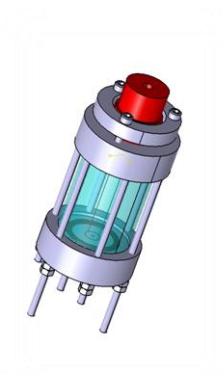
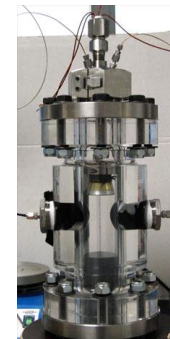
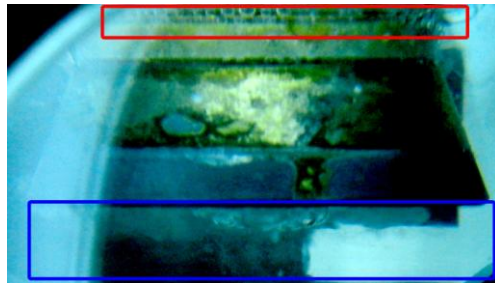
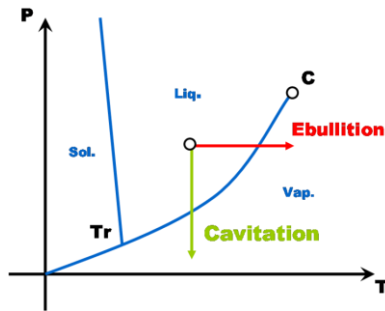


THERMODYNAMIC ANALYSIS OF HIGH-PRESSURE SONOREACTOR IMPACT OF CHOSEN TECHNIQS IN EFFICIENCY AND HEAT RELEASE PROBLEM

Bertrand GUATARBES, Laurent MARLIN, Guillaume BAREIGTS, Frederic PLANTIER

Laboratory of Thermodynamics and Energetics of Complex Fluids LFCR UMR 5150





Bubbles creation:

- Temperature increase: Boiling
- Pressure decrease: Cavitation

Cavitation, destructive effect but useful in nature and in industry:



→ Erosion

Pistol shrimp



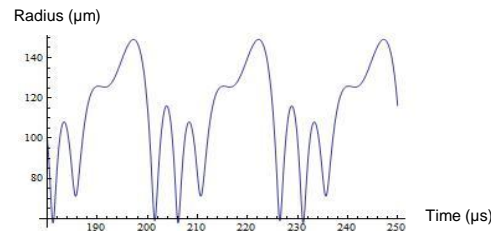
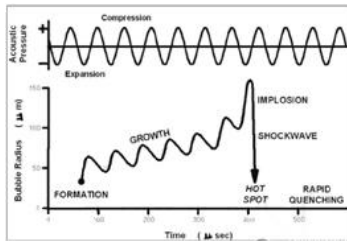
→



Acoustic cavitation

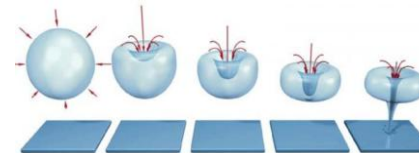


Sonochemistry* / Sonocrystallization...



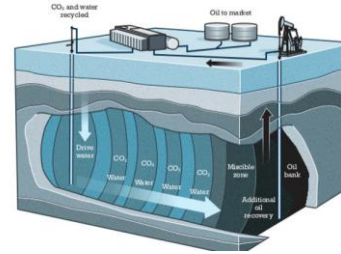
$$R \frac{dR}{dt} + \frac{3}{2} \dot{R}^2 = \frac{1}{\rho} \left(P_g - P_0 - P(t) - 4\eta \frac{\dot{R}}{R} - 2 \frac{\gamma}{R} \right)$$

*Bubble in instable state:
T ~ 10000 K and P ~ 1000 Bar*

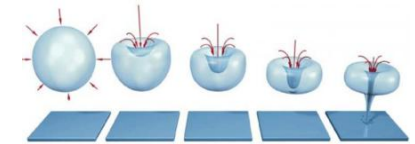




*Initial study:
Enhanced oil recovery **



Acoustic Cavitation



Problematic:

Study of acoustic cavitation at laboratory scale for high pressure till

150 Bar

***Development of
high-pressure
sonoreactor***



Utilization of piezoelectric transducer

$f_R = 40 \text{ kHz}$
 $P = 50 \text{ W}$
 $m = 286 \text{ g}$



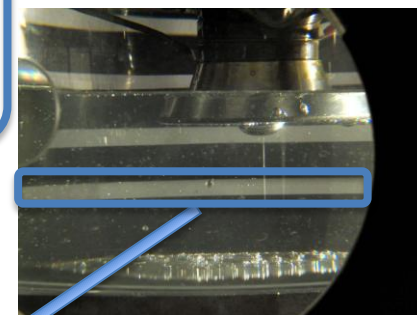
PZT Material
 Aluminum horn



Technique easier to enforce at ambient pressure* than at high-pressure

H₂O+CO₂ degassed in a crystallizer

main training plane of cavitation bubbles



Design of high-pressure sonoreactor:

