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Señores

DELEGATURA PARA NUEVAS CREACIONES

Superintendencia de Industria y Comercio

Asunto: **Respuesta a observaciones Artículo 45 Decisión 486**Expediente: **2013-25761**

JORGE ENRIQUE FORERO SANABRIA identificado como aparezco al pie de mi firma, mediante este escrito y en uso del término dispuesto por la ley de 60 días hábiles presento a ustedes la respuesta a las observaciones presentadas por esta delegatura de la siguiente manera:

La observación presentada por la Delegatura respecto de los requisitos de patentabilidad se efectuó mencionando los siguientes antecedentes:

Los requisitos de Patentabilidad de la presente solicitud están afectados así:

Item	Documento	Reivindicaciones afectadas	Requisito que afecta
D2	WO2008/147050	1, 2, 5	Nivel Inventivo
D3	US6054048	1, 2, 5	Nivel Inventivo

Consideramos respetuosamente que los documentos indicados por la delegatura no afectan el nivel inventivo de las reivindicaciones mencionadas por lo siguiente:

Manifestamos respetuosamente que el documento D2 es un sistema DAF la cual necesita succión de gas por medio de un elemento rotativo, en este caso una bomba especial. Con una bomba estándar D2 perdería un gran porcentaje de eficiencia o no podría operar, este factor que es inexistente en nuestra solicitud, ya que existe una sección (8) que es la cámara de inyección de agua y generación de vacío para la succión de gas que está formado por un contenedor, que puede ser cilíndrico, que dispone internamente de una o varias boquillas aerodinámicas, esta cámara de inyección de agua y generación de vacío para la succión de gas, puede ser formada por una o varias etapas de succión. En esta cámara se conforma también la primera etapa de mezcla entre el gas y el líquido.

El hecho de no requerir bombas especiales costosas sino bombas estándar de bajo costo hace que nuestra solicitud sea innovadora debido a que no se requiere de gases de baja corrosión, o inertes, como si se requiere si se usan elementos rotativos, que son altamente limitados por la calidad del gas, tanto que se pueden destruir muy fácilmente si este gas reactivo o es un gas corrosivo, situación que no afecta nuestro proceso, debido a que la bomba solo maneja líquidos.

En cuanto al documento D3, es un sistema que puede operar por succión inducida de gases, sin embargo existe una gran diferencia conceptual con nuestra solicitud, y es que D3 no tiene como objetivo saturar el líquido con gas y mantener un flujo en estado líquido para en una etapa posterior generar micro burbujas usando nucleación heterogénea, para hacer separación de partículas en el agua u otros fluidos (se consideran así las burbujas de diámetro menor a 100 micras), y menos aún si se usa múltiples etapas de mezcla para lograr generar gran cantidad de estas, así como tampoco podría usar cualquier tipo de gas solamente puede usar gases que contengan alto contenido de oxígeno, ya que según su operación, su objetivo no es separar fases sino que es aumentar el contenido de oxígeno en el agua, arrastrando gas para mejorar los procesos de oxidación, de impurezas solubles e insolubles, lo cual es conceptualmente diferente a nuestra solicitud, ya que podemos usar cualquier gas, preferiblemente aquel que sea mas recomendable para el agua, en el caso de la industria del petróleo no se deben usar gases ricos en oxígeno en la mayor proporción de casos de tratamiento.

Se debe mencionar que la formación de burbujas tanto en los documentos D2 y D3 se realiza casi totalmente por nucleación homogénea, que tiene como característica que requiere muy alta energía y las burbujas generadas tienen baja o nula concentración de micro burbujas (menores a 100 micras), su distribución de tamaño es muy disperso, su número es bajo, lo que quiere decir su aplicabilidad para separar pequeñas partículas de líquidos como el agua es baja, especialmente en aquellas generadas por D3.

