Energy and mass transfer in gas-liquid reactors.

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Why Energy Studies?

Energy input controls the flows established in a reactor.

Liquid Circulation

Residence time distributions.

Energy develops turbulence.

Global energy input to gas liquid systems relates:

Mass transfer rates ($k_L a \propto \varepsilon_M^{\alpha 1} * v_s^{\beta 1}$)

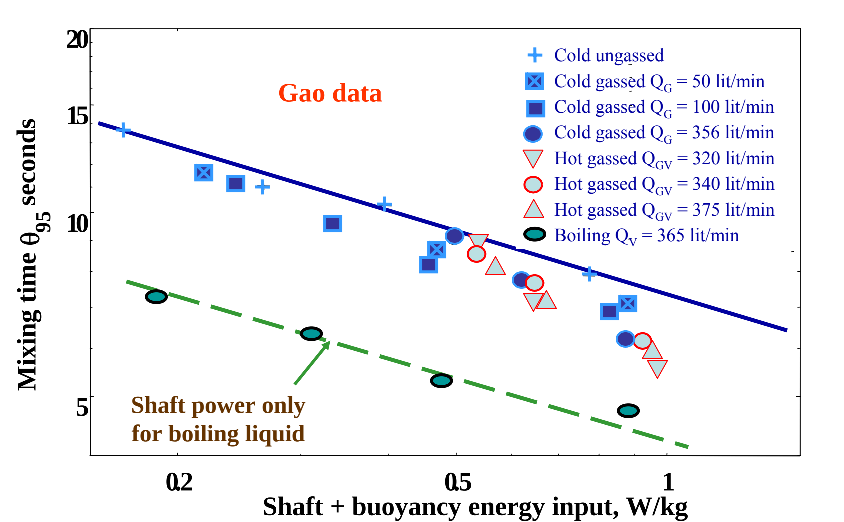
Retained gas fraction ($\varepsilon_G \propto \varepsilon_M^{\alpha 2} * v_s^{\beta 2}$)

Local energy input and the rate of micromixing

controls selectivity of complex single phase reactions.

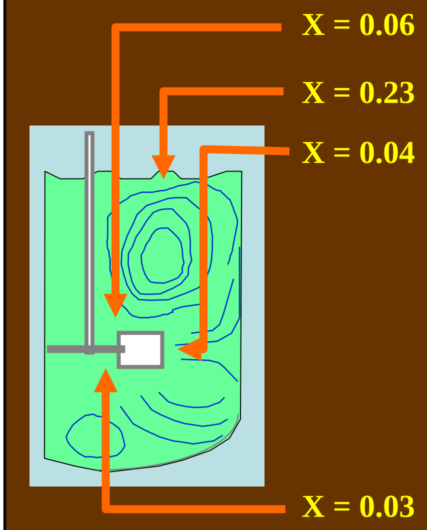
The distribution of energy input and the effects on micromixing in gas-liquid systems have not been considered in detail.

Macromixing times, total power basis, single CD-6



Mixing is about twice as fast if truly boiling than when sparged.

Selectivity in single phase reactions, typical results.



The selectivity (proportion of unwanted secondary product) highlights the potential losses from poor design or operation.

There is significant cost in making and disposing of 23% of unwanted product.

Process yield is improved from 77% to 97% by using a dip feed pipe at points of intense energy dissipation.

Energy dissipation in gas – liquid reactors

The second phase affects the energy distribution of the system.

Localised dissipation may affect selectivity.

1. At the point of gas injection or vapour generation.
2. During bubble rise.
3. As bubbles burst at the free surface.

There are also important differences between truly boiling and gas evolving or sparged systems

Boiling systems

Vapour generation in an unsparged boiling reactor occurs

1. near the free surface,
2. where there is local superheat, e.g. around heating elements or in regions of low pressure near impeller blades,
3. as evaporation removes heat of reaction.

Bubbles are usually not stable at great depth.

The rise in liquid surface level resulting from bubble formation does not greatly alter the potential energy of the system.

