “toughness”** (impact strength) of PVC and polypropylene (PP) copolymer without compromising rigidity
- Calcium carbonate (CaCO<sub>3</sub>) nanoparticles
  - Using a process developed at Beijing University of Chemical Technology licensed by Singapore's NanoMaterials Technology Pte Ltd. (Key advantage: Production costs)
  - Other suppliers: Solvay, Brussels, Belgium, and Shiraishi Calcium Kaisha Ltd., Osaka, Japan
- **The 15 to 40 nm dia. Particles** are produced by **reaction of calcium hydroxide and carbon dioxide** in a rotating reactor (the rotating packed bed, or RPB, process). **Proprietary surface modification techniques are then applied to the nanoparticles** to enable compounding of masterbatched. The masterbatches can be manufactured using standard twin-screw compounding equipment.
- Nano-CaCO<sub>3</sub> masterbatches, in which particle loadings are typically 70 to 80%, can then be utilized **to enhance the impact properties of products such as PVC window profiles**, where they can **partially replace impact modifiers** such as chlorinated polyethylene (CPE) and poly-methacrylate-butadiene-styrene (MBS). Interestingly, **flexural modulus is typically enhanced, as well.**

Sample	Composition (pph)			Single-Notch Impact Strength (kJ/m <sup>2</sup> )	Flexural Modulus (MPa)	Tensile Strength (MPa)
	PVC	Nano-CaCO <sub>3</sub>	CPE			
1	100	0	8	14.9	2180	38.8
2	100	8	8	81.4	2210	38.6

**Table 1:** Properties of nano-CaCO<sub>3</sub>/PVC/CPE compounds.

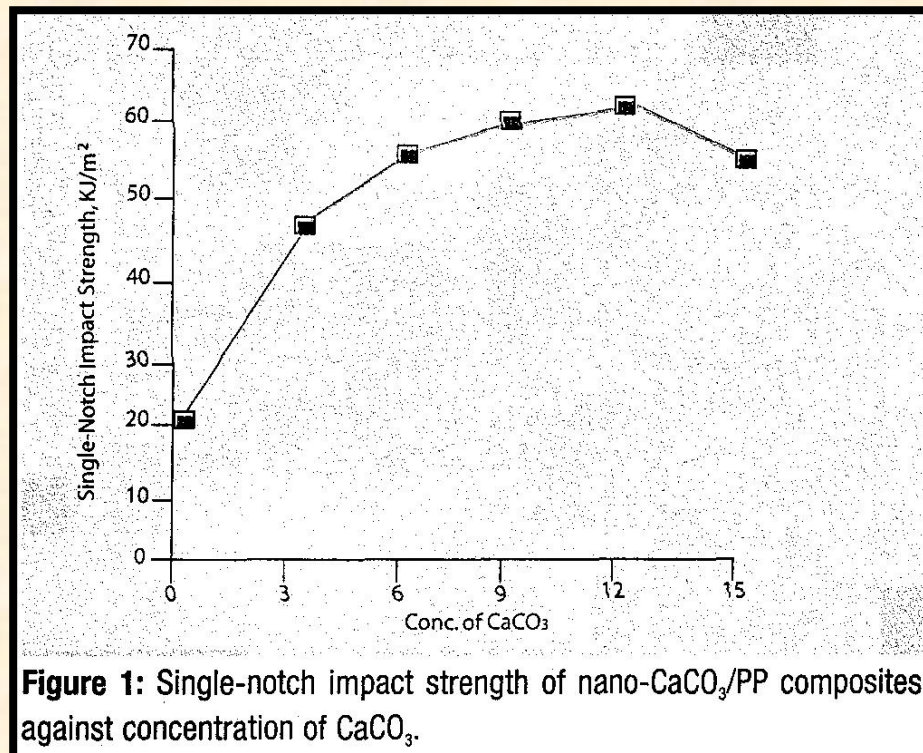


# A COMMERCIAL APPLCATION OF NANOPARTICLES

- The key in using Nano- $\text{CaCO}_3$  to increase the toughness of plastics lies in **the dispersion of these nanoparticles in the polymer matrix**. They possess very high surface activity, resulting in a tendency for the particles to agglomerate

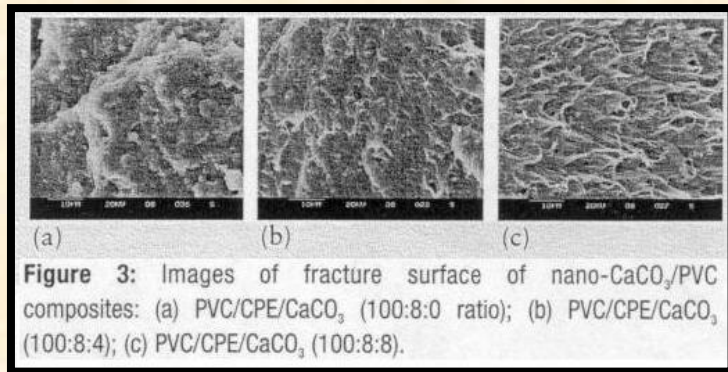
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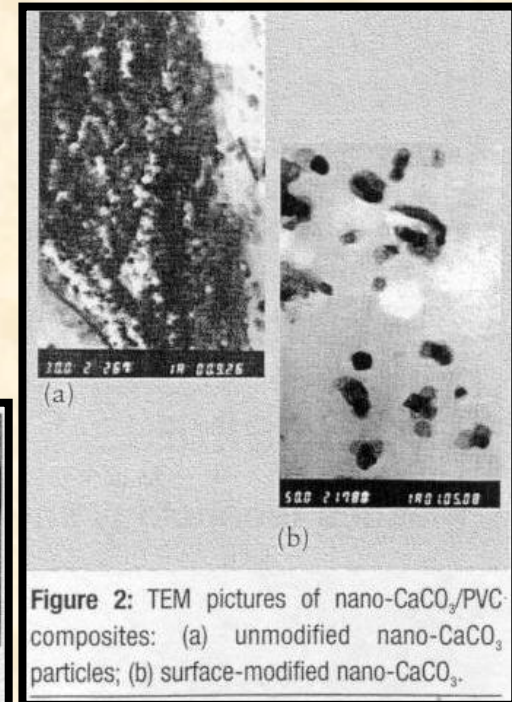
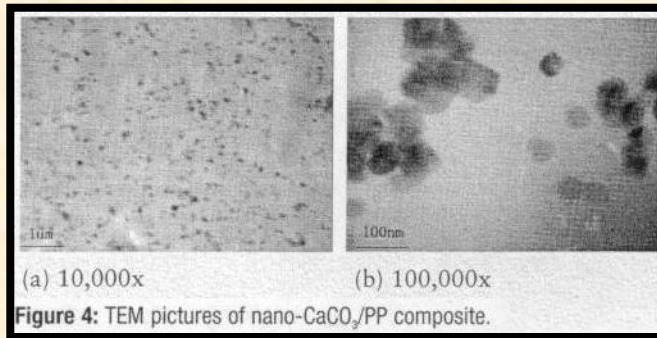
# A COMMERCIAL APPLICATION OF NANOPARTICLES

- It is generally thought that the **mechanism of plastics toughening through nanoparticles is the large surface area of the nanoparticles**, which causes a large amount of crazing (**microfracturing**) within the polymer matrix. **These microfractures act to dissipate impact energy**
- At the same time the matrix in the **internanoparticle space is thought to undergo plastic deformation on impact**, which also results in dissipation of external impact forces, hence achieving toughness
- However, the plastic-toughening effect of inorganic nanoparticles does require the polymer matrix to have an inherent toughness.
- In a brittle plastic (PVC), a small amount of **impact modifier (e.g. CPE)** is needed in the formulation
- The nano-CaCO<sub>3</sub>, and the CPE then **exhibit a synergistic toughening effect** within the nano-CaCO<sub>3</sub> / PVC/ CPE composite system (in commercial application: 4 pph of CPE and 4 pph of nano-CaCO<sub>3</sub> is considered optimum)



When no nano-CaCO<sub>3</sub> is used, the fracture surface of the composite is uneven, the typical appearance of a brittle fracture. When 4pph is added, fibrils begin to appear on the fracture surface of the PVC composite. At 8pph, **obvious fibril form on the fracture surface on impact, indicating large amount of craze generated in the PVC matrix**

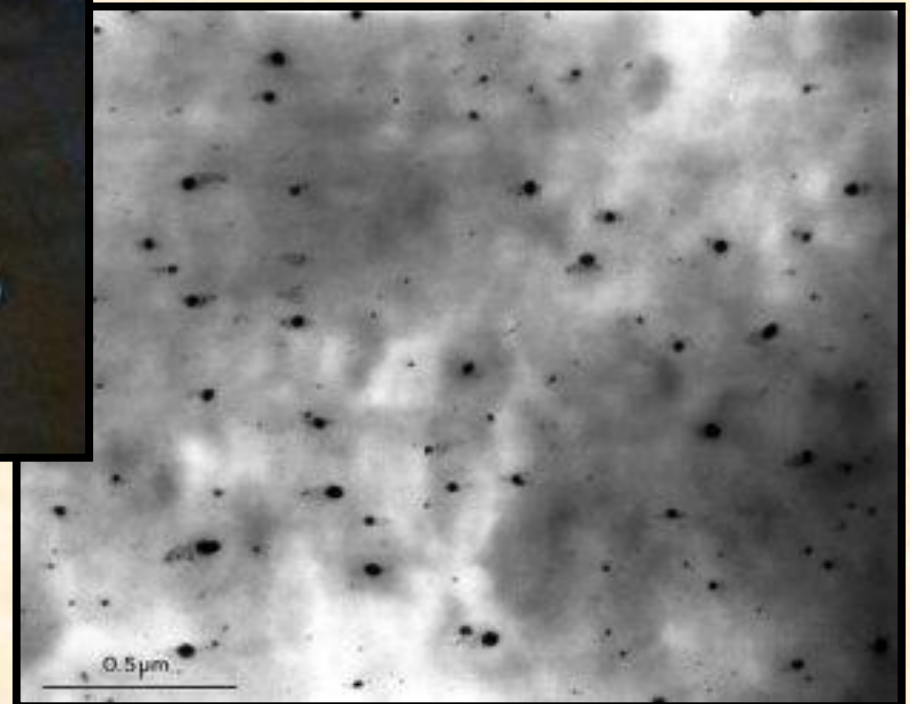
Shows dispersion of nano-CaCO<sub>3</sub> particles in PP. It can be seen that CaCO<sub>3</sub> are **evenly dispersed within PP matrix**, with the particles properly spaced out. There is also a little agglomeration (CaCO<sub>3</sub> particle agglomeration is at less than 100 nm), indicating that **effective dispersion at nanoscale is achieved**.





## ANOTHER APPLICATION OF NANOPARTICLES

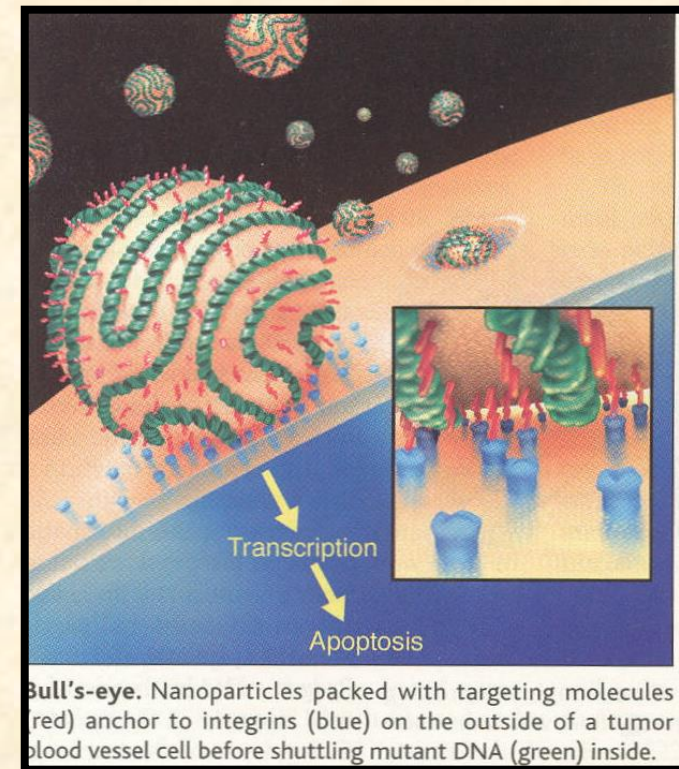
- Total hip replacement is a common operation. The, "socket", of the implant usually made of Ultra-high molecular weight polyethylene (UHMWPE)
- However, the surface of this polymer can degrade as the, "ball", moves around in the, "socket", leading to the production of tiny particles of UHMWPE that can cause problems and lead to implant failure.
- Poliakoff's group developed a supercritical fluid method for putting tiny metal particles into the polymer in an attempt to improve the properties of the UHMWPE (see Figure).
- They have developed silver precursors for the preparation of silver/UHMWPE composites by impregnation using  $\text{scCO}_2$ .
- Once these composites have been made they can be tested for biological response.



# YET ANOTHER APPLICATION OF NANOPARTICLES

## Nanoparticles Cut Tumors' Supply Lines

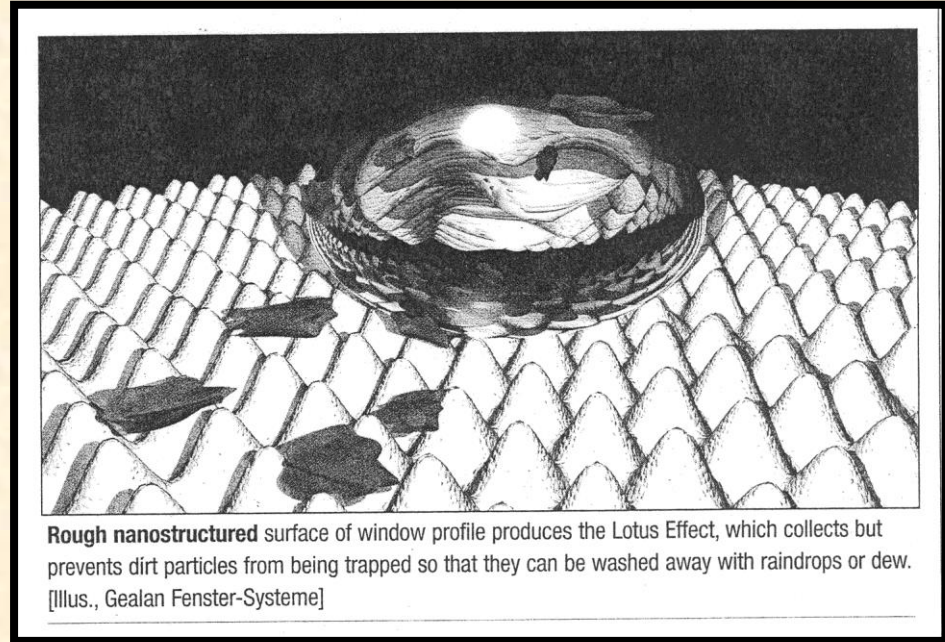
- Tumors hungry for sustenance need new blood vessels to deliver the goods. Cancer researchers have spent years working to starve tumors by blocking this blood vessel growth, or *angiogenesis*, with mixed success (*Science*, 22 March, p. 2198). Now a team has tackled the problem of choking off tumor vessels from a novel angle: The researchers packed a tiny nanoparticle with a gene that forces blood vessel cells to self-destruct, then they "mailed" the nanoparticle to blood vessels feeding tumors in mice.
- "It is a very provocative paper, which I think will become a landmark in angiogenesis research," says antiangiogenesis pioneer Judah Foikman of Children's Hospital in Boston. Adds Philippe Leboulch, a gene flierapist at Harvard Medical School in Boston:
- "They achieved tumor regression—and they started with tumors [that were] quite large for mice." Despite their enthusiasm, however, researchers are treading gingerly around the landmines in cancer treatment, where hopes have been raised and dashed many times.
- The study, reported on page 2404 and led by vascular biologist David Cheresh of the Scripps Research Institute in La Jolla, California, draws on research in a number of fields. In the mid-1990s, Cheresh and others found signatures specific to different types of blood vessels that they used as target "zip codes." One of these, belonging to a class of membrane proteins called integrins, is apparently always present on angiogenic, or newly growing, blood vessels but rarely on established ones. The integrin,  $\alpha v \beta 3$ , has another quality that would turn out to be convenient: It can propel viruses or other small particles into cells.
- Cheresh's team, assisted by organic chemist and radiologist Mark Bednarski of Stanford University, designed a lipid based nanoparticle that would target new blood Vessels. The nanoparticle's surface is studded with molecules that bind to  $\alpha v \beta 3$  and embedded with copies of a mutant form of the **Raf 1** gene that disrupts Raf's normal activity





# YET ANOTHER APPLICATION OF NANOPARTICLES

- Clean After Rain **Vinyl windows with self-cleaning technology** (coming near you by Gealan Window Systems, 2004)
- Surface has hydrophobic microstructure that reduces particle adhesion thus eliminate the need for periodic cleaning
- All PVC profiles contain surface irregularities that collect soot and thus require regular washing
- Gealan **created a surface irregularity profile that could clean itself with rain or dew**
- The surface coating provides the so-called **Lotus Effect**
- Through addition of a proprietary water-repelling “attribute,” rain droplets retain their spherical form when they fall onto the profile’s surface
- **The drops roll off the surface, carrying dirt with them. The effect is enhanced by a cushion of air between the droplets and the surface** created by the microstructure as it reduces the contact area
- Challenge: Because coating cannot be repaired if damaged, need to provide a durable surface that is not damaged during installation
- **CleanHT Troplast:** Worked on **nanostructure method**
- Proprietary **post-extrusion coating of TiO<sub>2</sub> nanoparticles** that function with UV light and moisture to **provide cleaning**
- Developed a formula and size for the TiO<sub>2</sub> nanoparticles
- **UV interaction with surfaces of the nanoparticles causes activation of an electron to form a peroxide and oxidizes it.**
- **This prevents soot from attaching to the vinyl profile and slides it away**
- Normal daylight (even cloudy days) provides sufficient reaction to activate the cleaning effect
- All that is needed is moisture in the form of humidity or dew
- Systems using Lotus Effect require rain. Parts of profiles under eaves may not get enough rain to clean themselves





# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

- RESS Process: **Dramatic change in dissolving power experienced by a solute as it rapidly expands from supercritical** (*significant dissolving ability*) → **subcritical** (gas) (*negligible dissolving ability*). Subsequently, **rapid nucleation and growth** of low vapor pressure solute particles, if sufficient solute density exists in expansion jet.
- Rapid solute condensation ( $10^{-5}$ s) during RESS → Solute **nucleation & Particle growth** processes
- Qualitative effects of solute concentration & presence of electrolytes on physical characteristics of material formed were analyzed
- RESS applicable to both inorganic ( $\text{SiO}_2$ ) and organic materials (polymers) → **for formation of powders, thin films, and fibers.**
- Also, it is shown that an intimately mixed powder of two inorganic materials ( $\text{SiO}_2$  & KI) or an inorganic and organic combination (KI and poly(vinyl)chloride) can be obtained → **feasibility of unique amorphous mixtures**
- **SCF:** Can dissolve solutes with negligible vapor pressure
- **RESS(highly diluted)** → Allows transfer of individual molecular species of low volatility to the gas phase, where mass spectroscopic techniques may be used for their study
- **RESS(more concentrated)** → Containing low vapor pressure solute **can be used to produce powders and films** due to homogeneous nucleation of the solute species present in the solution prior to expansion
- **Desired: A degree of control over solute nucleation and growth processes during expansion**
- Understanding the RESS expansion processes which affects nucleation & growth, hence physical properties of the products, aid for **better control of these properties**

# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

## ■ System:

- SiO<sub>2</sub> - water
- Autoclave at  $T_{\text{subcritical}}$  & ~ 590 bar kept for several hours to equilibrate (Critical Point water: 374 C & 221.2 bar)
- Open valve
- Heat the tube  $T \rightarrow T_{\text{supercritical}}$
- Expansion nozzle: 5mm length, 60 microns i.d. s.s. tubing
  - Fused silica ( 25 micron i.d. ) nozzle were used for **polymer solutions** using organic solvents, and no back pressure regulation was needed
- Powder samples were collected inside a partially evacuated chamber ( 0.1  $\rightarrow$  1 bar) to minimize **potential health hazards** associated with presence of airborne silica particles.
- Variation: For systems other than SiO<sub>2</sub> - water a premixed solution is pumped and no autoclave is used or collection is done at 1 atm inside a fume hood.
  - Premixed solution: Only when there was sufficient solubility in a liquid solvent at the ambient temperature and pressure and where solubility did not decrease to a point where the solute precipitated as the solution was heated to  $T_{\text{supercritical}}$

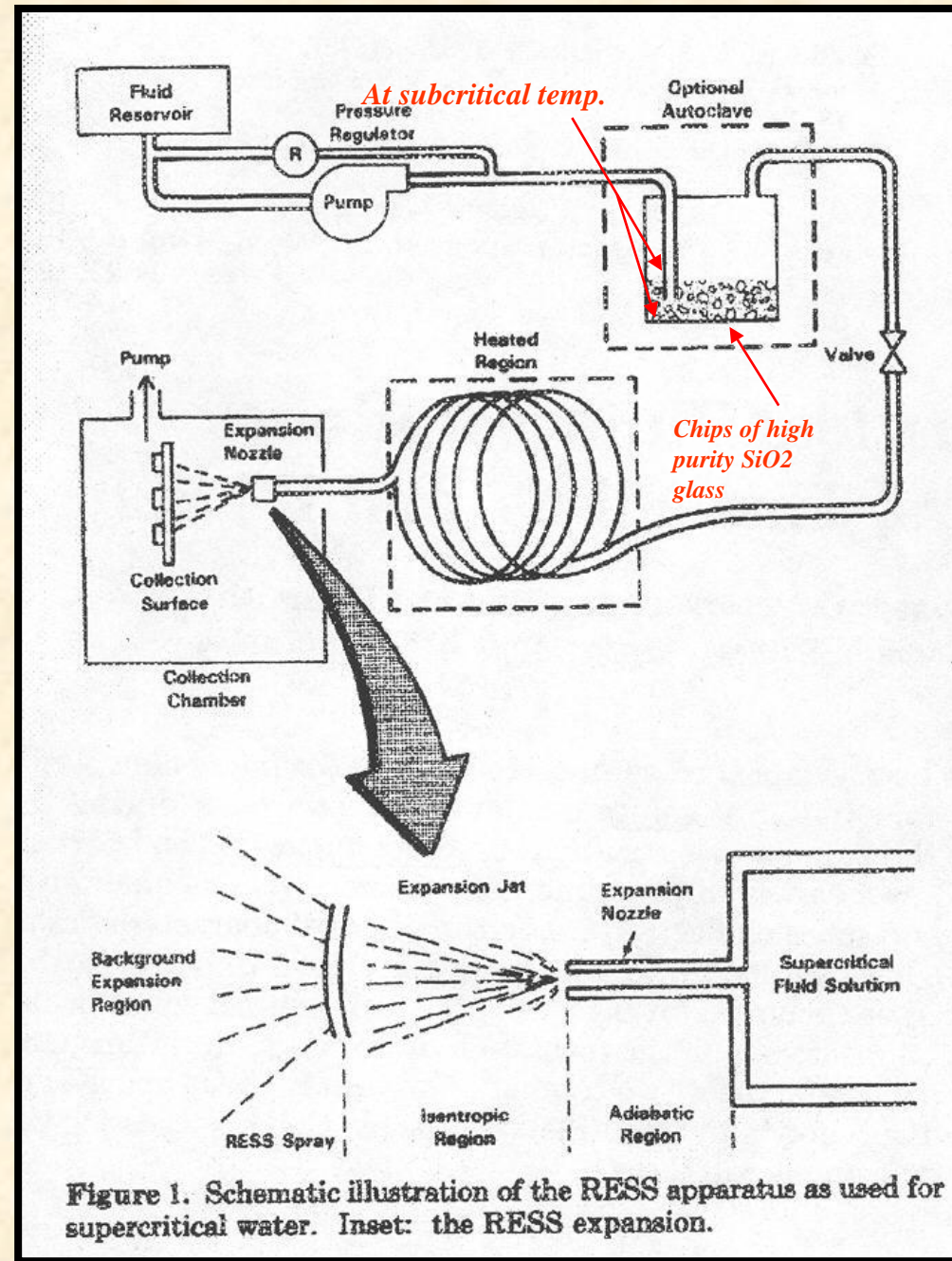


Figure 1. Schematic illustration of the RESS apparatus as used for supercritical water. Inset: the RESS expansion.

# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

## ■ Product characterization

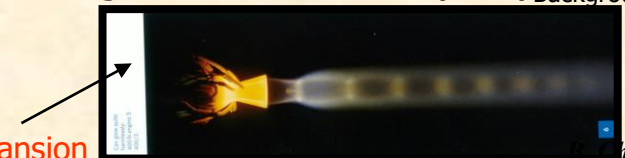
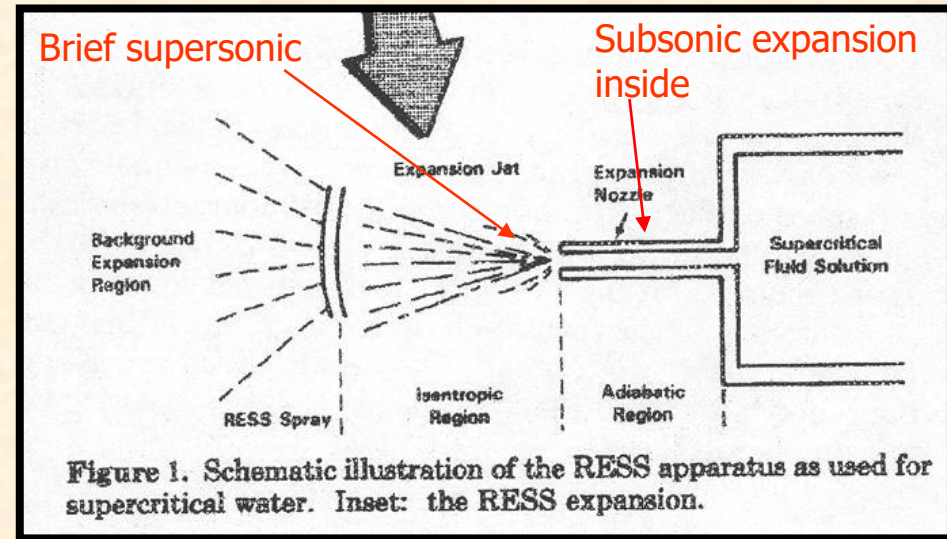
- Optical microscopy
- SEM, TEM for detailed morphology
- Qualitative X-ray fluorescence for elemental analysis of particulates
- Specific surface area of powder sample by nitrogen gas adsorption (BET method)
- Phase characteristics of powder samples were probed in the bulk by X-ray powder diffraction and at the micro structural level by using Dark Field TEM analysis
- IR-analysis; find the extent of solvent inclusion in RESS polymer products
- Melting point of polymer products: were determined and compared with that of polymers initially loaded into the autoclave to establish the extent of fractionation which might have occurred by selective solvation of lower molecular weight oligomers during the dissolution-extraction process



# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

## ■ RESS Process

- RESS process is characterized by the characteristics of the fluid expansion process, i.e.  $= f(\text{flow properties})$
- Stages for the expansion process:
  - **Subsonic expansion**: Through the length of the nozzles itself
  - **Brief supersonic** "free jet" expansion: immediately upon exiting the nozzle
  - Final Stage; Jet interacts significantly with background gas in the expansion region
- Flow through the nozzle is choked  $V_{\text{fluid}} < V_{\text{sound}}$
- For  $L/D \sim 400$  ( $\rho_{\text{Exit}} / \rho_{\text{Inlet}} \sim 0.5$  &  $P_{\text{Exit}} / P_{\text{inlet}} \sim 0.4$ ), **Fluid expands adiabatically in the tube** and reaches  $V_{\text{sound}}$  at the exit
- **A set of shock front separates the isentropic supersonic region from the other downstream part:**
  - Barrel shock wave
  - Reflected shock waves
  - Shock front is perpendicular to the jet axis (the **Mack Disk**)
  - Distance from the nozzle to the Mack Disk  $\sim 0.67 D (P_0/P_1)^{0.5}$ ; where  $P_0$ : initial preexpansion fluid pressure and  $P_1$ : background pressure in the expansion region
  - Beyond the Mach Disk, significant mixing between the jet & background gases contributes to entropy increase in the jet
- Within the supersonic region, the expansion process is complex and **jet may enter the 2-phase expansion region**
- The density of a single phase H<sub>2</sub>O fluid at the **Mach Disk** is estimated to be on the order of 50 times  $<$  than  $\rho_{\text{Nozzle Exit}} \rightarrow$  A significant fraction of the expansion occurs within the isentropic expansion stage
- **Beyond Mach Disk**: Turbulent flow of the jet rapidly mixes background gases with the fluid ( $T, P$ )<sub>Background gas</sub> large effect on the condition within the jet

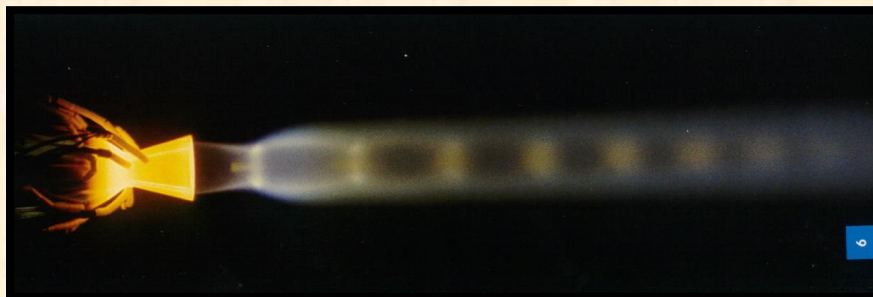
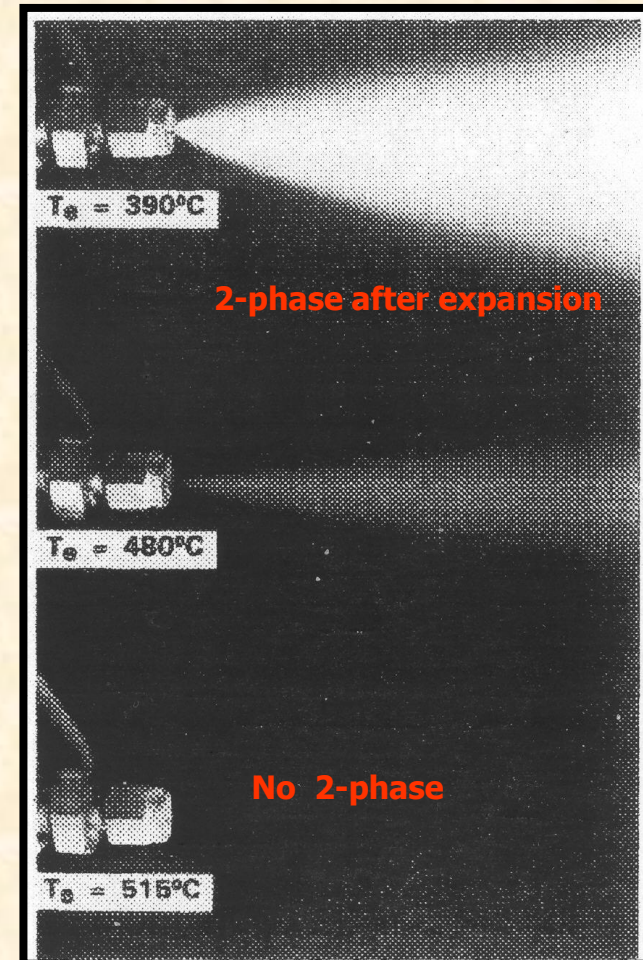
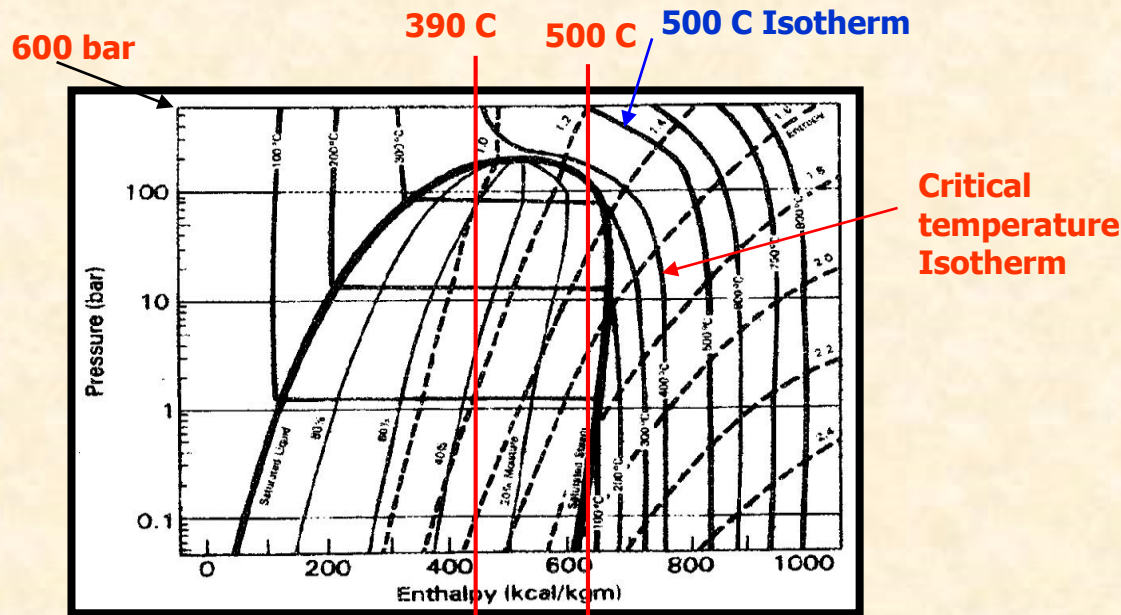


Similar shock patterns in Rocket exhaust expansion

# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

## ■ RESS Process (Cont.)

- Phase behavior of the expanded gas (considering low concentration of solute):
  - See Figure; If  $P_{\text{at Exit}} = 600 \text{ bar}$ :
    - $T_{\text{exit}} < 490 \text{ C}$  2-phase
    - $T_{\text{exit}} > 530 \text{ C}$  single-phase (if assuming  $T_{\text{background}} > T_{\text{exit}}$ ; see Fig. for experimental verification of these phase predictions)
- Operation of RESS process at **single phase** solvent expansion mode **allows the advantage of collecting solute products in the "DRY" state, with no liquid solvent incorporated in the product structure**

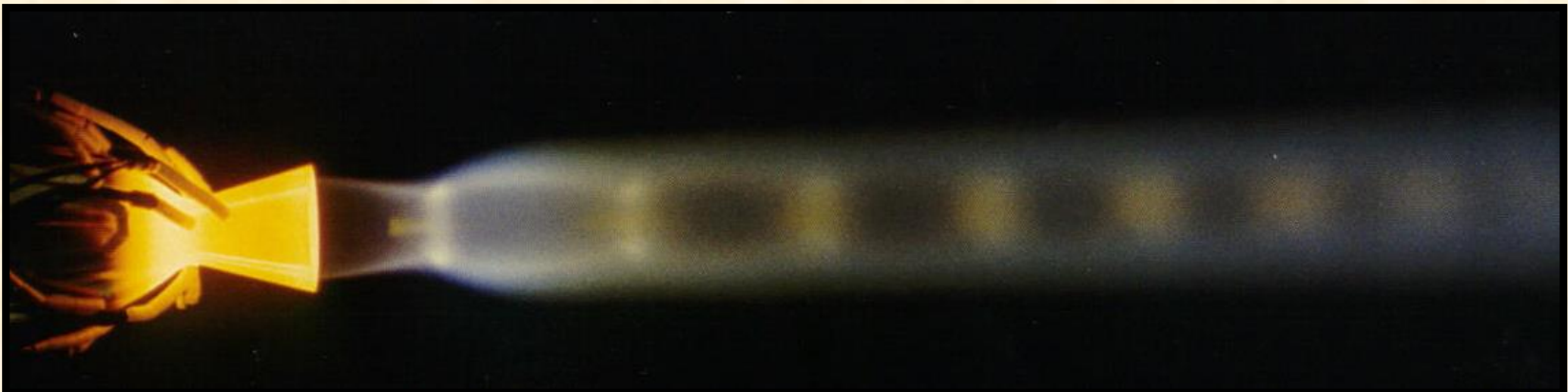




# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)



**Some similarities between the shock patterns in Rocket exhaust expansion and RESS**





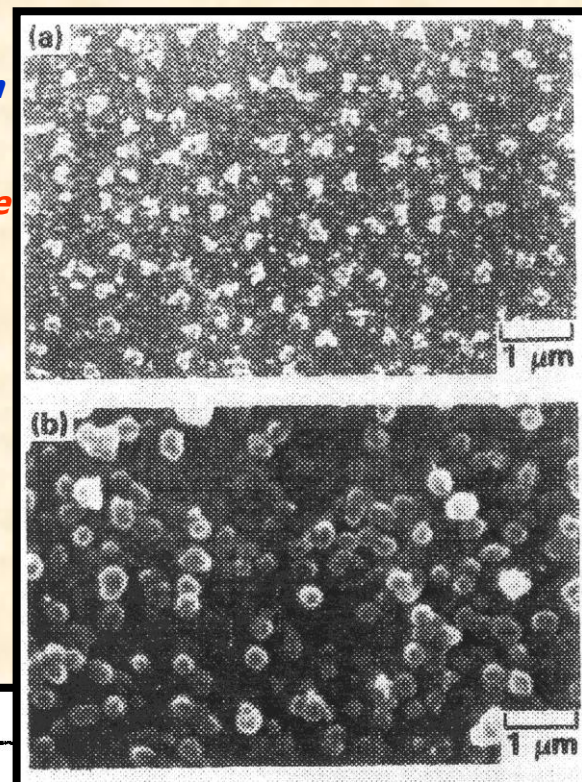
# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

## ■ RESS Products

- **Inorganic products:** Particularly oxides in which ability to generate uniform fine powder or/and thin film is advantageous. Silica is chosen as the model for this class
- **Polymers:** Many polymers exhibit significant solubility in CO<sub>2</sub> or low-M HC's at conditions where these solvents exist as SCF (McHugh & Krukonis)
- See Table
- Size of silica particles **nucleated** and **condensed** in jets of expanding supercritical SiO<sub>2</sub> – Water solutions were strongly function of silica concentration in SCF prior to expansion, see (a) and (b) in the **Figure**. Silica concentration is controlled via T of autoclave
- Also, GeO<sub>2</sub> (has high solubility than SiO<sub>2</sub> in water ) was used.

*Low  
concentration  
of silica:  
significantly  
smaller in size*

*High  
concentration  
silica: X-ray  
amorphous  
silica  
particles ~ >  
0.2 micron*



**Table II. Experimental Parameters and Product Morphologies of Some RESS Deposited Materials<sup>a</sup>**

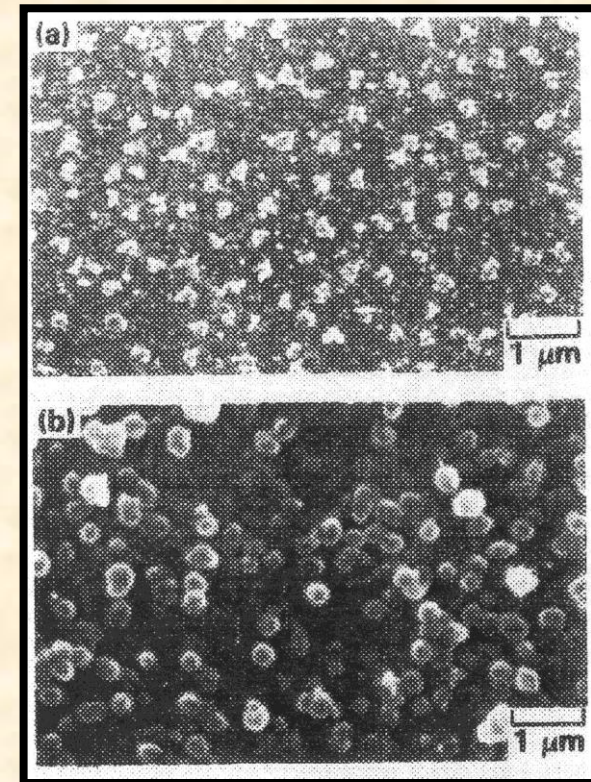
solute-solvent	auto-clave, temp, °C	system pressure, bar	preexpansion temp, °C	product morphology
SiO <sub>2</sub> -H <sub>2</sub> O	260	580	450	>1.0 μm thick film
SiO <sub>2</sub> -H <sub>2</sub> O	300	590	470	0.1-0.5-μm-diameter spheres
GeO <sub>2</sub> -H <sub>2</sub> O	25	580	475	5-μm agglomerates
GeO <sub>2</sub> -H <sub>2</sub> O	25	580	445	0.5-1.3-μm-diameter spheres
SiO <sub>2</sub> , KI-H <sub>2</sub> O	385	580	500	20-μm agglomerates <sup>b</sup>
Si-NH <sub>3</sub>	250	284-415	350	d
SiO <sub>2</sub> -NH <sub>3</sub>	285	204	350	d
ZrO(NO <sub>3</sub> ) <sub>2</sub> -ethanol	c	175	375	~0.1-μm particles
Si <sub>3</sub> N <sub>4</sub> -NH <sub>3</sub>	160-385	136-306	280-410	d
polystyrene-pentane	200	170	350	20-μm-diameter spheres <sup>c</sup>
polystyrene-pentane	200	170	200	1-μm-diameter fibers of 100-1000-μm length <sup>c</sup>
polypropylene-pentane	225	170	200-400	1-μm-diameter fibers of 100-1000 μm length or 0.5-1.0-μm particles <sup>c</sup>
poly(carbosilane)-pentane	g	102	375	1-μm-diameter fibers of 80-160-μm length
poly(carbosilane)-pentane	g	238	250	<0.1-μm particles
poly(phenyl sulfone)-propane	125	170	150	agglomerated spheres (each sphere ~0.5-μm diameter)
poly(methyl methacrylate)-propane	125	170	125-300	1-μm diameter fibers of 100-1000-μm length or 0.5-1.0-μm particles <sup>c</sup>
poly(vinyl chloride), KI-ethanol	250	170	350	7-μm-diameter spheres <sup>b</sup>



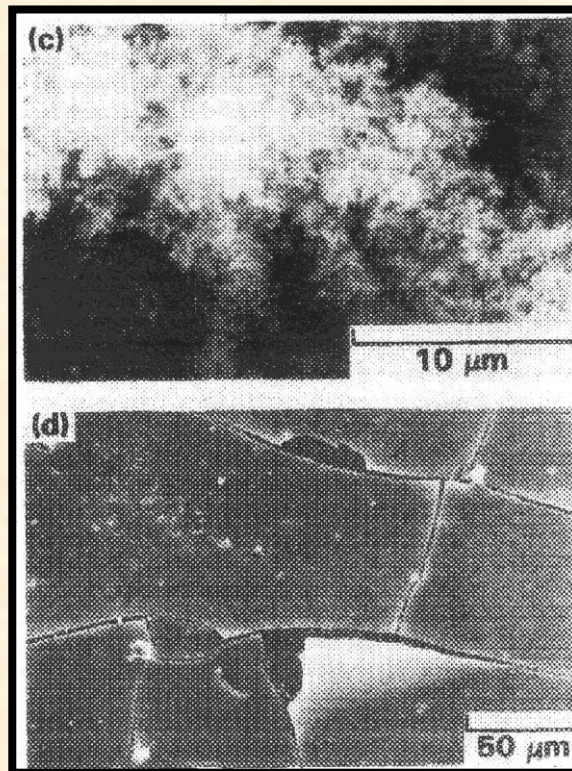
# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

Low  
concentration of  
silica:  
significantly  
smaller in size

High  
concentration  
silica: X-ray  
amorphous silica  
particles  $\sim > 0.2$   
micron



Significantly  
lowered size with  
higher  
agglomeration of  
particles



A thick film  $> 1$   
micron on  
surface of  
Millipore filter  
when RESS  
visibly produced  
2-phase jet.  
Cracks due to  
later flexing of  
substrate

**Figure 4.** Examples of silica particles deposited from supercritical water solutions under different experimental conditions. (a)  $\text{SiO}_2$ -water system with the autoclave operating at 75 °C and the supercritical output line at 500 °C; (b)  $\text{SiO}_2$ -water system with the autoclave at 225 °C and the supercritical output line at 500 °C; (c)  $\text{SiO}_2$ -0.001 M KI in water with the autoclave at 385 °C and the supercritical output line at 500 °C; and (d)  $\text{SiO}_2$ -water system with the autoclave at 280 °C and the supercritical output line at 450 °C. For each of the above samples, the system pressure was  $\sim 590$  bar and the background pressure was  $\sim 0.1$  bar. A 5-mm-long by 60-μm-i.d. expansion nozzle was used for all samples.

# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

- Use of supercritical fluid in manufacturing fine particles.
- Using the **Rapid Expansion of Supercritical Solutions (RESS)** method, the solute is dissolved in supercritical fluid and then is expanded through a nozzle to a low density in the vicinity of atmospheric pressure.
- **Ball-shaped or fibrous fine particles are obtained.**
- **Kobe Steel** has developed a process for manufacturing fine silica particles or minute fibrous material, in which the monocrystalline silica is dissolved in supercritical water. In addition, an **improved version of the RESS method** is used.

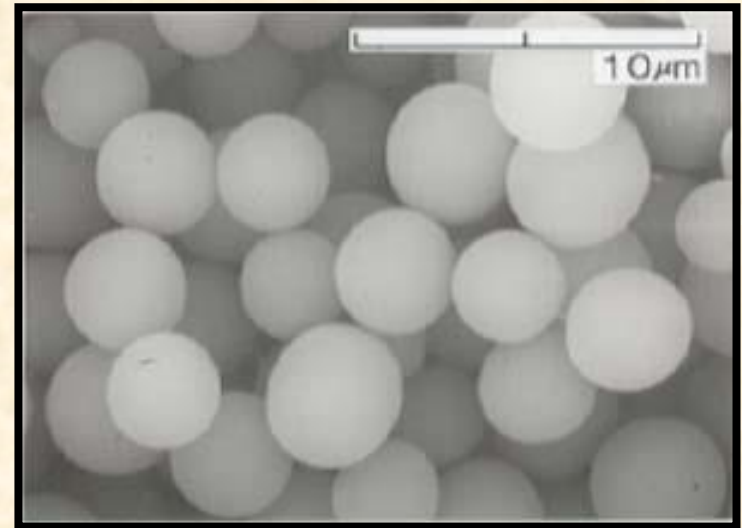


Photo 3 SEM image of SiO<sub>2</sub> particles (823K, 100MPa)

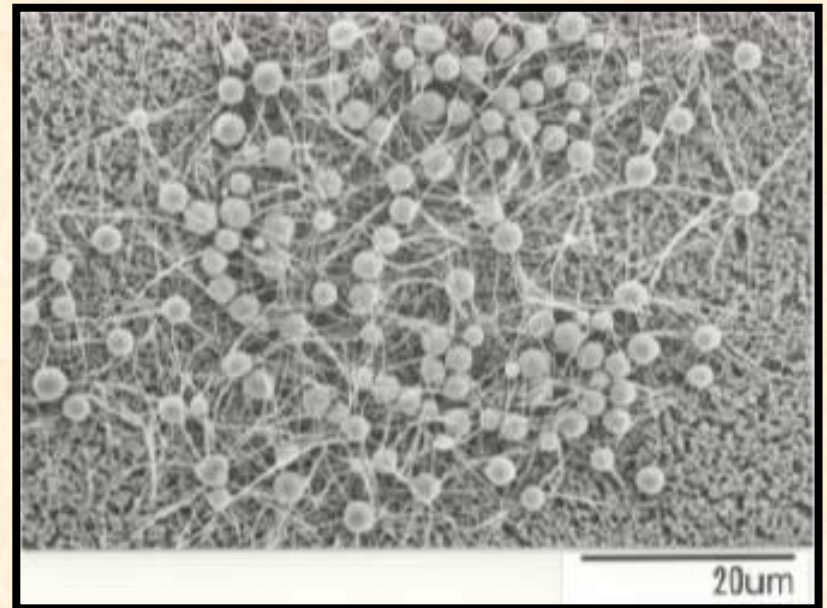


Photo 4 SEM image of SiO<sub>2</sub> particles (823K, 63MPa)

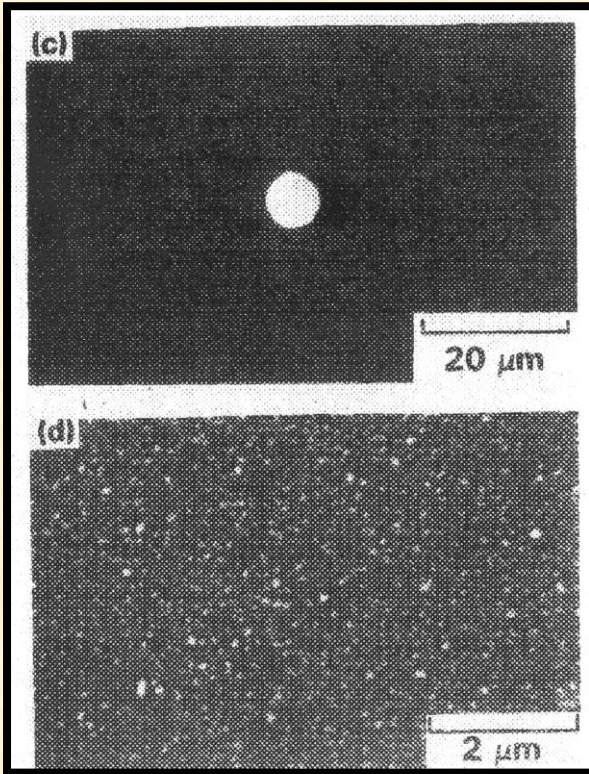


# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

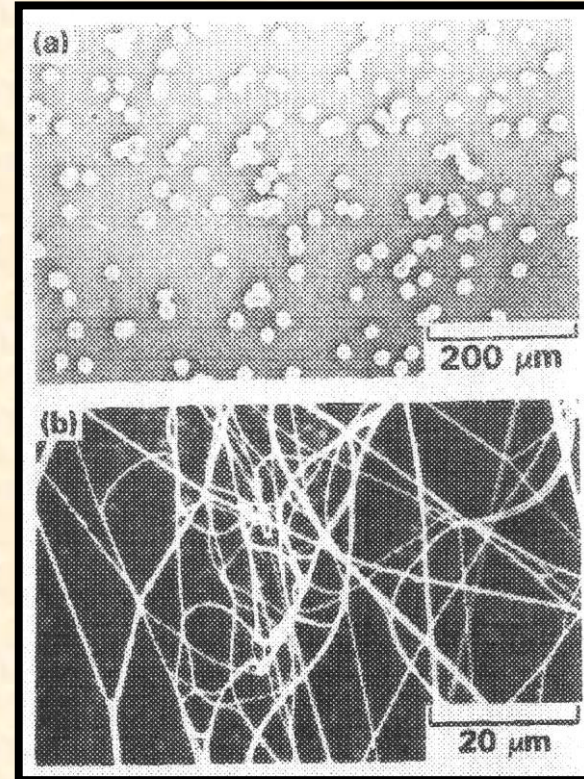
## ■ RESS & Polymer materials:

- Their solution differ from low-M inorganic. Why ?
- Molecular size
- **Solution process:** Typically involves formation of a **swollen** “gel” and then “true solvation” if the intermolecular forces between polymer molecules (caused by cross-linking, crystallinity, or strong H-bonds) are overcome by strong polymer-solvent interaction
- Concentration of polymer does affect the end-product morphology during expansion
- Polymer solubility is easily controlled via varying autoclave temperature . However, in some cases:
  - In poly(carbosilane), premixed polymer solution can be prepared.
- Product morphology = f( characteristic of solute, expansion process, .....)
  - **Precise mechanism by which the final particle product is formed, however, has not been fully established**
  - Also, observations regarding the mechanism of formation of film, fibers **remain largely empirical**
  - Initial nucleation: may be considered as homogeneous (without presence of additional surface)
    - Formation Rate (stable critical-sized solute) = f(Degree of Solute Supersaturation)
    - Homogeneous nucleation equation assuming equilibrium gives a **rate of nuclei formation equation**,  $I_f$  of the following form:
      - $I_f = (\dots\dots) e^{(\dots\dots)}$ ; where  $(\dots\dots)$  is related to molecular collision frequency, and  $e^{(\dots\dots)}$  is surface free energy of nucleus
      - Use of this equation is questionable due to nonequilibrium nucleation processes during RESS
    - **NEITHER**, 1. Degree of supersaturation (occurs during RESS expansion prior to significant particle nucleation), **NOR**, 2. Location at which nucleation occurs w.r.t. nozzle exit has been well established

# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)



(c) Poly (vinyl chloride) (77,800 MW) + potassium iodine **from an ethanol solution** at 170 bar with the autoclave and **supercritical** output line at 250 C



(a) Polystyrene spheres (300,000 molecular weight) **from a pentane solution** at 170 bar with the autoclave at 225 C and the **supercritical** output line at 350 C

(b) Polystyrene fibers (50,000 MW) **from a pentane solution** at 150 bar with the autoclave at 250 C and the **supercritical** output line at 260 C

(d) Poly(carbosilane) (1420-1450 mean MW) **from a pentane solution** (34.8 ppm by weight poly(carbosilane)) at 240 bar with the **supercritical** output line at 250 C.