En el caso de D1 esta eficiencia es mejor, pero en ningún caso las burbujas generadas por nucleación homogénea pueden superar la calidad y la cantidad, de aquellas generadas por nucleación heterogénea a las mismas condiciones de procesamiento y consumo de energía. Esta generación por nucleación heterogénea es tal vez la innovación mas grande en nuestra solicitud, ya que opera principalmente según el principio de generación de micro burbujas a partir de la obtención de un líquido metaestable (sobresaturado) que se pone en contacto con placas de superficie activa (nanotecnología) para la nucleación heterogénea, fija, controlada y simultáneamente con el fenómeno de aplicación de esfuerzos cortantes controlados. El desarrollo de estas placas es uno de las tareas que ha tomado mas recursos de investigación y desarrollo, ya que se requirió de muchas evaluaciones para lograr encontrar materiales y tratamientos que aseguraran alta calidad en este tipo de superficies, según el objetivo planeado (ver artículos anexos)

En D2 no existe línea de conducción de agua a presión, como en nuestra solicitud, allí existe un fluido mezclado de líquido y gas entrando a la bomba (fig 2, línea 4, 6,7,7a), esta particularidad de operar una bomba con líquidos y gases, genera un fenómeno que se conoce como cavitación, el cual es un fenómeno muy destructivo, aun si la bomba esta construida en materiales especiales y costosos, situación que seguramente es un requerimiento para la operación del sistema D2, ya que si se opera con una bomba estándar seguramente tendrá un vida útil muy corta (par de semanas o meses). Tambien es importante resaltar que la descripción de D2, es errónea, manifiesta que la línea 10 es un línea para conducción de agua, y lo real es que en esta línea se conduce agua y gas, generando inestabilidad en el flujo, que también afecta de manera notoria la generación de burbujas adecuadas para la separación.

En nuestra solicitud no se presentan estos fenómenos (cavitación e inestabilidad en el flujo) , debido a que la bomba es un equipo estándar y que a esta no llegan gases en su línea de succión, por lo tanto esta bomba podrá operar por tiempos prolongados sin ningún problema (años), esta diferencia conceptual es fundamental en estos dos procesos, por lo tanto demostramos que hay innovación en nuestra solicitud..

En D2 el contacto gas líquido se realiza especialmente en la bomba, (generando cavitación) y la segunda etapa se genera en el recipiente (20), mediante cambios de dirección, debidos a la presencia de tabiques y restricciones de flujo, lo que genera alto consumo de energía. En nuestra solicitud no hay presencia de gas a presión en la bomba, y el contacto se realiza en elementos estáticos, que no generan problemas de degradación de los materiales, lo que reduce muy significativamente el mantenimiento del equipo y el consumo de energía, y hace nuestro proceso innovador.

En D3 hay un contacto gas líquido en una sola etapa y se realiza en las tuberías de conexión del venturi, con el objetivo principal de succionar el gas rico en oxígeno y distribuirlo en el agua a tratar como fase gaseosa, en la solicitud se hace mezcla o contacto en múltiples etapas, con el fin de saturar el líquido con el gas presente, sin que esta fase gaseosa pase a la zona de formación de microburbujas, ya que afectaría la calidad de estas para realizar el proceso de separación, para las cuales se requiere, condición que no existe en D3, que es un proceso de transferencia de masa esencialmente y **no** de generación de microburbujas para separación de partículas suspendidas, como lo es la solicitud en mención.

En nuestra solicitud existe una válvula (7) que es un elemento regulador de presión , el cual opera en caso de que el tanque contenedor (9) alcance una presión mayor a la definida, En el caso de D3 esta válvula no existe , porque el contenedor de este proceso no es hermético y no genera presiones que requieran este tipo de elementos, en el caso de D2 las válvulas que se presentan como reguladoras de presión, no son realmente sistemas de control de presión, las válvula 14 y 16 son válvulas de control de flujo hacia la bomba y de cheque, si estas válvulas fallan seguramente habrá limitaciones menores, que solo afectaran la eficiencia del equipo por flujos no apropiados, tarea que es muy diferente a la válvula (7) de la solicitud que tiene como función principal proteger la integridad del equipo generador específicamente.