Thermal mixing in turbulent reactors

Turbulent mixing times are generally short; thermal equalisation may limit local temperature differences to less than 1 deg C

Near 1 bar, hydrostatic pressure increases the BP of water by about 3 ^{o}C per metre of submergence.

At **1 bar** operating pressure, **0.3 ^{o}C superheat** therefore allows bubbles to survive only to a **depth of about 10 cm**.

BUT NOTE

the corresponding depth at **10 bar**, (~175 ^{o}C) is **~ 70 cm.**

In large, high pressure reactors, vapour bubbles will be distributed over a greater depth, more like conditions in a sparged reactor

Cavitation number and local pressure

The vapour pressure of boiling liquid is the same as that at the free surface, P_o. Cavitation can occur within the liquid if the local pressure is below P_o, usually only close to the impeller.

The pressure at a stationary impeller at a depth S is $(P_o + \rho g S)$. Impeller motion (tip velocity v_t) modifies the local pressure field by amounts proportional to $^1/_2\ \rho v_t^2$

The agitation cavitation number is the ratio between the <u>reduction in pressure</u> that permits cavitation, and the <u>local changes</u> generated by impeller motion.

$$\boxed{\frac{2gS}{v_t^2}}$$

Bubbles released from a cavitating impeller are likely to collapse.

Incoming gas and potential energy.

Q_G $m^3 s^{-1}$ of gas or vapour introduced at depth S in liquid of density ρ_L raises the free surface.

Potential energy increase $= Q_G * \rho_L * g * S$

At high gas loadings this may exceed the shaft power.

It will be further increased by expansion due to evaporation

The kinetic energy of the sparged gas can usually be neglected.

Perhaps the kinetic energy of displaced liquid should not be.

Sparging into hot liquids

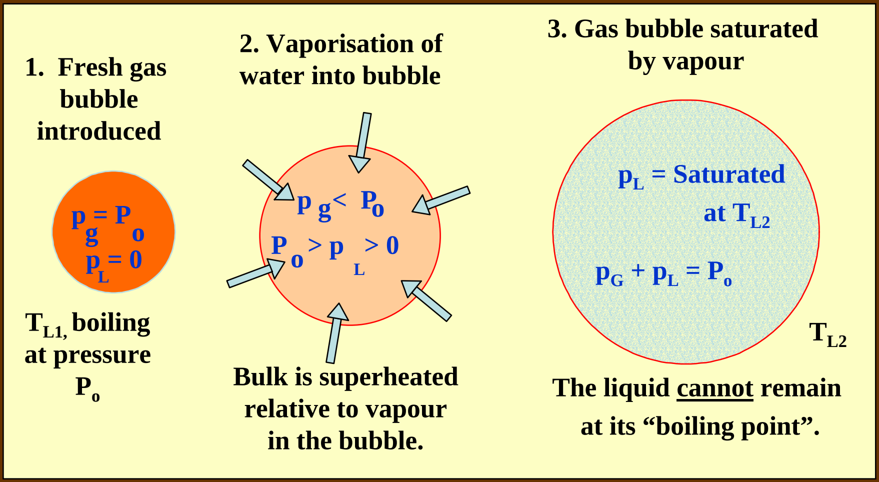
Evaporated vapour adds to the volume of gas entering the reactor.

The liquid temperature (vapour pressure) important.

If the (vapour free) gas volume rate is Q_V at a total pressure of P_0 with a liquid vapour pressure of p_L, the partial pressure of the injected gas in a saturated bubble will be $p_G = (P_0 - p_L)$.

True gas volume rate = $Q_V * P_0 / (P_0 - p_L)$

Injection of Gas into Boiling Liquid



1. Fresh gas bubble introduced

$p_g = P_o$

$p_L = 0$

$T_{L1,}$ boiling at pressure P_o

2. Vaporisation of water into bubble

$p_g < P_o$

$P_o > p_L > 0$

Bulk is superheated relative to vapour in the bubble.

3. Gas bubble saturated by vapour

p_L = Saturated at T_{L2}

$p_G + p_L = P_o$

T_{L2}

The liquid <u>cannot</u> remain at its “boiling point”.

What determines liquid temperature?