Outside transducer



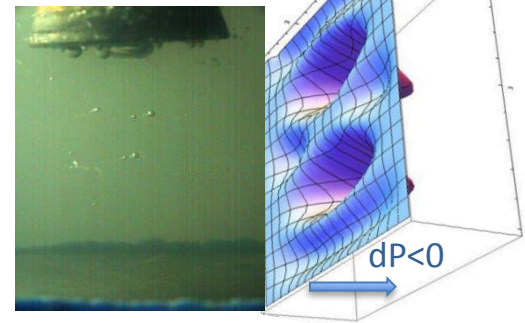
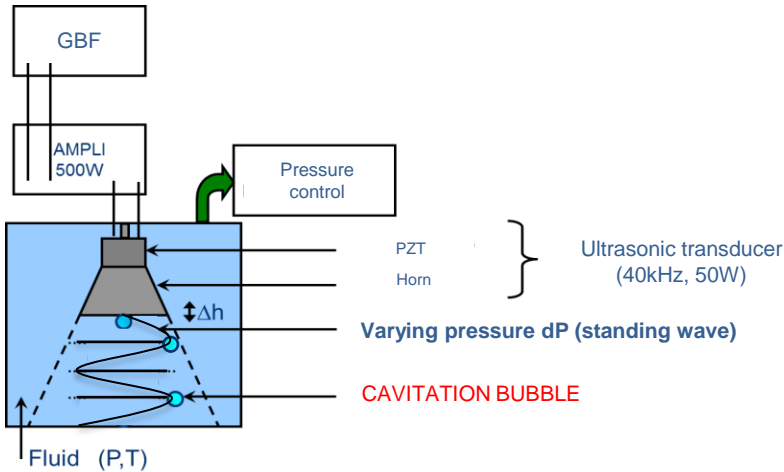
Impact
of
Temperature!

Inside transducer

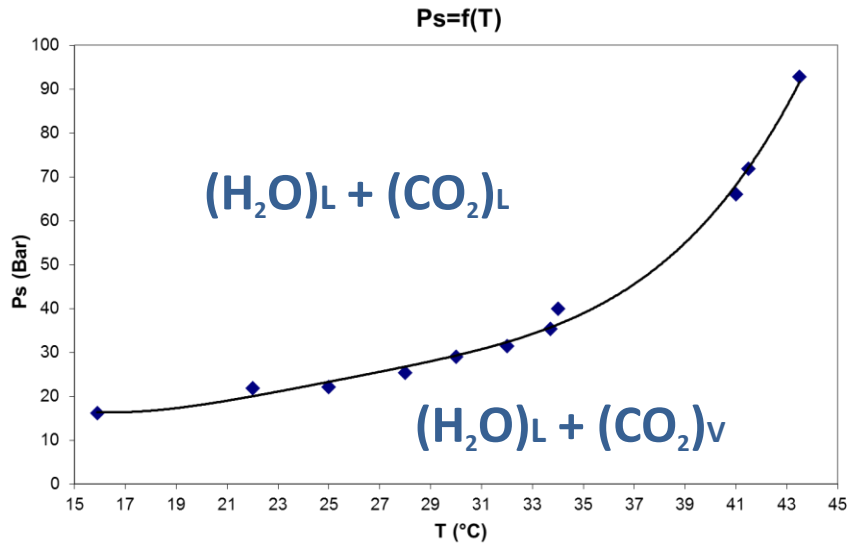


← Calorimetric study

Phenomenological study →

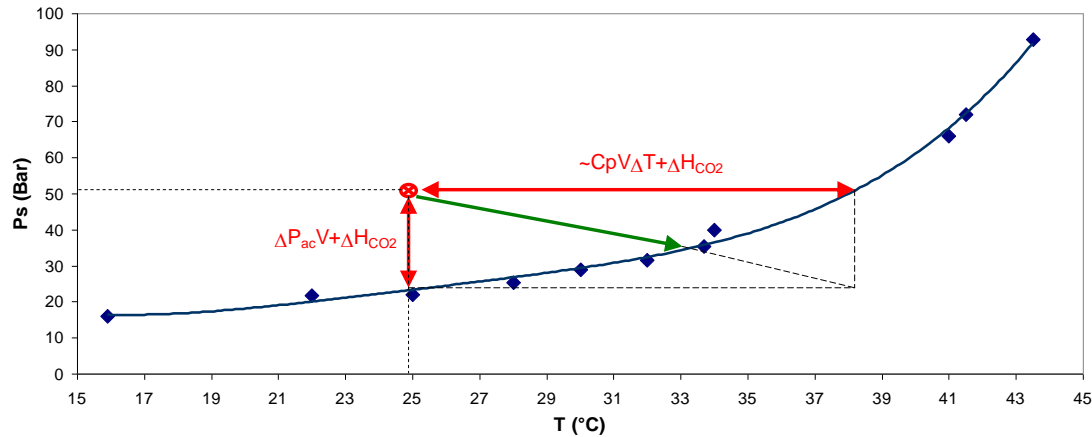


CO₂ dissolved in pure water



➔ Binary mixtures $\text{H}_2\text{O} + \text{CO}_2$
at (T, P_s)