El sistema de succión de D3, es un sistema de baja presión que tiene como objetivo inyectar gas (oxígeno) al agua que está en tratamiento y no a relacionar relaciones de flujo gas líquidos según se requiera, operan con bajos índices de recuperación de presión, generalmente solo pueden operar en una etapa y es un sistema ampliamente conocido como eyectores, de los cuales hay muchas marcas y modelos en el mercado, sin embargo el sistema de succión de la solicitud, tiene unos elementos específicos de operación selectiva, que operan en una o varias etapas a condiciones que permiten mantener presiones altas y mantener una relación gas líquido según diseño, con el fin de incrementar la producción de la burbujas, ya que exceso de gas o defecto de este limita la calidad y cantidad de la burbujas generadas, D2 no tiene este tipo de elementos, que hacen nuestra propuesta innovadora y eficiente.

En la solicitud se presenta un dispositivo (10) que controla la interface liquido-gas en el contenedor, factor clave para controlar la operación de generación de microburbujas de manera eficiente, sin embargo este elemento no existe en D2, la parte (18) que se menciona en la comunicación de la superintendencia no es un indicador de nivel de interfase de gas, realmente se refiere a un medidor de flujo, lo cual muestra nuevamente que nuestra solicitud es innovadora.

Asimismo, el documento D2 divulga las características de las reivindicaciones dependientes así:

- Reivindicación 2. Sistema de generación de micro burbujas que opera con una sola fuente de presión (10) (D2: Fig. 3; Pág. 50).
- Reivindicación 5. Contactor de placas (D2: Fig. 4; Párr. 58, 60, 64).

Por lo anterior, dichas reivindicaciones dependientes 2 y 5 no proporcionan al objeto de la reivindicación independiente 1 ningún efecto sorprendente, y en consecuencia no tienen nivel inventivo.

Se menciona que el documento D2 tiene placas de contacto, lo cual conceptualmente no es valido, las placas presentes en esta invención, son placas de contención, de division de zonas de diferente presión, tabiques de separación o de limitación de flujo, llamadas en el documento original partitions, lo cual traduce partición, pared, muro, medianera, valla, tapia. En nuestra invención las placas tienen como función principal actuar como zonas de reacción o contacto que incrementan la transferencias de masa entre los fluidos, hasta la metaestabilidad en el caso del contactor primario o de disponer de una zona activa (superficie modificada) para que se genera la nucleación heterogénea, por el contacto de un liquido metaestable con una superficie modificada y activa para generación de microburbujas. Para mejorar el contacto los fluidos viajan de manera paralela a las placas.

En el documento D2 estas placas que tienen como objetivos separar cámaras de condiciones de flujo diferente y de limitar el flujo por algunas zonas de la cámara de saturación. Además el flujo es normalmente ortogonal al eje de las placas causando choques y altas caídas de presión, que no se presenta en nuestras placas elementos de contacto.

Se menciona que el documento D2 tiene en su estructura un bloque de placas con puntos de nucleación en línea, lo cual no es cierto ni valido, las placas con puntos de nucleación en línea como objetivo principal incrementar la cinética de generación de las microburbujas, controlar su calidad y cantidad los fluidos viajan de manera paralela a las placas, sin embargo en el documento D2 las placas que existen son realmente tabiques de separación o de limitación de flujo, llamadas en el documento original partitions, lo cual traduce partición, pared, muro, medianera, valla, tapia.

En cuanto a la manifestación arriba mencionada y teniendo en cuenta las explicaciones y análisis anteriores, respetuosamente manifestamos, que la reivindicación 2, si es innovadora, porque tenemos "- (7) una válvula de seguridad y/o reguladora de presión, que mantiene el sistema a la presión deseada, según las condiciones de saturación deseadas de los fluidos (líquido y gas)", la cual se demostró no esta contenida ni en el D2 ni en D3 y que es fundamental para el control de calidad de la microburbujas y para asegurar la integridad del equipo, que tiene como variable de control la presión de generación de microburbujas por nucleación heterogénea. Además En la reivindicación 2, se están comparando las bombas de Cavitación y flujo multifásico del documento D2, con una bomba centrífuga estándar que tiene como único objetivo aumentar la presión de un fluido monofásico (líquido), las cual son conceptualmente totalmente diferentes.

