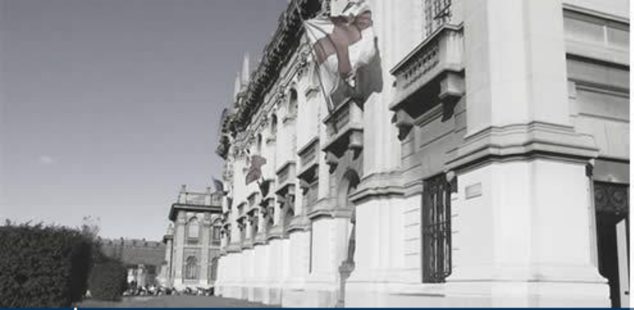


School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

# Unusual Forms of Energy in Synthesis: Ultrasound irradiation.

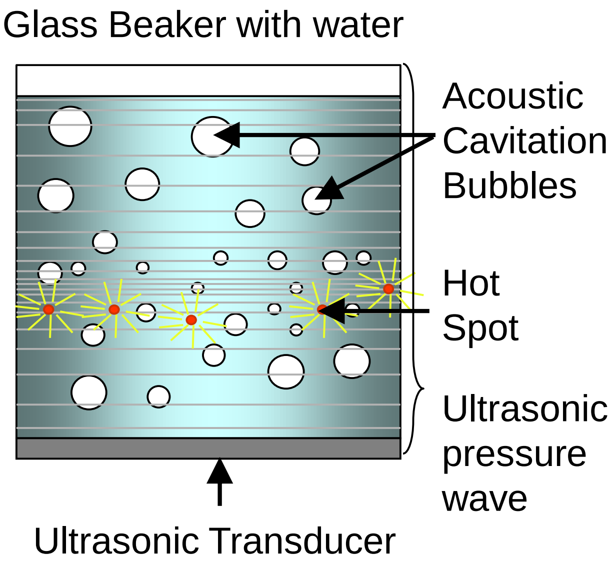

Prof. Attilio Citterio

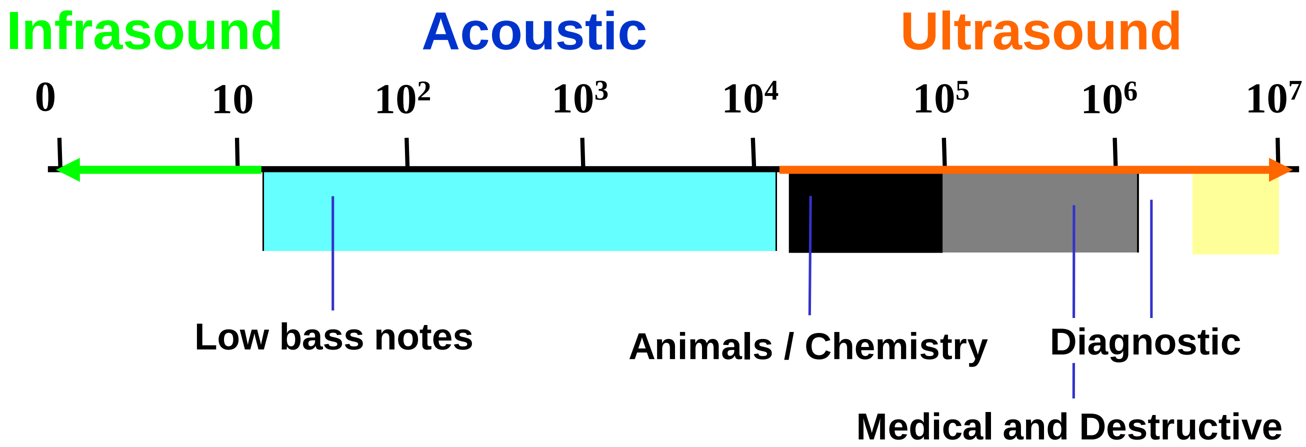
Dipartimento CMIC “Giulio Natta”


http://iscamap.chem.polimi.it/citterio/education/course-topics/

# Ultrasonics

- Ultrasounds (radiation at 20-10 000 kHz frequency)
- 1880 Piezoelectricity (Curie brothers)
- 1893 Galton-1912 TITANIC
- 1912 Behm (Echo technique)
- 1917 Langevin (Ultrasonic variation, Icebergs, Submarines)
- 1945 Application in chemistry

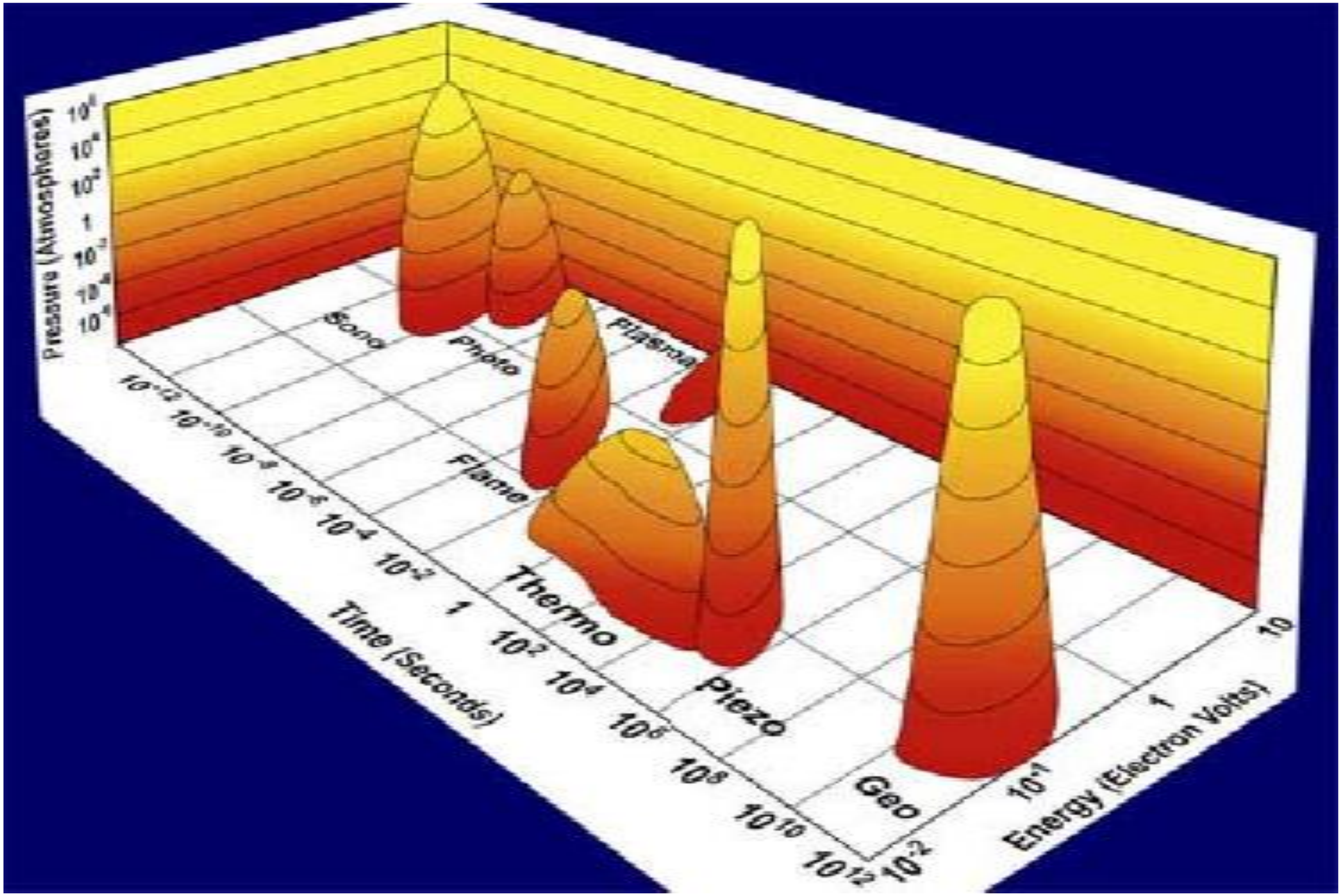





| | | |
|---|---|---|
| Human hearing | (cyan) | 16 *Hz* – 18 *kHz* |
| Conventional power ultrasound | (black) | 20 *kHz* – 100 *kHz* |
| Extended range for sonochemistry | (black/grey) | 20 *kHz* – 2 *MHz* |
| Diagnostic ultrasound | (yellow) | 5 *MHz* – 10 *MHz* |

## Frequency ranges of sound

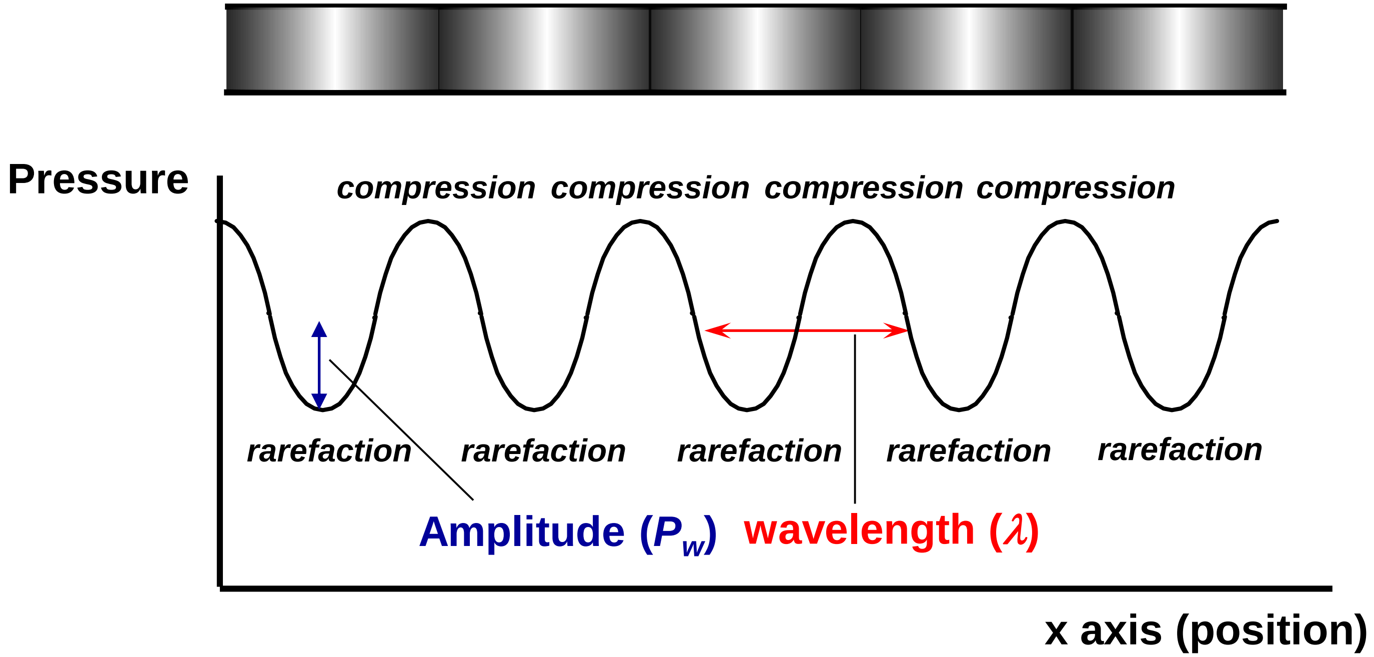
# Representation of Energetic Processes.