Initial state of experiment
 $P_{ini} = P_s + dP$

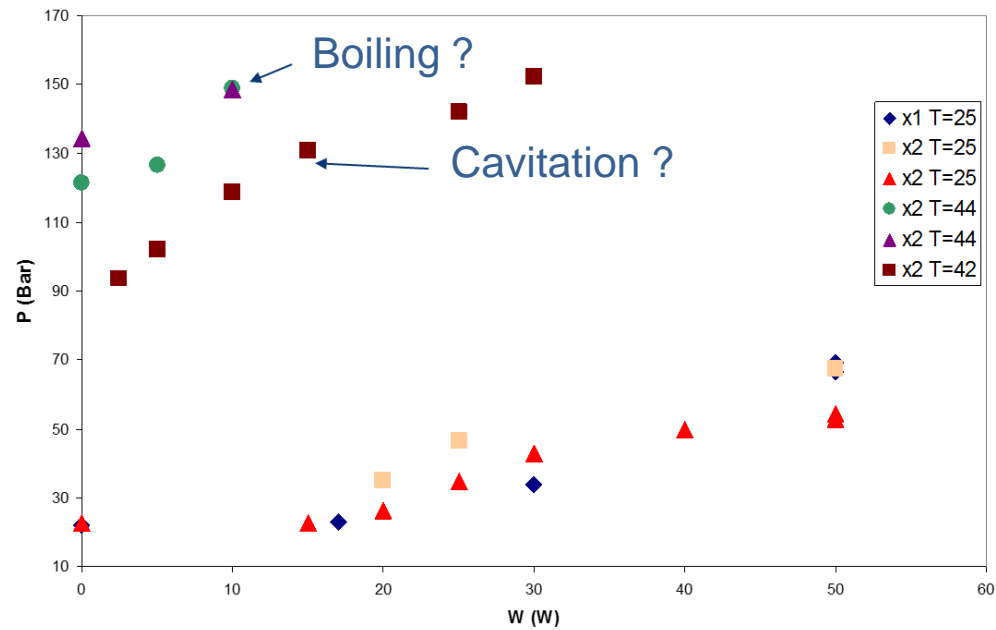


Switch on power W from 0 to 50W

Increase of pression → Degassing CO₂

Boiling or Cavitation Bubbles ?