En cuanto a la reivindicación 5, se menciona que hay un contactor de placas, sin embargo se demostró que estas placas no son contactores sino son realmente tabiques de separación o de limitación de flujo, llamadas en el documento original partitions, lo cual traduce partición, pared, muro, medianera, valla, tapia., en nuestra solicitud, efectivamente existe un contactor-reactor, que tiene como principal objetivo, generar nucleos, por el contacto del líquido-sólido que ha pasado por dos etapas de mezcla y se ha sobresaturado, que son los precursores de las microburbujas, Esta placas tienen una selección y un dimensionamiento definido basado en las propiedades de los materiales con que se fabrican, y claramente se observa que este tipo de placas no existe ni en D2 ni en D3, por lo tanto respetuosamente solicitamos el reconocimiento de esta innovación y nivel inventivo de esta reivindicación (ver artículos anexos)

También quiero manifestar que mediante correo del día 6 de Julio del 2014, se dio repuesta a las argumentaciones de oposición dadas el 14 de agosto de 2013 por la empresa opositora Exterran Holdings, Inc.

De igual manera con ocasión al presente escrito presento una modificación a la descripción y el resumen y las reivindicaciones y de igual manera anexo encontraran material de referencia para permitir a los examinadores un estudio más adecuado de la solicitud de la referencia.

ANEXOS

1. Documento de reforma del resumen, de reforma de la descripción y de reforma de reivindicaciones
2. Bibliografía complementaria que consideramos relevante para un mejor examen de la solicitud de patente:
 - 2.1.E.J Langham and Bj Mason The heterogeneous and homogeneous nucleation of supercooled water, Imperial College, London
 - 2.2.Ho-Young Kwak, Ki Moon Kang; Gaseous Bubble Nucleation Under Shear Flow; International Journal of Heat and Mass Transfer 52(2009) 4929 a 4937

- 2.3. Hanglin jo, Massoud Kaviany, Seol Ha Kim, Moo Hwan Kim; Heterogeneous Bubble Nucleation on Ideally-Smooth Horizontal Heated Surface; International Journal of Heat and Mass Transfer 71(2014) 149-157
- 2.4. Xavier Frank, Nicholas Dietrich, Jing Wu, Renaud Barraud, Huai Z Li; Bubble Nucleation and Growth in Fluids; Chemical Engineering Science 62(2007) 7090-7097
- 2.5. SF Jones, GM Evans KP Galvin; The Cycle of Bubble Production from a Gas Cavity in a Supersaturated Solution; Advances in Colloid and Interface Science 80 (1999) 51-84
- 2.6. JE Forero, OP Ortiz, Analisis Nucleacion Homogenea y Nucleacion Heterogenea, Documento interno, confidencial.
- 2.7. JE Forero, OP Ortiz, Presentacion Microburbujas por Nucleacion Heterogenea, Documento interno, confidencial

Atentamente



JORGE ENRIQUE FORERO SANABRIA
C.C. 91.227.105 de Bucaramanga

 Industria y Comercio SUPERINTENDENCIA	TESTIGO DOCUMENTAL	Folio: <u>7</u>
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Dependencia Jerárquica Del. Propiedad Industrial	Código	2000
Dependencia Productora :Dir Nuevas Creaciones	Código:	2020
Tipo de Radicación: Entrada: ☒ Salida: ☐ Traslado: ☐ Convenio: ☐		
Radicador: DAVID REINA		
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Nombre de la Serie / Subserie:		Código:
Expediente: 13-025761-28	Solicitante / <i>Quejoso</i> / <i>Demandante</i> / <i>otros</i> . JORGE ENRIQUE FORERO SANABRIA	
Prueba excluida: CD		
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Observaciones: Anexa CD contiene CINCO (9) ARCHIVOS TIPO .PDF y uno .PPSX <u>El cd contiene 9 Archivos PDF procesados y cargados al sistema.</u> <u>1 Archivo Power Point NO procesado</u>		Unidad de Conservación ☒ Bolsa ☐ Caja ☐ Libro ☐ Sobre ☐ Tomo ☐ Otro Soporte Documental ☒ CD ☐ Disquete ☐ DVD ☐ Folleto ☐ Periódico ☐ Plano ☐ Publicación Periódica ☐ USB ☐ Otro



Gaseous bubble nucleation under shear flow

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ABSTRACT

A decompression experiment of a water solution, saturated with methane gas at about 68 atm at room temperature, was done to investigate gas bubble nucleation under shear flow. A pressure reduction from 68 atm to atmospheric pressure is well below the decompression pressure required for spontaneous bubble nucleation of the methane gas, about 120 atm. The application of a shear flow from 5 min before to 1 min after the decompression induced active bubble formation and the final gas content in the solution was reduced substantially, even with the application of low shear rate of 25/s. However, the addition of the surfactant to the solution, which reduces interfacial tension considerably, hindered the bubble nucleation process.