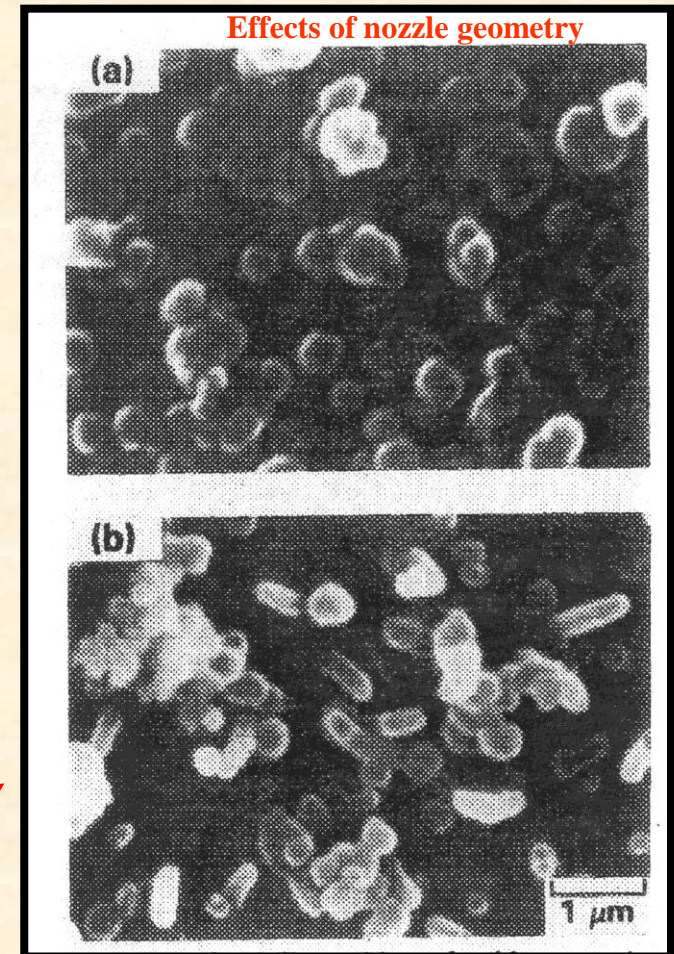
For each of the examples, a 5-mm long by 25 microns expansion nozzle was used , and the background pressure was 1.0 bar.



# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

## ■ Possibilities

- **Nuclei growth** via diffusion-controlled monomolecular addition mechanism is one reasonable process by which the ultimate RESS product takes place
- Extremely rapid expansion → Rapid drop in  $\rho_{\text{solvent}}$  → Massive **solute supersaturation** → simultaneous formation of large # of nuclei
- If no significant particle growth occurs subsequent to **nucleation**, products will be characterized by large # of very small solute nuclei
- **Coalescence of nuclei in jet**: Could produce much larger particles ( see Figures in previous slide)
- **Dimension of capillary nozzle: Affects the length in which RESS occurs**
  - Changing,  $1 \text{ mm} < L_{\text{nozzle}} < 10 \text{ mm}$  while  $L/D \sim 200$  : No effects on Particles ! Unexpected in view of differences in density gradient expected to be experienced by solution
  - If  $L/D \leq 1$  → Interesting (see **Figure 6**) RESS-generated particles could exhibit a brief plastic state if they are envisioned to form by the coalescence of solute nuclei
- **P & T of the SCF solution prior to expansion through nozzle affects products morphology**
- **P & T** : Affect the phase of the expansion jet
- **Phase effect**: Best result if the expansion jet is single-phase region than two-phase where solvent drops are formed



**Very very short nozzle (pinhole): Oblong shaped due to high shear in a brief plastic state**

**Figure 6.** Examples of silica particles produced from expansion of  $\text{SiO}_2$ -water solutions through different expansion nozzles. The nearly spherical particles shown in (a) are typical of those produced using capillary nozzles, whereas the elongated particles in (b) were produced using a very short nozzle and may indicate the existence of a transitory plastic state during particle formation. Both samples were collected from a system in which the autoclave was maintained at  $250^\circ\text{C}$ . The fluid expansion temperatures and pressures were maintained at approximately  $600^\circ\text{C}$  and 580 bar for (a) and  $675^\circ\text{C}$  and 580 bar for (b).



# RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTION (RESS)

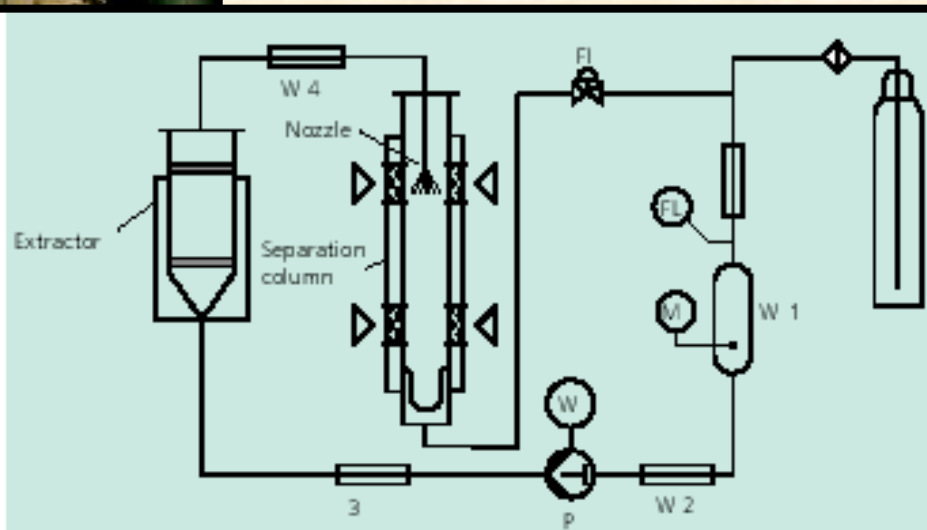
Fine Particle Formation  
using Supercritical Fluids  
(SCF)



**Fraunhofer** Institut  
**Chemische Technologie**

## We Offer

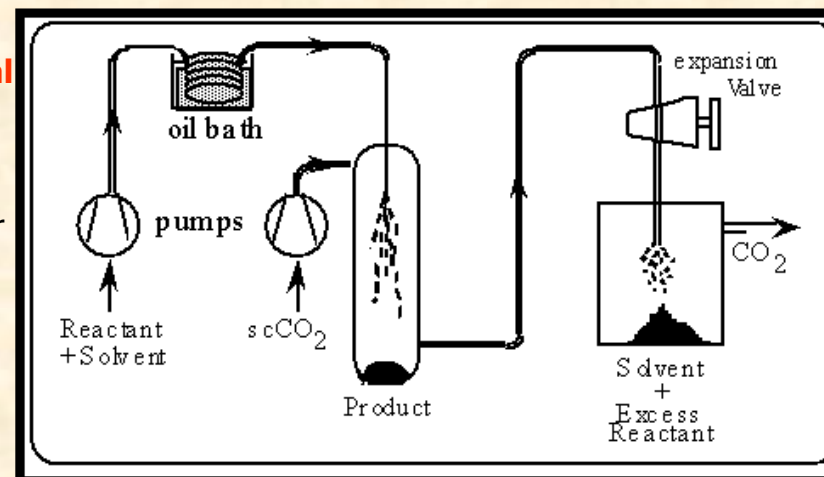
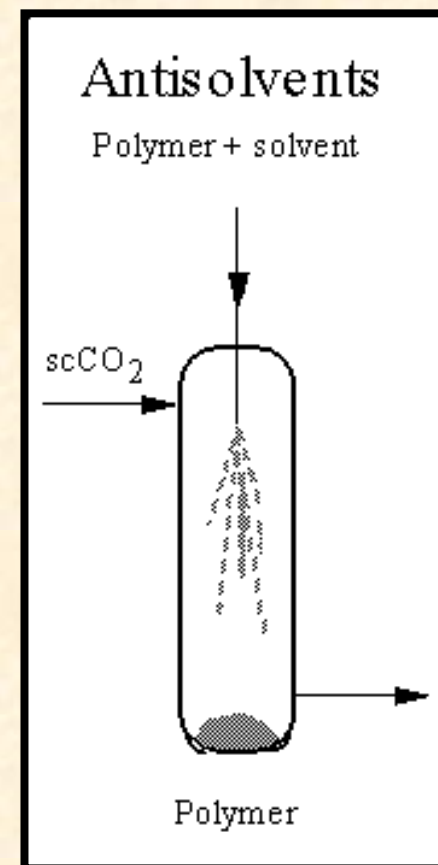
We offer application studies of the process and the development of custom made facilities. A pilot scale facility can be operated at a maximum pressure of 30 MPa and a maximum extraction temperature of 80 °C. A CO<sub>2</sub> mass flow rate up to 30 kg/h can be attained. A 600 ml fixed-bed-extraction-container or a 1l stirred vessel is used to premix and dissolve the material before introducing it into the process. The concentration of the solute can be measured on-line by spectroscopic and chromatographic methods. Relaxation processes in the nozzle produce very high local regions of supersaturation, which results in spontaneous formation of fine, narrowly distributed solid particles.



P: membrane pump, W: heat exchanger, FI: flow meter, FL: liquid CO<sub>2</sub> reservoir, M: Antriebsmotor, D: pressure control

# ANTISOLVENT METHOD

- The fact that many substances are insoluble in supercritical fluids has given rise to the use of the supercritical fluids as **antisolvents** to precipitate materials from conventional solvents.
- However, the significance of the **ROSA** (Reaction in Organics with Supercritical Antisolvents ) technique are:
  - The key advantage: the size and morphology of the particles can be manipulated by adjusting the parameters (flow rates, pressure, temperature of  $\text{CO}_2$ , etc.)
  - the same equipment can be used for almost any organic solvent without modification;
  - the apparatus is **inherently scalable** and reactions could be carried out on a much larger scale;
  - the technique **need not be restricted to organometallic chemistry** and a similar approach could be applied to widely different areas of chemistry.
- The principle is similar to the familiar use of aliphatic hydrocarbons to precipitate materials from a more polar organic solvent.
- The organic solution is injected essentially under conditions of laminar flow
- Particle formation in materials as diverse as polybutadiene, laser dyes and bucky balls ( $\text{C}_{60}$ ) were used
- A flow-reactor was combined with  $\text{scCO}_2$  antisolvent precipitation using conventional solvents for the synthesis of **organometallic** compounds.
  - The reaction is carried out in an organic solvent in a thermal flow reactor and the product is then precipitated by the  $\text{scCO}_2$  antisolvent, as shown in the Figure.
  - The high pressure of the  $\text{scCO}_2$  (typically 10 MPa) means that the organic solvent also has to be pumped at a pressure which is higher than the critical pressure of most organic liquids ( e.g. pyridine,  $P_c$  5.63 MPa, 56 bar.).
- The result is that the organic solvent can be heated right up through its critical temperature without boiling. Thus, it is possible to carry out reactions in highly superheated organic solvents without the use of conventional high pressure autoclaves.



# MICROEMULSION

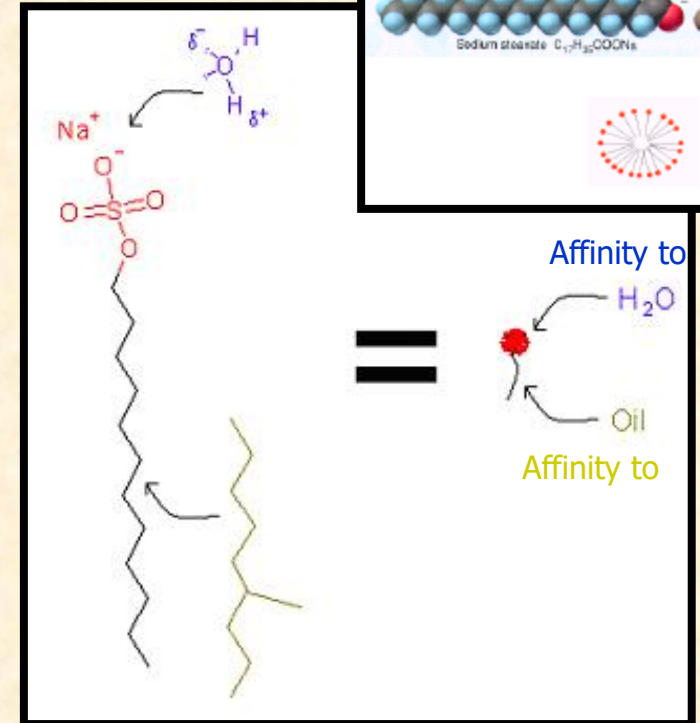
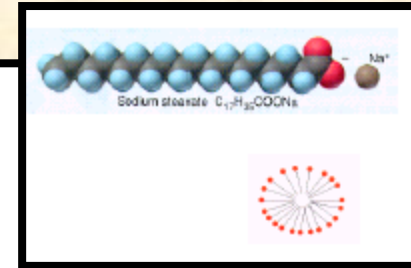
## WHAT DO WE GET WHEN WE MIX THINGS ?

continuous phase	dispersed phase	type	example
gas	liquid	aerosol	fog
gas	solid	aerosol	smoke
liquid	gas	foam	whipped cream
liquid	liquid	emulsion	milk
liquid	solid	sol	paint, blood, ink
solid	gas	solid foam	meringue
solid	liquid	solid emulsion	butter
solid	solid	solid sol	opal



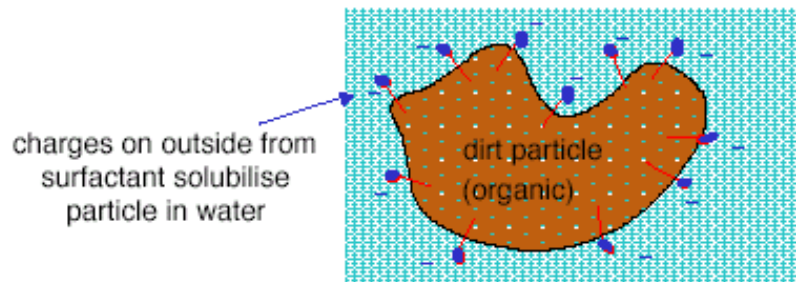
# SURFACTANTS: What are they ?

- A **surfactant** molecule is formed by two parts with different affinities for the solvents. One of them has affinity for water (polar solvents) and the other for oil (non-polar solvents).
- A little quantity of **surfactant** molecules rests upon the water-air interface and decreases the water surface tension value (the force per unit area needed to make available surface). That is why the **surfactant** name: "**surface active agent**".
- When water, oil and a **surfactant** are mixed, the **surfactant** rests at the water-oil interface.



## Surfactants

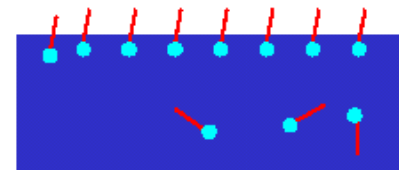
- "Dirt" is non-polar. Grease = long chain hydrocarbons
- However water is very polar and will not dissolve 'greasy dirt'
- Soaps, detergents (e.g. sodium dodecyl sulfate): emulsifying agent
  - Suspend normally incompatible grease in water



- Hence called **wetting agent** or **surfactant** (= surface-active agent)

## Surfactants at the interface

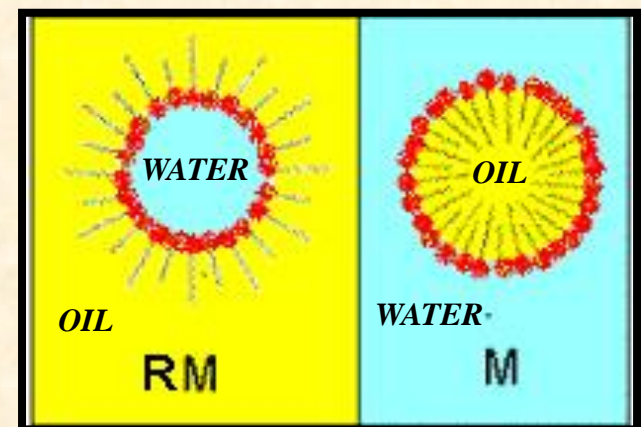
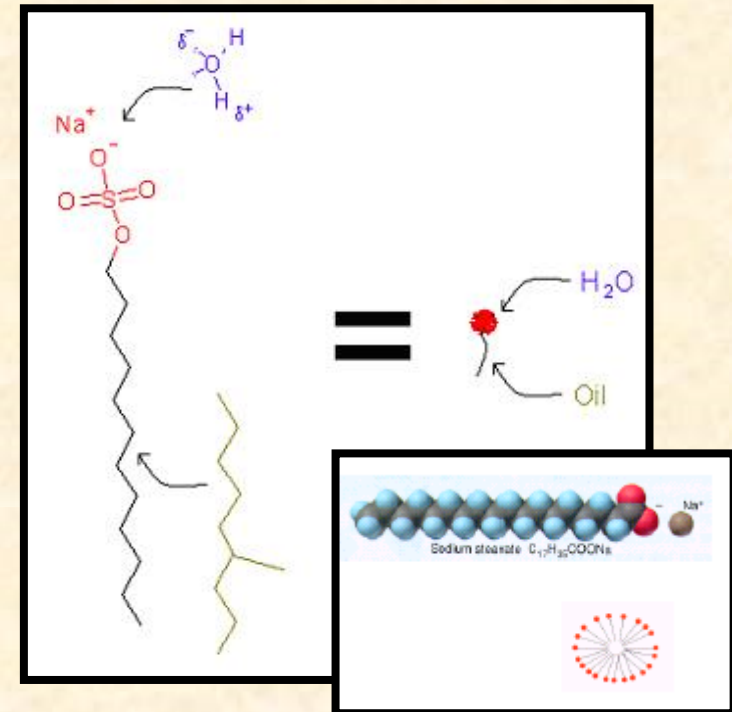
- Surfactants have **hydrophobic** and **hydrophilic** parts
- Hence both parts "happy" in micelles ("happy" = low free energy)
- Hydrophobic part also makes them accumulate at air-water interface (hydrophobic part is at least out of the water)



- Hence they lower the surface tension of water

# SURFACTANTS and Microemulsions (Micelles)

- A surfactant molecule is formed by two parts with different affinities for the solvents. One of them has affinity for water (polar solvents) and the other for oil (non-polar solvents).
- A little quantity of surfactant molecules rests upon the water-air interface and decreases the water surface tension value (the force per unit area needed to make available surface). That is why the surfactant name: "surface active agent".
- When water, oil and a surfactant are mixed, the surfactant rests at the water-oil interface.
- These systems depending on their stability are called emulsions or **microemulsions** (thermodynamically stable).
- Although, the properties for an emulsion and a microemulsion are different, both obey the same principle: **they try to form enough interface for preventing the polar non-polar solvent contact.**
- Microemulsions are very interesting systems, because the oil-surfactant-water interface forms a wide variety of structures to avoid the direct oil/water contact. **The sizes of these structures are in the range of a few hundreds of nanometers**, so the solutions are transparent.
- **Micelles** are the simplest structures: **spherical or cylindrical objects formed by surfactant molecules, separating oil and water.** Micelles are like drops of oil in water and **reverse micelles** are like drops of water in oil.



**Spherical micelle (M) and reverse micelle (RM). The oil is in yellow and the water is in blue.**

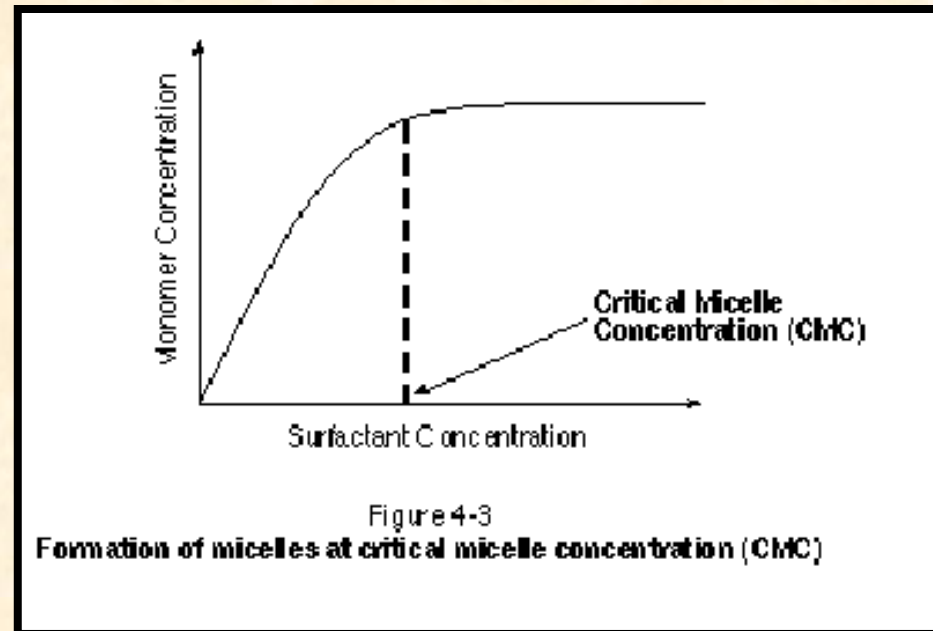
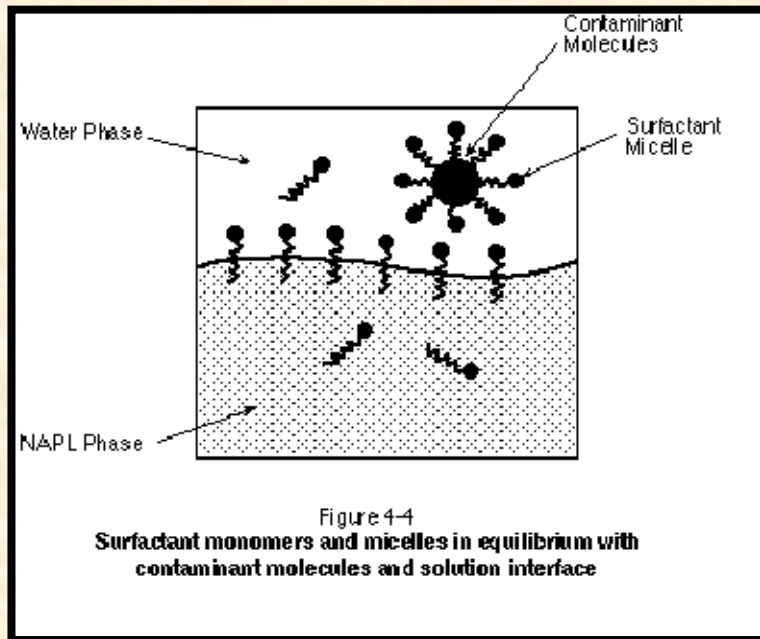


# Micelles and Microemulsions

- **Microemulsions (Micelles)** are clear, thermodynamically stable solutions that generally contain water, a surfactant, and an "oil".
- The "oil" in this case is the **supercritical fluid phase**.
- The water microdomains have characteristic structural dimensions between 5 and 100 nm. Aggregates of this size are poor scatterers of visible light and hence these solutions are optically clear.
- **Water-in-"oil" (w/o) microemulsions** can have a multitude of different microscopic structures including sphere, rod, or disc shaped aggregates.
- **Recently, microemulsions formed in liquid and supercritical CO<sub>2</sub> have emerged as a new type of solvent for industrial-scale processes. These CO<sub>2</sub> microemulsions, consisting of macromolecular surfactant aggregates, have profound implications for enabling new separations and reactions with virtually no detrimental environmental effects and with significantly reduced life-cycle energy content.**
- Microemulsions dramatically improve the solvent properties of CO<sub>2</sub> and other **supercritical fluids** to allow the dissolution of a wide range of polar species.
- PNNL is a recognized leader in the study of microemulsions in supercritical fluids and PNNL researchers were the first to address the solubility limitations by using microemulsions in **supercritical fluids**. CO<sub>2</sub> is environmentally benign, non-toxic, and is the second least expensive solvent available, next to water.
- The use of **supercritical CO<sub>2</sub>** by industry has been limited because, by itself, it will dissolve only a small number of compounds having low polarity and low molecular weight.
- **A microemulsion overcomes the major limitations of CO<sub>2</sub> or other supercritical fluids** by making it possible to dissolve highly polar, ionic, high molecular weight species

# Micelles and Microemulsions

- As surfactants are added to aqueous solution, they will **tend to accumulate at fluid-fluid and fluid-solid interfaces**. Some surfactant monomers also will exist in free solution in all phases present.
- **Once a sufficient amount of surfactant has been added** to aqueous solution, however, aggregations of surfactant monomers referred to as **micelles will form**.
- Micelles are often spherical in shape and can contain several hundred surfactant monomers.
- As shown in Figure 4-3, the threshold concentration at which micelles begin to form is termed the **critical micelle concentration (CMC)**.
- Beyond the CMC, any surfactant added to aqueous solution will not increase the number of monomers in aqueous solution, but rather will contribute to the formation of additional micelles.