$P=f(W)$

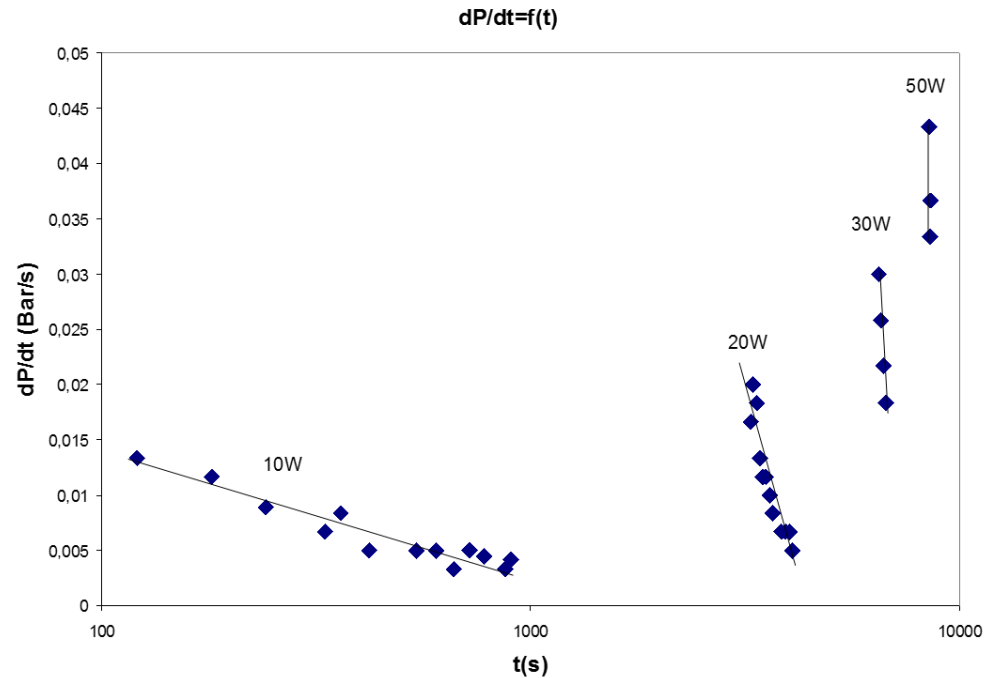


Impact of acoustic power for degassing

$$W + (P \cdot (dV/dt) + V \cdot (dP/dt)) = dU/dt$$

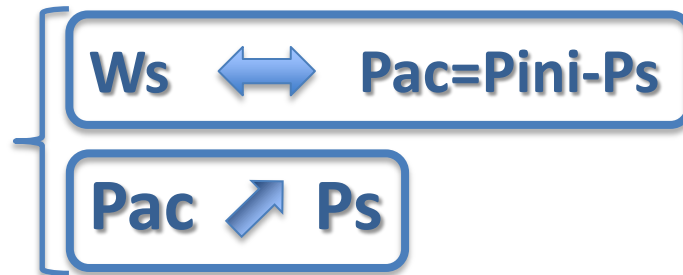
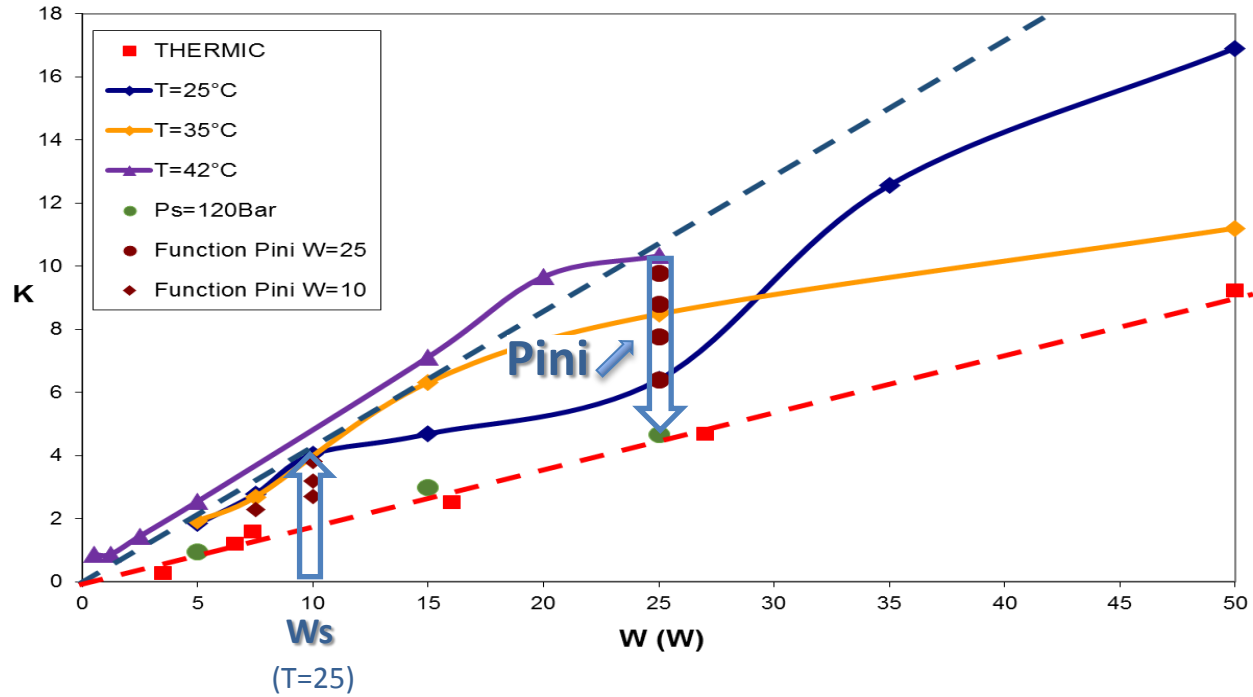