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1. Introduction

Understanding the degassing process from supersaturated liquid–gas solution is very important in many engineering applications. For example, industrial applications include degassing from molten metals [1] and the manufacture of foamed materials [2,3]. In the field of physiology, nitrogen bubble formation in blood vessels and tissue, as a result of an excessive rate of decompression, causes caisson disease [4]. Degassing from a supersaturated solution, the gaseous bubble is formed by an aggregation process involving the dissolved gas molecules, and is quite different from boiling or cavitation phenomena, a typical phase change process [5].

Systematic experiments on gas bubble formation from a highly supersaturated liquid–gas solution have been done by Hemmingesen [6,7]. He investigated bubble formation in a capillary tube (diameter of 0.15–2.5 mm) from a water–gas solution which was decompressed to atmospheric pressure from an initial saturated state at high pressure. After a series of such decompression experiments with different values for the initial saturation pressure, quite different threshold pressures for bubble nucleation were obtained for different dissolved gas species. These findings are quite contradictory to the predicted values from the classical nucleation theory. A condition of “massive bubble formation” was obtained when the initial saturation pressure was 20–30 atm higher than the threshold value. Also, it was observed that the capillary diameter affected the threshold value for bubble nucleation. For nitro-

gen, the threshold pressure dropped to 100 atm using a 2.5-mm diameter capillary tube, while the threshold value obtained was 170 atm for a 1.1-mm capillary. In these experiments, the pressure reduction time was reported as 2–3 s; however, the bubble formation time was not given.

Kaddah and Robertson [8] studied gas bubble nucleation in molten iron. In their experiment, a levitated molten iron drop was in equilibrium with dissolved gas at high pressure. By a sudden decrease in the pressure, the droplet becomes supersaturated. Nitrogen bubble nucleation in molten iron having an enormous high surface tension value was observed when the initial saturation pressure was about 53 atm, even though this result was not repeatable. On the other hand CO gas bubble nucleation in Fe–C–O melts was observed at an initial gas pressure as low as 10 atm, which cannot be explained by the classical theory of bubble nucleation with a macroscopic surface tension value [9].

The effect of shear on nucleation of bubbles, droplets, and of crystals has drawn some attention recently and is still a debated subject [10]. A theoretical study by Reguera and Rubi [11] revealed that shear flow may enhance the diffusivity of molecules and, correspondingly, the nucleation rate. Particularly, the shear promotes a drastic change in the crystallization process of polymers having high viscosity. However, the effect is expected to be unimportant in condensation. Indeed, a factor of 10 in nucleation of isoactic polypropylene was observed at a rate of shear 14/s compared with the stationary case [12]. Another computational study for a van der Waals fluid has revealed that shear affects the bubble growth rate due to enhanced molecular transport, but has little effect on the bubble nucleation process [13]. The nucleation and growth of a bubble in a Newtonian liquid having very high viscosity were

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Nomenclature

A_n	surface area of n -mer cluster	T	solution temperature
F_n	free energy needed to form n -mer cluster	T_a	Taylor number
f_L	lost degree-of-freedom of a dissolved gas molecule in solution	T_c	critical temperature of solution
H	Henry's constant	t_{nu}	duration of nucleation process
J_n	nucleation rate of n -mer cluster	V_g	molecular volume of a dissolved molecule
k_B	Boltzmann constant	x_f	mole fraction of methane gas in water solution after nucleation process
n	number of molecules in a n -mer cluster	x_i	mole fraction of methane gas saturated at 68 atm
n_b	number of molecules inside a bubble	x_o	mole fraction of methane gas in water solution saturated at atmospheric pressure
n_c	number of molecules in a critical cluster	<i>Greek letters</i> β_g	
N_g	number density of dissolved molecules in solution		accommodation coefficient
N_w	number density of water molecules in solution	σ_g	surface tension of solution
P_i	initial saturation pressure	σ_{LJ}	Lennard-Jones hard sphere diameter
P_f	final saturation pressure	ν	dynamic viscosity of liquid
R_1	radius of aluminum rod	Ω_1	rotation speed of the aluminum rod
R_2	radius of test tube		
r_g	radius of dissolved molecule		

