Towards energy efficient nanobubble generation with fluidic oscillation
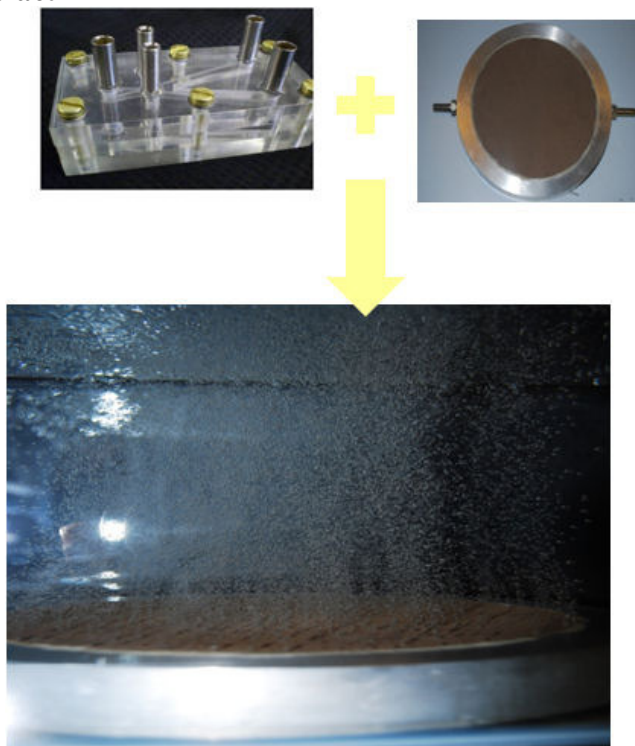
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Graphical Abstract

Caption: Recently, a 70+ year old problem in chemical engineering has been addressed: How to make the bubbles on the scale of the pore? Conventional nozzles produce bubbles from steady flow that are an order of magnitude larger than the hole from which the bubble emerged, and then coalescence generates larger bubbles still. Fluidic oscillation with a microporous (or nanoporous) diffuser system – an array of pores – produces bubble clouds on the size of the pore, so far down to the 20 micron scale. The bubbles are produced in an energy efficient way, since in any injection system, the cost of blowing the gas into the liquid must be incurred. With fluidic oscillation, the microbubble production is actually less energy consumptive than steady flow of the same rate producing larger size bubbles, by about 20% at best. This paper investigates the possibility of producing energy efficient nanobubbles and speculates on their potential value. The graphic should be interpreted as "fluidic oscillator" + "microporous diffuser" = "microbubbles on the size of the pore."

Abstract

Nanobubbles are a mystery as to their stability and longevity. So far their uses are limited to high value applications, such as medical imaging and controlled drug delivery and release.   The current methods of nanobubble generation and

understanding of nanobubble interfacial structure are reviewed. The analysis of the potential benefits of nanobubbles leads to the conclusion that if energy efficient nanobubbles that were flexible in injection and production were available, there would be widespread usage. The hypothesis that a recent methodology for energy efficient microbubble generation could be extended to nanobubble generation is presented and reviewed. The current applications and promising potential applications for energy efficient microbubbles are discussed, ranging from bioreactors to dispersal of ozone, through flotation separations and enhanced chemical reactions by reactive separation.

1. Introduction

Microbubbles have been a "hot topic" in engineering applications since the mid 1990s. However, the widespread, low cost, energy efficient production of microbubbles has been elusive, and generally limited their use to operations that cannot be achieved any other way. Nanobubbles have been a mystery as to their longevity and structure, but have mostly been limited to medical applications of ultrasonic imaging and ultrasound-mediated drug delivery, which are very high value uses that may have no other competing technology. The limitations to more widespread use are clear – ease of production, cost of the equipment, and energy efficiency of their production. In this paper, the trajectory of miniaturization of energy efficient microbubbles towards nanobubbles is reviewed. The paper is organized as follows. The recent explosive advances in nanobubble "sightings" and physic-chemical structure are reviewed in this section, along with their generation mechanisms. Section 2 reviews energy efficient microbubble generation by fluidic oscillation. Section 3 reviews the recent promise in innovations due to the advent of energy efficient microbubbles and the prospect of nanobubbles. The last section discusses the major themes and draws the conclusions to the paper.

§1.1 The benefits of nanobubbles

Nanobubbles are defined by their diameter – less than one micron and larger than a nanometer. However, the most distinguishing feature of a nanobubble is longevity. This longevity has two aspects. The obvious one is the virtual disappearance of buoyant force. Bubbles smaller than about 5 microns in diameter do not rise, since the buoyant force is smaller than any current in the liquid, and also swamped by the repulsive forces of such bubbles with each other and other interactive forces. The second, less obvious, aspect of longevity is physical stability: such bubbles do not dissolve away. They are a heterogeneity that is preserved, much like imperfections in a crystalline structure. The liquid molecules readjust their activities without interference with the heterogeneous regime. Nanobubbles, once formed, are highly persistent. This is both a blessing and a curse. The benefit that nanobubbles bestow are permanently within the system. Then again, the contents of the nanobubble are difficult to extract from the system once they are captured. The physical chemistry of this longevity is an observational mystery that is now attracting considerable attention. Ohgaki et al. [1] have prepared nanobubble solutions and studied the interfacial structure. Attenuated total reflectance infrared spectroscopy showed that the surfaces of the nanobubbles contain hard hydrogen bonds that may reduce the diffusivity of gases through the interfacial film. This is consistent with observations by Parkinson et al., [2], of single microbubble rise dynamics experiments with several gases, with the interesting result that the composition does matter in the sub

100micron size regime. Hence interfacial composition and structure are the likely explanation for the longevity of nanobubbles.