Usually the off gas is saturated or very nearly so.

The temperature of the bulk is

determined by the balance between

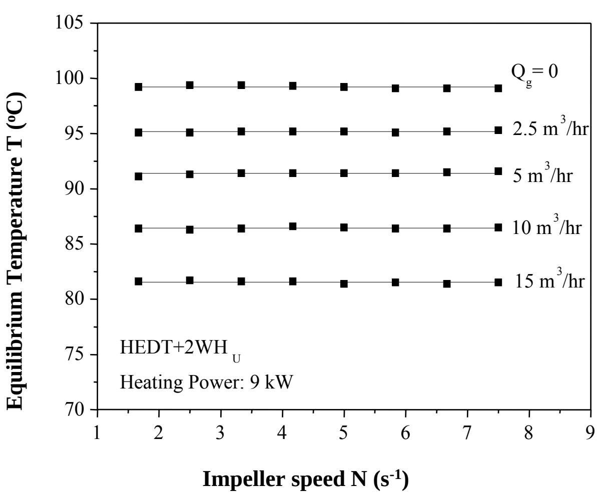
(a) heat SUPPLY (reaction and/or heating)

(b) heat removal as LATENT HEAT of evaporation.

The bulk temperature is not dependent on stirring rate.

The liquid temperature <u>does</u> depend on gas rate.

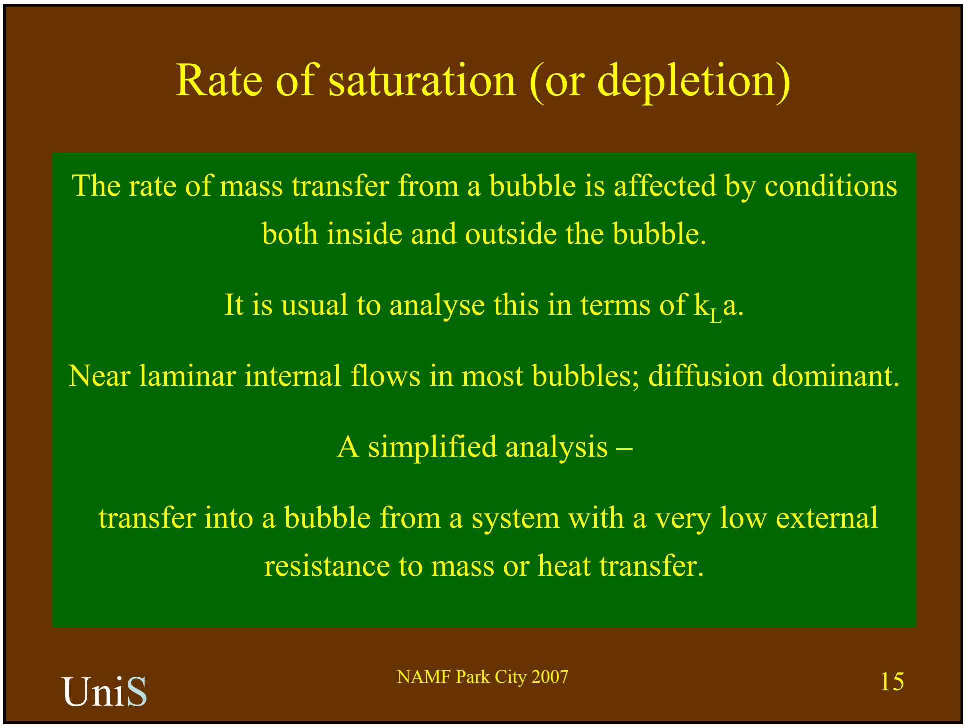
Hot sparging at constant heat input



This experimental result for a reactor with three impellers on a common shaft, (Bao, et al., 2007,) is consistent with rapid saturation of the gas.

The liquid side resistance to heat transfer is therefore not significant.