studied under simple shear and creeping flow using a Couette apparatus by Favelukis et al. [14]. They found that the growth rate of a slender bubble increases as the shear rate increases in the shear rate ranges between 2.0/s and 14.0/s.

In this study, decompression of a water solution saturated with methane gas at about 68 atm (1000 psi) at room temperature was done under shear flow. A shear stress by a Couette flow apparatus was imposed to investigate the shear effect on the bubble nucleation. This pressure reduction from 68 atm to atmospheric pressure is far below that required for spontaneous bubble formation for the methane gas, about 120 atm [5,15]. A shear flow was applied 5 min before to 1 min after the decompression and the final gas content in the solution was measured and it was found to be reduced substantially, even with application of a low shear rate of 25/s. For complete degassing, which is very hard usually, the decompression experiment at elevated temperature and accompanying with ultrasound irradiation was also performed.

2. Bubble nucleation theory

Classical nucleation theory was modified to produce a gaseous bubble formation model [5] and a vapor bubble formation model [15]. The essential element of these models is that the surface energy for formation of the critical cluster in the metastable state is formulated by molecular concepts, while the kinetic formalism of the classical theory is retained. However, a completely different physical mechanism is postulated for gas bubble formation in the gas-liquid solution and for vapor bubble formation in liquid [15]. For gas bubble formation in the supersaturated liquid-gas solution, the aggregation process of the dissolved gas molecules is the very first process for bubble formation.

Consider a liquid-gas solution saturated with gas at pressure P_i at temperature T . As a result of pressure reduction to P_f , the dissolved gases become supersaturated. In this metastable state, the dissolved gases aggregate into clusters. The driving force for this clustering process is just the chemical potential difference between the metastable state and the initial saturated state, which is given explicitly by

$$\mu_m - \mu_s = V_g(P_f - P_i) \quad (1)$$

Assuming that the chemical potential of the molecules in the clusters is the same as the chemical potential of the dissolved gas mol-

ecules in the metastable state, the free energy involved in the clustering process at the supersaturated condition due to the decompression process is given by [5]

$$F_n = -(P_i - P_f)nV_g + \frac{f_L}{2}k_B T n^{2/3} \quad (2)$$

The second term in the RHS of Eq. (2) represents the energy needed for the separation of the cluster from the solvent molecules. This energy is the part of translational motion energy constrained during the dissolution process [16]. A fact that the translational motion energy is the surface energy needed for one molecule cluster to overcome for bubble formation was shown by a heuristic approach [5]. Comparing the above equation to the capillary approximation, the molecular surface tension related to bubble nucleation of the dissolved molecules may be given as follows [17].

$$\sigma_g = \frac{r_g}{2} \left(\frac{f_L}{3} \frac{k_B T}{V_g} \right) \quad (3)$$

The “lost degree-of-freedom” f_L in Eq. (2) represents the degree of translational motion restrained in solution, given by [5,17]

$$\frac{f_L}{3} = \frac{\hat{V}_g}{V_g} \quad (4)$$

If a dissolved gas molecule occupies the equilibrium volume, $\hat{V}_g$ which is equal to $\pi(2^{1/6}\sigma_{LJ})^3/6$, all the three degree-of-freedom of translational motion is restrained. Somehow the molecule occupies more volume than the equilibrium volume, a part of the degree of translational motion will be restrained. The hard sphere diameter ($2^{1/6}\sigma_{LJ}$) for the volume that a single molecule occupies in solution is well defined quantity [18]. The condition for a maximum with respect to n in the free energy is found from Eq. (2) to be