Suslick, K.S. et al. Acoustic Cavitation and its Chemical Consequences *Phil. Trans. Roy. Soc*. 1999, 357, 335.

## Sound transmission through a medium

Ultrasound travels through a liquid as a longitudinal wave, i.e., the molecules of the liquid oscillate about their equilibrium positions in the direction of the motion of the wave. Therefore, the effective pressure in any given region of liquid is determined by the equation, $P_t = P_h + P_a$, where $P_t$ = the total pressure in a specific region in the liquid, $P_h$ = the hydrostatic pressure and $P_a$ = the acoustic pressure in a particular region and time.



# Ultrasonics/Sonochemistry – Basics (3).

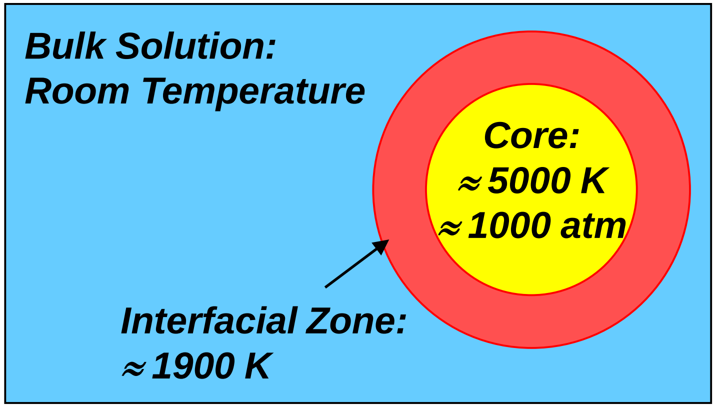
*Nucleation, Growth and Collapse of Microbubbles:*

- Pockets of gas are trapped on microscopic impurities (e.g., dust particles), inherently present in any liquid, or in imperfections on the wall of the vessel.
- The gas nuclei expand under the influence of the UW and detach to form in the liquid free microbubbles. These continue to adsorb energy from the wave and grow isothermally.
- When the microbubbles reach a critical size (approximately 2 to 3 times the resonance radius), they implode violently. Assuming adiabatic collapse, the temperature of the hot spot can be estimated using the equation below (note the importance of $\gamma$ in determining the collapse temperature and, being non adiabatic, thermal conductivity effect s $T_f$ ).

$$T_f = T_i \left( \frac{R_{max}}{R_{min}} \right)^{3(\gamma-1)}$$

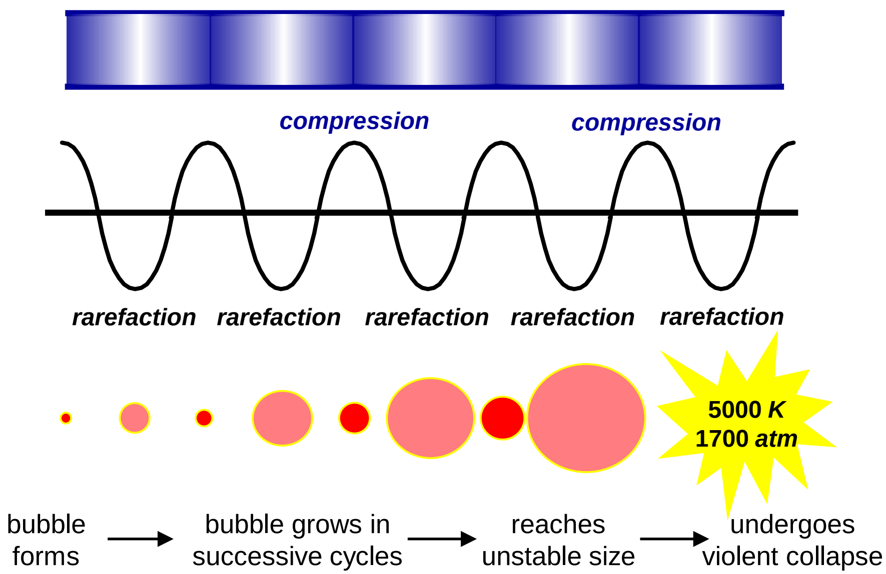
- Where, $T_f$ is the temperature of the core, $T_i$ is ambient temperature, $R_{max}$ and $R_{min}$ are the maximum and minimum bubble radius and $\gamma$ is the ratio of specific heats ($C_p/C_v$) of the gas inside the bubble. $\gamma$ = 1.67 for monoatomic gases and 1.40 for diatomic gases.

The Sonochemical Hot Spot*



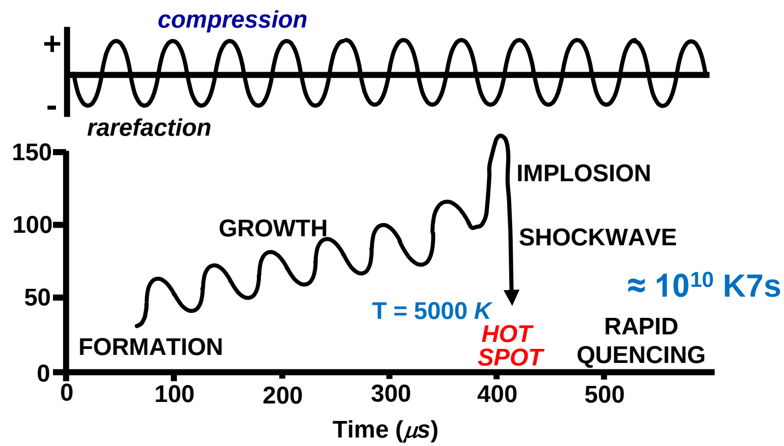

*Suslick, K.S. et al., *J. Am. Chem. Soc.*, **1986**, *108*, 5641.

# Ultrasonics/Sonochemistry – Basics (4).




**Formation of an acoustic bubble**
(in cavity extreme high *T* and *P*
In the media intense shear forces)

TRANSIENT CAVITATION:
THE ORIGIN OF SONOCHEMISTRY




Bubble size and cavitation dynamics

Transient cavitation

Suslick et al., *Chem. Mat*., 1996

# Sonochemistry: Bubble Dynamics.

*Cavitation bubble dynamics*: Rayleigh-Plesset equation

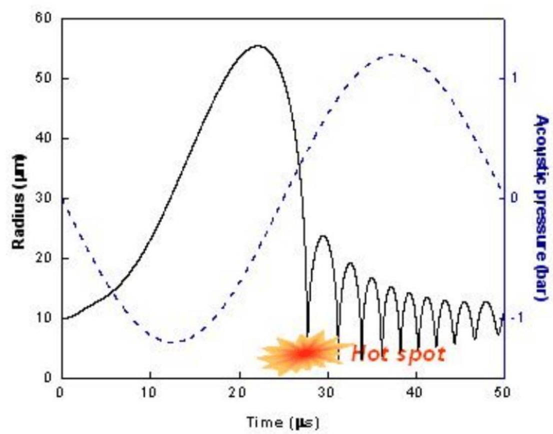
$$\rho\left[R\frac{\partial^2 R}{\partial t^2}+\frac{3}{2}\left(\frac{dR}{dt}\right)^2\right]=\left(P_h-P_v+\frac{2\theta}{R_0}\right)\left(\frac{R_0}{R}\right)^{3k}-P_k-P_a+P_v-\frac{2\theta}{R}$$

**ρ** - density of the solvent, **R –** bubble radius **$P_h$ –** hydrostatic pressure, **$P_a$ –** acoustic pressure, **$P_v$** – vapor pressure, **k= $C_p/C_v$** – polytrophic index, and **θ** complex parameter taking into account the surface tension

Time of the collapse:

$$t_i = 0.915R\sqrt{\frac{\rho}{\left(P_h+P_a-P_v\right)}}$$

ν = 20 kHz
I = 1 W/cm$^2$
**$t_i$ = 0.7-0.8 μsec**




Bubble radius:

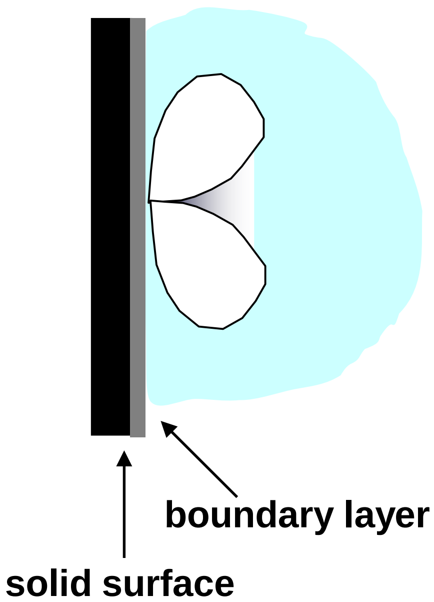
$$R_0=\frac{4}{3Wa}\left(P_A-P_h\right)\left(\frac{2}{\rho P_a}\right)^{1/2}\left[1+\frac{2\left(P_A-P_{h\partial}\right)}{3P_h}\right]^{1/3}$$