By comparison with microbubbles and fine bubbles, nanobubbles have very small carrying capacity. Where the fine bubble quite often leaves the system having transferred only a small fraction of its "cargo", the microbubble, due to its small carrying capacity and high transfer rates (surface area per unit volume increases with diameter), frequently becomes capacity-limited (Bredwell and Worden[3]; Worden and Bredwell [4]). Inevitably, transfer with microbubbles is a transient process, whereas the historic models of gas-liquid transfer processes assume pseudo-steady state (Bailey and Ollis [5]). With nanobubbles, transfer rates are enormous, so in fact, the delivery of bulk materials with nanobubbles is expensive. Yet, even nanobubbles expensively produced with high energy density techniques have high transfer efficiencies and performance (Masayoshi [6]). Nevertheless, quite a lot of the biomedical uses of nanobubbles stem from their ability to deliver materials in a controlled fashion. The migration of nanobubbles can be directed by ultrasonic fields, and their interfaces can be loaded with surfactant materials that are held by high interfacial affinity. Watanabe et al. [7] illustrate this paradigm beautifully by delivering genetic materials with ultrasound – a non-viral "vector" for genetic engineering. Controlled release of materials can be achieved optically with plasmonically induced nanobubble rupture (Anderson et al. [8]). Nanobubbles are also very useful for ultrasound imaging, providing the compressible surface for reflection of the irradiated waves. Imaging of tumors by a mixture of nanoparticles and nanobubbles, stabilized by block co-polymers, has proven a successful technique for medical diagnostics (Rapaport [9]).

For biomolecular separations, very small bubbles, termed aphrons, have shown particularly useful extraction properties. Lye and Stuckey [10], for instance, report large mass transfer coefficients in the extraction of erythromycin using colloidal *liquid* aphrons, an emerging technique for the recovery of microbial secondary metabolites, such as antibiotics in pre-dispersed solvent extraction (PDSE) processes. More typically, nano and microbubbles at the micron scale form colloidal *gas* aphrons are used for gas phase extraction, such as for lactoferrin and lactoperoxidase from sweet whey (Fuda et al. [11]). Protein separations are typically by interfacial affinity, rather than phase transfer. For instance, Noble et al. [12] showed that protein affinity to foams was largely chemical interactions, but to gas aphrons, electrostatic and hydrophobic interactions dominated. Oil recovery could benefit from gas-lift technology if sufficiently small microbubbles can be generated in situ downhole (Guet and Ooms [13]), driving such innovations as new pump cavitation mechanisms (Samuel and Saveth, [14]).

Most current applications for nanobubbles are high value added activities – such as drug delivery – for which the cost of production is a secondary issue. If energy efficient, low cost nanobubbles were available, commodity applications many be found that depend on the existence of the "permanent" heterogeneity in the liquid at the uniformly dispersed nanobubble sites. For instance, steam forms from nucleate boiling at flaws in the heat transfer surface in power stations, which are localized on the boundaries. This situation can lead to rapid local steam rising which can be explosive. "Homogeneous" nucleation – uniformly distributed in the liquid by nanobubbles – would be inherently much safer. Similarly, nucleation of crystals is

often seeded by impurities in the liquid medium. The high surface energy at imperfections in solid surfaces are attractive somehow at templating the pre-crystalline state and forming nucleates.

Nanobubbles have very large surface energies (estimates of MPa internal pressure due to the Young-Laplace equation driven by very steep curvature), and hence mimick solid surface imperfections. Typically, larger bubbles demonstrate substantial deformation and hence fascinatingly complex shapes (Celata et al. [15]). At nanoscales, the assumption is that the bubbles are nearly spherical, but given the scale of the interfacial Gibbs free energy, the fluctuations in surface energy must also be very large. Solutocapillary and thermocapillary effects (Zimmerman et al. [16]) are proportional to the gradients of surface tension, hence small concentration and temperature fluctuations induce very large surface energy fluctuations in nanobubbles. Consequently, nucleation of crystals should be enhanced with seeded nanobubbles. Similar to the lauded catalysis effects of nanoparticle activity, nanobubbles, with such large surface energies and fluctuations, could serve as uniformly distributed catalysis sites, particularly suited to two-phase reactions and for surfactant mediated catalysis.