$$dP/dt(t) = f(\text{ultrasonic power})$$

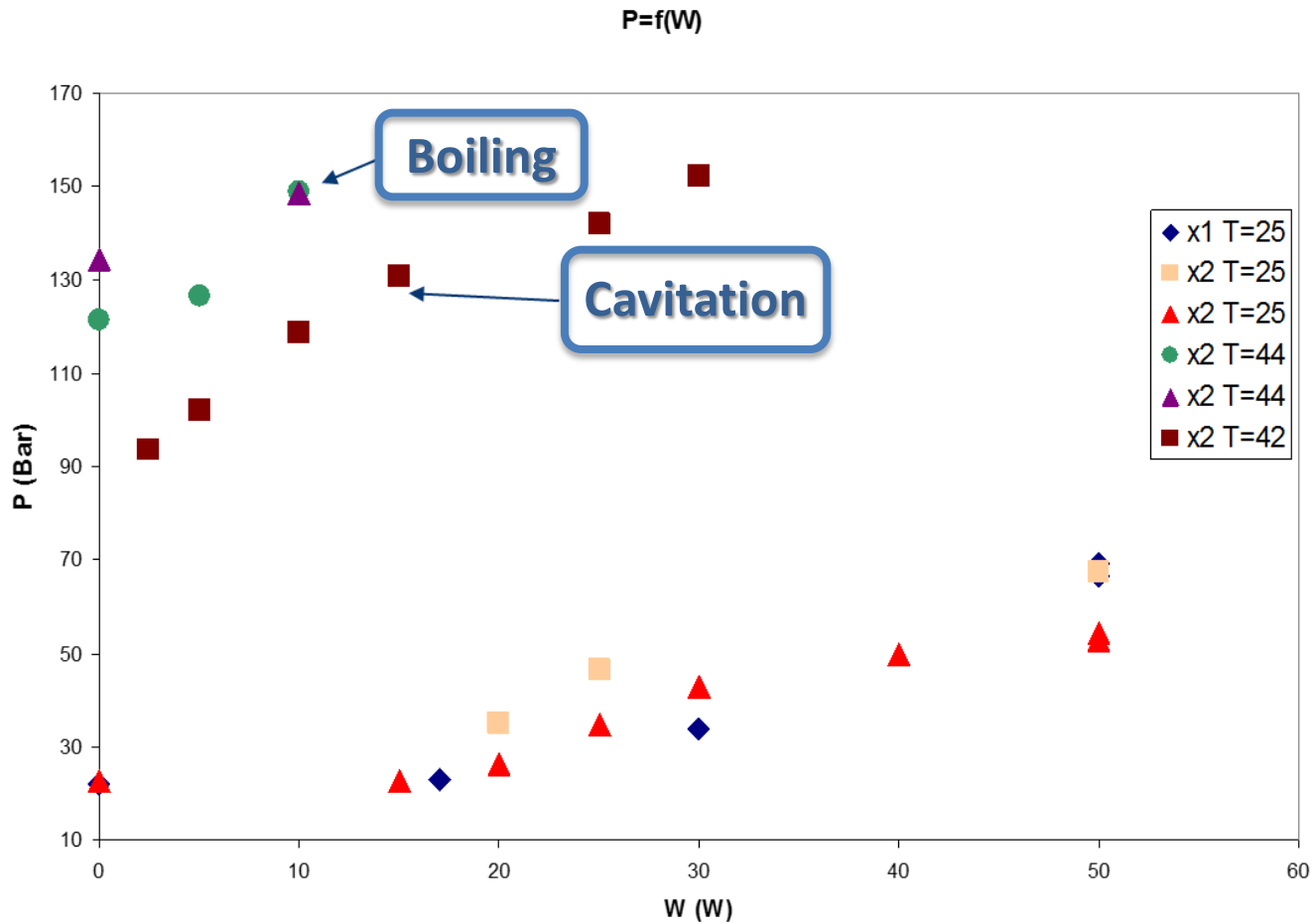


$$dP/dt = K(W) \cdot \ln(t/t_0)$$

K = Identification criterium of bubbles



Identification of bubble category



dPac/Ps for W=50W

Outside transducer



→ $dPac/Ps < 1/10$

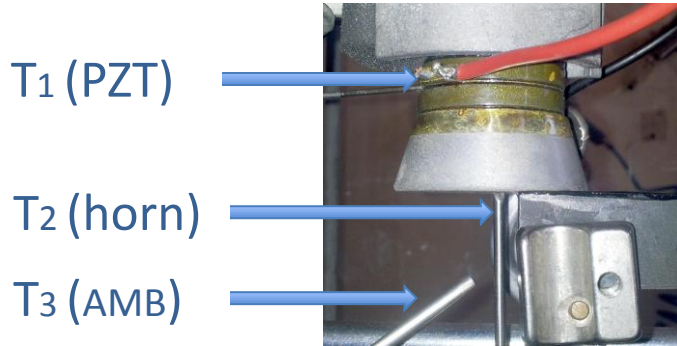
Inside transducer



→ $dPac/Ps \sim 1/2$

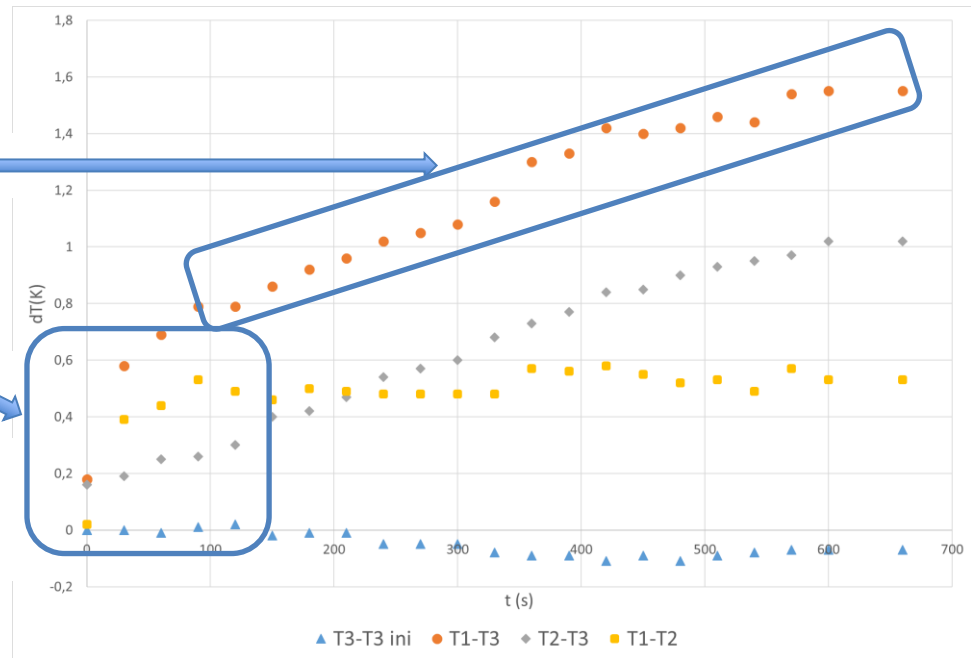
Inside transducer much better technicle for efficiency !