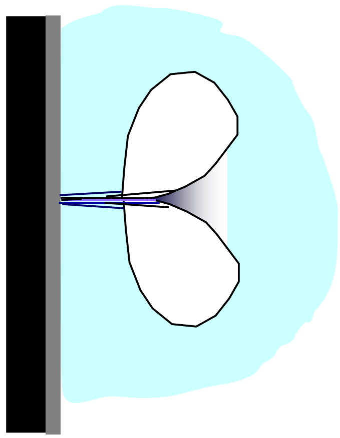
*Wa* = 2πFa  is applied circular frequency

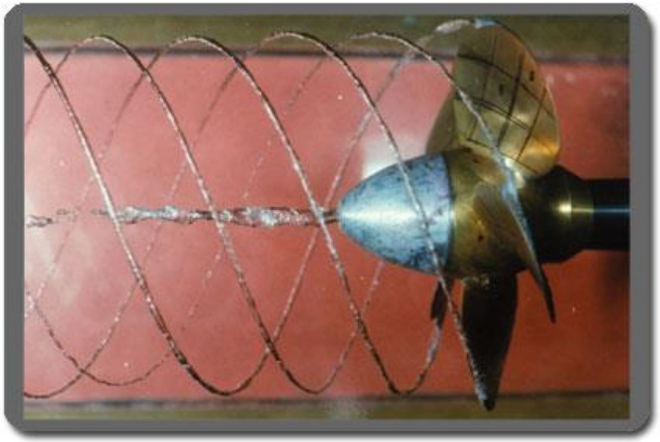
**$H_2O$:**

| ν, kHz | R, μ m |
|---|---|
| 18 | 150 |
| 1000 | 3.3 |

**In rush of liquid from one side of the collapsing bubble produces powerful jet of liquid targeted at surfaces**



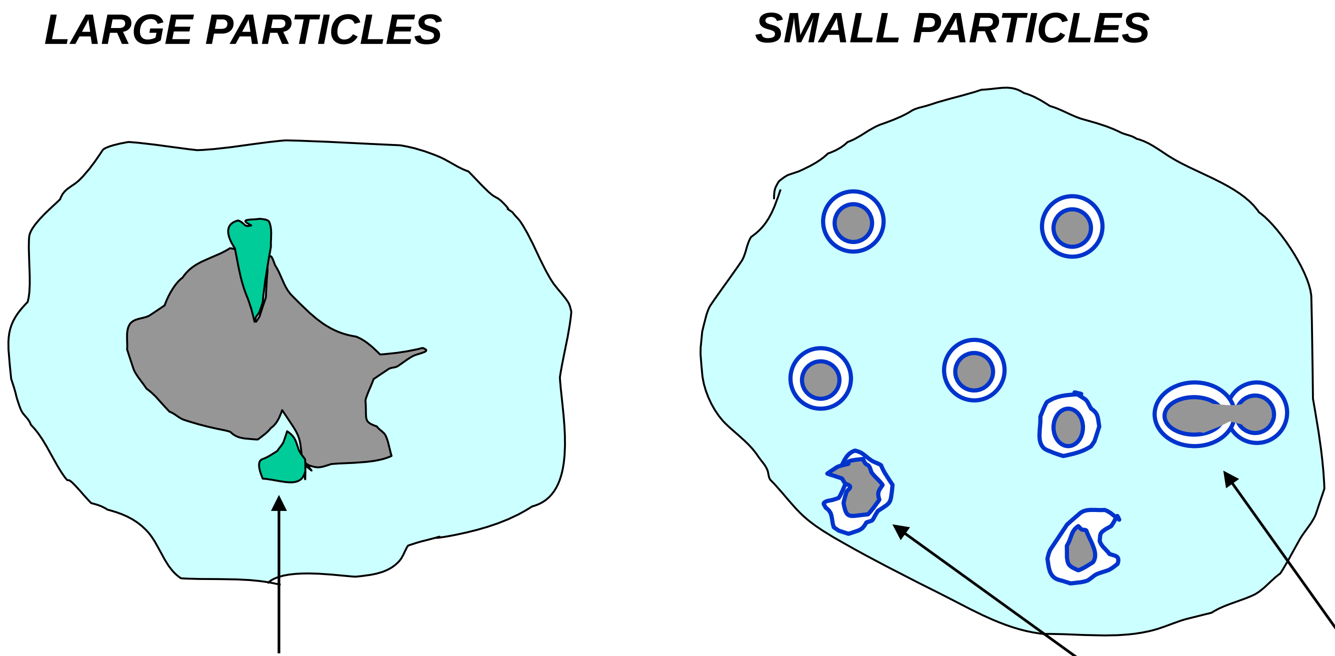





**Surface cleaning**
**destruction of boundary layer**
**Surface activation**
**Improved mass and heat transfer**

Acoustic cavitation in solid/liquid system

# Acoustic Cavitation (2).




Surface cavitation due to defects loading to **fragmentation**

collision can lead to **surface erosion** or **fusion**

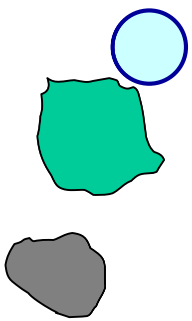
**Acoustic cavitation in solid/liquid system**

# Effects of Parameters on Cavitation.

| Parameter | Effect |
|---|---|
| Temperature | Increase in temperature leads to rise in vapor pressure and thus increasing cavitation and deceasing cavitation collapse. This allows cavitation to be achieved at lower acoustic intensity |
| US amplitude / Intensity | An increase in intensity will provide for an increase in the sonochemical effects. However intensity cannot be increase indefinitely. With increase in pressure amplitude, the bubble may grow so large on rarefaction that the time available for collapse is insufficient. May shift US behavior from far reaching effects to near reaching effects. |
| US frequency | As ultrasonic frequency is increased, the production and intensity of cavitation in liquids decreases. |
| External pressure / hydrostatic pressure | Increasing external pressure leads to both increased cavitation threshold and intensity of bubble collapse. |
| Flow rate | Since flow produces negative pressures, flow rate reduces the threshold for cavitation. Flow also disturbs standing fields. |
| Solvent | Vapor pressure and viscosity solvent dependent. High vapor pressure facilitates cavitation (see temperature effect on vapor pressure) |
| Viscosity / surface tension | Cavitation more difficult to produce in viscous liquids or liquids with high surface tension |
| Gas entrainment | Increase gas content in liquids leads to lowering of both cavitation threshold |

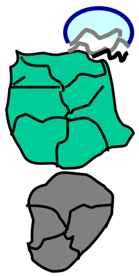
# Sono-Fragmentation (Size Reduction).