Another application where cheap, energy efficient nanobubbles could contribute is surge protection in pumped systems like long liquid pipelines. A small fraction of dispersed bubbles serve to mitigate surge waves, as the interfacial dynamics provide another mode of oscillatory motion that diverts the kinetic energy, slowing down the surge wave. In quantum statistical mechanics, it is well known that energy distributes itself equally in all pure quantum modes – a consequence of the linearity of the governing equations of quantum mechanics. For such composite modes as the interface of a nanobubble, the distribution need not be equipartitioned. Since anecdotally 1% holdup of fine bubbles can slow a surge wave ten-fold, it is likely to be a surface area effect, in which case a vanishingly small phase fraction of nanobubbles could bestow the same benefit.

§1.2 Nanobubble generation and structure
Early observances of nanobubbles were at imperfections on hydrophobic surfaces in oxygen super-saturated liquids (Attard et al. [17]). This feature of high energy interfaces is a recurring theme in the generation of nanobubbles and of their own utility. However, this mechanism of generating nanobubbles, for practical purposes, opposes their use as a bulk gas transfer mechanism. In most instances, the intention is to either dose the liquid with the content of the liquid, or degas the liquid by extraction in the bubble phase. Since these nanobubbles are formed from supersaturated liquid, they do not dose. Although they remove gas from the liquid, due to their practically permanent nature, they do not remove the gas completely from the domain, but rather persist as tracer elements, moving with the liquid.

Creation of small bubbles can be induced in a number of ways. The most common uses the cavitation mechanism with power ultrasound (Leighton [18]). Removing the ultrasonic field usually results in the collapse of the bubble, which can be used for cleaning effects or sonochemistry. Cameron [19] reports in the trade press about the development of nanobubble generation in the labs of Masatoshi Takahashi at the Institute for Environmental Management Technology at the National Institute of Advanced Industrial Science and Technology (AIST). Takahashi's 200nm diameter bubbles have been reported to have no propensity to rise and are stable for months,

having been formed by a process involves "physical stimulation leading to violent adiabatic collapse." It appears that this can be stabilized (Masayoshi [6]).

Most known methods of nanobubble production do so by creating vapour from the surrounding liquid. The nanosolutions study of Ohgaki et al. [1] suggests that many impure water solutions are riven with nanobubbles. Dzubiella [20] gives some theoretical insight as to why this is. Molecular dynamics simulations with hydrophobic solutes in water give rise to nanoscale capillary effects that generate water vapour in nanobubbles. The surprise is actually that, according to the hydrogen bonding mechanism proposed by Ohgaki et al. [1], the nanobubbles are stable rather than re-dissolved. One would, naively, expect that fluctuations induced in the liquid water structure would naturally disperse the very small volume of vapour material. That imperfections on hydrophobic solutes can generate nanobubbles lends substantial insight to the structure of water as a liquid, but it does not suggest that the applications promised by nanobubbles are achievable, since the nanobubble consisting of the same chemical constituency as the surrounding liquid are unlikely to provide the heterogeneities desired alone. The role that surfactants might have in stabilizing such fleeting nanobubbles and altering their interfacial chemistry suggests a whole new line of investigation.

The structure of water in particular is elucidated more clearly by hydrophobic interactions in the drainage of films between small bubbles, as the rupture during coalescence of the film can be analyzed by long range hydrophobic interaction theory (Nguyen and Nguyen [21]). The instability of the thin films between bubbles during coalescence has been argued that migration of gases inherently dissolved in water might cause the transient behavior of the water films at the short contact time. Nanobubbles may well be stable to this instability mechanism, either by their strong hydrogen bonding at the interface or the magnification of electrostatic repulsive forces which are proportional to surface area. Matsumoto [22] underscores this role of hydrophobic stabilization by molecular dynamics simulations. Ducker [23] addresses this stability as well, with particular attention to the role of the very low contact angle. A self-consistent explanation of both or these effects is that there is a film of contaminant at the air-water interface that decreases the surface tension and thus the contact angle, and also hinders diffusion of gases from the bubble, thereby increasing the lifetime. If, during the lifetime of the bubble, the surface tension increases faster than the area of the air-water decreases, the interfacial energy can lead to a stabilization of the bubbles.

Ultrasonication, as previously mentioned, is the source of many nanobubble production mechanisms. Inherently, as in the hydrophobic impurity mechanism illustrated by Dzubiella [20], ultrasonication results in nanobubbles of the vapour of the liquid medium. In order to create a chemical contrast, the liquid medium should be a solution for which only the most volatile component(s) flash into the vapour phase. Xing et al. [24] illustrate this approach by using a pair of contrast agents in a suspension. A mixture of Span 60 and polyoxyethylene 40 stearate (PEG40S) followed by differential centrifugation to isolate the relevant subpopulation from the parent suspensions created the impetus for nanobubble formation.

Farook et al. [25] report on the creating of phospholipid-coated microbubbles for medical applications using an electrohydrodynamic technique. The methodology

produced 1-50 micron sized bubbles. Potentially, this method can be miniaturized to nanobubbles. Zhang and Li [26] use a similar electric field focussing approach to generate microbubbles for medical imaging stabilized by addition of PEG additives.