$$(P_i - P_f)n_c^{1/3} = \frac{f_L}{3} \frac{k_B T}{V_g} \quad (5)$$

By substituting Eq. (5), the stability condition of the cluster, into Eq. (2), one may obtain the free energy needed to form the critical cluster such as

$$\frac{F_{n_c}}{k_B T} = \frac{f_L}{6} n_c^{2/3} \quad (6)$$

The growth of a cluster in the supersaturated solution depends on kinetic events within the liquid. Assuming that the mean velocity of the dissolved gas molecules and the number of activated gas

molecules per unit volume in solution depend on solution properties, one may get the steady state nucleation rate of the n_c -mer cluster by dissolved gases [19] with our surface energy as

$$J_{n_c} = Z_{fg} D_{fg} N_g \exp \left(-\frac{f_L}{6} n_c^{2/3} \right) \quad (7)$$

Here D_{fg} is rate that molecules strike the surface area of the cluster and Z_{fg} is the Zeldovich nonequilibrium factor [20]. D_{fg} in Eq. (7) is the rate molecules strike the surface area of the cluster, given by

$$D_{fg} = \frac{\beta_g}{4} \bar{V} \bar{N}_g A_n \quad (8)$$

In Eq. (8), $\bar{V}$ is the average speed of gas molecules within the solution, $\bar{N}_g$ is the number of activated gas molecules per unit volume and A_n is the n -mer cluster surface area given as $A_n = 4\pi r_n^2 = 4\pi r_g^2 n^{2/3}$. The accommodation coefficient β_g was taken to be unity. In fact, the pre-exponential factor in Eq. (7) is insensitive in determining the decompression amount for gaseous bubble formation.

The classical nucleation theory with macroscopic surface tension and the kinetic process by capturing or losing a molecule at the interface provides the following nucleation rate for the critical size bubble [9].

$$J_{r_c} = N_g \sqrt{\frac{\sigma}{2m_g B}} \exp \left[-\frac{4\pi r_c^2 \sigma}{3k_B T} \right] \quad (9)$$

where $B = 2/3$ and r_c in Eq. (9) is the radius of the critical size bubble, which is given by

$$r_c = \frac{2\sigma}{P_g - P_f} \quad (10)$$

The gas pressure inside the critical bubble may be obtained from the Kelvin equation such as [5,17]

$$P_g = P_i \exp \left[-\frac{V_g(P_i - P_f)}{k_B T} \right] \quad (11)$$

It should be noted that the decompression amount for the gaseous bubble formation with the classical nucleation theory given from Eqs. (9) and (10) by replacing P_g as P_i is about 1600 atm for any gas species dissolved in water having surface tension value of 0.072 N/m at room temperature.

A procedure to obtain the bubble nucleation rate from the molecular cluster model [5] is as follows. With an assumed value of the nucleation rate, J_{n_c} , one can calculate the number of molecules constituting the critical cluster, n_c from Eq. (7) and thereafter decompression amount, $P_i - P_f$ for bubble nucleation from Eq. (5) if the values of $\hat{V}_g$ and $V_g(T)$ are provided. The molecular volume $\hat{V}_g$ which restrains all the translational motion of a gas molecule in solution may be obtained from the hard sphere diameter of a molecule [5,17]. This molecular cluster model predicts pressure reduction required for bubble formation in various gas–water solutions, and that depends crucially on the occupied volume of the solute species in solution [6,7]. For example, a decompression amount of 360 atm is required for massive bubble formation in water for helium gas. On the other hand, it needs only 120 atm for methane gas. Furthermore, this model predicts the CO gas bubble formation in Fe–C–O melts [21] and bubble nucleation and subsequent formation of microcellular foam in polymer solutions [22]. More importantly, this model bridges the gap between the bubble embryo (a critical cluster) and the critical bubble [22,23], which was proposed in the classical theory. Once the transition from a cluster to a critical bubble takes place, subsequent growth to macroscopic size bubble can be done by diffusion process through the concentration defect at the bubble wall. A detailed exposition on the molecular cluster model can be found in Kwak [24].