Bubble



Particles

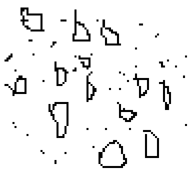
**Bubble Collapse due to Implosion**



**Particle Fragments due to**

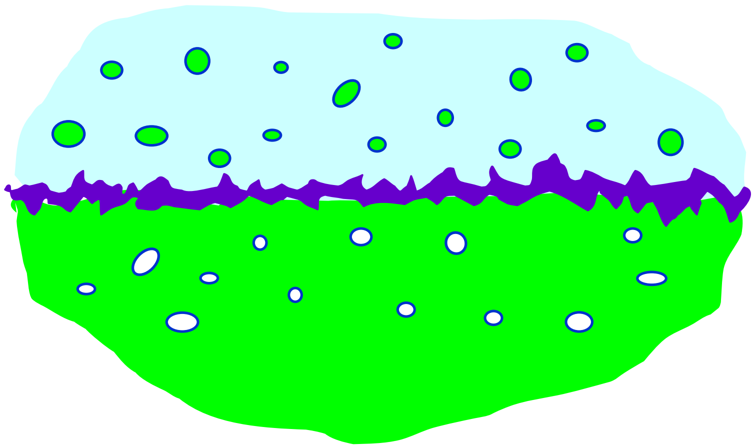
a) Violent bubble collapse

b) Inter-particle attrition



**Fragmented Particle**

## Acoustic cavitation in solid/liquid system



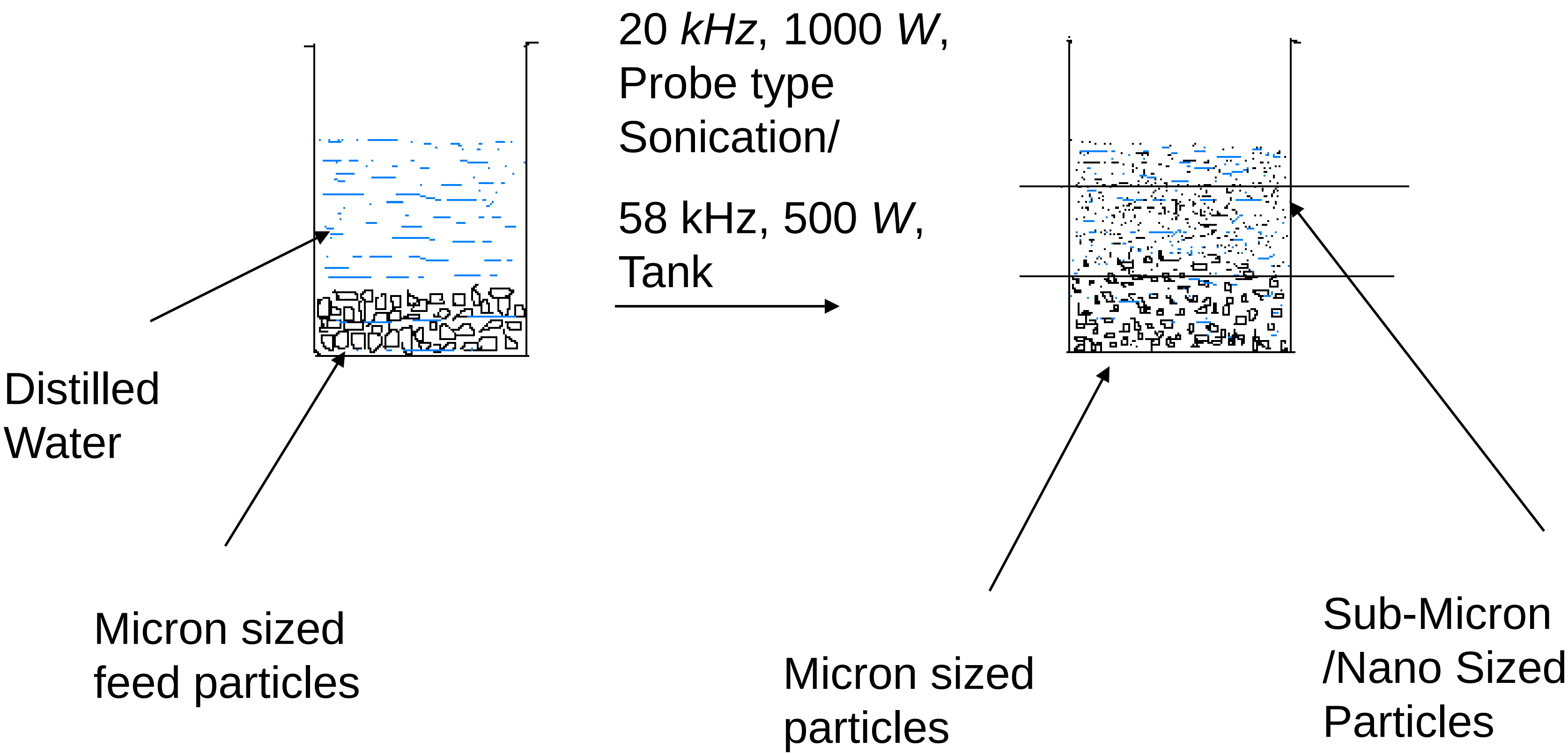
Powerful disruption of phase boundary

## Ultrasonic enhancement of the rate of dissolution:

$$-\frac{\delta C_a}{\delta t} = kS\left(C_A^* - C_A\right)$$

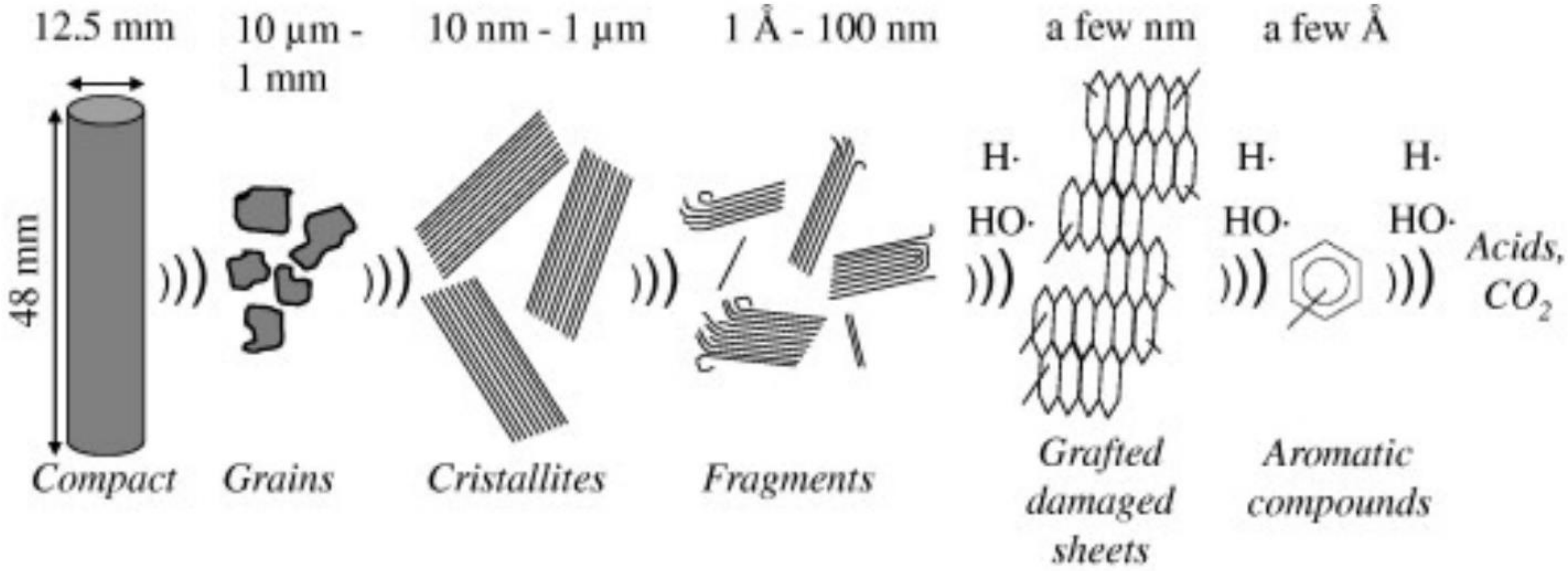
- $(C_A^* - C_A)$ → Increased solubility due to the local heating, supersaturation
- $S$ → Increased by erosion
- $k$ → Increased by microstreaming

# Sono-Processed Sample.

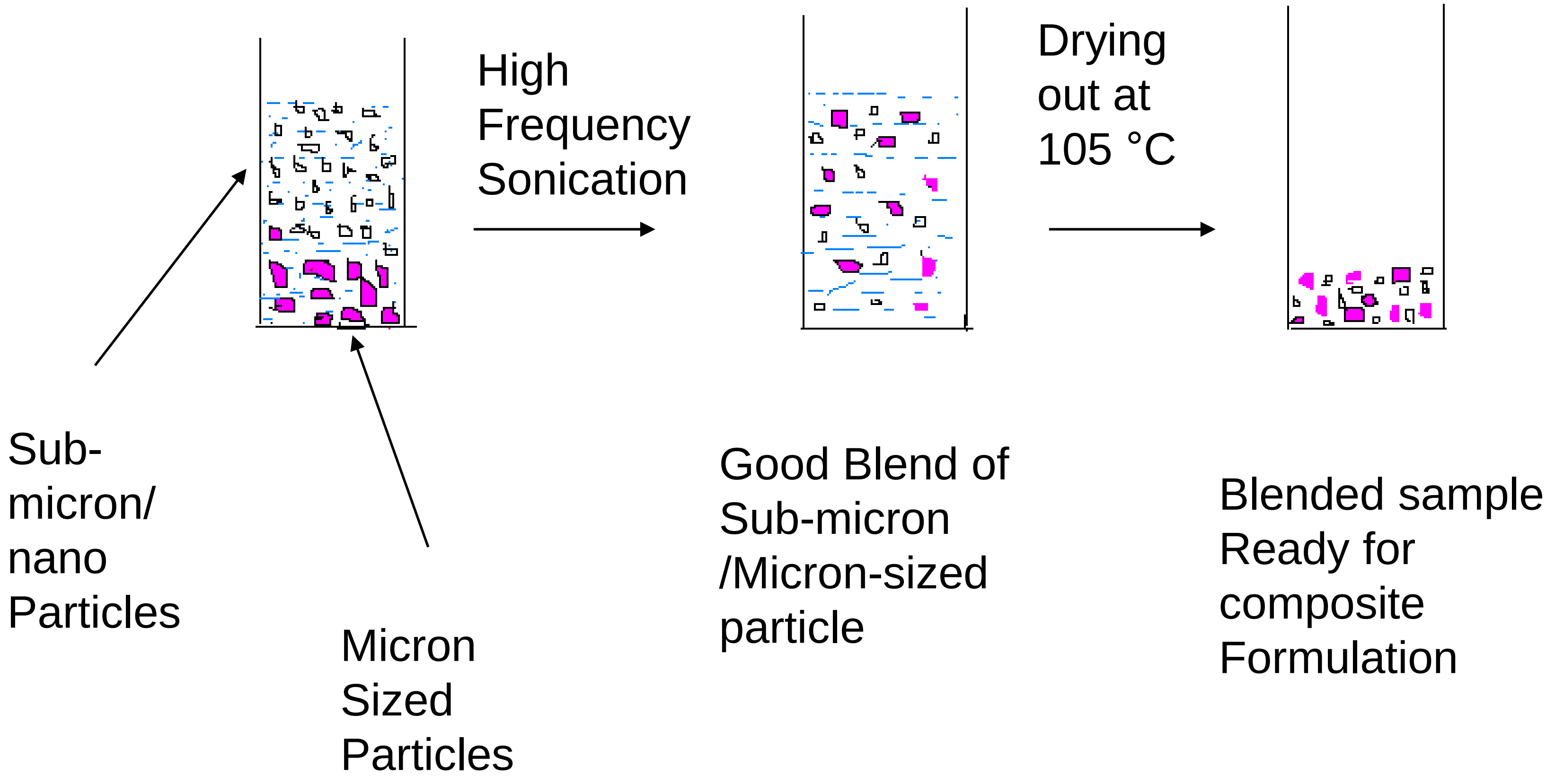


# Mechanical and Chemical Effects.

Sonochemistry of graphite in water

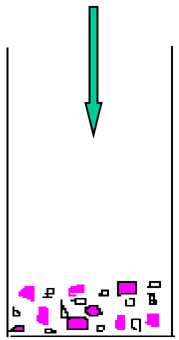


# Sono-Blended Particles For Composite Formulation.

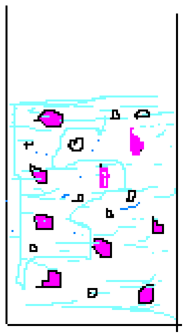


# Polymer Precursor and Polymer Composite Preparation.

Solvent
e.g. $CH_2Cl_2$



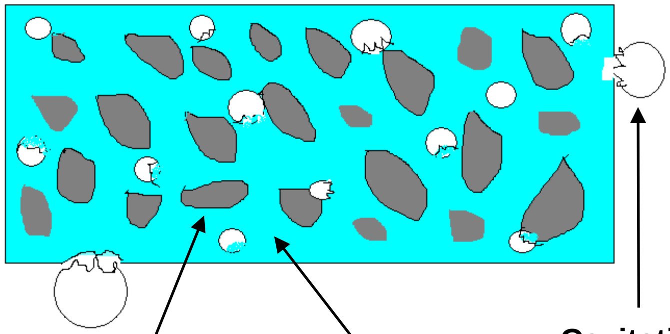
sonication
for 2 min



Blended sample
Ready for
composite
Formulation

Polymer
Precursor

(Particles
Dispersed in
solvent)