Kukizak and Goto [27] give a recipe for nanobubble production from uniform nanoporous membranes which achieves sub-100nm bubbles from c. 10nm pores using steady flow. As we will see in the next section, oscillatory flow has the promise to reduce the size disparity between the produced bubble and the pore by breaking the balance between buoyant forces and wetting forces that are typically attributed to the resultant bubble being released at a size an order of magnitude larger than the pore. With nanobubbles, as the rise forces are so small, buoyancy most likely plays no role in the production of nanobubbles. The release mechanism must be effective in "microgravity" conditions as all other fluid interaction forces dominate buoyancy at sub-micron scales.

§ 2 Energy Efficient Microbubble Generation by Fluidic Oscillation
Zimmerman et al [28, 29] report on an energy efficient mechanism for the generation of microbubbles on the size of the pore used to disperse the bubble by using a fluidic oscillator. A fluidic oscillator is a no-moving-parts valve that can control the frequency of the oscillation by the length of a feedback loop [30]. If the frequency of the oscillation is sufficiently high and the distribution of the antechamber before the bank of pores gives a good distribution, the bubble cloud generated is of the scale of the pore. Surface wetting properties have an influence on the size of the generated bubbles. In general, hydrophilic surfaces have a thin water film between the bubble and the pore material, and hence the hydrophobic gas (say air) does not adhere to the solid surfaces. The bubbles are observed to "shoot" out like bullets from the pores, rather than the conventional slow pushing out from the pore as under steady flow. The air pulses control the size of the bubbles.
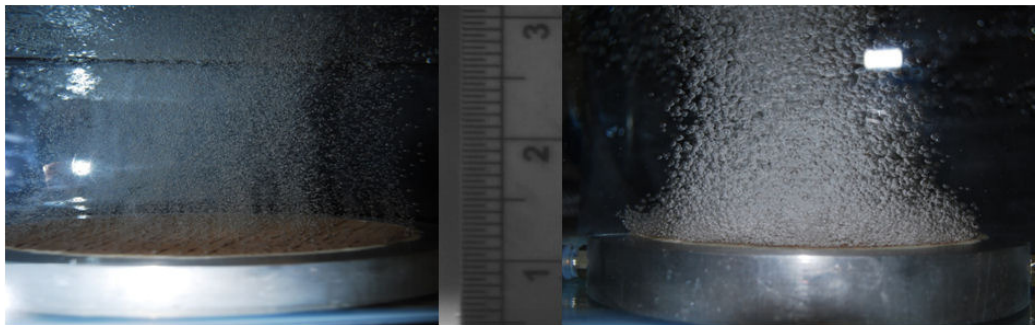

Figure 1 Comparison of fluidic oscillator driven microbubble generation.The right side of the figure shows the result of steady flow through a 15cm diameter microporous diffuser with 20 micron size pores. The bubbles are approximately 500microns in size from a combination of formation that is much larger than the pore, and from coalescence. The left hand side shows a closeup of the same diffuser with a fast oscillation (~90Hz) and flow rate tuned to the Stokes rise velocity. The resultant bubble cloud is non-coalescent, nearly uniformly dispersed, and with size tuneable from 20-100 microns and practically monodisperse. For some applications, energy efficiency is desired and the high transfer rates at low volumetric flow rates are highly desirable. For high throughput dissolution applications (such as CO_2 scrubbing), high flow rates are necessary, and potentially possible.

The limitation in the length of the pulse is a straightforward application of wave dynamics theory. The speed of the carrier wave is the linear velocity of the fluid,

hence division by the frequency of oscillation gives the "wavelength" of the pulse or half-width of the solitary wave of momentum (see Zimmerman and Rees [31]). Clearly, the linear flow rate must be as small as possible and the frequency as large as possible to miniaturize microbubbles to nanobubbles from this approach. As the oscillator used to create the microbubbles in Figure 1 achieves 1-100Hz fundamental frequencies, it is estimated that higher harmonics of the oscillation in the fluidic oscillator chamber are responsible for the smallest bubbles (c. 20 microns, see Figure 2) that are generated. Miniaturization of the fluidic oscillator could increase the oscillations to the kHz regime needed to produce nanobubbles. Other fluidic oscillator designs could achieve 10s of kHz. It should be noted that oscillatory flow is inherently different from classical calculations of droplet or bubble mass based on Tate's Law (see Hool and Schuchardt [32]):

$$W = 2\pi r \gamma$$

Where the mass W of the droplet or bubble is calculable directly by the pore size and surface tension. As the density of gas is so small, Tate's Law guarantees a much larger diameter bubble than the pore radius r unless surface tension γ is vanishingly small. Of course a predominant feature of water is its large surface tension. Thus, wetting effects are intrinsically different in a fluidic oscillator induced micro/nanobubble than in a conventional steady flow bubble generator.
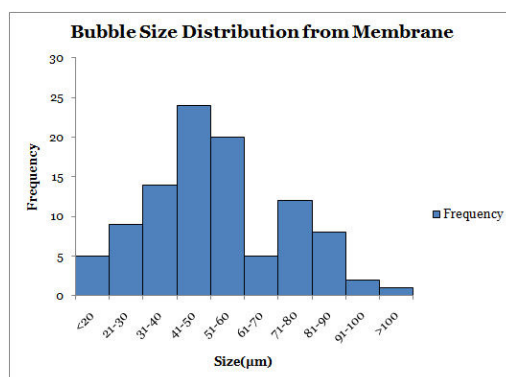

Figure 2 Bubble size distribution from a microporous nickel membrane diffuser with mean bubble diameter 47 microns from the 20 micron size pores. As small as 28 micron size mean diameter has been found with very low flow rates.