By increasing the total aqueous solubility of the target NAPL (nonaqueous phase liquid contamination), dissolution of the NAPL will be accelerated. Surfactant monomers in solution and monomers at solution interfaces will be in equilibrium with monomers in micelles, with a continuous movement of monomers between these various sites. This is illustrated schematically in Figure 4-4.



# TiO<sub>2</sub> Synthesis in SCF – CO<sub>2</sub>

Anionic Fluorinated surfactant  
to stabilize water dispersion in  
SCF\_CO<sub>2</sub>

Titanium alkoxides (dissolution  
in SCF\_CO<sub>2</sub> required)

+

Water (stabilization is required)

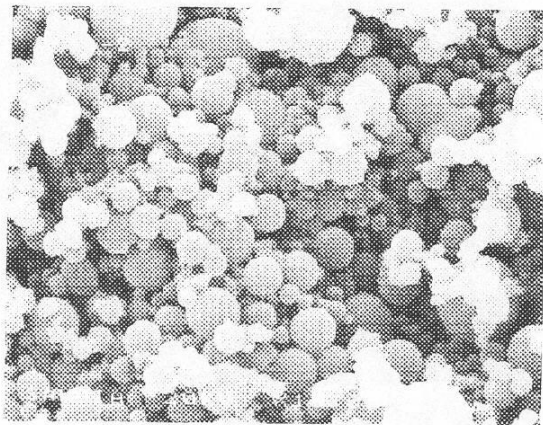
SCF\_CO<sub>2</sub> →

- Solubility of Titanium alkoxides in CO<sub>2</sub>: Parallel their vapor pressure = f (Oligomerization of unhydrolyzed alkoxides)
- Polydispersed particles: because of simultaneous nucleation & growth occurring owing to :

- Changes in degree of supersaturation during the transition from the liquid to supercritical state.

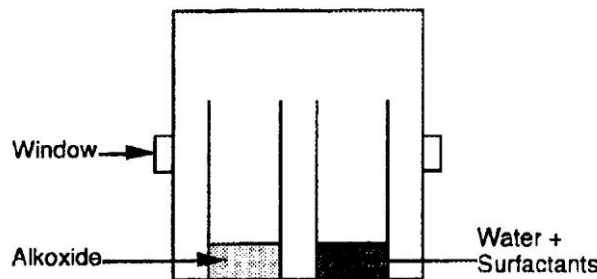
## ■ Problems:

- Since CO<sub>2</sub> is highly nonpolar:
  - Limits solubility of surfactants, and
  - Consequently, ability to stabilize polar molecules
  - HC-based surfactants have limited solubility → not useful for stabilization of aqueous droplets in SCF\_CO<sub>2</sub>
  - However, surfactants with low solubility parameter moieties like Fluorocarbon or Dimethyl siloxane groups are more soluble in CO<sub>2</sub>
  - Some of these surfactants were shown to enable formation of Reverse Micelles and Microemulsions in SCF\_CO<sub>2</sub>
  - Ability to stabilize aqueous droplets in SCF provides opportunity for a range of applications: Separation, Chemical Reaction, Synthesis or particulates materials:
- **Example:** Spherical submicron particles of Al(OH)<sub>3</sub> have been produced by reacting aqueous Al(NO<sub>3</sub>)<sub>3</sub> solutions present in the cores of RM with ammonia in SCF\_propane



**Figure 3.** Scanning electron micrograph of titanium dioxide particles prepared from Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> and aqueous solution of Zonyl FSJ in supercritical CO<sub>2</sub>. Magnification 10 K (1 cm = 1 μm).

A white powder was seen covering the walls of the reaction and the glass container. No hydrolyzable liquid was seen, meaning a complete reaction. Particles were examined with SEM: Polydispersed spherical 0.1 to 2 microns



**Figure 1.** Reactor schematics.

# FINE PARTICLES IN SCF & REVERSE MICELLE (SCF Propane)

**RAPID EXPANSION IS NOT USED HERE**

- **First work** of particle production using SCF\_Reverse Micelle.
- Also, **first example** of a chemical reaction occurring within RM dispersed in a SCF
- **Chemical reactions involving species present in the RM cores have allowed the production of colloidal-size particles ( 3 to 10 nm) for use in catalytic and semiconductor applications**
- **SCF Reverse Micelle phase stability is strongly dependent on the fluid pressure, and the amount of water that can be contained in the micelle core increases the pressure applied to the fluid.**
- At 100 bar / 103 C the max. water-to-AOT molar ratio for RM in a propane continuous phase is 4. The value increases to 12 at the same temperature and 300 bar.
- **Advantages of SCF + RM:**
  - Ability to manipulate the concentrations of reactants involved in the particle formation may allow capability to finely control the particle size
  - Operation in the SCF regime may allow high mass transfer rates of reactants to and across the micelle membranes, and should relax rate limitations when one of the reactants is a gas
  - Increased reaction rates are expected for diffusion limited reactions. High diffusion rates may reduce polydispersity by minimizing local concentration gradients due to incomplete mixing
  - Pressure dependence of the phase and density behavior in SCF systems may also allow additional advantages to be gained in the area of particle separation from the continuous fluid phase in which it is produced

Aqueous core in continuous nonpolar phase at SCF

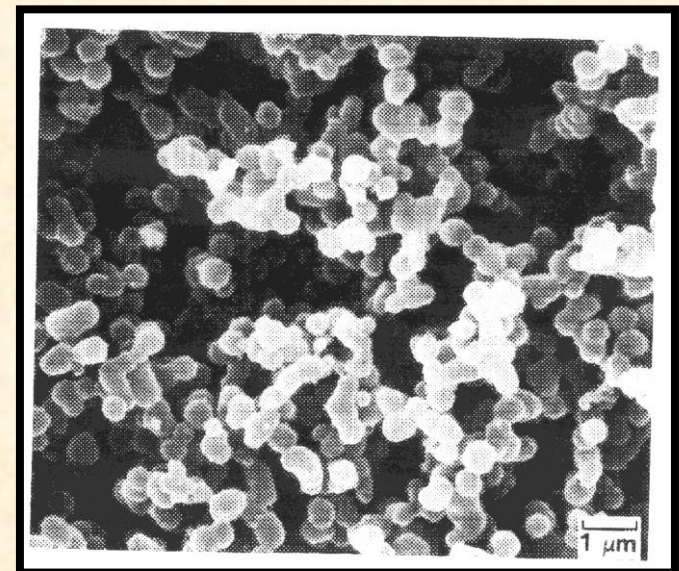
Spherical particles of  $\text{Al}(\text{OH})_3$  produced by precipitation. ).  
0.5 microns after introduction of  $\text{NH}_3$

Adding  $\text{NH}_3$  into RM system.  $\text{NH}_3$  shows high solubility in many SCF\_HCs

Aqueous  $\text{Al}(\text{NO}_3)_3$  in core of RM

**SCF\_Propane**

**AOT:** Sodium bis(2-ethylhexyl) sulfosuccinate)





# FINE PARTICLES IN SCF & REVERSE MICELLE (SCF CO2)

## ■ **First report on stable separation of nanometer sized metallic particles in CO2**

## ■ **SCF\_CO2: Only capable of dissolving nonpolar organic molecules**

- Add a cosolvent (acetone, ...) significantly improves solubility

## ● **Reverse Micelles & Microemulsions formed in liquid & SCF\_CO2 allow highly polar or polizable compounds be dispersed in the nonpolar fluid**

■ Conventional surfactants → do not form RM in CO2 → Why ? → Van der Waals interdroplet attractions are too high → **what to do ?** → Use a surfactant or co-solvent with fluorinated tail → **Why it works?**

→ Because it provides a layer of a weakly attractive droplet cores → preventing their short-range interactions that would destabilize the system → Use this method to synthesize & stabilize metallic silver nanoparticles ( 5 to 15 nm) in SCF\_CO2 using an optically transparent, water-in-CO2 microemulsion

## ■ **How do we measure the size of the particles in microemulsion ?**

- Use height & width of the **Surface Plasmon resonance band** in the UV-vis absorption spectra
- TEM measurements of offline samples confirmed the in situ measurements of Ag particle size

## ■ **Reverse micelles in SCF**

- Nanometer-sized water droplets could be thermodynamically stabilized in SCF of these ( alkanes, hydrochloro-fluorocarbons, Xenon)
- However, in past decade: formation of microemulsion in CO2 using variety of fluorinated surfactants
- Fluorinated chelates were used to "dissolve" a number of different metal ions in CO2
- **Dissolve a compound in SCF → do RESS → Nucleation process → get nanoparticles**
- Variation of above: produce Ag nanoparticle:
  - Precursor AgNO3 dissolve in SCF Ammonia → Spray it into a liquid ethanol solution containing reducing agent
- Nano & micro – sized metal oxide and metal sulfide particles were synthesized → in RM in SCF alkanes where colloidal attractive forces are much weaker
- Colloidal silver stabilization in SCF\_CO2 microemulsions (this study) has the following advantages:

## FINE PARTICLES IN SCF & REVERSE MICELLE (SCF CO<sub>2</sub>)

- Colloidal silver stabilization in SCF\_CO2 microemulsions (this study) has the following advantages:
  - Environmentally benign
  - High diffusivity → accelerated Reaction Rates
  - Ability to recover reaction products and the catalyst particles through manipulation of fluid density
  - Potential to synthesize the particles in the fluid → subsequently conduct catalytic reaction using these particles

CO<sub>2</sub>

**Co-surfactant** With fluorinated tail

Is very soluble in CO<sub>2</sub> but, by itself, is unable to form a microemulsion phase with large water core → so it acts as cosurfactant for AOT micelles

Surfactant system: { ( [AOT] + [PFPE-PO<sub>4</sub>] ) at Water-to-surfactant ratio of [H<sub>2</sub>O]/[AOT]=12 }

12.8 mM 25.3 mM

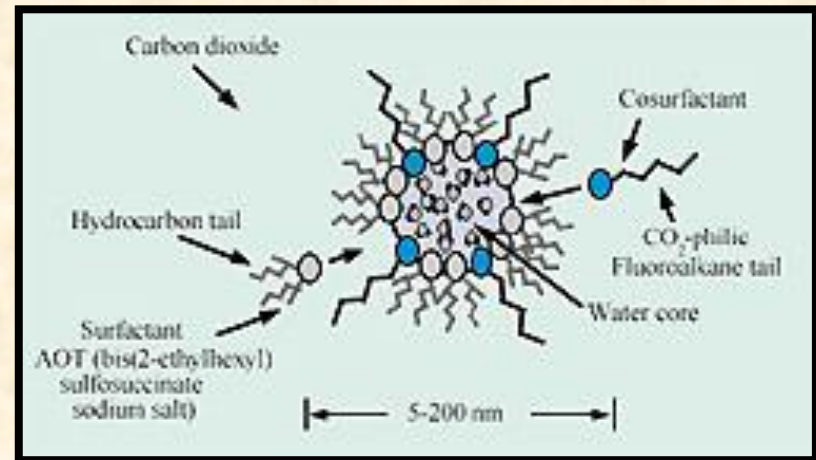
**Cosurfactant** in this case: Partitions into interface region with the AOT, and the fluorinated tails REDUCE the interdroplet attractive interactions to the point where AOT microemulsion droplets can be stably dispersed.

## Common reducing agents used in alkanes

Hydrazine ( $\text{N}_2\text{H}_4$ )

### Borohydeide ( $\text{NaBH}_4$ )

**Problem:** Both react with aqueous carbonic acid (PH 2.9) in the micelle core that is present as a result of the CO<sub>2</sub>/H<sub>2</sub>O equilibrium

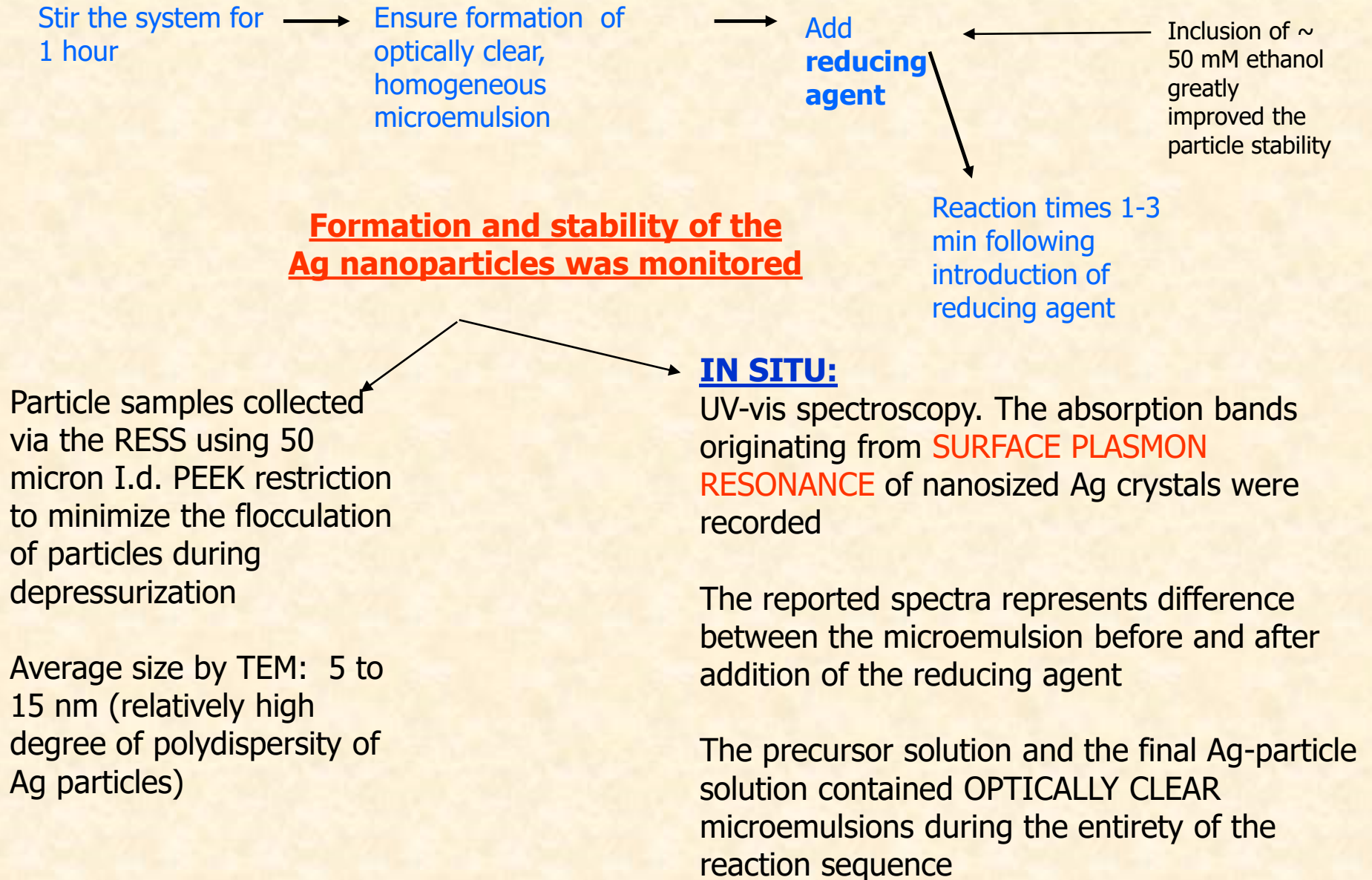


## Micelles and microemulsion in carbon dioxide

**The less CO<sub>2</sub>-reactive compound NaBH(OAc)<sub>3</sub> is used as reducer** both in liquid and in supercritical CO<sub>2</sub> ([AgNO<sub>3</sub>] = 0.33 mM; [NaBH(OAc)<sub>3</sub>] = 0.2mM )



# FINE PARTICLES IN SCF & REVERSE MICELLE (SCF CO<sub>2</sub>)



# FINE PARTICLES IN SCF & REVERSE MICELLE (SCF CO<sub>2</sub>)

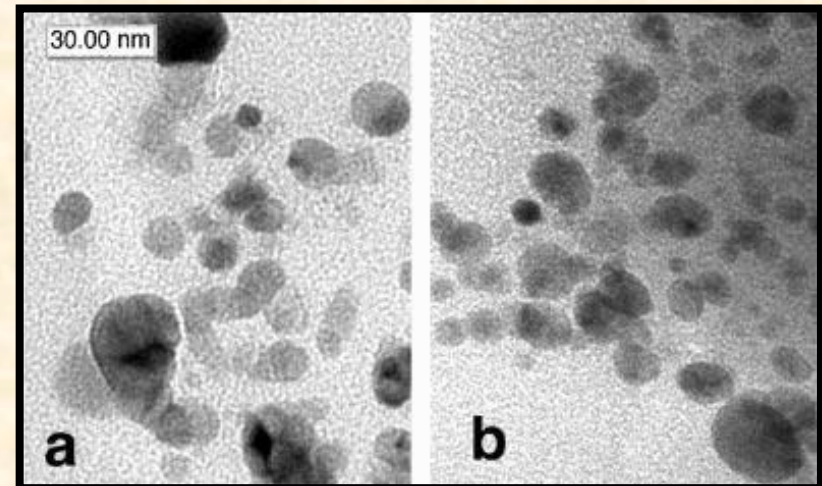
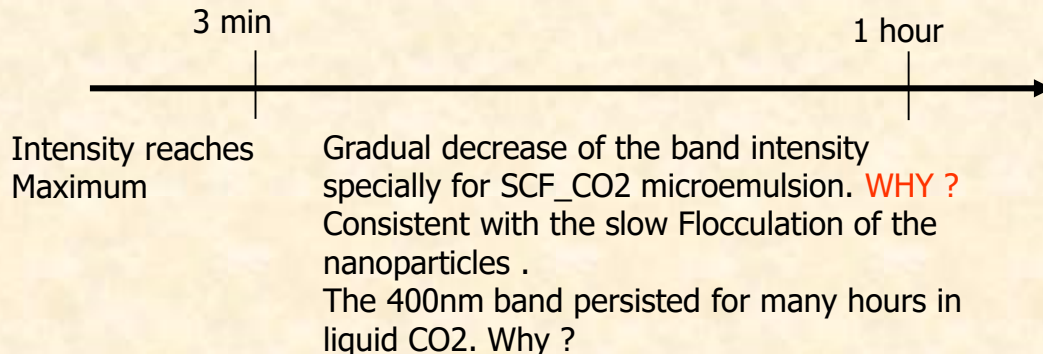
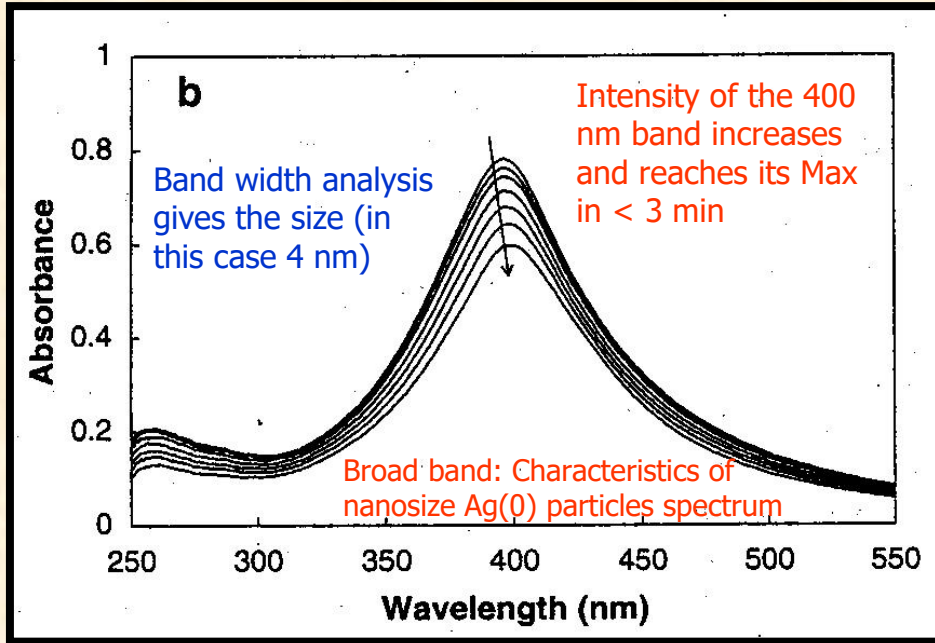
Formation and stability of the Ag nanoparticles was monitored

## IN SITU:

UV-vis spectroscopy. The absorption bands originating from **SURFACE PLASMON RESONANCE** of nanosized Ag crystals were recorded

The reported spectra represents difference between the microemulsion before and after addition of the reducing agent

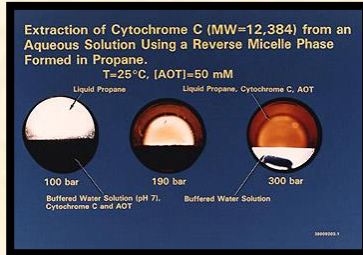
The precursor solution and the final Ag-particle solution contained **OPTICALLY CLEAR** microemulsions during the entirety of the reaction sequence



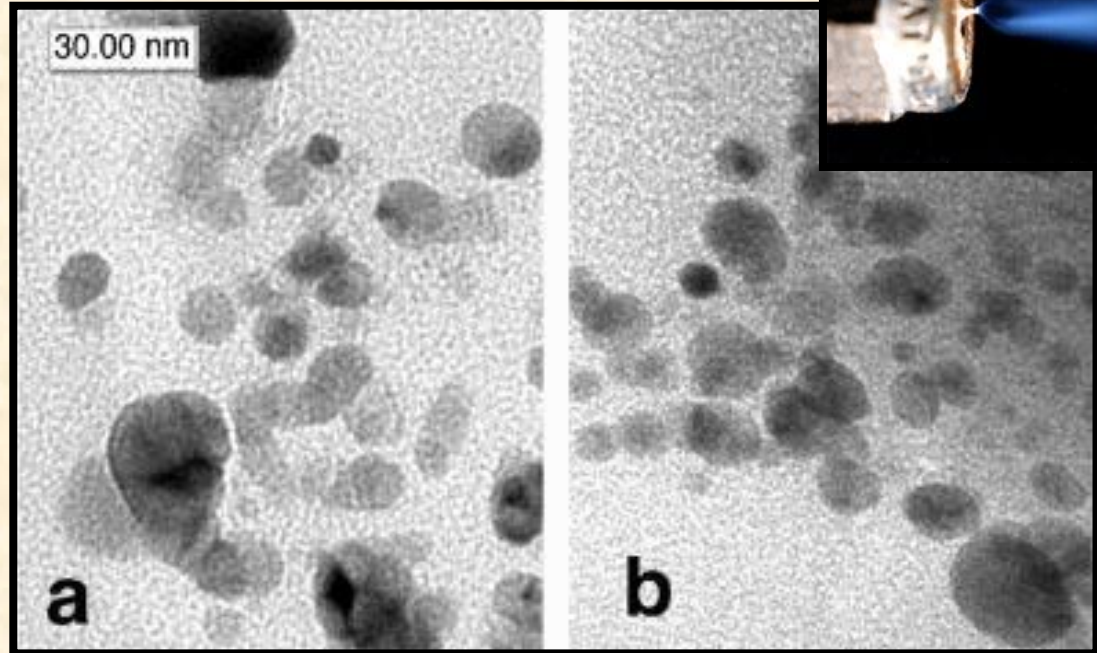
**Ultra-small silver particles synthesized and stably suspended in carbon dioxide.**