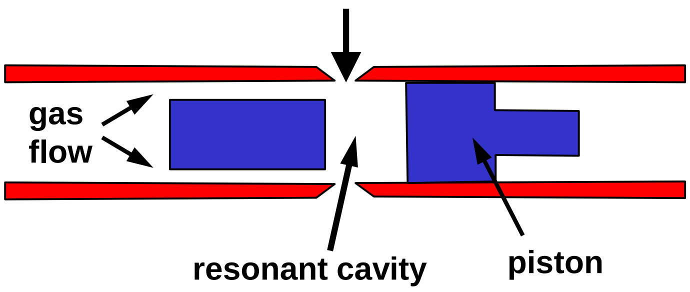


Particle

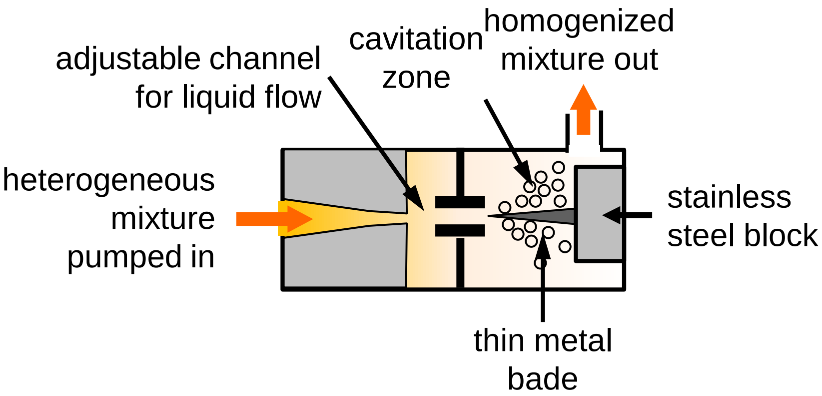
Polymer Matrix

Cavitation
Bubble

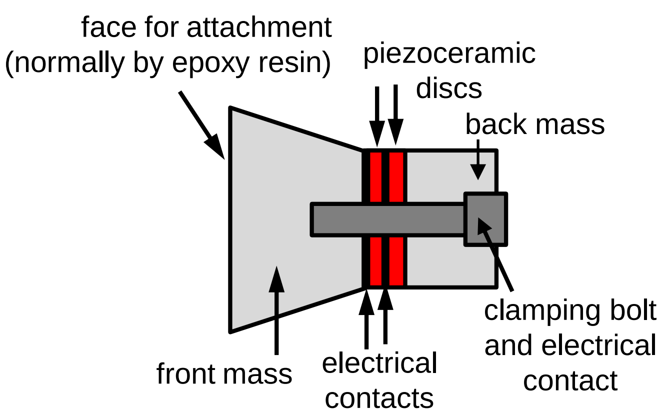
# Ultrasonics/Sonochemistry – Transducers.



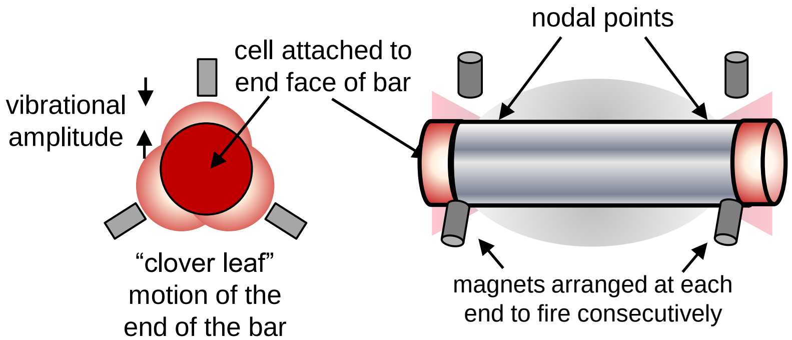

Galton whistle (physical)




Liquid whistle (physical)