Thermic study of ultrasonic transducer



Increase of T

Rapid differential T

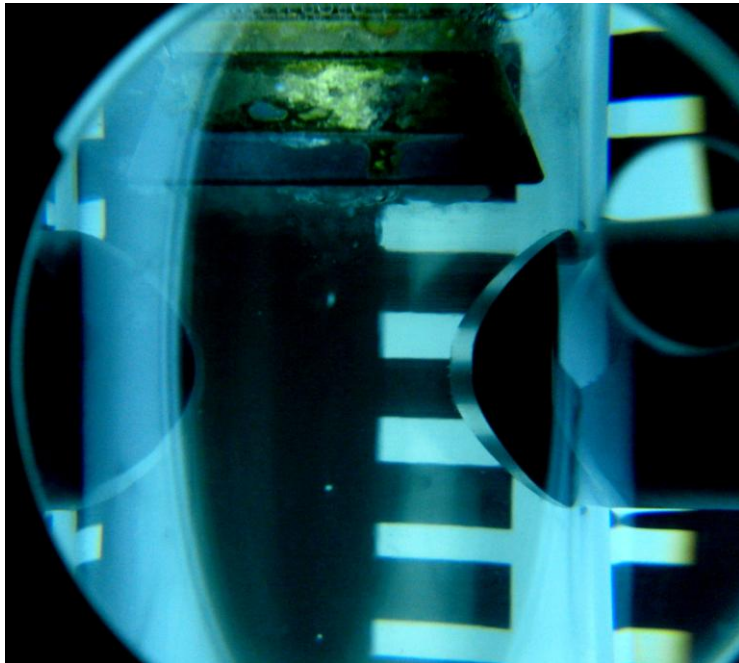


$$\text{Heat release/s} = W - m \cdot C_p \cdot dT/dt$$

$$\sim 50 - 0,9 \times 290 \times 0,01 \sim 48 \text{ J} \cdot \text{s}^{-1}$$

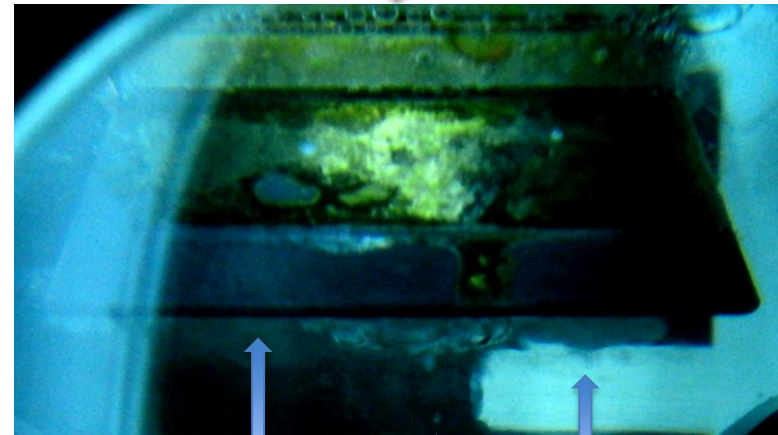
$$m (\text{H}_2\text{O}) = 600\text{g} \Rightarrow \text{Average } T \text{ increase} > 0,02 \text{ K} \cdot \text{s}^{-1}$$

Use of imaging to better understand



H_2O+CO_2 $P_{sat}(CO_2)=30\text{Bar}$ $T=25^\circ\text{C}$





Predominantly bubbles generated by boiling in contact with the PZT ceramic

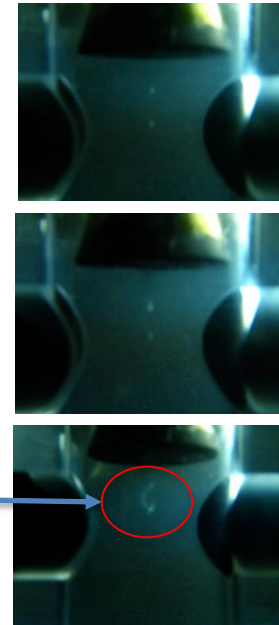


Predominantly bubbles generated by cavitation under horn and in liquid

A complex phenomenon !!!

possible evolutions
during the growth of bubbles

-  Archimedes' principle
-  Stable cavitation and streaming
-  Unstable cavitation
-  Coalescence



Coalescence of bubbles

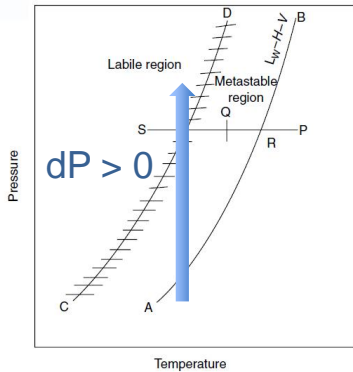
What is interesting for SONOCRYSTALLIZATION?