A similar result may apply to mass transfer



Rate of saturation (or depletion)

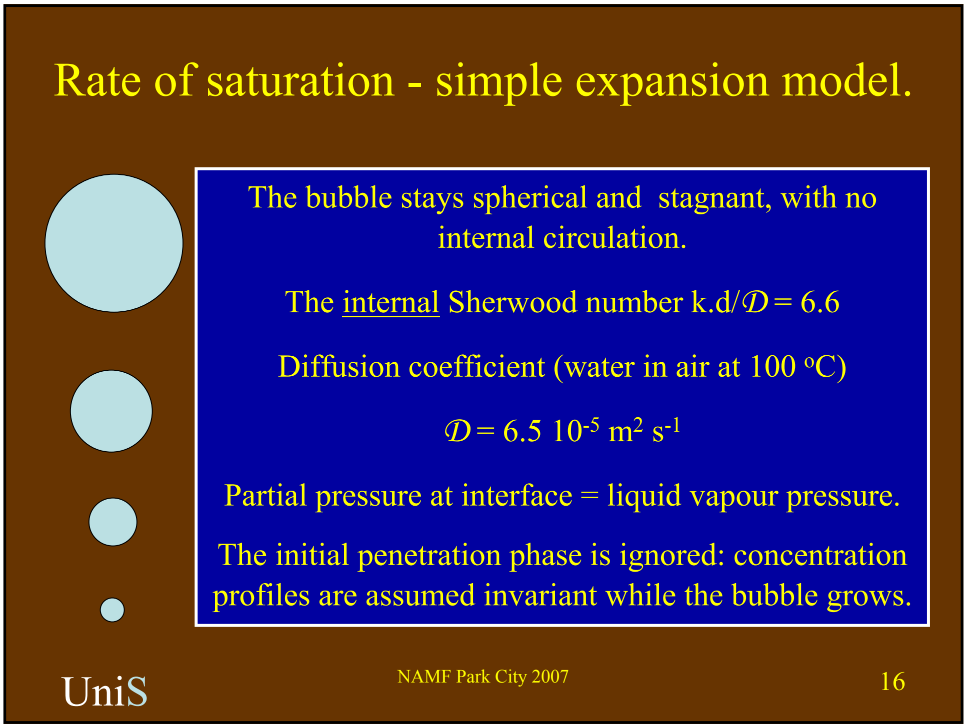
The rate of mass transfer from a bubble is affected by conditions both inside and outside the bubble.

It is usual to analyse this in terms of $k_L a$.

Near laminar internal flows in most bubbles; diffusion dominant.

A simplified analysis –

transfer into a bubble from a system with a very low external resistance to mass or heat transfer.



Rate of saturation - simple expansion model.

The bubble stays spherical and stagnant, with no internal circulation.

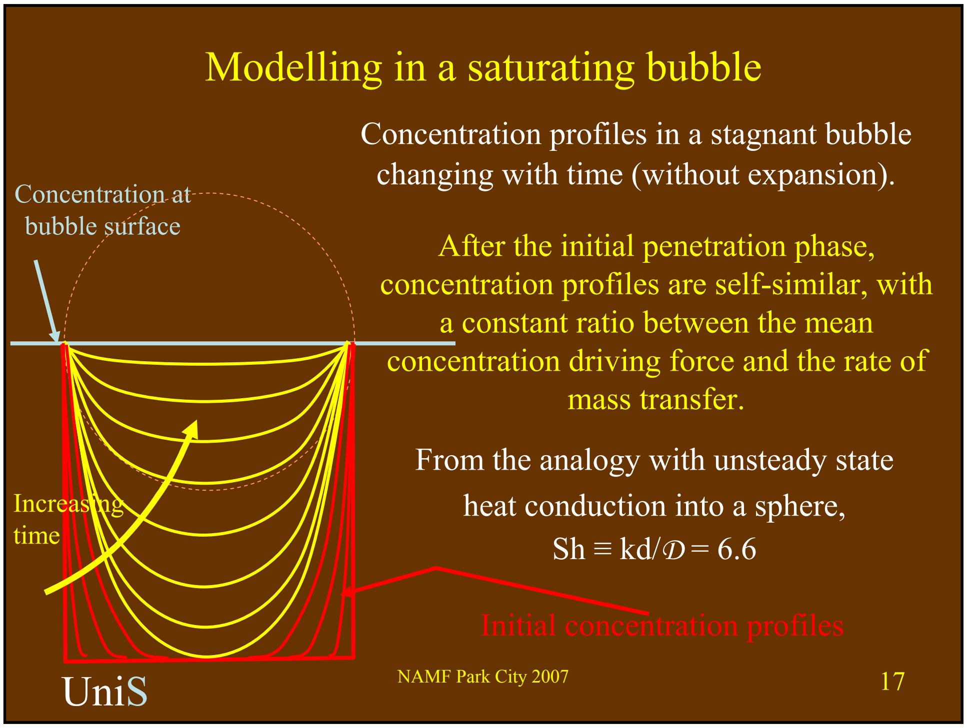
The <u>internal</u> Sherwood number $k.d/\mathcal{D} = 6.6$