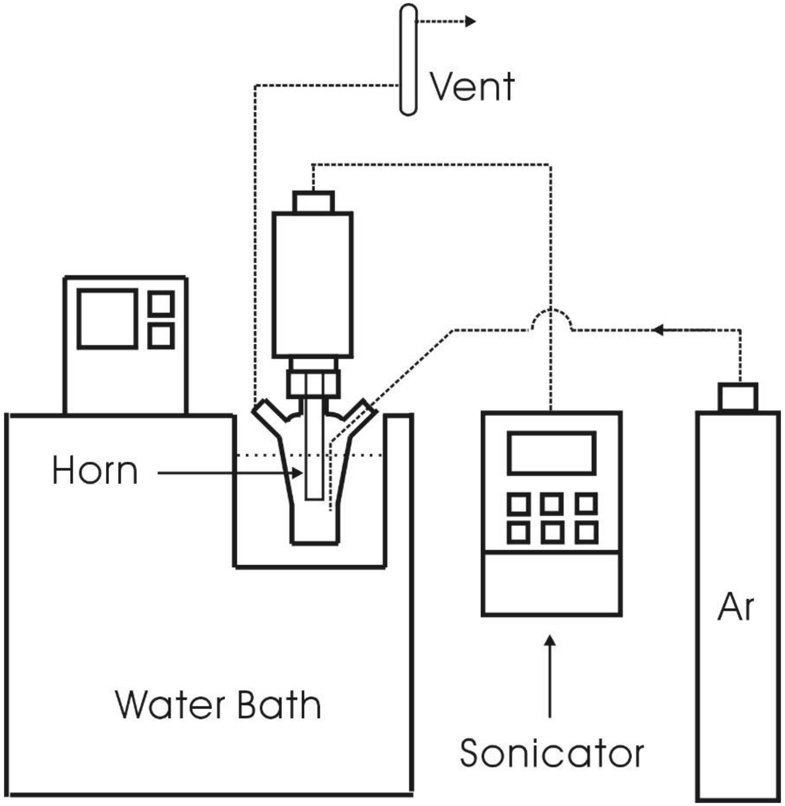



Piezoelectric sandwich transducer



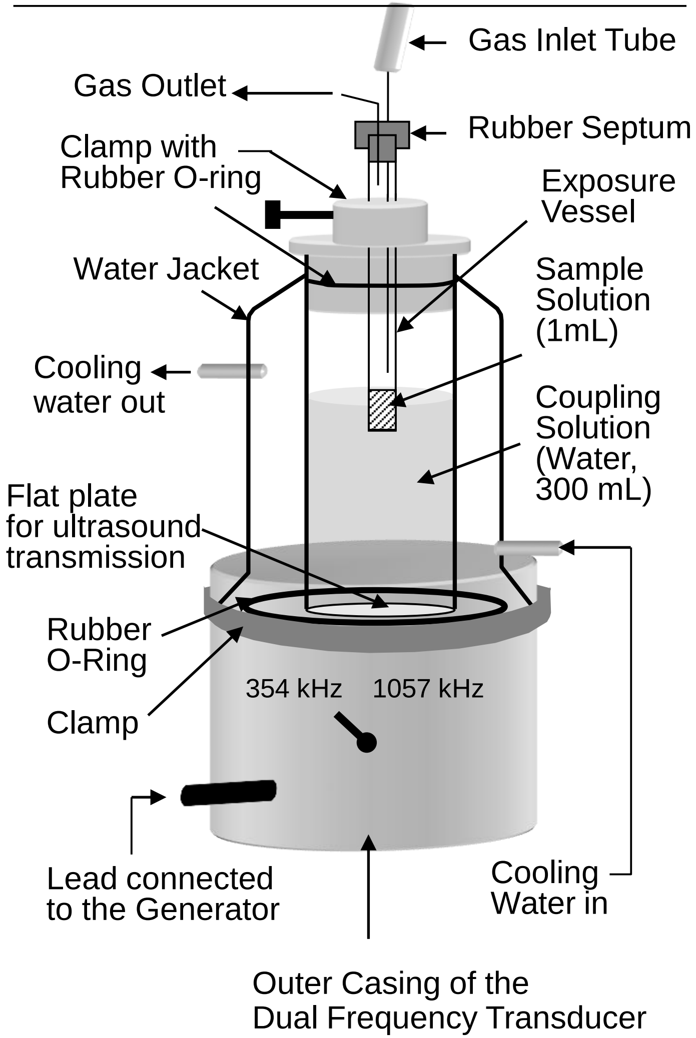

Magnetostrictive transducer

# Laboratory Set-up.




Suslick et al., *J. Am. Chem. Soc.*, 1998

**Figure 1**: Apparatus made by L3-Communications - ELAC Nautik GmbH, Germany.

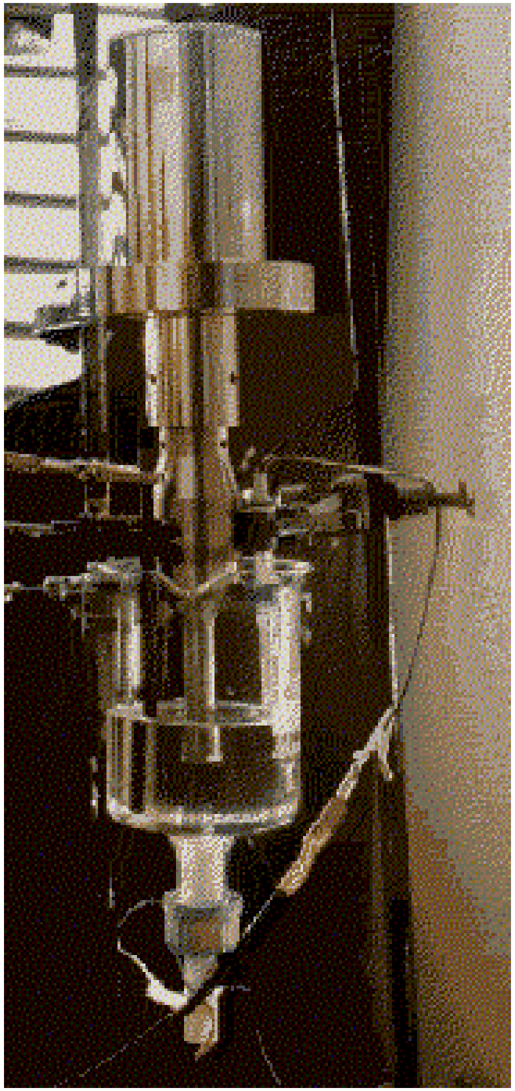


# Ultrasonics/Sonochemistry–Experimental Parameters.

| Experimental parameter | Physical parameter | Effect |
|---|---|---|
| Acoustic frequency | Period of bubble collapse | Change in the size of the bubbles |
| Acoustic power | Size of the reaction zone | The number of cavitation phenomena in a volume unit |
| Temperature | Vapor pressure of liquid<br>Thermal activation | The content of bubbles,<br>the intensity of collapse<br>Secondary reactions |
| Static pressure | Total pressure<br>Solubility of gas | Intensity of collapse<br>The content of bubbles |
| Gas | Politrop ratio<br>Thermal conductivity<br>Chemical reactivity<br>Solubility | Intensity of collapse<br>Primary / secondary reactions<br>Content of bubbles |
| Solvent | Vapor pressure<br>Surface tension<br>Viscosity<br>Chemical reactivity | Intensity of collapse<br>Limit of transient cavitation<br>Primary / secondary reactions |

# Ultrasonics/Sonochemistry–Applications.

- Electronics industry (coating with metals)
- Therapy (surgery), diagnostics
- Food industry (homogenization)
- Materials
  - metallurgy
  - ceramics
- Organic Synthesis
- Inorganic Synthesis
- Environmental applications



# Sonochemistry.

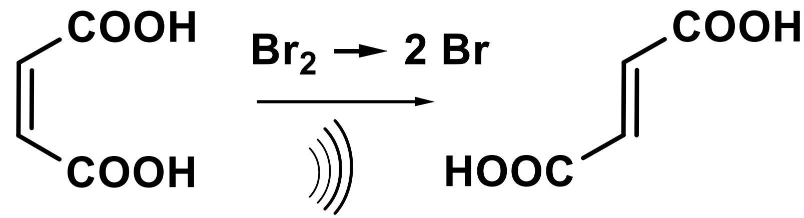
i) *The Three Regions of Chemical Activity:*

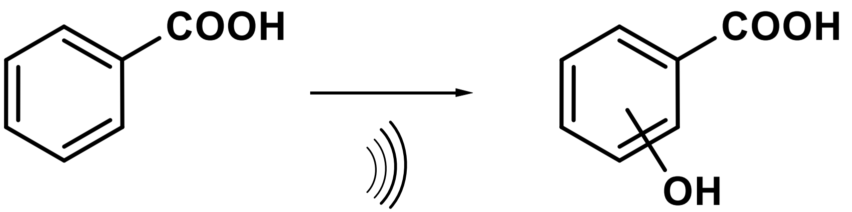
Sonochemical reactions can occur in three different regions:

- *Region 1*: interior of collapsing gas bubbles (i.e., the core) in which very high temperatures and pressures exist. Under these conditions the solvent vapor inside the bubble undergoes pyrolysis reactions.
- *Region 2*: interface between the collapsing bubble and the bulk solvent, where high temperature and pressure gradients exist. In aqueous solutions, the relative efficiency of non-volatile solutes to decompose thermally or to scavenge radicals formed in the hot spot depends on their ability to accumulate at the gas/solution interface of the growing microbubble.
- *Region 3*: bulk solution at ambient temperature. Free radicals formed in the hot regions may diffuse to the bulk solution and react to yield products similar to those found in aqueous radiation chemistry. Thus, sonochemistry can partly be understood in terms of a combination of combustion chemistry and radiation chemistry.

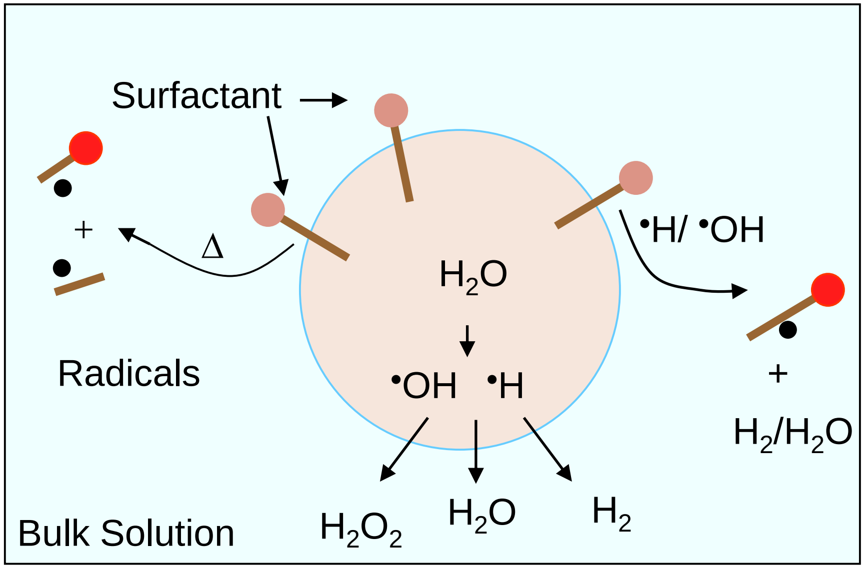
# Ultrasonics/Sonochemistry – Synthesis.

## Aqueous sonochemistry:




Collapsing Cavitation Bubble




$H_2O \longrightarrow H^{\bullet} + OH^{\bullet}$

$H^{\bullet} + OH^{\bullet} \longrightarrow H_2O$

$2\,H^{\bullet} \longrightarrow H_2$

$2OH^{\bullet} \longrightarrow H_2O_2$

$2OH^{\bullet} \longrightarrow O + H_2O$

$2O^{\bullet} \longrightarrow O_2$

$0{,}5\,O_2 + 2\,H^{\bullet} \rightarrow H_2O$

# Ultrasonics/Sonochemistry – Synthesis (2).

**Non aqueous sonochemistry**

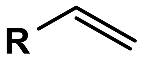
**Scheme I: Rice Mechanism of Radical chain[a]**

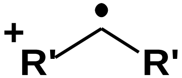
**Initiation:**

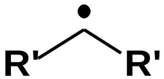
$C_{10}H_{22} \rightarrow 2\,R^{\bullet}$ (1)

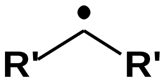
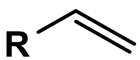
**Propagation:**

$R^{\bullet} \rightarrow R'^{\bullet} + C_2H_4$ (2)

$R^{\bullet} \rightarrow$  $+ H^{\bullet}$ (3)

$R^{\bullet} + C_{10}H_{22} \rightarrow RH +$  (4)

$H^{\bullet} + C_{10}H_{22} \rightarrow H_2 +$  (5)

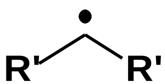
 $\rightarrow$  $+ R^{\bullet}$ (6)

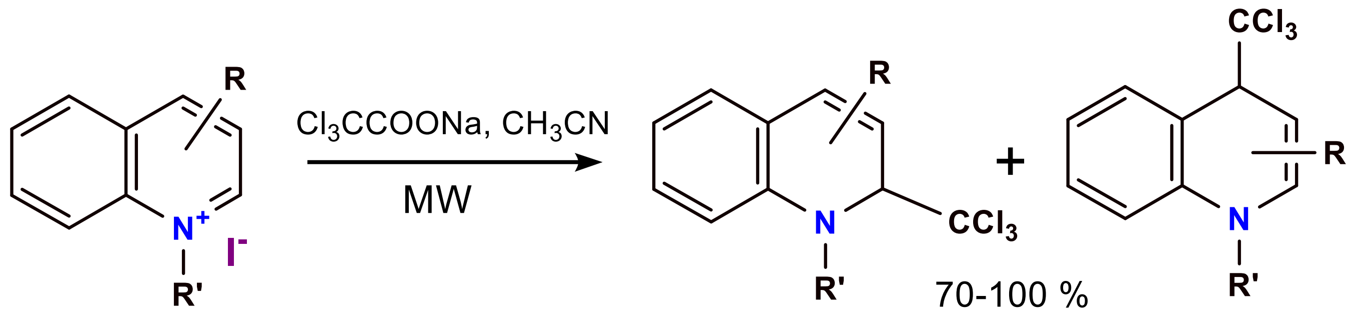
**Termination:**

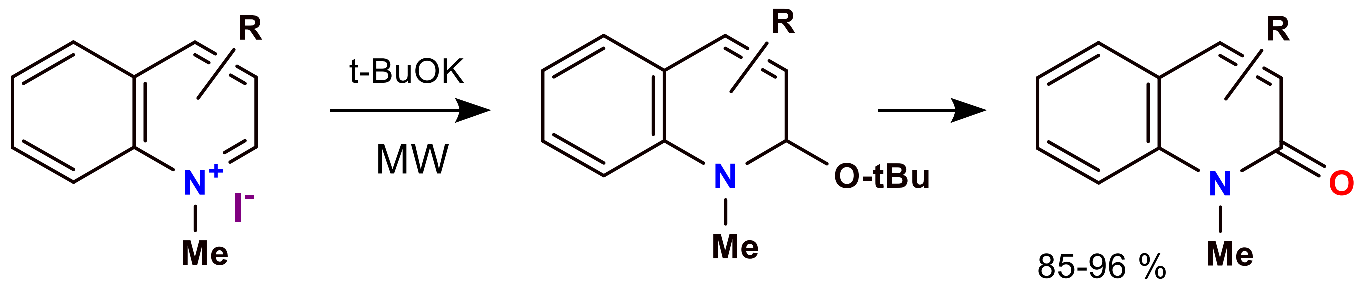
$R^{\bullet} + R^{\bullet} \rightarrow R\text{-}R$ (7)