# FINE PARTICLES IN SCF & REVERSE MICELLE (SCF CO<sub>2</sub>)



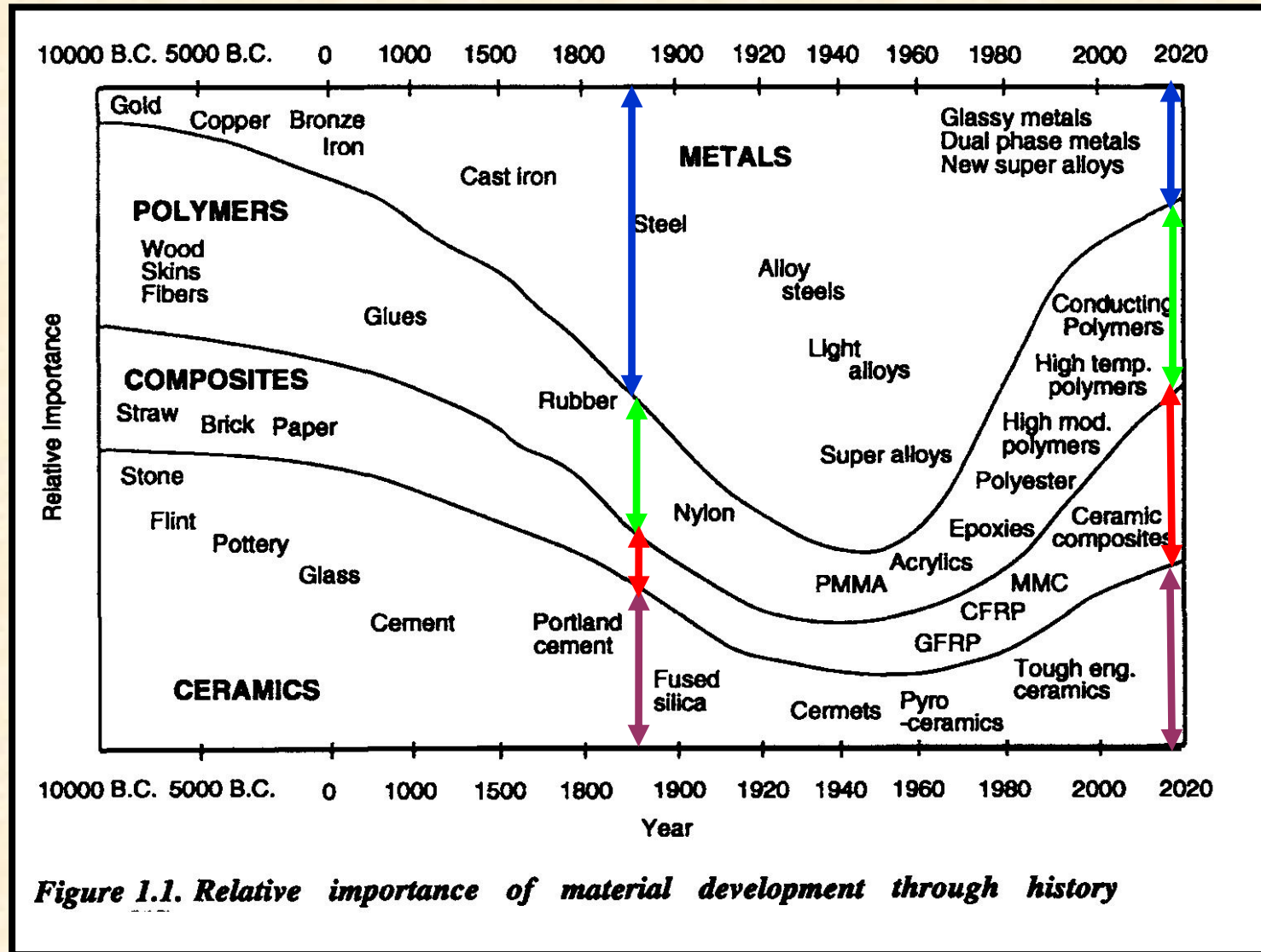
Extraction of a biomolecule using a propane microemulsion



Ultra-small silver particles synthesized and stably suspended in carbon dioxide.

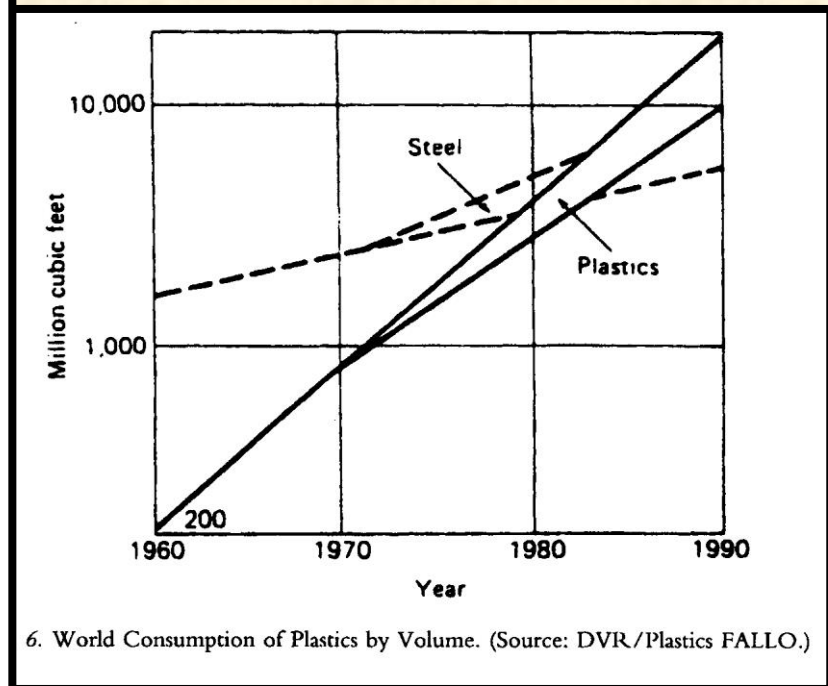
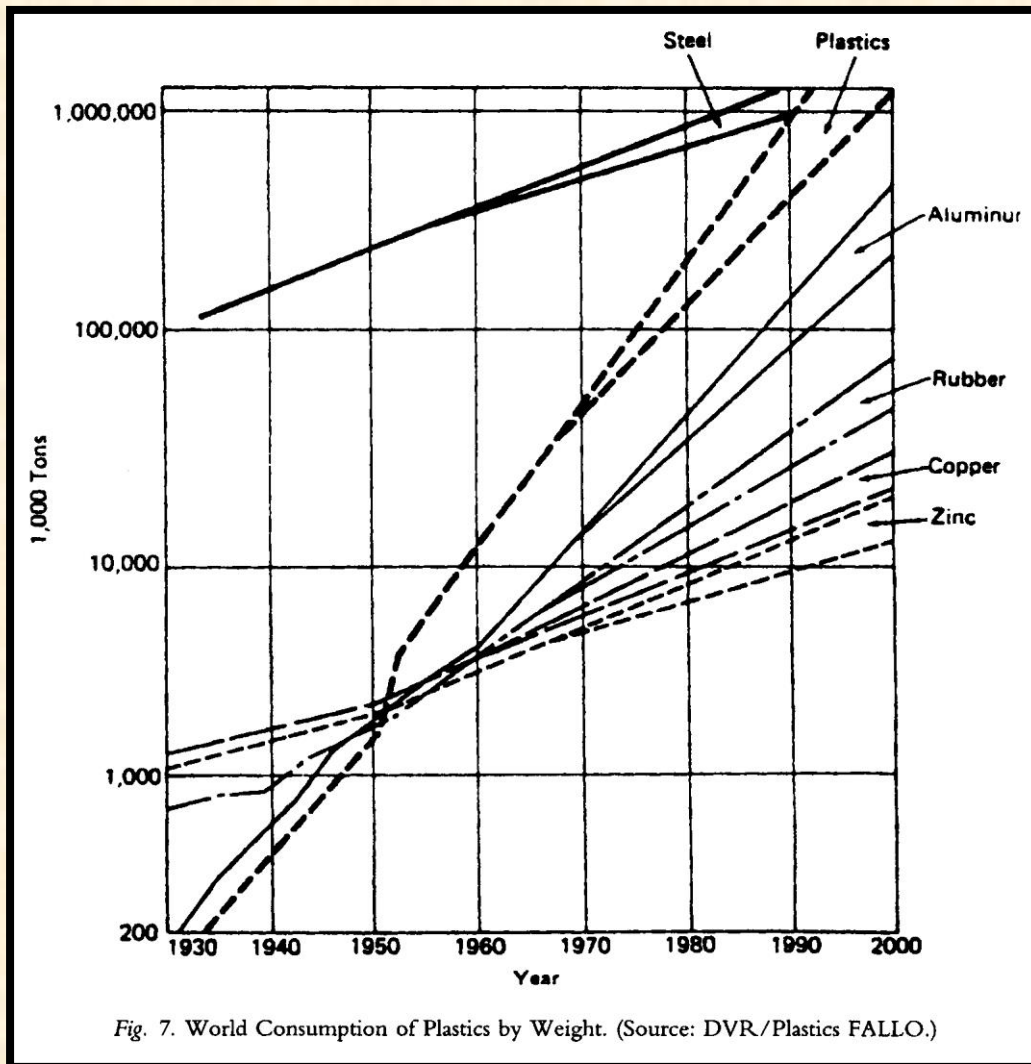
- Recently reported results: Ag nano-crystals (5 - 15 nm size) were synthesized and stabilized in CO<sub>2</sub>.
- This finding opens a broad range of potential synthesis routes for a variety of different nanoparticles that provides a simple, effective means for removal of the solvent (CO<sub>2</sub>) from the particles.
- In addition to developing the particle chemistry suitable for a CO<sub>2</sub> solvent, the colloid stability is controlled by the proper choice of surfactants, co-surfactants or capping agents.
- Initial studies on the measurements of the micelle size and structure were conducted using light scattering on alkanes and CO<sub>2</sub> micelles.
- At PNNL, the early realization of the importance of using angstrom-wavelength radiation (neutrons and x-rays) for characterization of micelle structures led to the first SANS and SAXS studies of these 62 colloidal systems in fluids.

# HISTORICAL RELATIVE IMPORTANCE OF DIFFERENT MATERIALS





# HISTORICAL CONSUMPTION OF POLYMERS



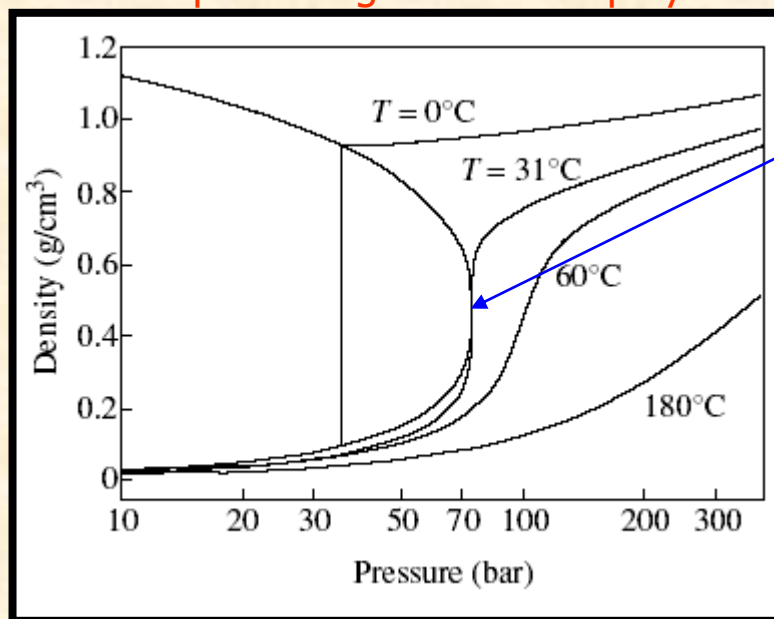
Consumption rate of the composites can be approximately and indirectly inferred through consumption of plastics

- World consumption of plastics by weight and by volume
- Relatively high growth rate of plastics and its high absolute consumption volume with respect to steel are made clear from the above two figures

# SUPERCRITICAL FLUIDS AND POLYMERS

- Single-phase solvents play an important role in many processes where phase separation would be undesirable because of the appearance of meniscus and the capillary forces that could play a negative role in some of the processes of mass transport (e.g. drying) within porous materials
- Although SCF remains single-phase, its density can be easily “tuned” from gas to liquid values merely by changing the pressure. This tunability of the SCF without changing the molecular structure makes SCF a unique solvent for adjusting many facets of process operation via “density tuning”
- Pioneering SCF work of relevance to polymers: Ipatiev at the beginning of the 20<sup>th</sup> century discovered that when ethylene is heated above its critical temperature in a high pressure autoclave, it can oligomerize noncatalytically into higher molecular mass alkanes. Further works on this were done by ICI and DuPont
- **Over the past decade:** It has been shown that CO<sub>2</sub> is an attractive alternative to traditional organic solvents used in polymer synthesis. DuPont has recently announced a major investment into the use of supercritical CO<sub>2</sub> for producing fluorinated polymers

**C&EN 2002 Industry Review:**  
“Novel polymers also came from DuPont, which offered fluoropolymers made with a new supercritical carbon dioxide-based polymerization process, ...”



Critical Point

CO<sub>2</sub> phase diagram



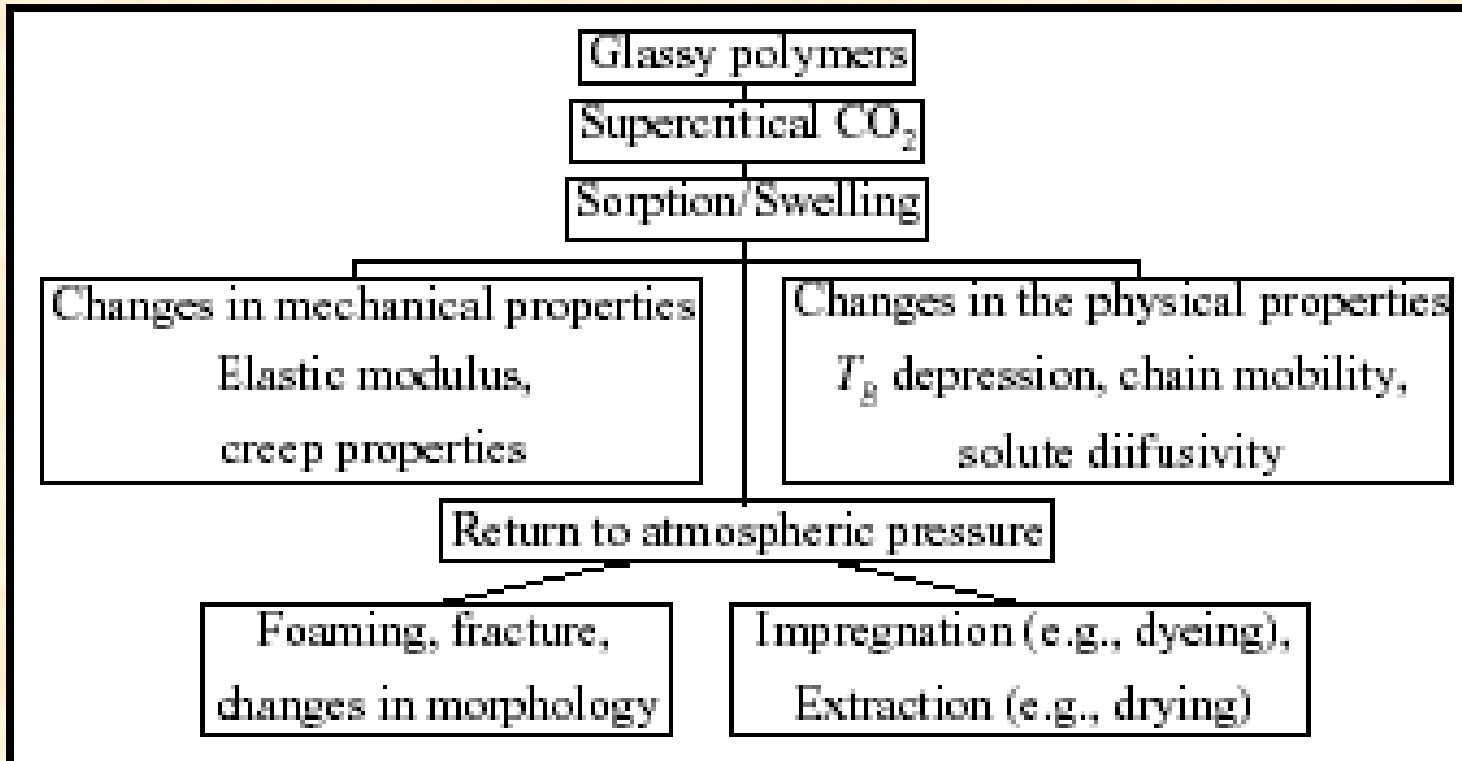
# SUPERCRITICAL FLUIDS AND POLYMERS

- Plasticization of polymers with SCF
- Implications of CO<sub>2</sub>-induced Plasticization of polymers:
  1. Extraction and drying
  2. Impregnation and dyeing
  3. Polymer blends
  4. Crystallization
  5. Foaming of glassy polymers
  6. Applications to optical materials
- Polymer processing
  - Viscosity reduction
  - The use of other SCFs in polymer processing
- Outlook

# SUPERCritical FLUIDS AND POLYMERS:

## Plasticization of polymers with SCF

- The sorption of SCF\_CO2 into polymers results in their **swelling** and changes the polymer mechanical and physical properties; Most important effect is the reduction of the "glass transition temperature,  $T_g$ ", of glassy polymers subjected to SCF\_CO2, often **simply called plasticization**.
- SCF-induced **plasticization impacts many polymer processing operations**:
  - Viscosity reduction for polymer extrusion and blending
  - Enhancement of the diffusion of additives through polymer matrices for impregnation and extraction
  - Enhancement of monomer diffusion for polymer synthesis
  - Foaming of polymers
  - Changes in polymer morphology due to induced crystallization
- See Figure for the overall effect of SCF\_CO2 on glassy polymers



● **Plasticization** is characterized by increase segmental and chain mobility and by an increase in interchain distance

● The plasticization of SCF\_CO2 is due to ability of CO2 molecules to interact with basic sites in polymer molecule.

● **Examples demonstrate that the effect of SCF\_CO2 is to mimic the effect of heating the polymer**

● Plasticization of polymers is accompanied by the **swelling of the polymer matrix** with consequent increase in free volume of the polymer



# Implications of CO<sub>2</sub>-induced Plasticization:

## 1. Extraction and drying

- The most common example of supercritical fluid extraction is decaffeination of coffee
- High diffusivity, low surface tension, polymer plasticization, and swelling in polymers caused by SCF, considerably enhance the rates of the extraction of residual solvent, oligomer or monomer, or other unreacted species from polymeric samples.
- Recent works:
  - Extraction of copper ions using SCF\_CO<sub>2</sub>-soluble chelating agents
  - The use of SCF\_CO<sub>2</sub> in a degreasing process in leather industry

# Implications of CO<sub>2</sub>-induced Plasticization:

## 2 . Impregnation and dyeing

### ■ Two different mechanisms of impregnation

- **Simple deposition of a compound soluble in SCF into polymer matrix:** A polymer matrix is subjected to an SCF containing a solute and when the vessel is depressurized, CO<sub>2</sub> molecules quickly leave the matrix, leaving the solute molecules trapped inside the polymer matrix ( good for solutes highly soluble in SCF\_CO<sub>2</sub> or when glassy polymers are used, because the plasticizing ability of SCF\_CO<sub>2</sub> also enhances solute infusion)
- **For when solute has low solubility in SCF:** Then the high affinity of these solutes for certain polymer matrices can result in preferential partitioning of a solute in favor of polymer over fluid. (the high partition coefficient of polar molecules played a crucial role in the success of SCF dyeing)

### ■ Some applications:

- Supercritical fluid impregnation of organometallic compounds into polymer matrices. Also, used to produce polymer films with highly reflective surfaces. (Motivated by potential applications of polymer films with highly reflective surfaces in aerospace devices).
- SCF impregnation of platinum complexes for preparation of metal-containing **nanocomposite materials**. Metal clusters with size ranging from 10 to 100 nm with uniform distribution of these clusters throughout the film has been achieved
- Copper compound has also been impregnated resulting in improved tribological properties of the modified polymer.
- Grafting or a specific group onto polymer surface.
- Infusion of a monomer and an initiator into a CO<sub>2</sub>-swollen polymer matrix with subsequent polymerization of a monomer within the polymer matrix (**Polymer blending discussed later**)

# Implications of CO<sub>2</sub>-induced Plasticization:

## 2 . Impregnation and dyeing (Cont. )

### ■ Some applications (Cont.):

- Using a solution of polymers diluted with SCF\_CO<sub>2</sub> for powder-coating applications. Formation of polymer powder by RESS with consequent precipitation, and the morphology of these powders, have also been reported
- Great potential for coating applications (due to reduction or elimination of VOC during spray painting). Union Carbide developed a process for spray coating using SCF\_CO<sub>2</sub> as a solvent. Gives improved film coalescence and quality of the coating as compared to conventional alternative powder coatings. The coating materials are dissolved in SCF\_CO<sub>2</sub> and released through a specially designed nozzle from the spraying head as an atomized spray. This process produces a highly uniform spray with a narrow droplet size distribution. Unfortunately solubility of many compounds used in coating is quite low in SCF\_CO<sub>2</sub>. Hence some methanol was used as organic cosolvent to increase solubility. Alternatively, stabilizers can be used (similar to their use in dispersion polymerization reaction). Fluorinated acrylate polymers may act as an effective stabilizer. There are other stabilizers (block or graft copolymers) that can be used in dispersion polymerization or in mixtures of SCF coating processes mentioned above.
- Successful suspension of poly(20ethylhexylacrylates) in SCF\_CO<sub>2</sub> formed by dispersion polymerization with a PDMS-based surfactant was reported. These suspensions were sprayed through nozzles from 30 to 200 microns in diameter. The suspensions formed uniform circular films. Effects of nozzle size, spray duration, spray distance, fluid velocity, etc. Which may affect the quality and pattern of the film were investigated. Spray pattern changed little as a function of nozzle size but changed significantly with spray distance and fluid velocity. They also reported that the SCF\_CO<sub>2</sub>-induced viscosity reduction of the dispersed phase is crucial for producing fine droplets in the spray atomization process and for droplet coalescence and film formation on the surface.



# Implications of CO<sub>2</sub>-induced Plasticization:

## 2 . Impregnation and dyeing (Cont. )

### ■ Some applications (Cont.):

- SCF has recently been used for preparing polymer substrates with drugs. At 3M, developed an interesting modification of the SCF impregnation of polymeric materials. SCF\_CO<sub>2</sub> is used as an agent to enhance the diffusivity of water soluble solutes into various substances by performing the process in water pressurized with SCF\_CO<sub>2</sub>.