Diffusion coefficient (water in air at 100 °C)

$\mathcal{D} = 6.5\ 10^{-5}\ m^2\ s^{-1}$

Partial pressure at interface = liquid vapour pressure.

The initial penetration phase is ignored: concentration profiles are assumed invariant while the bubble grows.



Modelling in a saturating bubble

Concentration at bubble surface

Increasing time

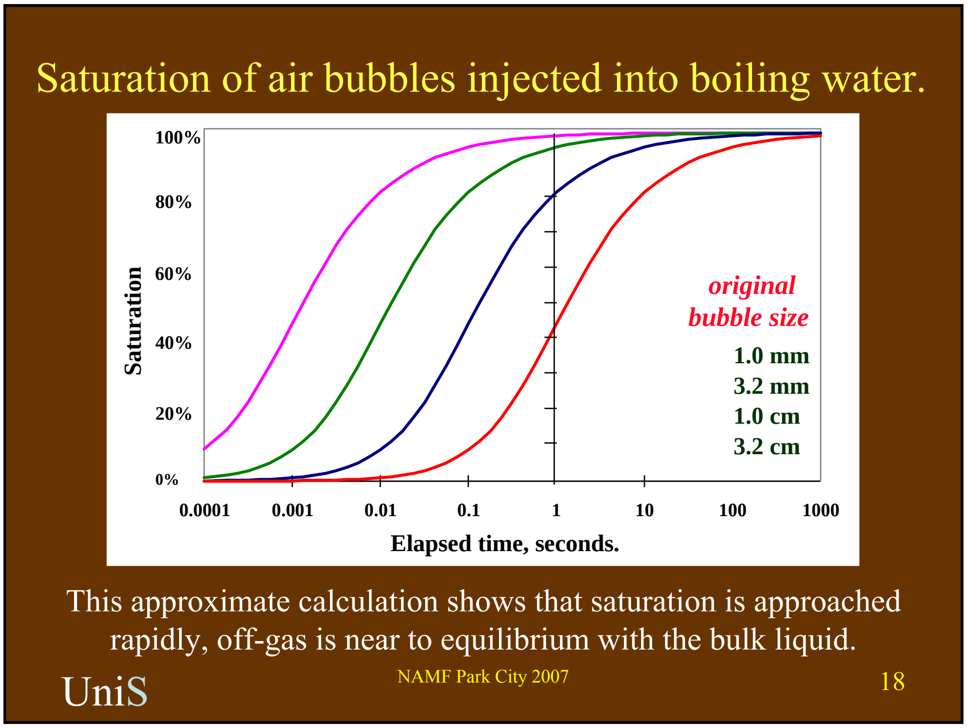
Concentration profiles in a stagnant bubble changing with time (without expansion).

After the initial penetration phase, concentration profiles are self-similar, with a constant ratio between the mean concentration driving force and the rate of mass transfer.

From the analogy with unsteady state heat conduction into a sphere,

$\mathrm{Sh} \equiv kd/\mathcal{D} = 6.6$

Initial concentration profiles



Saturation of air bubbles injected into boiling water.

This approximate calculation shows that saturation is approached rapidly, off-gas is near to equilibrium with the bulk liquid.