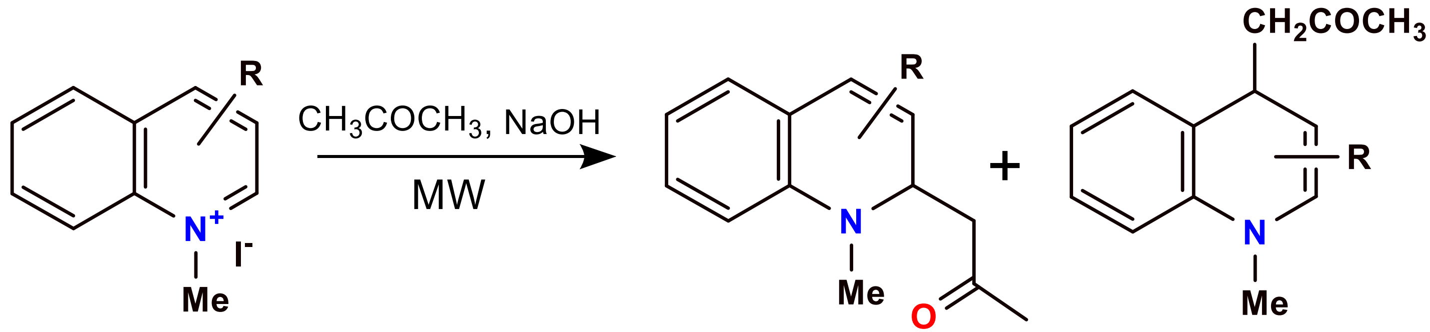
$R^{\bullet} + H^{\bullet} \rightarrow R\text{-}H$ (8)

$H^{\bullet} + H^{\bullet} \rightarrow H_2$ (9)

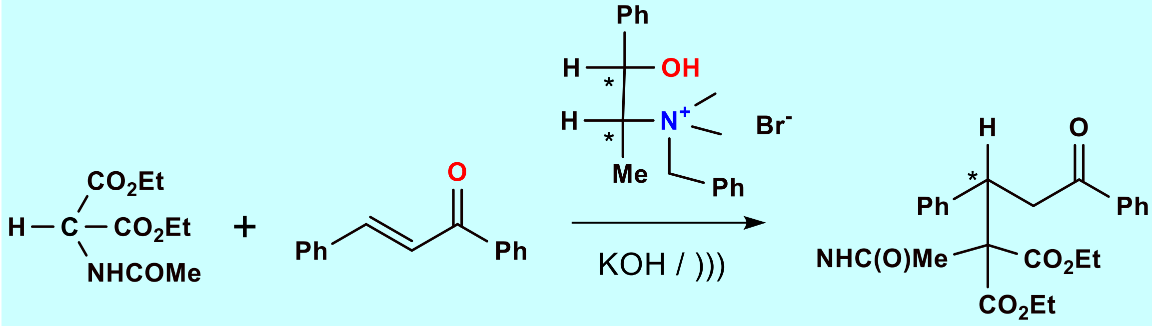
[A] R• = terminal radical,  = internal radical.


R
N+
I-
R'
Cl3CCOONa, CH3CN
MW
R
N
R'
CCl3
70-100 %
+
CCl3
R
N
R'

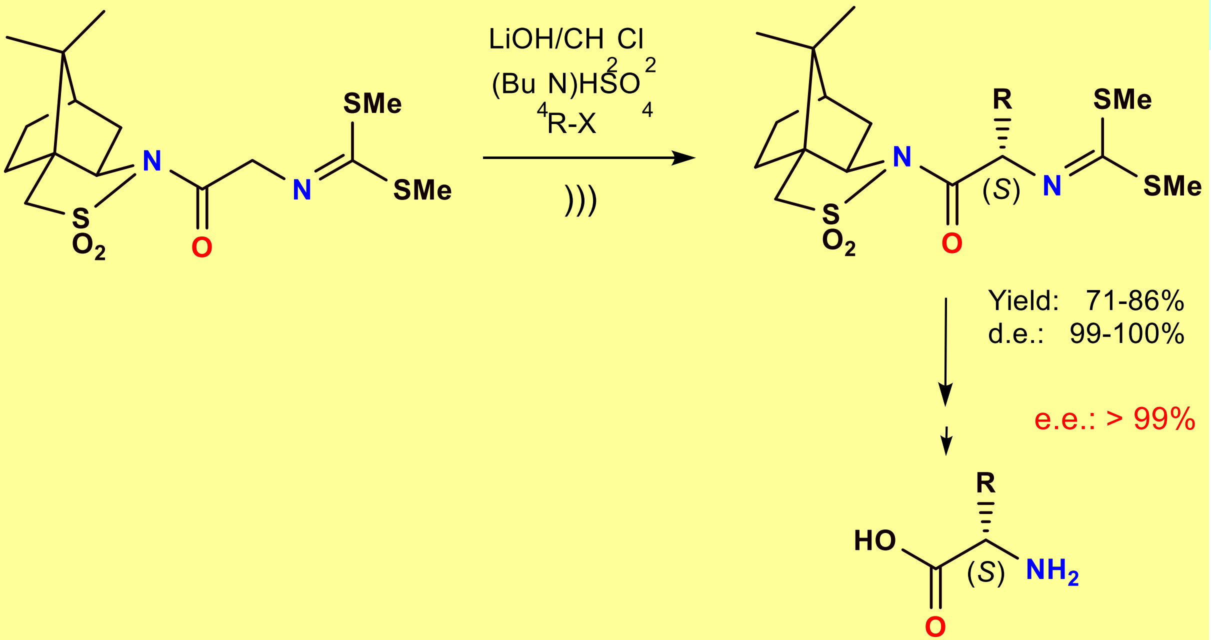

R
N+
I-
Me
t-BuOK
MW
R
N
Me
O-tBu
R
N
O
Me
85-96 %


R
N+
I-
Me
CH3COCH3, NaOH
MW
R
N
Me
O
+
CH2COCH3
R
N
Me

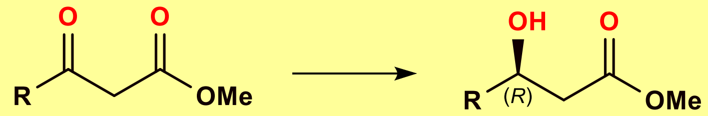
# Ultrasonics/Sonochemistry – Synthesis (4).



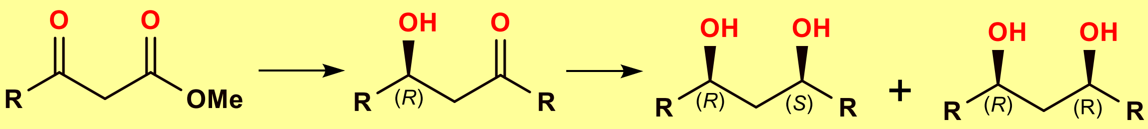

| | silent | ))) |
|---|---|---|
| Yield: | 70% | 82% |
| e.e.: | 40% | 40% |



# Ultrasonics/Sonochemistry – Synthesis (5).

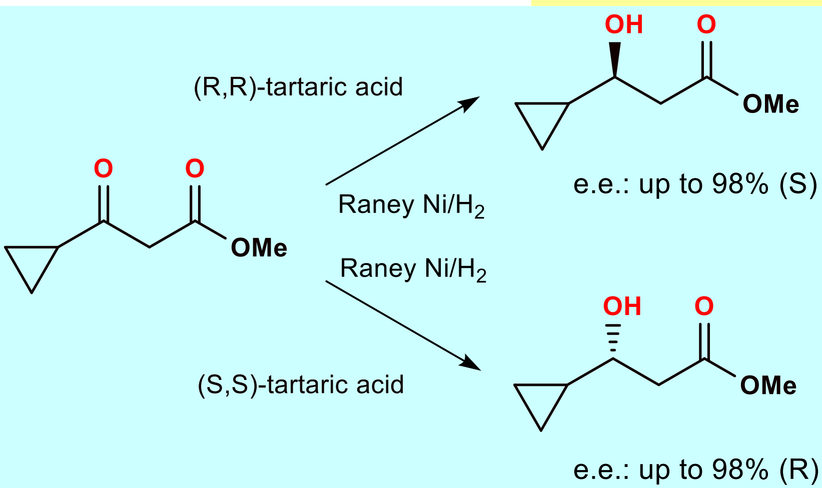



| | silent | ))) |
|---|---|---|
| $e.e._{max}$: | 86% | 94% |



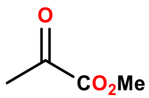
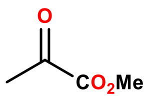
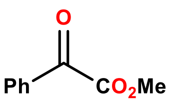
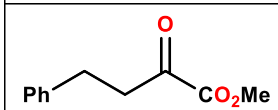
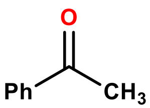
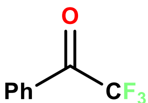
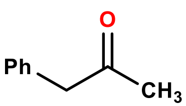
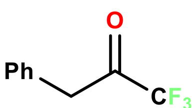
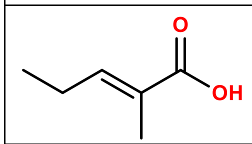

| | silent | ))) |
|---|---|---|
| Resa: | 52% | 62% |
| $e.e_{max}$: | 86% | 94% |