# Implications of CO<sub>2</sub>-induced Plasticization:

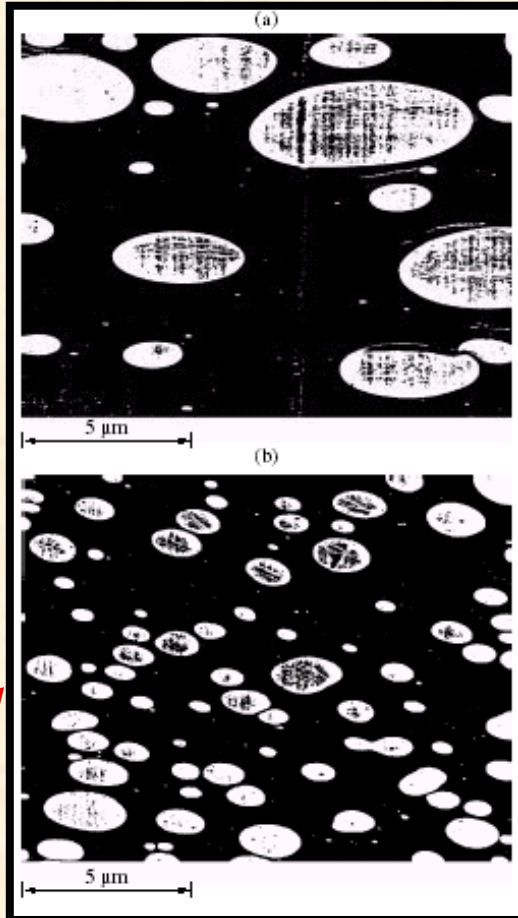
## 3 . Polymer blends

- Impregnating the monomer and initiator from an SCF\_CO<sub>2</sub> solution into a polymer matrix with subsequent polymerization of the monomer within matrix has led to formation of polymer blends not easily obtainable by conventional methods
- Polystyrene-polyethylene composite has been prepared via radical polymerization of styrene within SCF\_CO<sub>2</sub>-swollen high density polyethylene:
  - The SCF\_CO<sub>2</sub>-assisted blending process does not affect the crystalline structure of HDPE, but does affect the spherulitic structure (Polystyrene were observed in spherulite centers → there is a lack of crystallinity there)
  - Process is described as polystyrene forming a “scaffold” that reinforces the polyethylene spherulites → Results to significant increase in modulus and strength improvement but with a penalty, that is, loss in fracture toughness
- The tunable solvent power of the SCF can be used to manipulate the properties of the blends and composites using the blending process described above
  - Hence, it is important to understand the phase behavior of polymer blends and the implications for their miscibilities
- SCF\_CO<sub>2</sub> interacts differently with components of the polymer blend → also have different effect on glass transition temperature of each component → different plasticizing effects → improving the mixing of these components:
  - It has been demonstrated that SCF\_CO<sub>2</sub> can assist in polymer blending both in batch and continuous processes:
    - PMMA-polystyrene: Higher solubility of CO<sub>2</sub> in PMMA → greater plasticizing effect will occur for PMMA → Could lower the viscosity of PMMA more than polystyrene
    - See figure for batch mixing

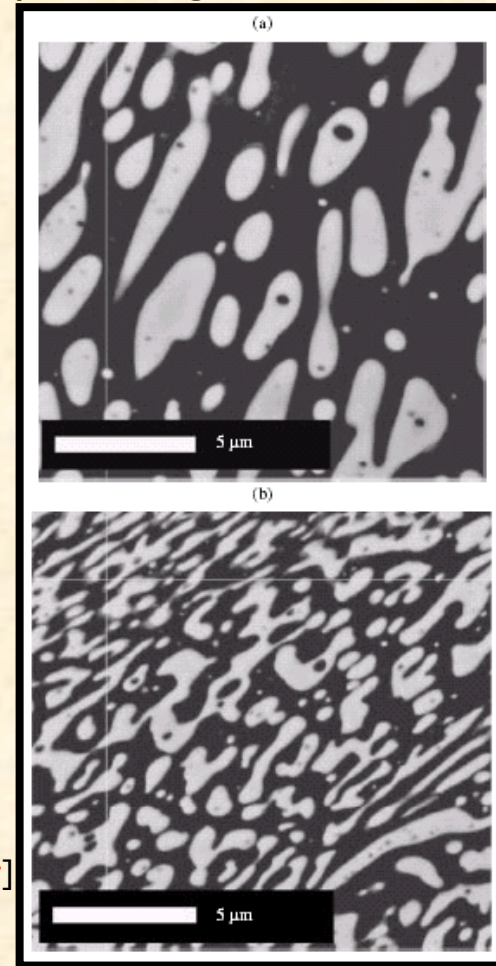
# Implications of CO<sub>2</sub>-induced Plasticization:

## 3 . Polymer blends (Cont. )

- SC\_CO<sub>2</sub> interacts differently with components of the polymer blend → also have different effect on glass transition temperature of each component → different plasticizing effects → improving the mixing of these components:
  - It has been demonstrated that SC\_CO<sub>2</sub> can assist in polymer blending both in batch and continuous processes:
    - PMMA-polystyrene: Higher solubility of CO<sub>2</sub> in PMMA → greater plasticizing effect will occur for PMMA → Could lower the viscosity of PMMA more than polystyrene
      - See Figures for batch mixing and continuous (single- & twin- screw extruder) mixing
      - The addition of SCF\_CO<sub>2</sub> has a pronounced effect on the morphology of PMMA-polystyrene blend
      - The domains of the PMMA have been reduced in size and are more evenly distributed as a result of addition of SCF\_CO<sub>2</sub> into system at 200 C. Why ?
      - As a result of lowered polymer viscosity and possibly affecting the interfacial surface tensions between these polymers



TEM micrograph of blends of 25/75 PMMA/Polystyrene (a) without CO<sub>2</sub>, (b) with CO<sub>2</sub>.  
[Batch mixer]



TEM micrograph of blends of 50/50 PMMA/Polystyrene prepared from twin screw extruder (a) without CO<sub>2</sub>, (b) with CO<sub>2</sub>.  
[Continuous mixer]



# Implications of CO<sub>2</sub>-induced Plasticization:

## 3 . Polymer blends (Cont. )

- Effects of SCF\_CO<sub>2</sub>-induced viscosity reduction on polyethylene-polystyrene have also been studied
  - It was found that the size of the dispersed polystyrene domains in the blend decreased when 5% of CO<sub>2</sub> in polystyrene was injected, and no further increase was observed at concentrations of CO<sub>2</sub> up to 10 wt. %
  - Also, a number of experimental difficulties associated with the extrusion setup were overcome in these elegant experiments
  - They found that this polymer system was foamed upon exiting the die of the extruder, and cell structures and the mechanism of formation are discussed
  - The work by this group (Lee, Tzoganakis, and Park) had an important impact on stimulating interest in SCF-assisted polymer processing (foaming, extrusion, blending)

# Implications of CO<sub>2</sub>-induced Plasticization:

## 4 . Crystallization

- The phenomenon of SCF\_CO<sub>2</sub> –induced plasticization of glassy polymers has important implications for semicrystalline polymers: **SCF\_CO<sub>2</sub> induced plasticization may induce crystallization in certain polymers**
  - This happens when the CO<sub>2</sub> –induced mobility for polymer chains allows them to rearrange into kinetically favored configuration, thus forming crystallites
  - Poly(ethylene terephthalate): PET-based materials are widely used in production of soft drink bottles and synthetic polyester fibers
  - Morphology and degree of crystallinity of PET affect gas permeability of these products (critical for CO<sub>2</sub>-saturated drinks !)
  - Morphology of PET-based fibers play an important role in determining mechanical properties of fibers used in textile industry
  - Degree of crystallinity of polyester fibers may affect the ability of the fibers to be dyed
  - In situ near\_IR spectroscopy: CO<sub>2</sub>-induced crystallization was observed in initially amorphous PEET films at 28 C and 50 C, however, it did not occur at 0 C
  - **It is important that the morphology of the PET processed with SCF\_CO<sub>2</sub> could be different from the morphology of PET processed by heat or drawing to open up a new approach to modifying the material properties**
  - Japanese researchers: Demonstrated that how plasticizing effect of high pressure CO<sub>2</sub> could facilitate drawing of glassy polymers without heating
- SCF dyeing of polymer-based materials shows much promise in attempts to prevent pollution because it is environmentally friendly process

# Implications of CO<sub>2</sub>-induced Plasticization:

## 5 . Foaming of glassy polymers

- Use of high pressure gases in the **production of microcellular polymers** (Closed cells < 10 microns and cell density 10<sup>8</sup> cells/cm<sup>3</sup>)
- May have properties superior to those of unfoamed polymers (e.g. **higher impact strength**)
- **Applications:** insulation of lightweight materials, biomedical devices, adsorbents, etc.
- Pioneering work on foaming using high pressure gases or SCF by Russian scientist Skripov and coworkers (work began 30 years ago)
- Polymer is subjected to high-p gas and when the pressure is suddenly decreased or the temperature is rapidly increased, the gas attempts to escape from the polymer, causing antiplactization. This rapid escape of gas can **cause the nucleation and growth of bubbles within polymers**. Once a significant amount of gas is escaped, the T<sub>g</sub> of the polymer drops and “freezes” the foamed structure
- **Interesting recent work:** Preparation of a very fine structure of foamed PMMA with an average cell size of 0.35 micron and cell density of 4.4x 10<sup>13</sup> cells/g (the retrograde vitrification phenomenon was used)
  - Handa and Zhang used the existence of of a rubbery state at low temperature to generate foams by saturating the polymer with CO<sub>2</sub> at 34 bar and at temperatures in the range –0.2 to 24 C followed by foaming at temperatures in the range from 24 to 90 C.
  - They showed that the solubility of CO<sub>2</sub> in the polymer plays an important role in controlling cell density and size.
  - The work was the **first to comment on formation of ultramicrocellular (Nano-) foams at relatively low saturation pressures**
  - They recently reported the analysis of foaming glycol-modified PET (PRTG) with SCF\_CO<sub>2</sub>
- **The process of SCF\_CO<sub>2</sub>-assisted polymer foaming has also been coupled with polymer extrusion and is being commercialized**



# Implications of CO<sub>2</sub>-induced Plasticization:

## 5 . Foaming of glassy polymers (Cont. )

### ■ Beckman approach:

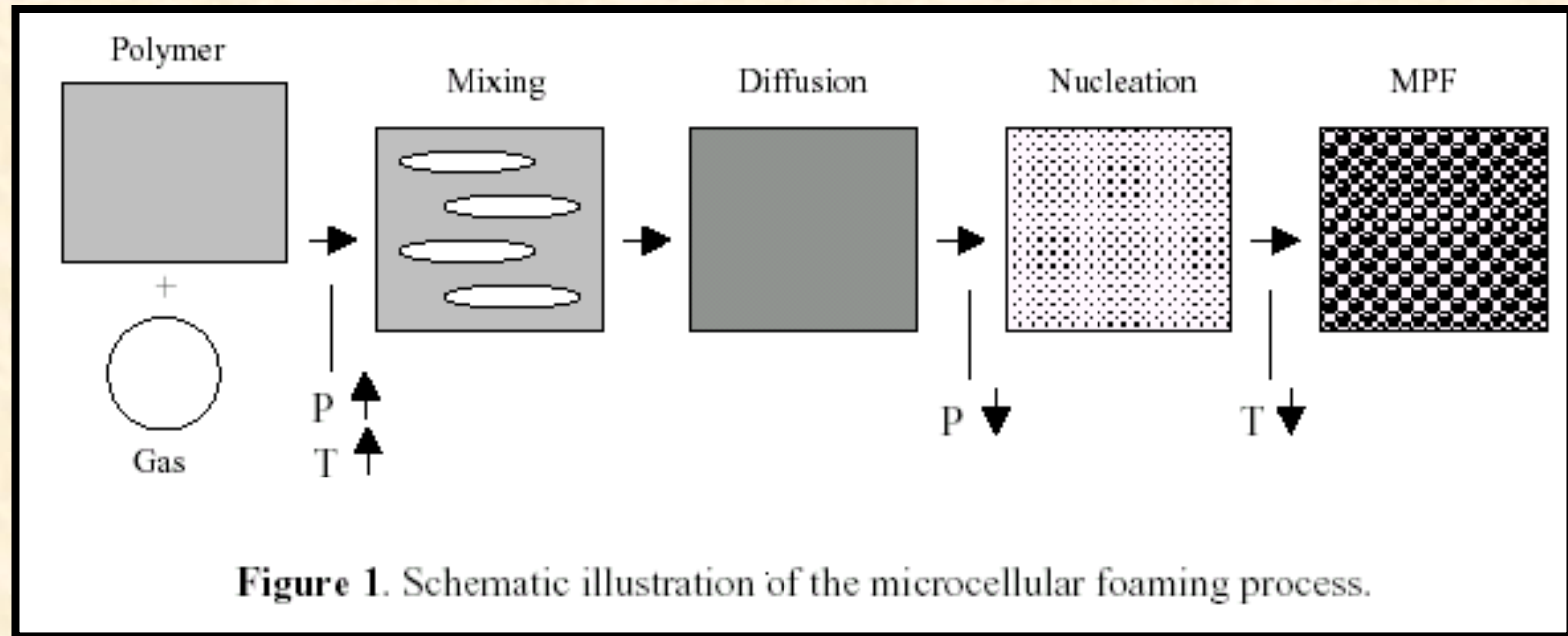
- **First**, synthesize a number of chemicals soluble in SCF\_CO<sub>2</sub> or liquid CO<sub>2</sub> (these chemicals have a number of “monomers” containing 1 or 2 urea group and fluorinated “tail” to enhance solubility in CO<sub>2</sub>.)
- **Second**, when they are dissolved in CO<sub>2</sub>, their self-association (or assembly) led to formation of gels.
- **Third**, removal of CO<sub>2</sub> by depressurization resulted formation of foams with cells average dia. < 1 micron
- Bulk density reduction of these foams were 97% compared to parent materials
- Note that gelation in SCF\_CO<sub>2</sub> has been reported in SOL-GEL polymerization in porous silica aerogel

- CO<sub>2</sub>-assisted foaming of biodegradable polymers (such as, Poly(lactide-*co*-glycolide) (PLGA) copolymer) represents an exciting opportunity for **formation of sponge scaffolds for medical applications**. Past work generated high-surface-area fibrillar scaffolds that were then used to generate liver tissue

- Bioabsorbable polymer scaffolds for tissue engineering capable of sustained growth factor delivery. Gas treatment of amorphous copolymers produced matrices with porosity up to 95%. The work also demonstrated that **ONLY CO<sub>2</sub> among the other gases used ( N<sub>2</sub>, He, ..) created highly porous polymer structures in the copolymers tested.**

# Implications of CO<sub>2</sub>-induced Plasticization:

## 5 . Foaming of glassy polymers (Cont. )



**Microcellular Polymeric Foams (MPF)**

- The **first step**, is the saturation of a polymer melt with an inert gas, such as CO<sub>2</sub>, under high pressures, followed by thorough mixing.
- Thermodynamic instability is then rapidly induced so that numerous vapor nuclei form within the polymer matrix. This can be accomplished either by a **pressure quench** or a **sudden temperature increase**.
- The **final step** in the process relates to the **growth of the large number of stable bubble nuclei and the subsequent development of a desired microcellular morphology under controlled temperature conditions.**

# Implications of CO<sub>2</sub>-induced Plasticization:

## 5. Foaming of glassy polymers (Cont.)

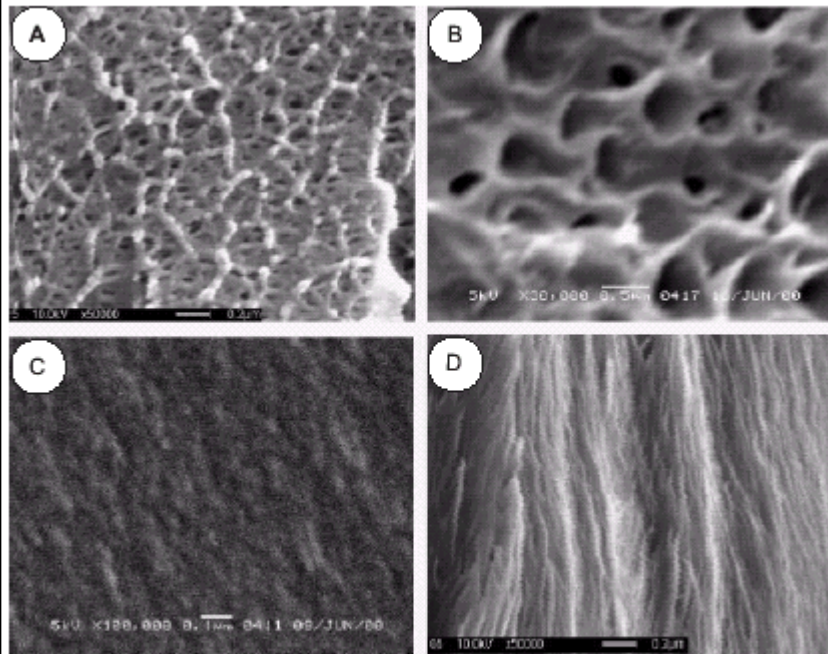


Fig. 2. SEM images: A) Matrimid (1) foamed at 270°C. Magnification 50000, white horizontal bar equals 200 nm. B) 6-FDA-4,4'-6F (3) saturated at 25°C and foamed at 250°C. Magnification 30000, white horizontal bar equals 500 nm. C) 6-FDA-4,4'-6F (3) saturated at 0°C and foamed at 250°C. Magnification 100000, white horizontal bar equals 100 nm. D) Kapton HN (5) foamed at 300°C. Magnification 50000, white horizontal bar equals 200 nm.

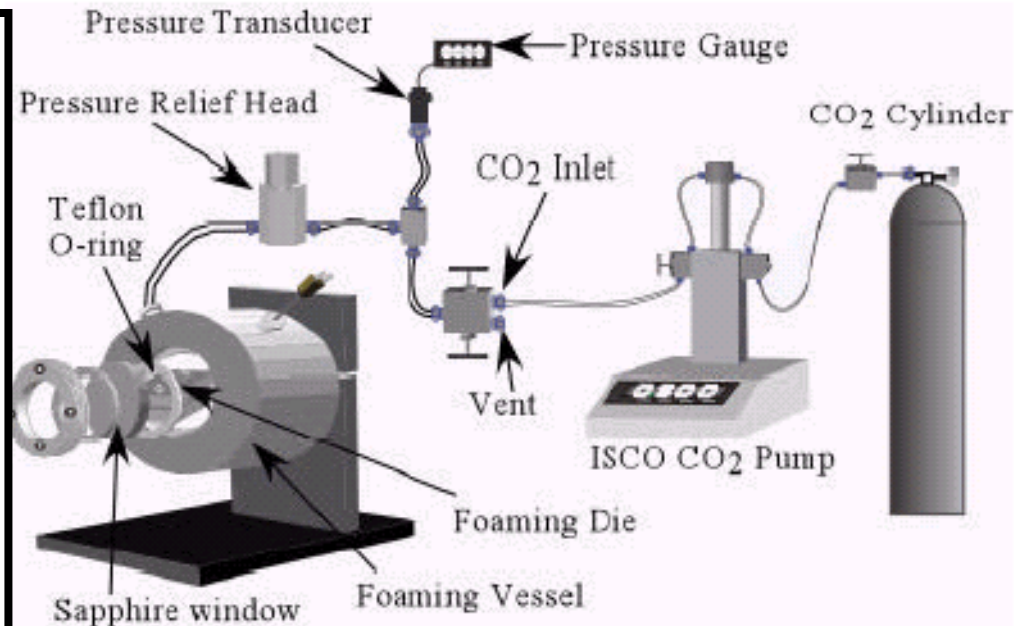


Fig.1: Schematic of the foaming experimental setup

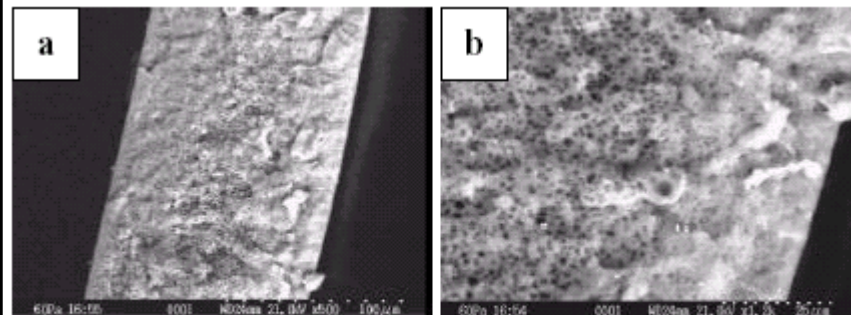


Fig. 2(a) & (b): PMMA film foamed at 5000 psi and 40°C

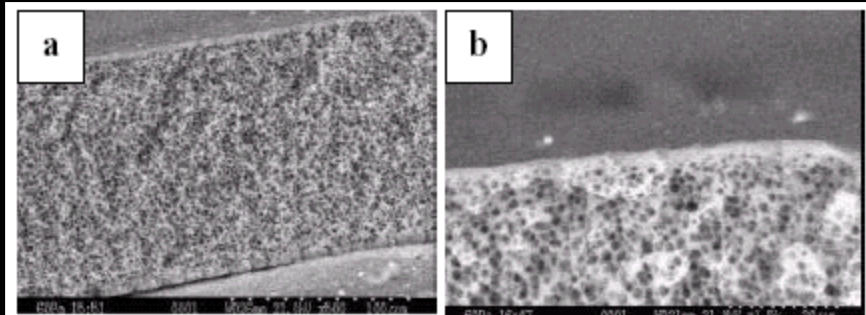
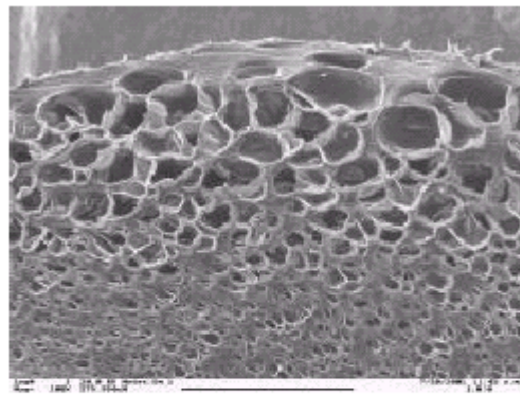


Fig. 4(a) & (b): PMMA film foamed at 5000 psi and 40°C with diffusion control

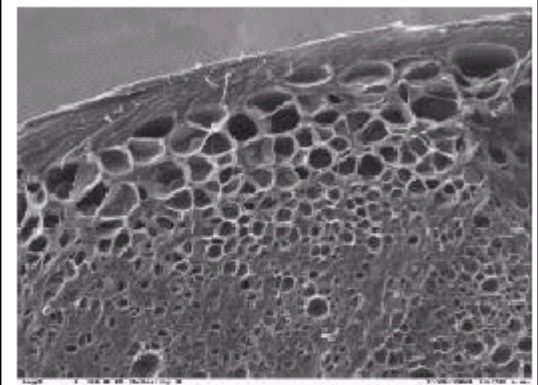


# Implications of CO<sub>2</sub>-induced Plasticization:

## 5 . Foaming of glassy polymers (Cont. )

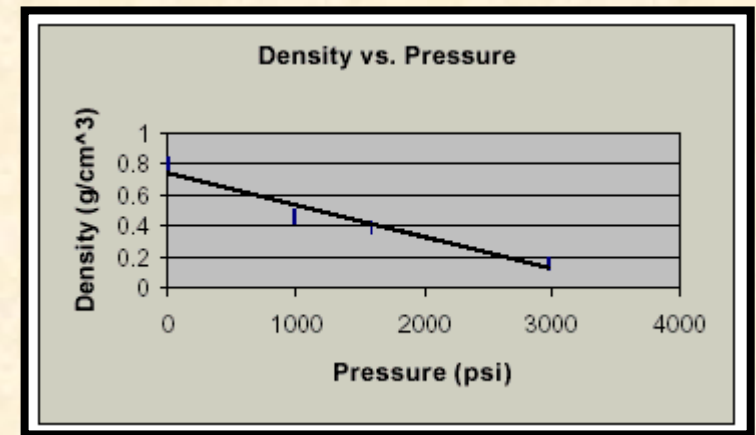


276 μm  
Figure 2.  
EVA 350 @ ~ 1100 psi  
Under SC conditions  
(100x)



276 μm  
Figure 3.  
EVA 350 @ ~ 2500 psi  
Under SC conditions  
(100x)

Elvax 350 or Ethylene Vinyl Acetate (EVA 350) was exposed to supercritical (SC) carbon dioxide to alter their properties in this investigation. These samples were all exposed to SC CO<sub>2</sub> at varying pressures of 982 psi, 1590 psi, and 2971 psi. As shown in figures, it was found that the density of these materials varied inversely with the pressure of CO<sub>2</sub> that they were exposed to. In Figure 2. and Figure 3. the Scanning Electron Microscopy (SEM) imaging showed that as CO<sub>2</sub> pressure increased, foaming penetrated more deeply into the core of the polymer.