§3 Conventional uses of microbubbles as potential applications for energy efficient nanobubbles

In order to recognize the drivers for energy efficient nanobubbles and microbubbles, we have listed some of the major potential applications below, with a short description of the rationale for the innovation by their introduction.

§3.1. Bioreactors: Algal biofuels production.

Zimmerman et al. [29] describe the design of an airlift loop bioreactor (ALB) that has been used for the enhanced production in laboratory trials of algal biomass production with microbubble generation [33]. These studies showed that microbubbles dissolve CO_2 faster and therefore increase algal growth. Microbubbles also extract the inhibitor O_2 produced by the algae from the liquid so that the growth curve is wholly exponential. The algal culture with the fluidic oscillator generated bubbles had ~30%

higher yield than conventionally produced bubbles with only dosing of one hour per day over a two week trial period.
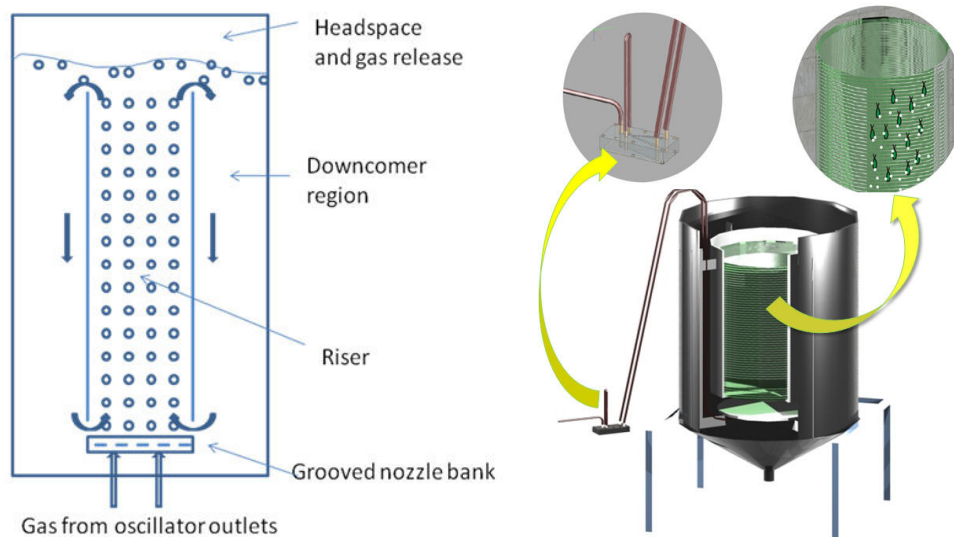

Figure 3 Use of energy efficient microbubbles to generate airlift loop effect, suspension of algae by flotation, and gas exchange – CO2 dosing and O2 stripping. The operating regions of the flow structure induced by microbubble rise and liquid released by the bursting of the bubbles causing the downcomer flow. The fluidic oscillator is external to the device. Nanobubbles would not rise naturally by the airlift loop effect, but would be entrained by microbubbles. A hybrid micro-nano-bubble distribution would benefit from nanobubble flocculation on very small microalgae for transport, gas exchange, and suspension. Flocculation and flotation separations could be used for the algal dewatering stage, which is currently a major energy use in algal biofuels production.

Because the microbubbles are so small and rise slowly and smoothly, they dissolve the gas at a much higher rate. The air-lift loop design manages to corral the strong momentum transfer effects by creating a global stirring motion for rapid overall mixing. The schematic to the left shows how the airlift loop effect is driven by the rise of microbubbles. The cloud of microbubbles is well distributed over the microporous diffuser pair at the bottom of the central, annular region of the reactor. As the bubbles rise, they attach to the surface of cells or other particles and keep them in suspensions, floating some to the top surface. The bubbles can spread out along the top surface, and will drop the particles as the burst at the top surface. The bubbles also drag liquid with them to the top surface. The released liquid or cells/particles drop to the bottom when the bubble bursts, so the inner region has both rising and falling particles and liquid, which makes it vertically well mixed. The horizontal spreading at the top, however, only drops liquid/particles over the outer, downcomer region. They are then entrained at the base of the shell wall back into the riser region.