Catalytic system: Raney Ni (presonicated)
( *R*,*R*)-tartaric acid-NaBr

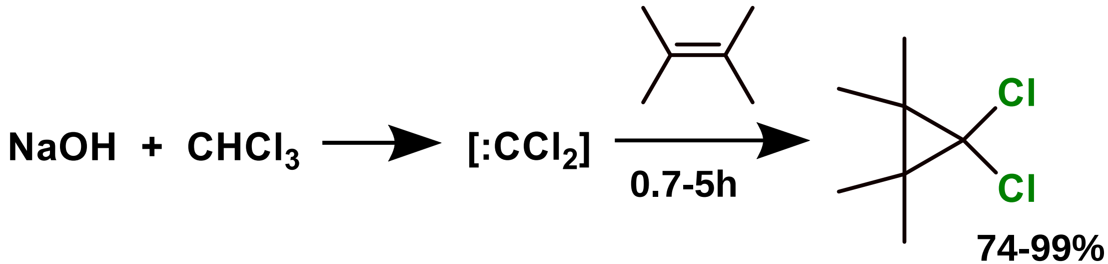


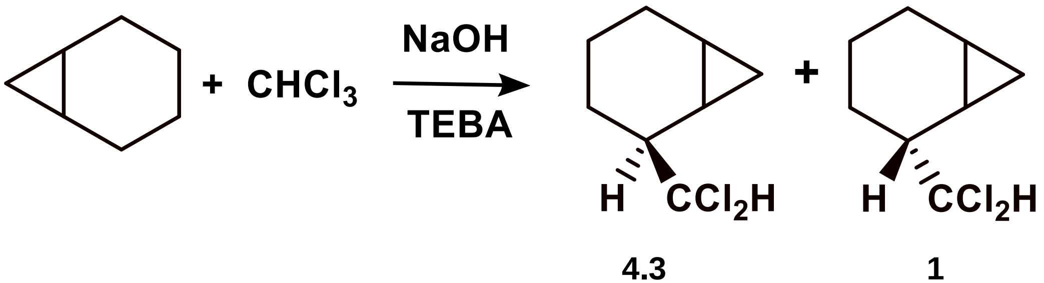
# Ultrasonics/Sonochemistry – Synthesis (6).

**Sonochemical and silent enantioselective hydrogenation of activated ketones, ketoesters and unsaturated carboxylic acids over 5% Pt/$Al_2O_3$ (C=O doubl$_e$ bond) and 5% Pd//$Al_2O_3$ (C=C double bond) using different cinchona modifiers under hydrogen pressure**

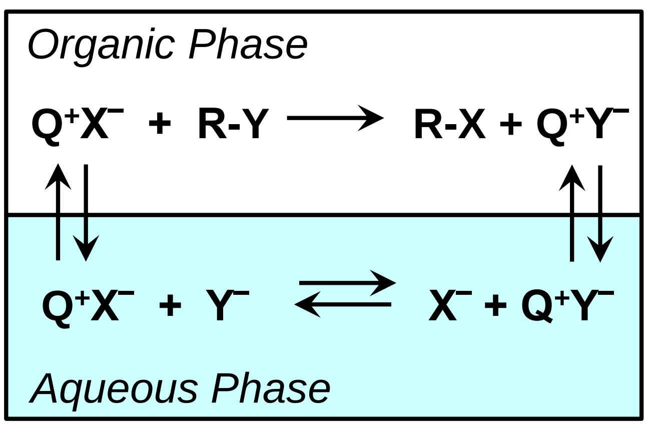
| Substrate | modifier | Catalyst | Hydrogen pressure (bar) | Solvent | Major product | Optical yield (ee%) | |
|---|---|---|---|---|---|---|---|
| | | | | | | No MW | MW |
|  | CD | E4759 | 10 | AcOH | R | 94 | 95 |
|  | CD | E40655 | 10 | AcOH | R | 85 | 97 |
| | MeOH/CD | E40655 | 10 | AcOH | R | 78 | 98 |
|  | CD | E4759 | 10 | AcOH | R | 88 | 92 |
|  | CD | E4759 | 10 | AcOH | R | 79 | 96 |
| | CN | E4759 | 10 | AcOH | S | 85 | 92 |
|  | CD | E4759 | 10 | DBC | R | 6 | 8 |
|  | CD | E4759 | 10 | DBC | R | 46 | 49 |
|  | CD | E4759 | 10 | DCB | R | 7 | 8 |
|  | CD | E4759 | 10 | DCB | R | 18 | 18 |
|  | CD | E4759 | 50 | Toluene | S | 50 | 62 |

# US in Phase Transfer Catalysis.




stirring 9 h 15%
sonication, 3h 83%




**Phase transfer catalysis**

$Q^+$ = TEBA = $^+N(n\text{-}Bu)_4$ cation

# Sonochemical Nano-Synthesis.

- **Sonochemistry**: molecules undergo a chemical reaction due to application of powerful ultrasound (20 *kHz* – 10 *MHz*)
  - Acoustic cavitation can break chemical bonds
  - "Hot Spot" theory: As bubble implodes, very high temperatures are realized for a few nanoseconds; this is followed by rapid cooling ($10^{11}$ *K/s*)
  - High cooling rate hinders product crystallization, hence amorphous nanoparticles are formed
- **Superior process for**:
  - Preparation of amorphous products ("cold quenching")
  - Insertion of nano-materials into mesoporous materials
    - By "acoustic streaming"
  - Deposition of nanoparticles on ceramic and polymeric surfaces
  - Formation of proteinaceous micro- and nano-spheres
    - Sonochemical spherization
  - Very small particles

# Sonochemical Nano-Synthesis: Examples.

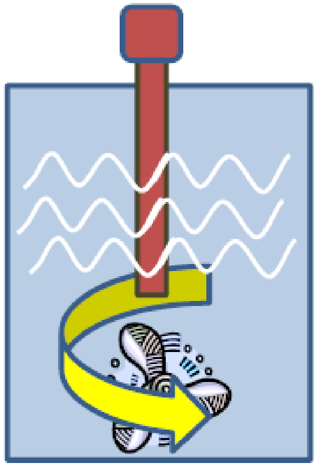
- $S^{-2}$, $Se^{-2}$, $Te^{-2}$
  - used in non-linear optic detectors, photorefractive devices, photovoltaic solar cells, optical storage media
- Gold, Co, Fe, Pt, Ni, Au/Pd, Fe/Co
- Nanophased oxides (titania, silica, ZnO, $ZrO_2$, $MnO_x$
  - More uniform dispersion, higher surface area, better thermal stability, phase purity of nanocrystalline titania reported
- MgO coating on $LiMn_2O_4$
- Magnetic $Fe_2O_3$ particles embedded in $MgB_2$ bulk
- Nanotubes of C, hydrocarbon, $TiO_2$, $MeTe_2$
- Nanorods of $Bi_2S_3$, $Sb_2S_3$, $Eu_2O_3$, $WS_2$, $WO_2$, CdS, ZnS, PbS, $Fe_3O_4$
- Nanowires of Se

# Effects of US on Crystallization.

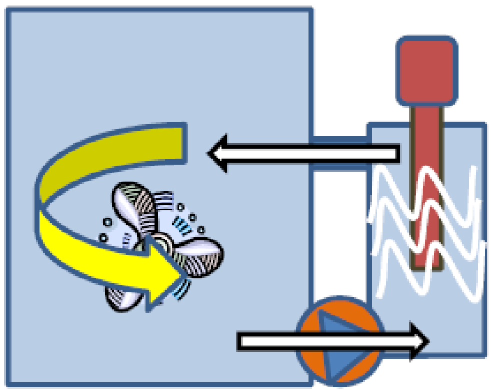
- Controls onset of crystallization (initiate seeding)
  - Cavitation bubbles acting as nuclei for crystal growth
- Controls subsequent crystal growth
- Produces more uniform crystals of designated homogenous crystal size
- Provides controlled and uniform crystallization speed throughout the super-saturated solution
- Produces a disruption of seed
  - increasing the number of nuclei present in the medium
- Prevents inclusions
- Prevents encrustation of crystals on cooling elements in liquids and hereby ensures continuous efficient heat transfer through cleaning action of cavitation.

# US Equipment.

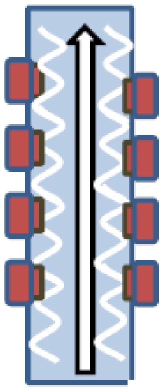
## Possible assemblies of US crystallization reactors



Batch processing
**closed system**



Batch processing
**recirculation system**

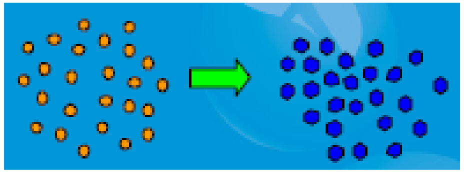


**Continuous** processing
open flow reactor

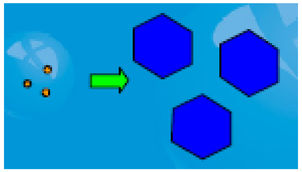
# Control of Crystal Size with Sono-crystallization.

ULTRASONIC TREATMENT OF A SUPERSATURATED SOLUTION

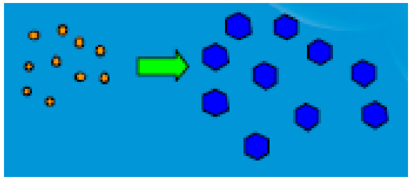
1. Continuous insonation produces many nuclei resulting in small crystals



2. Initial insonation produces finite nuclei which can be grown into large crystals

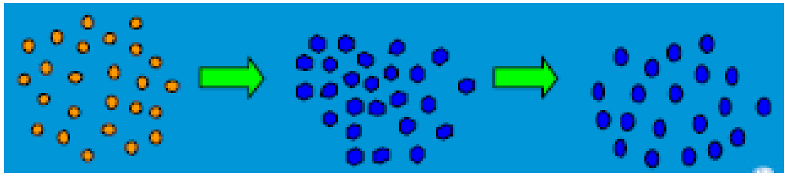


3. Pulsed insonation gives tailored crystal size



ULTRASONIC TREATMENT BEFORE AND/OR AFTER CRYSTALLIZATION

4. Continuous insonation throughout supersaturation produces many nuclei resulting in small crystals. Application of ultrasound thereafter can condition the crystals produced



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