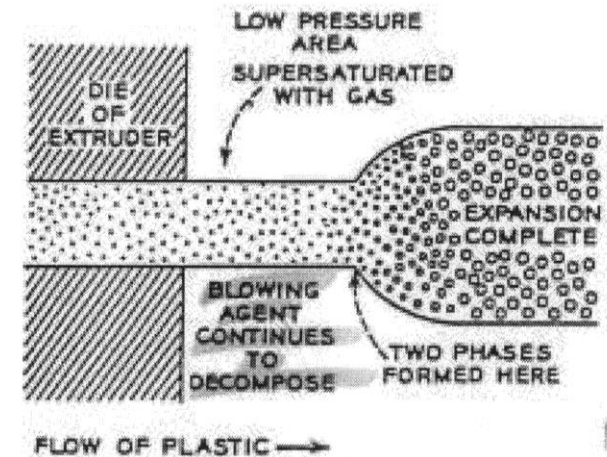
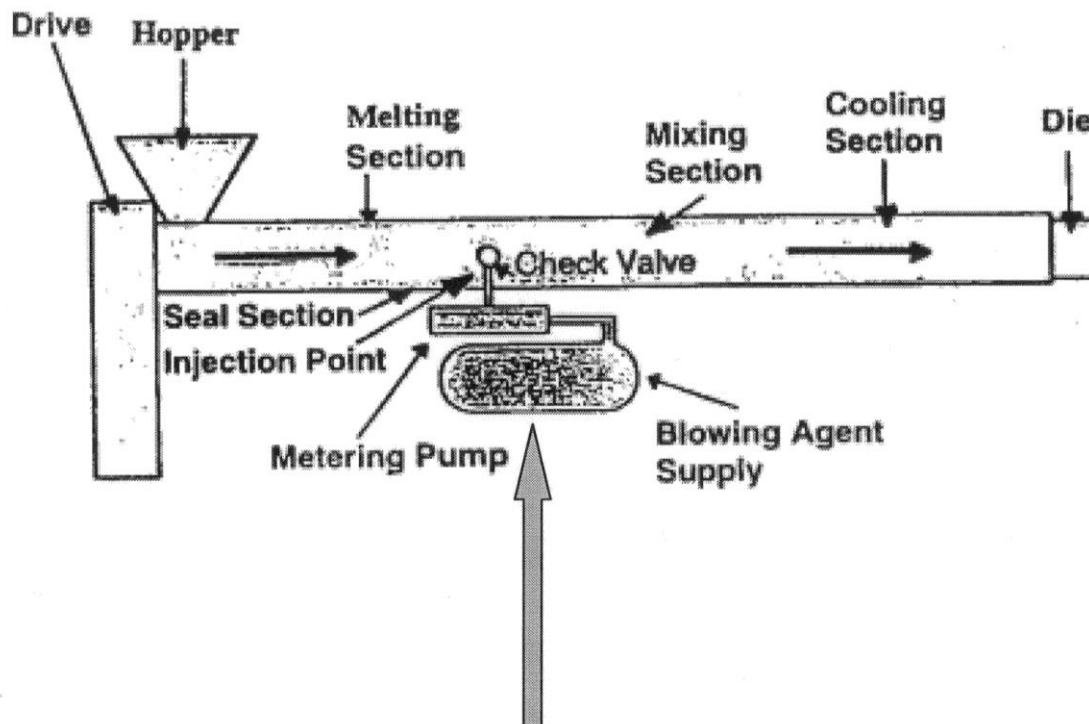


# Implications of CO<sub>2</sub>-induced Plasticization:

## 5 . Foaming of glassy polymers (Cont. )



### Foam extrusion: single/twin-screw or tandem extruders



Cell nucleation /  
bubble growth /  
bubble stabilized

\* Blowing agent

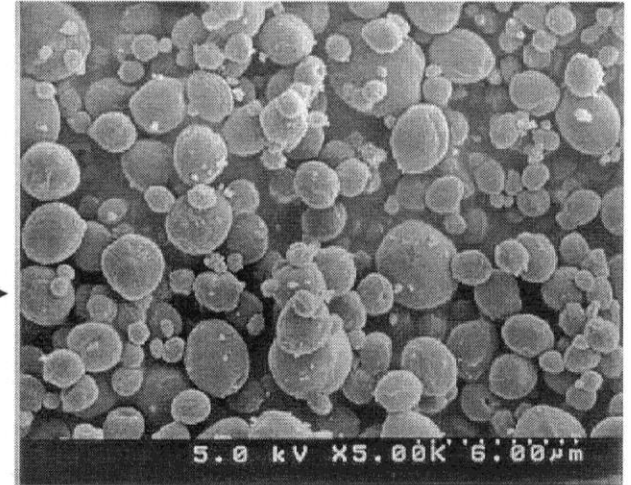
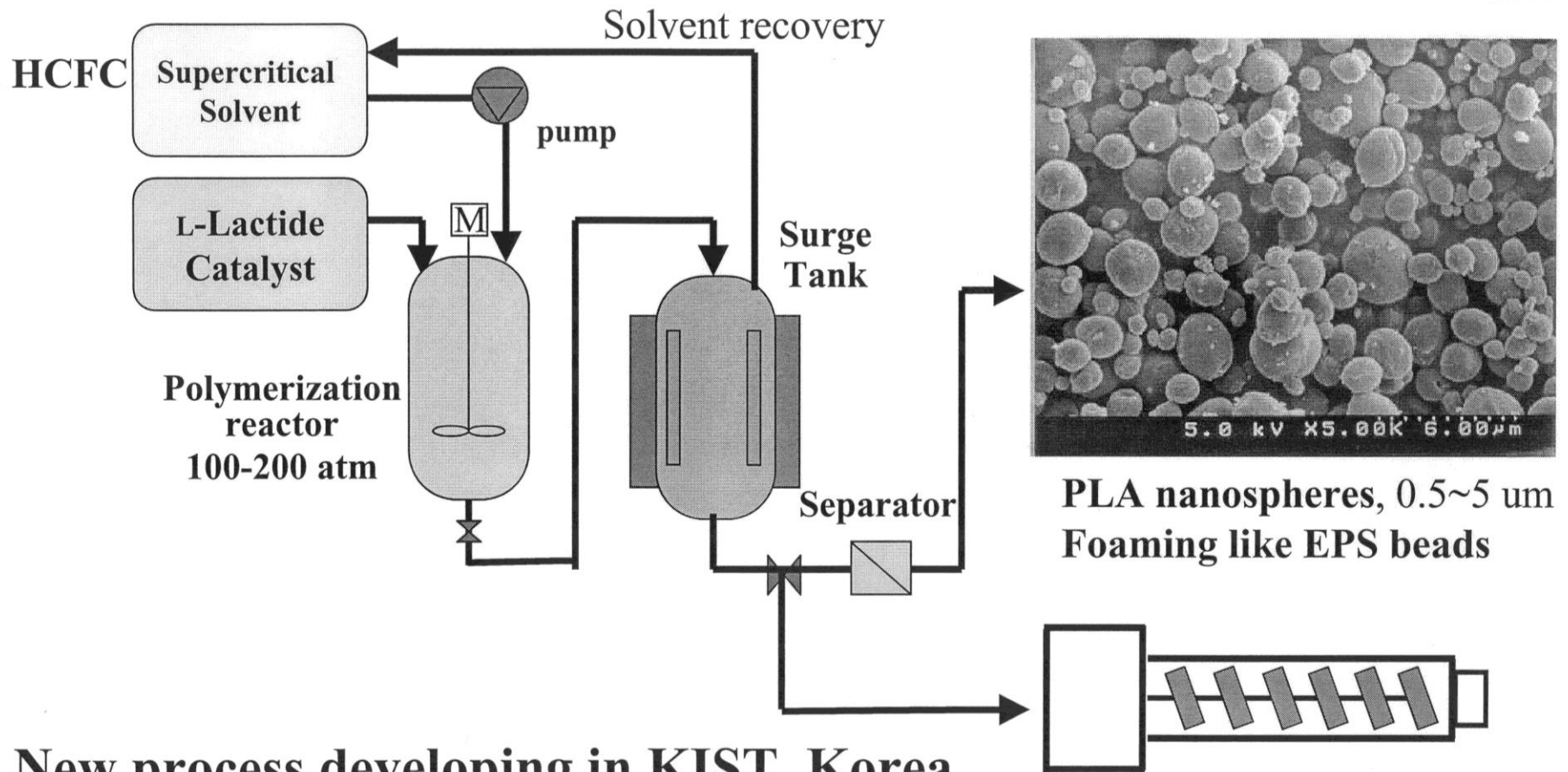
- Physical: Gas (CO<sub>2</sub>, N<sub>2</sub>, air), Hydrocarbons (pentane, butane, Freon)
- Chemical: azo/diazo compounds, inorganics such as carbonates



# Implications of CO<sub>2</sub>-induced Plasticization:

## 5 . Foaming of glassy polymers (Cont. )

### In situ foaming of PLA polymerized in a supercritical state



**PLA nanospheres, 0.5~5 um**  
**Foaming like EPS beads**

**New process developing in KIST, Korea**  
**Advantages:**

- Direct process: short way to PLA spheres or foam
- Eco-friendly process: complete solvent recovery
- Functional process: easy to add chemicals/additives



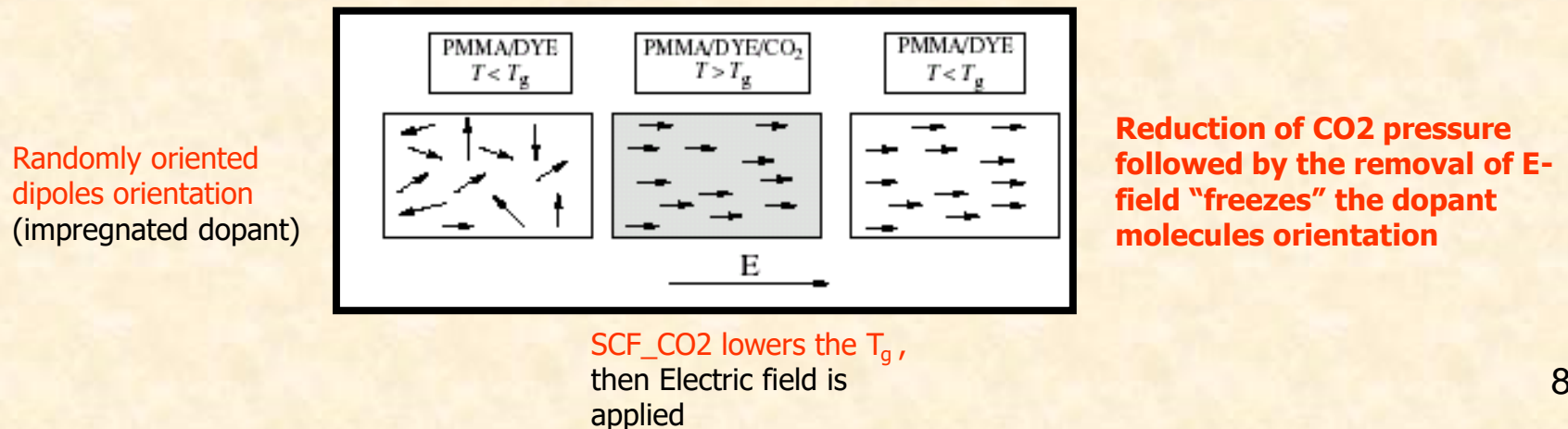
# Implications of CO<sub>2</sub>-induced Plasticization:

## 6 . Applications to optical materials

■ Plasticization of glassy matrix by SCF\_CO<sub>2</sub> opens new opportunities for optical applications

■ **Example:**

- Azobenzene derivatives are frequently used as dopants in NLO devices for second harmonic generation
- To have NLO effect, one needs to orient impregnated azobenzene chromophores
- This orientation is usually achieved via “poling” at temperatures near  $T_g$  of the polymer matrix
- **The ability of CO<sub>2</sub> to reduce the  $T_g$  of glassy polymers offers an exciting opportunity to perform such “poling” at room temperatures**
- Also, azobenzene derivatives can be isomerized by visible light. Such photoisomerization induces a change in the refractive index of the system and, most importantly, can increase 2<sup>nd</sup> harmonic generation
- The mobility of the polymer chain and segments and its free volume play an important role in these processes
- *Barry and Soane* (used azo-dye): The key idea of CO<sub>2</sub>-assisted orientation of NLO dopants within polymer matrix by electric poling at room temperature is presented in the Figure.
- Presumably, the reduced thermal energy in an SCF\_CO<sub>2</sub> plasticized polymer matrix assisted in better orientation of dye molecules than would have been achieved by poling at higher temperatures by heating the polymer



## POLYMER PROCESSING: Viscosity reduction

- One of the major factors that affect the processing of polymers is the effective viscosity of the bulk materials
  - Example: High  $\nu$  is a major issue in processing of high MW polymers or complex mixtures of particle-filled polymers or pastes. **Usually this is handled by:**
    - **Increase temperature** (problem: requires energy and may lead to thermal degradation), and/or
    - **Addition of plasticizers** (usually remains in the product, affecting its properties and performance)
- Also, the desired removal of some intrinsic plasticizers such as fat from dough systems in food processing or organic solvents from ceramic paste, results in increase of bulk and interfacial viscosity
- **The plasticizing effects of the SC-CO<sub>2</sub> on polymers reduces their viscosity.** Why?
  - Presumably due to the reduction of chain-chain interaction, and
  - Increases in the interchain distance
  - CO<sub>2</sub> also weakly solvates the molecular segments of the polymers, thus acting as a “molecular lubricant”
  - Recently, these phenomena were used in the extrusion of polyethylene-polystyrene blends and for foam extrusion of thermoplastics polyurethane elastomers and other polymers

# **POLYMER PROCESSING:** Viscosity reduction

## ■ **Food industry**

- SC\_CO2 is used for extrusion in the cooking of foods. It is important as it demonstrates the feasibility of combining SCF with extrusion processing of starch-based materials
- The combination of SCF extraction of fat with viscosity reduction are particularly useful in food processing using a diverse product set (bakery products, chocolate, egg yolk)
- Furthermore, the SCF-assisted extrusion also facilitate addition of flavors, colorings, and other additives without the use of organic solvents

## ■ **Ceramic paste**

- Plasticizing effect to modify the properties of polymeric additives such as binders in the ceramic paste processing
- Since some pastes are suspension of particles in a polymer solution, the effect of SC\_CO2 on the polymer phase will modify mechanical properties of the paste
- Hence, viscosity reduction:
  - Lower extrusion or injection pressure
  - Reduction of residual stresses
  - Improved accuracy of formation
- Also, once ceramic paste processing is completed, the polymeric binders and solvents have to be removed prior to sintering

- Clearly, SC\_CO2 may be used in polymer-ceramic composites to influence the processing rheology of these pastes, as well as in the supercritical fluid extraction and drying of the paste



## **POLYMER PROCESSING:** The use of other SCFs in polymer processing

### ■ **SC\_methanol** ( $T_c = 513 \text{ K}$ ; $P_c = 7.95 \text{ MPa}$ )

- To decompose PET into monomers
- To decompose PET (a widely used material in soft drink bottles due to its excellent processing and gas permeability properties)
- Advantage over SC\_water: lower CP thus simplified operation
- Ozaki studies reaction of phenol resin in SC\_methanol: Conversion above  $400^\circ\text{C}$  was  $> 80\%$ . The liquid product was found to include phenols, while solid product showed a high concentration of carbon

### ■ **SC\_water**

- It is more challenging to recycle thermosetting resins due to their highly crosslinked structure
- SCF for recycling tires is very promising in terms of both economic and environmental benefits
- Park et al. reported SC\_water oxidation to partially break down rubber materials of used tires
- They claimed that these materials can be converted to alcohols, aldehydes, and ketones under certain experimental conditions
- German researchers: feasibility of SC\_water for plastic recycling
- Eyerer et al. discussed the use of SC\_water for energetic materials (such as explosives or pyrotechnics), treatment of contaminant soil, plastics and additives, and other organic materials
- Hydrolysis and oxidation of epoxy resin in sub- and super-critical water has been studied in both reactors: use in nuclear waste as epoxy is used as coatings for materials in nuclear plants

# RECENT AND POTENTIAL BREAKTHROUGHS IN THE APPLICATIONS OF SCF IN POLYMER PROCESSING

## **Recent** Breakthroughs in the Applications of SCF to Polymer Processing

1. Structure/Properties and Characterization
  - Solubility of polymers in SCFs
  - Models of SCF-induced polymers plasticization
  - High-Pressure *in situ* methods for the characterization of polymer/SCF systems
2. Synthesis
  - Dispersion and emulsion polymerization
  - Polymerization with CO<sub>2</sub> as solvent and reactant
  - Polymerization in SCF-swollen polymer matrices
  - **Dendrimers**
3. Surfaces and Interfaces
  - Cleaning with SCFs using surfactants
  - Surface modification via impregnation
  - Coatings (e.g., UNICARB process)
4. Materials
  - Polymer—metal composites
  - Bone replacement materials
  - Dyeing
  - Foaming
  - Impregnation of microporous materials
  - **Nanoscale casting using SCFs and lithography**
  - Gelation
5. Biopolymers
  - Food processing
  - Biodegradable polymers
  - Scaffolds for tissue engineering
6. Pharmaceutical applications
  - Production of protein powders
  - Preparation of biodegradable microparticles
  - Aerosol formation
7. Polymer extrusion
  - SCF-induced viscosity reduction
  - SCF-assisted polymer blending
8. Recycling the polymeric materials

## **Potential** Breakthroughs in the Applications of SCF in Polymer Processing

1. Structure/Properties, and Characterization
  - Development of novel *in situ* high-pressure techniques for polymer/SCF systems
  - Theories of polymer solubility in SCFs
2. Synthesis
  - Combining ionic liquids and SCFs for two-phase mixtures polymer synthesis
  - Novel hybrid systems
3. Surfaces and Interfaces
  - Novel SCF-soluble surfactants for coatings
  - **Novel SCF-soluble polymers for lithography**
4. Smart materials
  - Processing of shape-memory polymers
  - Metastable polymer systems
  - Non-linear optical materials
  - Chemical vapor deposition of new optical materials from SCF solutions
  - **Molecular imprinting**
  - Systems for controlled release
5. Biodegradable polymers for environmental, ecological applications and medical applications.
  - SCF-assisted processing of plastic wastes
  - SCF-assisted processing of personal care products
  - Extrusion of biodegradable polymers
6. Pharmaceutical applications
  - Formation of particles with complex morphology (e.g., multi-layer system) for controlled drug release
  - SCF-impregnation of bio-active substances into biomedical or personal care products (e.g., contact lenses, tooth brushes, bone cements, etc.)
7. Polymer extrusion
  - Combining catalysis and SCF-assisted extrusion for polymer systems
  - Extrusion of ceramic pastes
  - Extrusion of food materials with simultaneous impregnation of fragrances and colorings
8. Converting polymer waste into useful materials

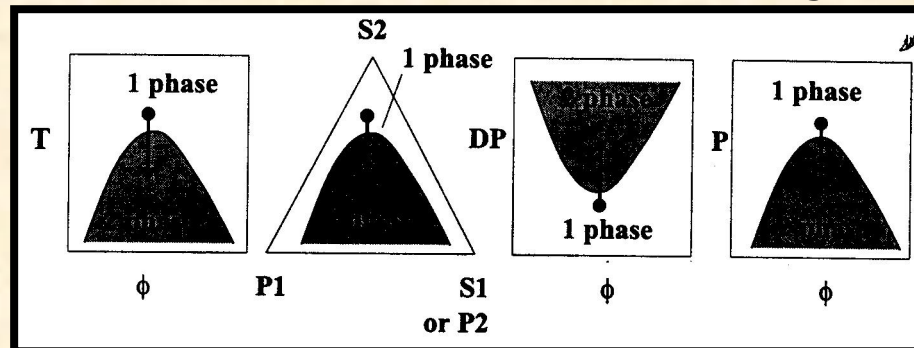
- Pressure-induced **miscibility** and **phase separation** constitute the integral steps in a wide range of applications that **use supercritical or near-critical fluids as a process or processing medium for polymers**
- **Pressure** becomes the practical “**tuning parameter**” that transforms a fluid or a fluid mixture from behaving like a solvent to one behaving like a non-solvent, thereby inducing miscibility or phase separation
- Dynamics of phase separation becomes very important if transient (nonequilibrium) structures are to be pinned by proper matching of the process conditions with the onset of transition in material properties such as the vitrification or crystallization in polymers
- Pressure-induced phase separation in Poly(dimethylsiloxane) + SCF\_CO2 and polyethylene + n-pentane solutions
- **Unique applications of polymer miscibility and phase separation:** Impregnating a host polymer that is swollen in a fluid with a second polymer that is dissolved in the same fluid at high pressures. The **dissolved polymer is in-situ precipitated and entrapped in the matrix by pressure-induced phase separation** (new route for blending of otherwise incompatible polymers: Polyethylene with Poly(dimethylsiloxane) in SCF\_CO2)



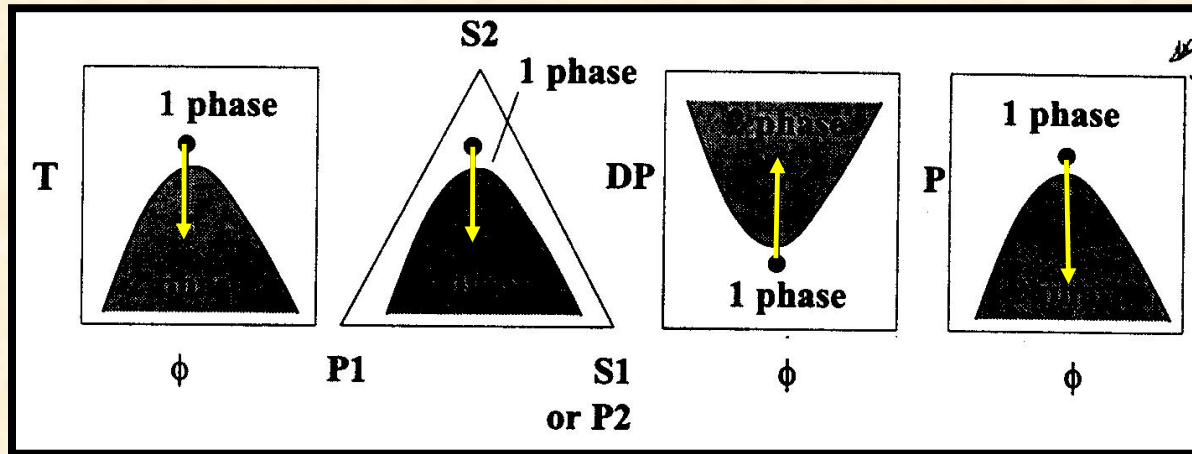
# SUPERCRITICAL FLUIDS, POLYMERS, MISCIBILITY, PHASE SEPARATION

## ■ How do we induce miscibility or phase separation?

- By a **change in T**
- By a **change in composition** (adding a third component such as a solvent or a non-solvent, or as a result of progress of a reaction)
  - T and solvent-induced phase change is common in membrane formation and processes that lead to porous materials
  - Reaction-induced phase separation is used in polymerization, particularly when system undergoes crosslinking where a homogenous system may enter the 2-phase region
- **Changes in P:**
  - Essentially unavoidable integral step in all processes using near- or super-critical fluids. Because at some point the pressure must be reduced either to recover a product or the processing fluid
  - **Important differentiating feature:** Pressure changes can be brought about **uniformly and very fast throughout the bulk of a solution**. This would not be so in other separations due to mass and heat transfer limitations that would influence the rate of phase separation in case of T- and solvent- induced separations
  - Applied fields such as shear may also induce phase separation
- T-, solvent-, reaction- induced separation are also available at elevated pressures if desired. Therefore:
- All modes of phase separation methods are of interest when working with near- or super-critical fluid systems



# SUPERCRITICAL FLUIDS, POLYMERS, MISCIBILITY, PHASE SEPARATION



T- induced phase separation

Solvent-induced phase separation

Reaction (i.e. polymerization) – induced phase separation. 2-phase region is entered with increasing degree of polymerization

P- induced phase separation

## Shaded area:

Arrow direction:

Reverse arrow direction:

$\phi$ :

S1 and S2:

P1 and P2:

## 2-phase regions

Shows paths for phase separation

Shows paths for miscibility

Polymer concentration

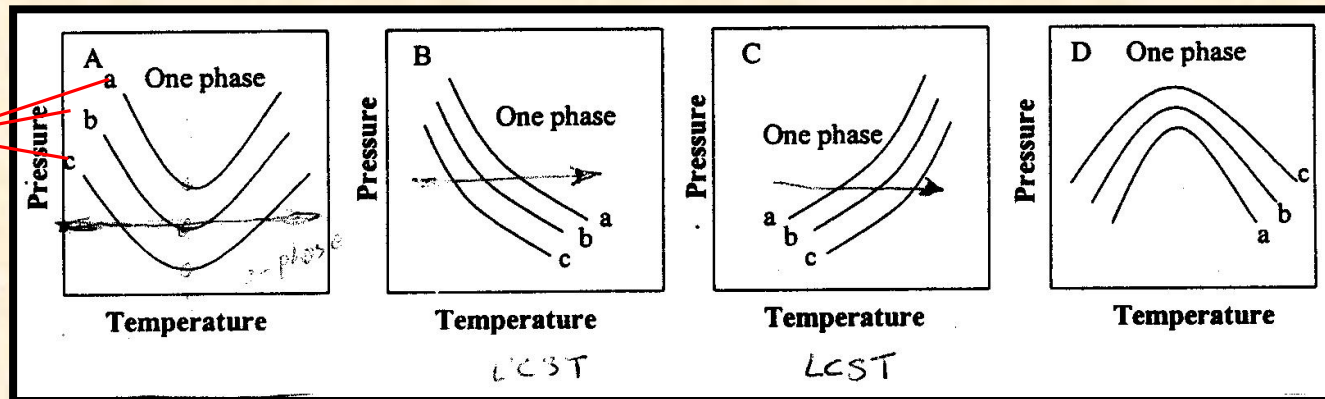
Solvent and nonsolvent

Polymer 1 and polymer 2

# SUPERCRITICAL FLUIDS, POLYMERS, and MISCIBILITY

- Miscibility in fluid mixtures containing CO<sub>2</sub> is of particular importance in applications that aim to reduce use of traditional organic solvents in polymer processing
- Miscibility of polymer in the near- CP =  $f(T, P, \text{polymer concentration, MW, MW distribution, polymer type, nature of the solvent fluid})$
- High-P miscibility results are shown as “**MIXING CURVES**”. How experiments are done ?
  - Data taken in variable volume view cell
  - Polymer + fluid mixture corresponding to target polymer concentration is first brought into 1-phase homogenous conditions
  - Pressure is then slowly decreased
  - The incipient phase separation condition is visually or optically noted through the window of the cell
- Depending upon the polymer + solvent system, the shape of these demixing curves differ

Different concentrations



The system that may be in the two-phase region may become one-phase increasing temperature, but further increase in T may force into 2-phase region