For algal bioreactors, this global stirring motion makes possible the precession of the suspended algae around the top and outer walls, so that external lighting provides the impetus for photosynthesis. Access to light is a key limitation in other photobioreactors. Here, the microbubbles cause the stirring motion. In mammalian cell bioprocessing, airlift loop bioreactors are preferred as the cells are fragile and lyse in high shear rates. Mixing is needed to disperse the dissolved oxygen. The higher transfer rates with very low shear rates (flows of 10^{-4}m/s) are attractive for such culturing. The biochemistry of nearly all bioreactors could be intensified by

microbubble sparging, not just for the delivery and dispersal of gaseous nutrients, and for liquid phase mixing, but also for the removal of gaseous byproducts by extraction. Most such byproducts will inhibit the growth of the biomass and provide a biochemical resistance to greater production of the desired products.

With biofuel production, the lionshare of the energy goes into the biomass production, with a small fraction into the biorefinery. Algal biofuels promise to provide a sustainable fuel source, but suffer from large footprint requirements to make use of the concentrated CO_2 sources from power stations, for instance. Hundreds to thousands of hectares of land are required for the ponds. Our engineered bioreactor makes use of energy efficiently produced microbubbles to grow the algae to high density and with high growth rates. We know how grow a population to high density -- we do it with cities. We provide public services. An engineered bioreactor with microbubble dosing does this too. It delivers the food -- CO_2 -- in small packets that dissolve very quickly. The bubbles mix the nutrients well and suspend the algae so that it "parades" around the lighted services: public transport! Finally, the bubbles remove the major waste product: O_2, which inhibits the algal growth and is eventually toxic in high concentrations (public waste removal system). Follow up pilot trials on steel stack gas has recently achieved a remarkable uptake of CO_2, greater than 30% of the 40litre/min stack gas stream in a 2 cubic metre pilot bioreactor on a steel plant, achieving very high density, with our novel fluidic oscillator microbubble generator that makes ten-fold smaller bubbles with less energy use than traditional fine bubble diffusers. Since the CO_2 has to be dosed anyway, why not provide energy efficient "public services" while doing it?

§3.2. Wastewater aeration.
In the developed world, on the order of 1% of electricity usage is to power aeration of wastewater systems. The activated sludge process is widely accepted as the most common form of biological treatment of wastewater from both domestic and industrial sources in the developed world. From conception in the late nineteenth century to the first full scale application in 1913 (Ardern and Lockett[34]) the process has been widely adopted (Hanel [35]; Gray [36]) and many versions now exist (Tchobanoglous and Burton [37]). Interestingly the analogy of biological treatment is likened to that of the natural river environment by Gray [36]. Aeration, and actually stripping of the produced CO_2, simply accelerate the natural life cycle of the bacterial consortium and facilitate growth by provision of nutrients and extraction of waste products. This is, of course, the opposite of the cycle for which micro/nanobubbles can contribute to the plant gas exchange in algal bioreactors.

Nanobubbles have the promise in wastewater aeration of creating the "permanent" benefit of gas exchange, which would then no longer require large open tanks to achieve. Wastewater treatment plants of the future could be organized as largely horizontally arrayed pipework networks (i.e. the existing sewerage duct system) with injection streams for nanobubbles enriched in O_2. The product stream would be nutrient rich with CO_2 enriched nanobubbles, which would be an excellent growth medium for algal bioreactors. Zimmerman et al. [29] report some of the preliminary studies on wastewater aeration efficiency.

By analogy to either the CO_2 dosed algal bioreactor or O_2 dosed wastewater aeration system, it is clear that any dosing with any gaseous nutrient for an arbitrary bioreactor

would benefit from energy –efficient microbubble or nanobubble generation and dispersal system. But what about anaerobic systems, where the anaerobic "blanket" is not dosed, but simply maintains an oxygen-free environment? Two types of such schemes are anaerobic digesters and the anammox ammonia removal processes. Anaerobic digesters produce CO_2, H_2, and CH_4 in general. They would benefit, conceptually, by stripping with N_2 micro/nanobubbles. The general principle is that of Le Chatelier, in which a reactive separation of a product favors the production of more product, hence higher metabolic rates and yields. Similarly, anammox produces N_2, which would benefit from extraction with CO_2, again by Le Chatelier's principle. The massive surface area of micro/nanobubbles should make the transfer rates sufficiently high that only a very small bubble phase holdup is required to achieve significant performance enhancement. Yeast production and beer and (bio)ethanol production are also large volume operations that would benefit from the same principle.

§3.3 Ozone dosing by microbubbles: Low power consumption ozone generation by plasma microreactors

Ozone is a strong oxidation and disinfection agent, but its use is limited by conventional high power consumption and the requirements of vacuum operation and high voltage. In recent years, Zimmerman and co-workers (Zimmerman [38]; Lozano and Zimmerman, [39]) have been developing plasma microreactors that operate under atmospheric pressure, low voltage, and room temperature. In seeking to miniaturize plasma reactors onto microchips, they constructed a purpose-built plasma source and impedance matching network, which has the benefit of greater operational flexibility than conventional plasma sources. The upshot was that it allowed the discovery of recipe for low power consumption in the operation of the plasma microreactor for ozone formation, by exploiting the fast kinetics of the chemical reaction. A prototype dosing lance which multiplexes the plasma reactors for greater throughput, and crucially permits high dispersal rates of the ozone through microbubble delivery (Zimmerman et al. [40]). Since microbubbles have a low carrying capacity and ozone is highly reactive, it should be possible to tune the production and dispersal so as to completely consume all the ozone generated, removing the necessity for costly plant rooms for unspent ozone destruction.