Sonocrystallization of gas clathrate, also a complex process*...

- ➡ Process used for a long time but little understood
 - ➡ Fundamental action: **nucleation** help (but counterproductive in growth phase)
 - ➡ Bibliography: several ways to analyze

1st vision of phenomenon

Local Supersaturation



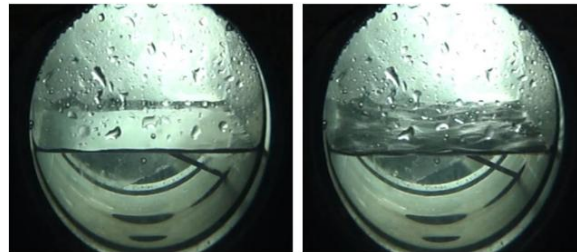
hydrate formation as a function of subcooling relative to the equilibrium line (AB) and the spinodal line (CD; supersaturation limit).

Clathrate Hydrates of natural gases 3rd edition

E. Dendy Sloan Carolyn A. Koh

2nd vision of phenomenon

Interface area increase between gas and liquid**



(a) 0W

(b) 150W

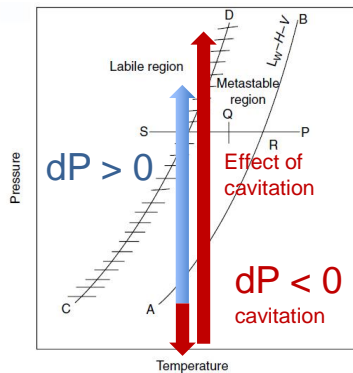
Surface photograph of the distilled water.

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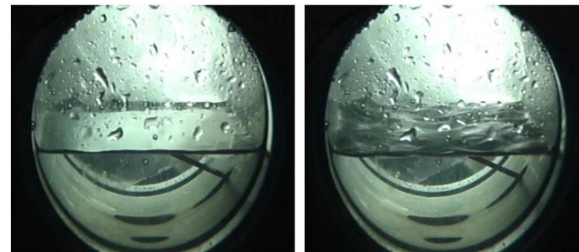
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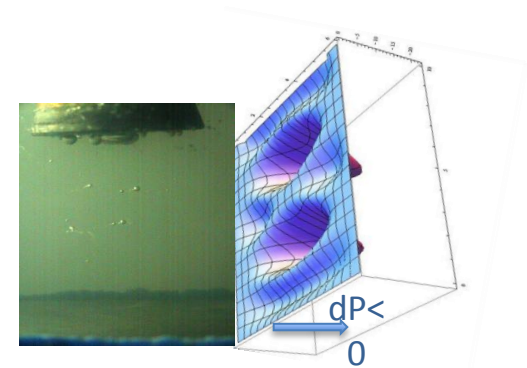
(a) 0W

(b) 150W

Surface photograph of the distilled water.

...

Primary reason ?



Local fall of pressure: cavitation

From simple emulsion to cavitation...

In order:

- Emulsion H₂O/Cyclopentane 640fr/s (=Slow motionX25)
- Comparison with/without ultrawave
- Emulsion H₂O/Cyclopentane 24fr/s
- Cavitation Cyclopentane 640fr/s
- Cavitation H₂O/CO₂ Ps=30Bar

Always presence of bubbles ?

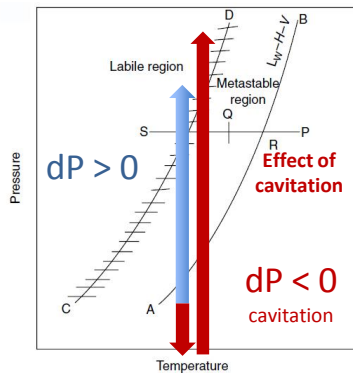


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Local Supersaturation



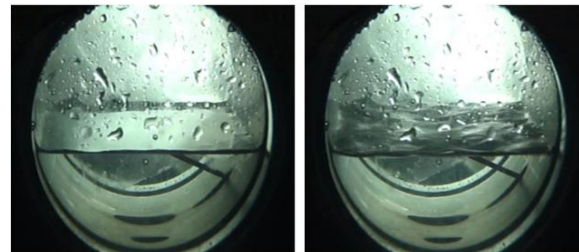
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Interface area increase between gas and liquid**



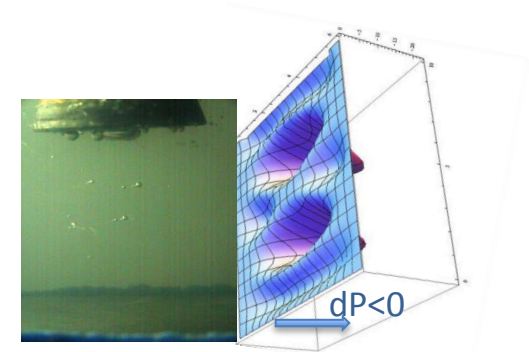
(a) 0W

(b) 150W

Surface photograph of the distilled water.