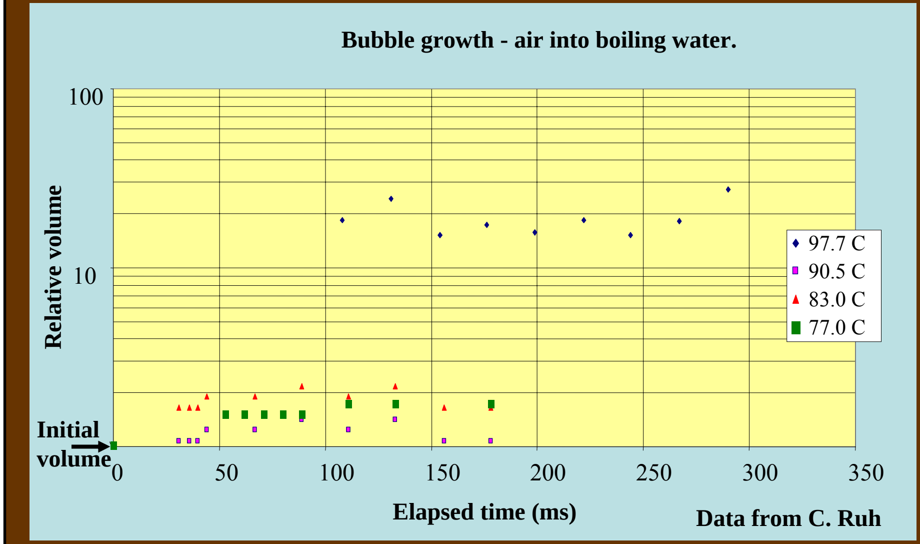
Experimental

Air carried by a mercury stream is injected into hot water and their release and subsequent growth followed with high speed video at ca 1000 pps.

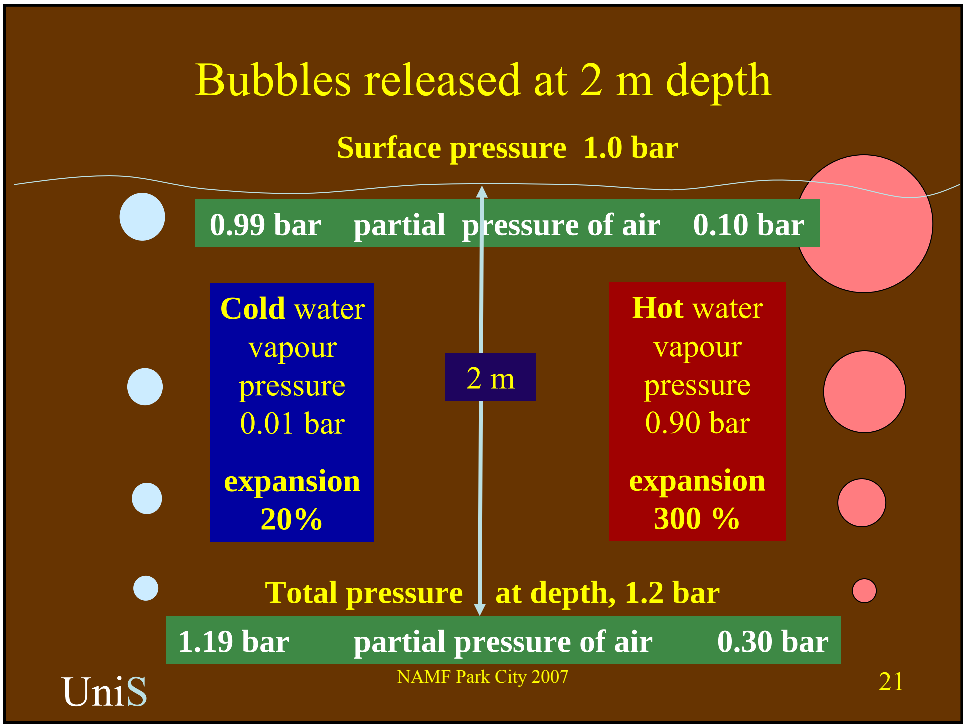
Original bubbles in the range 0.7 to 1 mm diameter

Experiment was unsuccessful in detail though the images are sufficient to confirm the rapid saturation of the bubbles.