Two equilibrium liquid phases are converted to a single phase. Upper Critical Solution Temperature (UCST)

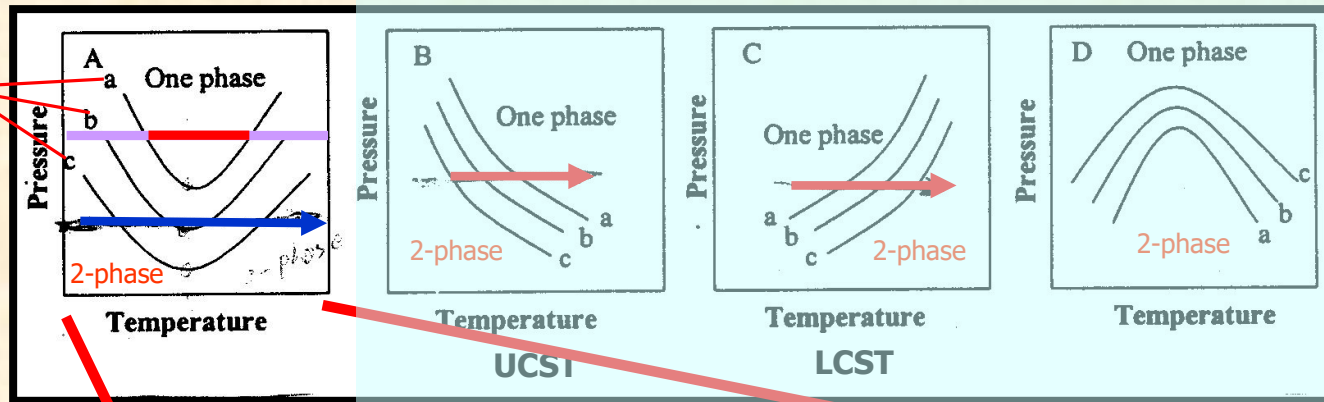
A single liquid phase separated into 2-phase. Lower Critical Solution Temperature (LCST)

Not very common

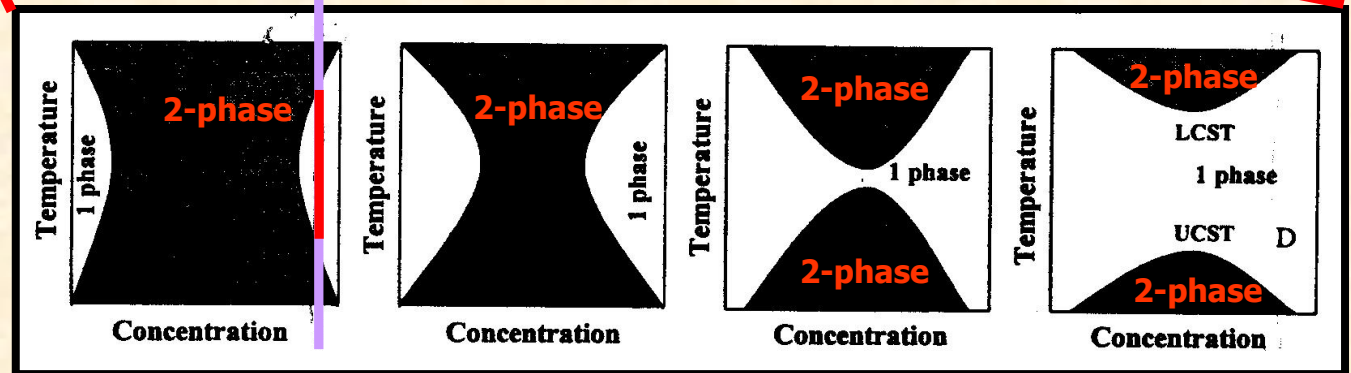


# SUPERCRITICAL FLUIDS, POLYMERS, and MISCIBILITY

Different concentrations



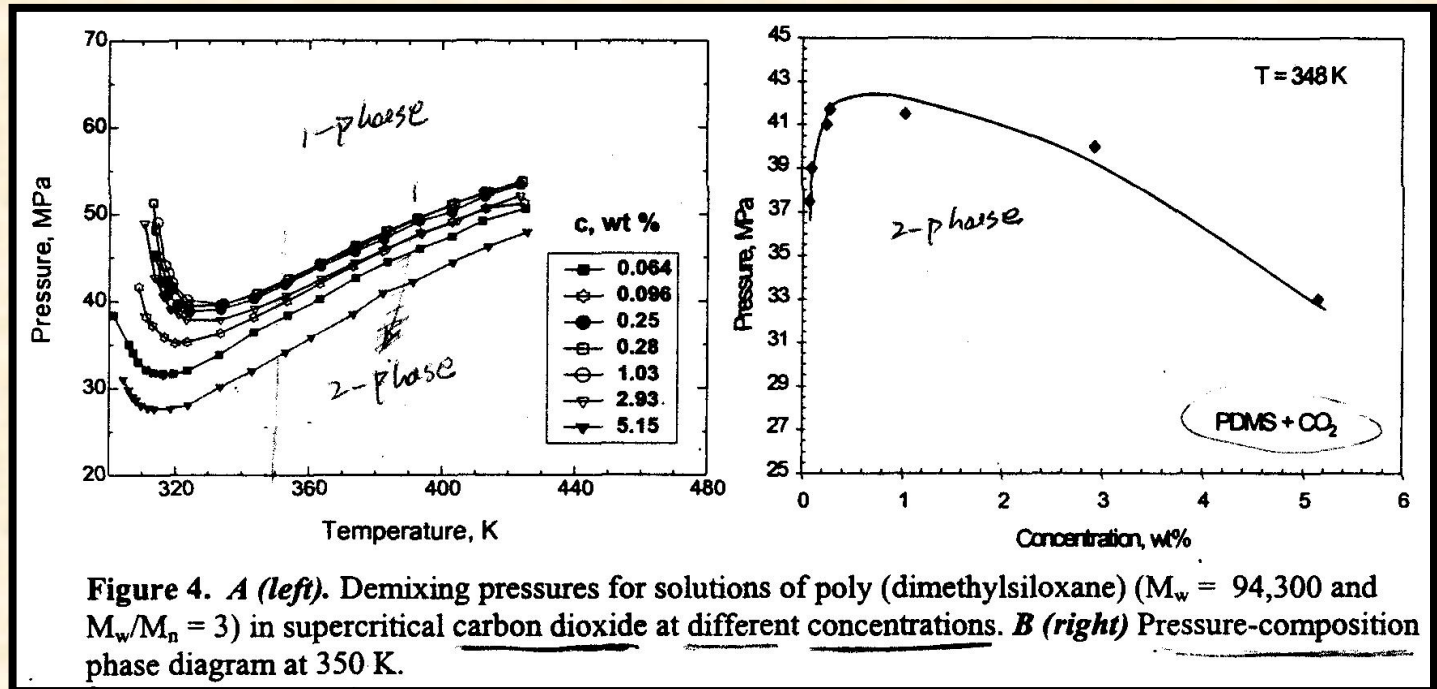
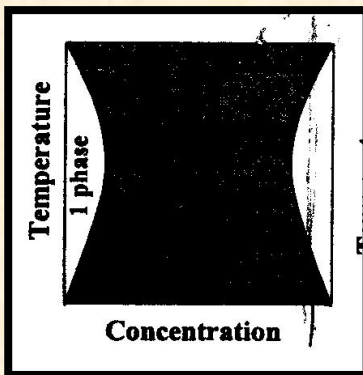
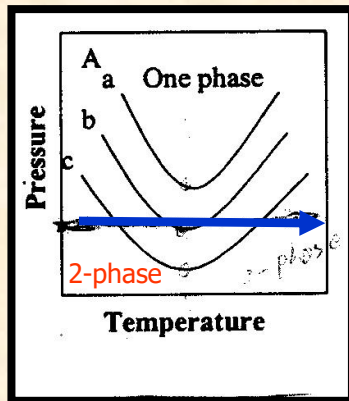
T-Composition phase diagrams in polymer solutions that display liquid-liquid demixing pressures of the type shown in the first left frame of the P-T demixing plots shown above



Increasing pressure

- **From left to right:** Progressive improvement in degree of miscibility as pressure is increased
- **Example of polymer-solvent showing this behavior:** Poly(dimethylsioxane) solutions in SC\_CO2

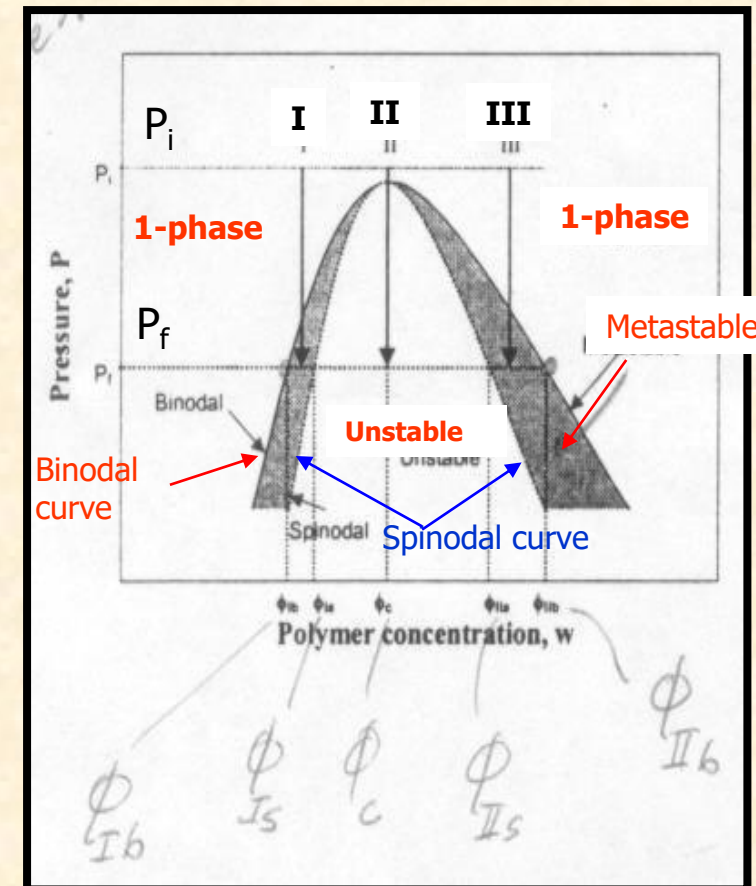
# SUPERCRITICAL FLUIDS, POLYMERS, and MISCIBILITY



- Example of polymer-solvent showing this behavior: Poly(dimethylsiloxane) solutions in SC\_CO2

# SUPERCRITICAL FLUIDS, POLYMERS, and PHASE SEPARATION

- Figure shows a **general representation of the pressure-composition (equilibrium) diagrams for systems that display liquid-liquid phase separation**
- The binodal boundary represents the equilibrium demixing pressures for monodisperse polymer system
- The binodal and spinodal envelopes determine the **metastable region (shaded area in the Figure)**. They merge at the critical polymer concentration ( $\phi_c$ )
- The equilibrium compositions of the two phases that form when pressure is reduced from  $P_i$  to  $P_f$  are given by binodals  $\phi_{Ib}$  and  $\phi_{IIb}$ . **The solution phase separates into a polymer-lean and polymer-rich phases**
- For different pressure quench paths I, II, and III that end at the same final  $P_f$ , the compositions of the coexisting phases are given by the same binodal compositions, even though the concentrations of the initial 1-phase solutions are different
- The difference in the initial compositions shows itself in the volumes of the coexisting phases rather than the compositions
- Figure is for equilibrium and does not describe the transient structures that may form along different pressure reduction paths before final equilibrium conditions are reached





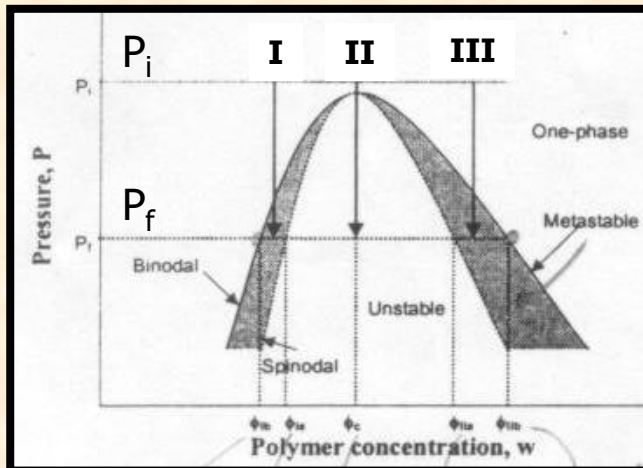
# SUPERCRITICAL FLUIDS, POLYMERS, and PHASE SEPARATION

■ **Along paths I and III**, the system enters the metastable regions where the mechanism of phase separation is by **nucleation** and **growth**

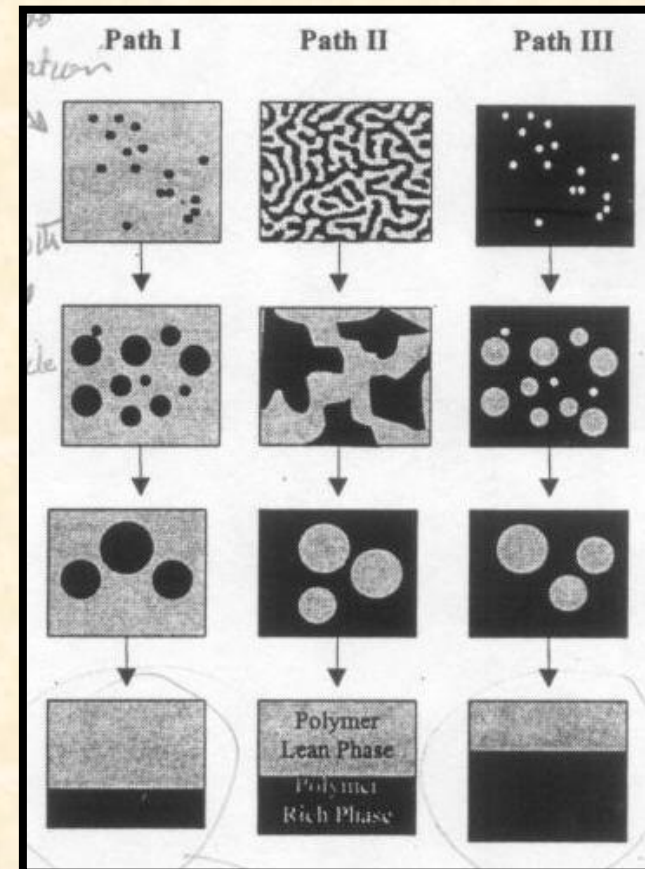
- In solutions of low polymer concentrations **along path I**, the polymer-rich phase nucleates in the polymer-lean phase, and grows
- In contrast, in the more concentrated polymer solutions **along path III**, the polymer-lean phase nucleates in the polymer-rich phase and grows
- The particles of polymer-rich phase (path I), or the bubbles of polymer-lean phase (path III) unless frozen may eventually collapse, settling into the two coexisting phases with compositions fixed by the binodal values

■ **Along path II** which corresponds to the critical polymer concentration,

- the system immediately enters the spinodal region where the phase separation is spontaneous and in the initial stages a co-continuous texture of polymer-rich and polymer-lean phases forms.
- In time, the structure coarsens and may eventually collapse



Understanding the **time scale** of new phase formation and growth and devising methods to quench and pin a system in one of its equilibrium transient states are important considerations in producing micro-structures materials, for example, structures with specific pore size, distribution or morphologies



# SOME FUTURE TRENDS in NANOTECHNOLOGY

## ■ TOOLS

- **Nanomanipulators** (*3rdTech*): Marriage of Virtual Reality (VR) and AFM. It is expected to tremendously facilitate research in nanomaterials

## ■ FABRICATION/PROCESS

- **Self assembly** (Examples: (Ghadiri, *Adaptive Therapeutics*), (Belcher, *Semzyme*), etc.)  
☞ Nearly half of the 994-page April 16, 2002 issue of the **Proceedings of the National Academy of Sciences** was devoted to supramolecular chemistry and self-assembly.
- **Supercritical**: (Fulton, Chehroudi ?) Nanoparticle formation using microemulsion under supercritical produces particles having extremely homogeneous size. Also, substantially simplifies thin film CVD process

## ■ NANOELECTRONICS

- **Terabit storage**: IBM demonstrated 20 times greater data density than the best magnetic storage available. It is rewritable
- **Molecular logic & Memory**: HP group using molecular switching demonstrated the first molecular logic and memory can work together on the same nano-scale circuits. Also, built the assembly using a candidate technology for volume manufacturing.

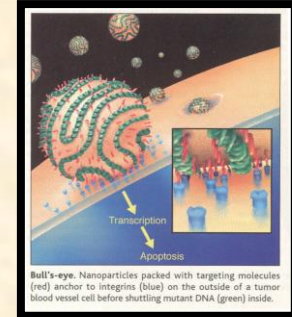
# SOME FUTURE TRENDS in NANOTECHNOLOGY

## ■ MATERIALS

- Polyhedral Oligomeric Silsesquioxane (POSS) and Nanocomposites (AFRL, HybridPlastics)
- Nanocrystalline H<sub>2</sub> (hydrogen) storage
- Nanocrystalline corrosion-resistant

## ■ NANO/BIO

- Use of nanoparticles (Cheresh):
  - ☞ Polymer nanoparticles carry deadly weapon (a mutant DNA) to the cancer cell. Scripps and Stanford have applied for patents on the technology, which Merck KGaA of Darmstadt, Germany, has licensed
  - ☞ Human tests will follow
- Use of Q-dots
- Self assembly & Supramolecular assembly
- Nanodevices (Example: nanofluidic chips by H. Craighead (Cornell) and Turner (president) formed *Nanofluidics* startup):
  - ☞ Tiny channels (50 nm) on silicon chip through which single strand of labeled DNA can barely squeeze through (key feature of the device). As DNA passes down the nanochannel, an optical detector identifies the labels
  - ☞ Protein analysis bio-chips (IBM's nanocantilever beams)





# SOME FUTURE TRENDS in NANOTECHNOLOGY

## ■ TRAINING

- Educational institutions are beginning to feel **the need for courses in nanotechnology**
- In light of the fundamental knowledge required for nanoscale science and the **interdisciplinary nature of the field**, specialized degrees (MS or PhD) are needed.
- **Truly multidisciplinary centers are being formed** (Example: MESA+ Research Institute, Netherlands)

# FUTURE OF SUPERCRITICAL FLUIDS IN NANOTECHNOLOGY

- SCF solvents show great potential for the creation of nanostructures.
- As recognized for many years in the field of aerogels, **surface tension and capillary forces can be highly destructive at the nanoscale.**
- Also, complex supramolecular structures are typically formed in solution, and the self-assembly process is invariably influenced by solvent variables such as density, dielectric constant and polarizability.
- **All of these variables can be fine-tuned in compressible SCF solvents, and the control of molecular self-organization is likely to be one of the new frontiers for this technology.**

## SUMMARY AND CONCLUSIONS

- **Nanotechnology will have a revolutionary impact** in a number of key technologies
- The growth of nanotechnology to a large extent depends on how the key **tools to manipulate, "see", and fabricate the nanoworld** develops (both technologically and commercially). Reduction of acquisition costs and their availability **will largely determine the growth time scale** in many areas.
- Solubility of supercritical fluids increases with increasing density (i.e. with increasing pressure)
- Rapid expansion of supercritical solutions leads to precipitation of a finely divided solid (**nanoparticles**). This is a key feature.
- SCFs offer opportunities for purifying proteins, producing micro- and **nano- particles** via rapid expansion and antisolvent precipitation, creating protein powder, preparing liposomes encapsulating water-soluble compounds, and for aerosolization for fine powder generation and drug delivery
- SCF\_CO2 for fabricating 0.2 micron feature size using **fluorinated polymers**: High solubility of fluorinated block copolymers in SCF\_CO2 and the selectivity of SCF\_CO2 to both polarity changes and the molecular structure of the polymer were used to develop an environmentally friendly **lithographic process** which could be superior to that of non-green aqueous-based systems
- Supercritical fluids have solvent power similar to a light hydrocarbon for most solutes. However, **fluorinated compounds** are often more soluble in SCF\_CO2 than in hydrocarbons; this increased solubility is important for polymerisation.
- The fluids are completely miscible with permanent gases (e.g., N<sub>2</sub> or H<sub>2</sub>) and this leads to much higher concentrations of dissolved gases than can be achieved in conventional solvents. This effect has been exploited in both organometallic reactions and hydrogenation.
- In general, the SCF will play an increasingly important role in the production of high-value-added polymeric materials
- **SCFs offer a marvelous opportunity for exciting research** with a good potential for utilizing the results in industrially important processes for sustainable development in the new millennium
- Clearly, SCF\_CO2 may be used in **polymer-ceramic composites** to influence the processing rheology of these pastes, as well as in the supercritical fluid extraction and drying of the paste



# **BACK-UP SLIDES**

# **FACTS ABOUT SUPERCRITICAL SOLUTIONS**

- Supercritical CO2 fluid extraction produces natural nutritional extracts.
- Supercritical CO2 fluid extraction is used in the development of new and improved nutraceutical components achieving extraction specifications which cannot be achieved through other extract processing methods.
- Supercritical fluid extraction uses CO2 as its extraction media eliminating the use of harmful solvents during the processing of nutraceutical extracts.
- The Supercritical CO2 extraction removes the essential oils and phytochemicals from nutraceutical botanicals and other horticultural materials. The botanicals are placed in extraction vessels where CO2 is infused. The Supercritical CO2 solvent flows into the separators where the extracted material is collected. The extracted material from the separators goes to degassing holding tanks and eventually to product packaging and storage. The CO2 is recycled back into the process and returned back to the extractors. Nearly 100% of the CO2 is recycled.
- Carbon-dioxide as a solvent is non-toxic, odorless, tasteless, colorless, non-flammable, and easily removed from the extract. One of the primary benefits of this extraction process is that carbon dioxide leaves no solvent residues in the product. This is not achieved with conventional solvent extraction procedures. This allows the extract to meet natural product standards.
- Extracts produced by the supercritical CO2 fluid process are of superior quality and command a higher market value when compared to a solvent derived extract.
- The Supercritical CO2 extraction process works at low temperatures. It eliminates the need for an evaporation process that can damage the extracted phytochemicals. Supercritical technology has no effect on the taste or quality of the extract and produces more pure phytochemical.
- The extracts are highly concentrated, more stable and have a longer shelf life than standard solvent extracts.
- Supercritical fluid processes are easily and efficiently reproduced. This means duplication of a finished product and a more reliable processing procedure.
- Supercritical CO2 fluid extraction concentrates more of the beneficial phytochemicals and oils from the botanical raw material sources.

# TERMINOLOGY

## ■ Vit·ri·fi·ca·tion

- 1. **conversion into glass:** the process of converting materials to glass
- 2. CERAMICS **point where fired pot loses porosity:** the point at which a pot loses its porosity during a firing
- **Vitrification:** Point at which a system becomes a glassy solid, and its molecules become immobilized, except for vibrations. At vitrification, the reaction rate (kinetics) drops off quickly

## ■ O·lig·o·mer

A polymer that consists of two, three, or four monomers.

## ■ **Nutraceutical:**

The term nutraceutical was coined in the 1990's by Dr. Stephen DeFelice. He defined nutraceutical as: 'A nutraceutical is any substance that is a food or a part of a food and provides medical or health benefits, including the prevention and treatment of disease. Such products may range from isolated nutrients, dietary supplements and specific diets to genetically engineered designer foods, herbal products, and processed foods such as cereals, soups and beverages. It is important to note that this definition applies to all categories of food and parts of food, ranging from dietary supplements such as folic acid, used for the prevention of spina bifida, to chicken soup, taken to lessen the discomfort of the common cold. This definition also includes a bio-engineered designer vegetable food, rich in antioxidant ingredients, and a stimulant functional food or pharmafood.' Since the term was coined, its meaning has been modified. Health Canada defines nutraceutical as: 'a product isolated or purified from foods, and generally sold in medicinal forms not usually associated with food and demonstrated to have a physiological benefit or provide protection against chronic disease.' **Examples:** beta-carotene, lycopene

## ■ **"lotus effect":**

The way water dropping on lotus leaves forms beads which simply roll off, leaving no trace. In the same fashion, the spray repels water and stops dust and grime sticking. As the water droplets roll off the surface they pick up dirt and carry it away. The "lotus effect" was discovered in the 1990s by German botanist Professor Wilhelm Barthlott. He showed that lotus leaves are covered in tiny bumps or "nanoparticles" five to 10 thousandths of a millimetre high and coated by a waxy film. Water droplets touch the rough surface at only a few points. Because of the small contact area, they roll off easily under their own weight. A rolling droplet gathers dirt like a snowball, unlike water sliding over a smooth surface.



# SUPERCRITICAL AND ENVIRONMENTAL ISSUES

- Recently reported results: Ag nano-crystals (5 - 15 nm size) were synthesized and stabilized in CO<sub>2</sub>.
- This finding opens a broad range of potential synthesis routes for a variety of different nanoparticles that provides a simple, effective means for removal of the solvent (CO<sub>2</sub>) from the particles.
- In addition to developing the particle chemistry suitable for a CO<sub>2</sub> solvent, the colloid stability is controlled by the proper choice of surfactants, co-surfactants or capping agents.