Dispersal of ozone

Conventional dosing of ozone is by insertion of a gas jet into the water stream, with subsequent in-line mixers used to disperse the gas. The mass transfer is enhanced by turbulent entrainment of the gas stream, but this procedure is plagued by low mass transfer rates. A substantial quantity of the ozone remains unspent and must be destroyed for safety reasons in a post-processing plant room. Greater dispersal rates of ozone are promised by microbubble dispersal. Zimmerman et. al [29] demonstrate the use of a new fluidic oscillator technique in the design of bioreactors, but the technique has much wider applicability. Aeration rates in wastewater treatment and CO_2 dosing and O_2 extraction in algal biomass growth have been shown to benefit from much higher mass transfer rates with microbubbles due to the much higher surface area with the same volumetric flowrate. Delivering ozone with such a microbubble dispersal system has the promise of such high dispersal rates, particularly since ozone is reactive and dissociative (see Beltran, [41]) upon dissolution, so that the rate limiting step is typically mass transfer. As microbubbles

have only a limited capacity for carrying ozone, it should be possible to tune the dosing rate so as to completely consume all ozone generated.

Ozone generation in plasma microreactors

Zimmerman (2010) chronicles the iterative development of the microreactor operation, coupled with the plasma source and matching network optimization. Through many laboratory experiments in developing a glow discharge, we found that ozone could be reliably produced with a low voltage (170VC AC) at atmospheric pressure and room temperature, with a 100Hz AC electric field. Conventional plasma sources off-the-shelf operate at 13.56MHz to sustain the plasma continuously. Our low frequency, 100Hz, operation draws approximately $1/10^{th}$ the specific power for ozone yield compared to conventional ozone generators. We attribute this phenomenon of low power consumption operation to a proper respect of the kinetics of the ozone formation reaction (Lozano-Parada and Zimmerman [39]). As the pathway for ozone formation is well studied due to its environmental importance, it was demonstrated that under these reaction conditions, ozone forms to 99% of its equilibrium yield in 0.01s. Since their reactor is 1cm long, with a 1m/s superficial velocity, the residence time in the reactor is 0.01s. The 100Hz operation means that the electric field forming the glow discharge plasma is "on" for 0.01s. Conceptually, this is a recipe for low power operation which is simply to power the plasma only as long as the reaction requires, and then provide fresh reactants. The only potential threat to this operation is extinction of the plasma at the walls. The diffusion velocity of the ions in the plasma can be estimated as 1cm/s. Since the electrodes are 800 microns apart, the time to extinction is ~0.1s, by which time the reaction is long over. The plasma has done its job, so how it extinguishes is of no concern. By contrast, in conventional plasma reactors, designed for continuous plasma stability, the reactor walls are far apart so as to minimize the extinction of the plasma on the walls.

Ozone dosing is used for the final stage of disinfection in only a few countries in water purification pants, but in most water purification plants it is used for organics removal – breaking down complex organic molecules dissolved in the clear but not pure water sources. Dual ozone-UV breakdown of organics such as pesticides or metallocyanides is another use, where only the dual mode treatment generates sufficient hydroxyl radicals to be reactive enough. Ozone dosing for wastewater disinfection is rare, with UV seen as the more tractable option. There are many sterilization uses for ozone, and some cleaning, such as ozone dosing in HF for cleaning solution for silicon wafers. In each of these applications, microbubble dispersal enhances the performance, but nanobubble dispersal would enhance the reactivity and effectiveness, hence reducing the need for high levels of ozone dosing. Selective oxidation based on control of ozone levels in organic synthesis or for analytic chemistry (ozonolysis) and green chemistry with ozone and hydrogenation reactions are other potential applications where micro/nanobubble dosing would benefit.

§3.4 Flotation separations

Gas-Induced Flotation Technologies are the use of gas bubbles in water to convert suspended matter and some colloidal, emulsified, and dissolved substances to floating matter (Nemerow, [42]). This technology which was developed and first applied in the mining industry for many years has become the preferred technology for secondary oil and water separation in industry today (Owens and Lee [43]). The basic

principle behind this technology is that the microscopic gas bubbles (while rising) attach themselves to the oil droplets, thus reducing the effective specific gravity of the oil droplets in the Stokes' Law hence increasing their rising velocity. This ensures faster separation rate with respect to time and efficiency. Gas flotation technologies are very versatile and they are able to handle upset conditions. Because gas flotation technology units are relatively smaller in size per unit of flow treated, compared to other gravity separation technologies, they can be used in both offshore and onshore applications. Two methods are commercially available. They are the dissolved air flotation (DAF) and the dispersed (Induced) air flotation (IAF). Other available gas flotation technologies include electro flotation, nozzle flotation, column flotation, centrifugal flotation, jet flotation, cavitation air flotation, e.t.c. Of all these technologies, the dissolved air flotation method is the most employed in practice because it can produce bubbles in the 40-70 micron range (Cheremisinoff [44]), which tend to have more surface area-to-volume ratio compared to the bubbles generated by other methods, thereby resulting in better separation efficiency. However, this system despite being very efficient (about 99%), has some major drawbacks like being labour intensive and expensive (Cheremisinoff [44]).