Ruh experiment air in mercury jet into hot water



Data from C. Ruh



Bubbles released at 2 m depth

Surface pressure 1.0 bar

0.99 bar partial pressure of air 0.10 bar

Cold water vapour pressure 0.01 bar

expansion 20%

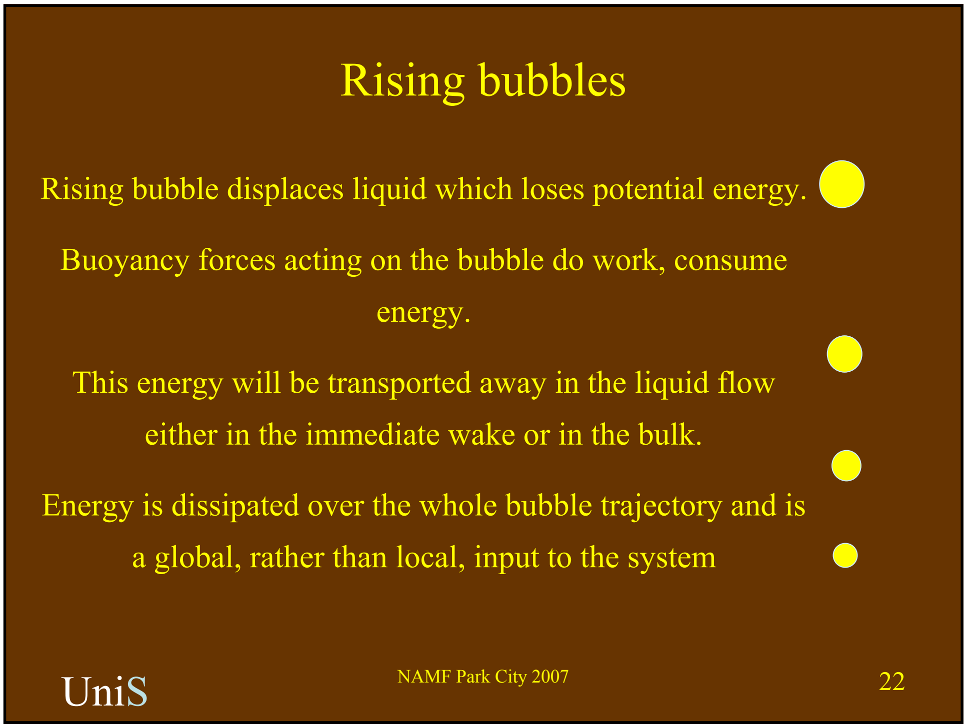
2 m

Hot water vapour pressure 0.90 bar

expansion 300 %

Total pressure at depth, 1.2 bar

1.19 bar partial pressure of air 0.30 bar



Rising bubbles

Rising bubble displaces liquid which loses potential energy.

Buoyancy forces acting on the bubble do work, consume energy.

This energy will be transported away in the liquid flow either in the immediate wake or in the bulk.

Energy is dissipated over the whole bubble trajectory and is a global, rather than local, input to the system

Bubbles bursting at the free surface

When a bubble of film thickness δ bursts, the surface energy is concentrated (at least momentarily) in the mass of liquid contained in the film, $\rho_L * \delta * A$.

A two-sided liquid film has a surface energy of $2\gamma * A$. If

$\gamma \approx 70$ mN m^{-1}, a half bubble of 1cm diameter bursting at the surface releases about 280 J kg^{-1}

If $\delta \approx 0.5$ µm and bursting takes 10 ms, 28 kW kg^{-1} is released.

Integrity of fragile particulates? Rapidity of micromixing?

Thickness of bubble film at burst?

Consequences for boiling liquids.