...

Primary reason ?



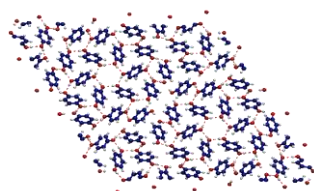
Local fall of pressure: cavitation

For sonocrystallization, heat release to avoid !!!

- ➔ **Strong difference of efficiency with inside and outside ultrasonic transducer**
- ➔ **With inside ultrasonic transducer: heat release problem**
- ➔ **In sonoreactors, different complex phenomenons**
- ➔ **Sonocrystallization, complex process with primary reason: cavitation ?**
- ➔ **For sonocrystallization, outside ultrasonic transducer better choice**

Sonocrystallization of CO₂ clathrate hydrate or organic

Gas Clathrate = Host molecule that traps guest molecule
(if host molecule H₂O = hydrate)



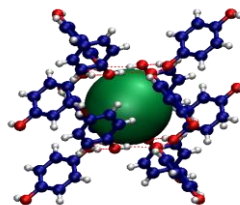
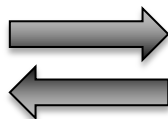
α-Hydroquinone

Native form,
stable under ambient
conditions of P and T



Guest Molecule

Ar, Kr, N₂, CH₄, Xe, H₂S,
CO₂, ...



β-Hydroquinone

Clathrate form,
Stable in presence of guest
molecule under ambient
conditions of P and T

Applications:

- CO₂ capture and separation
- Phase change materials

Development of new high-pressure sonoreactor without release heat problem

With ultrasound, can we promote synthesis ?



Thanks



Video at various speed acquisition (24 à 1200 frame/s)

In order:

Mixture $\text{H}_2\text{O}/\text{CO}_2$ $P_s=30\text{Bar}$

- Slow motion (X4)

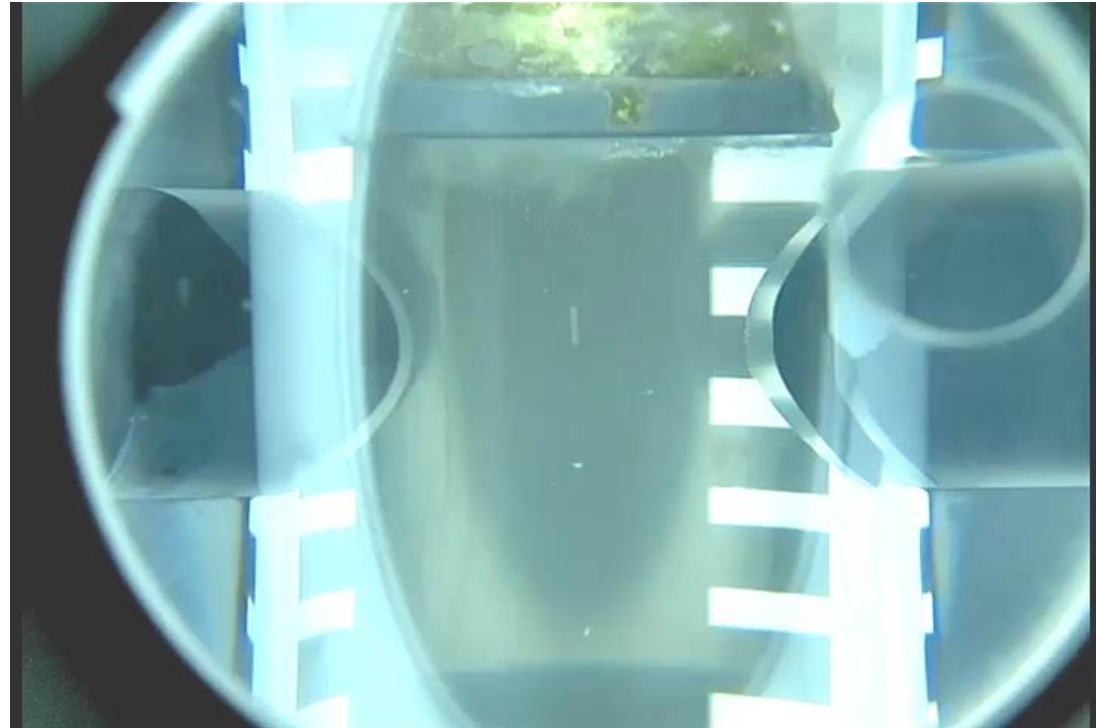
(Stationary bubbles, streaming, coalescence)

- Normal speed

- Central bubble 1200im/s neon light (cycle 0,01s)

- Central bubble 1200im/s zoom

(homogeneous nucleation, coalescence)



$\text{H}_2\text{O}+\text{CO}_2$, $P_{ini}=P_s(\text{CO}_2)=30\text{Bar}$