Grammatika and Zimmerman [45] review generalized flotation processes, and in particular conclude that particle-bubble pairs must be within an order of magnitude of each others size for collection to be possible, irrespective of the flocculation surfactant chemistry. Microbubble flotation (and potentially nanobubble foam flotation) have the potential to replace dissolved air flotation by achieving the same scale of bubble size distribution (see Figure 2), but by simply blowing air rather than pumping saturated liquid. Given the 1:1000 density ratio, the former is much less energy consumptive than the latter. The current DAF process generates microbubbles by compression of air to 6bar, contacting recycled clear water in a saturator, and then releasing the saturated liquid from 6bar into the clarifying tank. The nucleated bubbles are 40-70 microns in diameter when created with a strong turbulent flow, attach to the flocculated solids, and the whole floc floats by buoyant force and is skimmed off the top, leaving the water nearly solid-free.

As a consequence of the energy efficient microbubble generation methodology Zimmerman et al. ([28], the compression stage and saturation may not berequired. Microbubbles of the appropriate scale, crucially without the turbulent release (laminar flow), will allow flotation separation without the saturated recycle flow, which is 90-95% of the electricity cost for the DAF process. The saturator would no longer be required, which has a capital cost per unit of $500k, and a similar cost of pumping systems could be saved.

In addition to solids removal in water purification, such DAF processes are currently used in minerals engineering, oily effluent treat (fats, oils, and grease, for instance), offshore oil-water separations, and in particulate removal. There is a clear potential for algal dewatering as well. Gas-lift enhanced oil recovery (requires 30-50 micron size bubbles, cheaply produced) is another possible application (Guet and Ooms [13]).

§3.5 Other applications: Chemical reactions, heat transfer, vaporization, enhanced oil recovery

Since one third of chemical processes and nearly all biochemical processes are gas-liquid systems, many industries will benefit from low cost, energy efficient microbubble transfer processes. Some further potential applications:

- Microbubble dosing / extraction replacing gas-liquid spargers/scrubbers in commodity chemicals production, potentially CO_2 dissolution in carbon capture and utilization systems.
- Heterogeneous chemical reactions at gas-liquid interfaces (see Deshpande and Zimmerman [46,47])
- CO_2 flooding for enhanced oil recovery with microbubbles which avoids the channelling instability.
- Hot gas microbubble injection for enhanced oil recovery which achieves similar improvement.
- Drag reduction in oil pipelines.
- Microfoam production for processed foods.
- Oxygenation of oxygen depleted water recycled through PEM hydrogen fuel cells.
- Rapid humidification such as needed in desalination plants or solar air conditioning systems.
- Rapid heat transfer uniformly distributed through the medium rather than from heat transfer surfaces.

§4 Discussion and Conclusions

Clearly, recent advances in nanobubble technology are fascinating and encouraging. Nanobubble structure in water solutions is now much better understood due to molecular dynamics simulations and careful microscopy studies. The role of hydrophobic materials in generating nanobubbles as dispersed heterogeneities throughout liquid structure leads to insight into many nucleation processes. For instance, Leighton [18] computes that the breaking strength of pure water by cavitation to induce sonochemistry is several orders of magnitude higher than the observed power ultrasound required. Nanoscale impurities are an intrinsic feature to aqueous solution structure.

Although nanobubbles are now known to be common, this does not mean there are sufficient quantities for all the purposes desired. Common generation mechanisms create nanobubbles of the volatile components of the liquid, with the exception of electrolysis, but do not inject fresh material, hence are limited in the scope of commodity operations. In order to exploit nanobubbles more fully, we must move towards energy efficiently and conveniently produced nanobubbles with low cost methodologies. This paper has reviewed recent advances in fluidic oscillator induced, energy efficient microbubbles to demonstrate the promise that miniaturization of that approach holds. The key bottleneck is the extension of the currently used fluidic oscillator regime from the 100Hz to several tens of kHz regime, maldistribution at the nanoscale of gas flows, potentially wetting effects, and other surface forces that do not manifest strongly in the microscale. Acoustic and ultrasonic focussing may be possible to use the "chamber" of the pore for additional "shredding" of the microbubble with existing micro/nano fabrication methods.

The scope for micro and nanobubbles to impact current industrial scale processes, such as biofuels production, water treatment, chemicals production, and other gas-

liquid transfer processes to save energy and enhance performance / production rates is very promising. The engineering exploration through application oriented industrial development is currently outstripping the fundamental physical chemistry and engineering science of both microbubbles and nanobubbles. It is the sincere hope of the authors that this article will spur greater investigation of the underpinning science.

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