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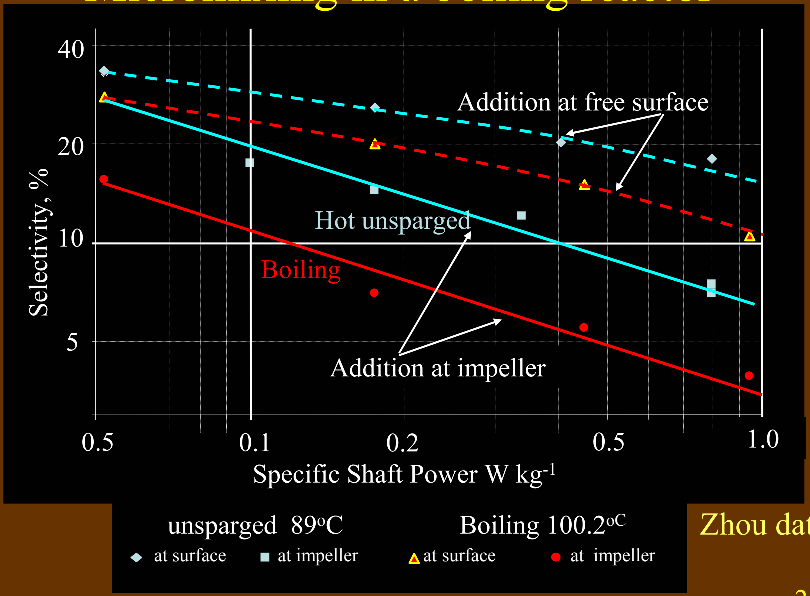
Micromixing in a boiling reactor



Zhou data

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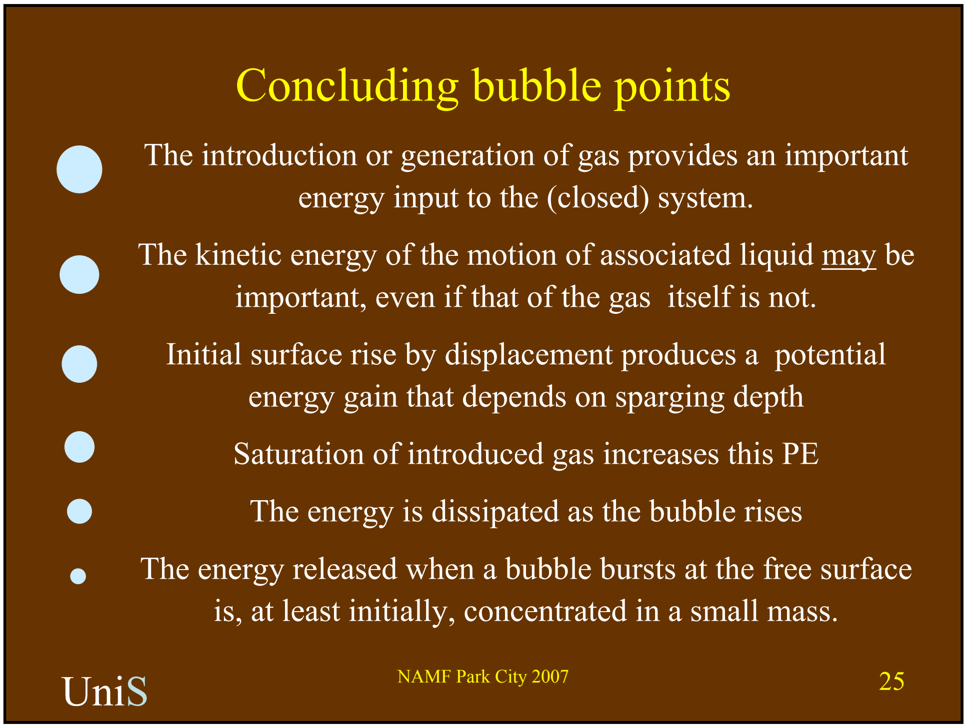

Concluding bubble points

- The introduction or generation of gas provides an important energy input to the (closed) system.
- The kinetic energy of the motion of associated liquid may be important, even if that of the gas itself is not.
- Initial surface rise by displacement produces a potential energy gain that depends on sparging depth
- Saturation of introduced gas increases this PE
- The energy is dissipated as the bubble rises
- The energy released when a bubble bursts at the free surface is, at least initially, concentrated in a small mass.