3. Experimental apparatus and procedures

A schematic diagram of the test equipment for the decompression experiment is shown in Fig. 1. The test chamber is made of carbon steel. Two flat glass window 17.7 mm thick allow viewing of the sample during the decompression experiment. To receive the sample solution, a test tube was inserted into the test chamber from the bottom.

The saturated water–gas solution was prepared in a separate mixing cylinder (500 cc), made of stainless steel. The cylinder was filled with deionized water. A magnetic stirrer was used to mix the water and methane gas. Mixing was started by opening valve (5) slowly. The typical mixing time was 6 h. Next, the test chamber was purged and pressurized with methane gas by opening valve (2). After mixing was accomplished, the valve (2) is closed and the test section pressure was decreased slightly by

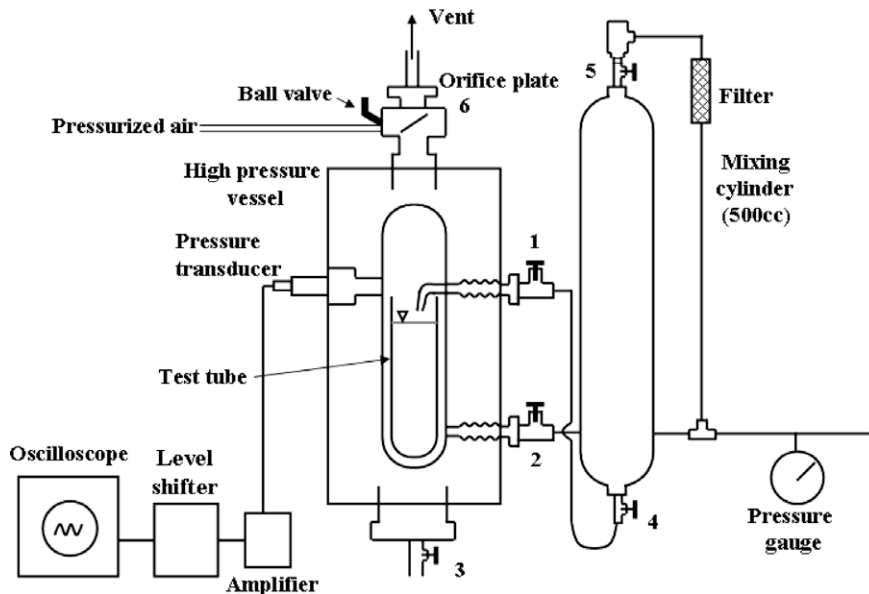


Fig. 1. Schematic diagram of decompression experiment.

opening valve (3). Then the mixture flows into the test tube by opening valve (1) and (4). About 6 cc of the water–methane gas solution was used in each experiment. After filling the test tube with the solution, valve (1) and (2) were closed to isolate the test chamber.

A Couette flow apparatus imposes a shear stress in a fluid without changing the pressure in the fluid, as shown in Fig. 2. The apparatus consists of an annulus formed by inserting a mirror finished aluminum rod with diameter of 7.94 mm into the center of the test tube. The shear flow is set up by rotating the rod by a small electric motor. The motor located at the top of the test chamber was attached to a gear box, and the speed was controlled by a variable DC voltage. The rotating rod was connected to a gear box with a 22:1 gear ratio. To eliminate the friction of the rotating rod, the end of the test tube was made of aluminum and fitted with a bearing.

The speed of the rotating rod was measured with a digital strobe, and found to be 240–1200 rpm. Speed below 240 rpm could not be operated. The corresponding shear rates are 20–100/s and Taylor numbers are 37,120–928,000. The rotating speed of the rod was found to be linearly dependent on the input voltage to the motor. It is known that a secondary flow called a Taylor vortex occurs if the rotation speed is above a critical value of the Taylor number, 33,000 in this case. The Taylor number for this particular case of rotating of inner cylinder only is defined as

$$T_a = \frac{4\Omega_1^2 R_1^4}{\nu^2 (1 - \eta^2)^2} \quad (12)$$

where $\eta = R_1/R_2$ and the radius of aluminum rod, R_1 is 3.97 mm and the radius of the test tube, R_2 is 6.75 mm. The Taylor vortices were observed at all rotation speeds tested and at a speed of 600 rpm, the

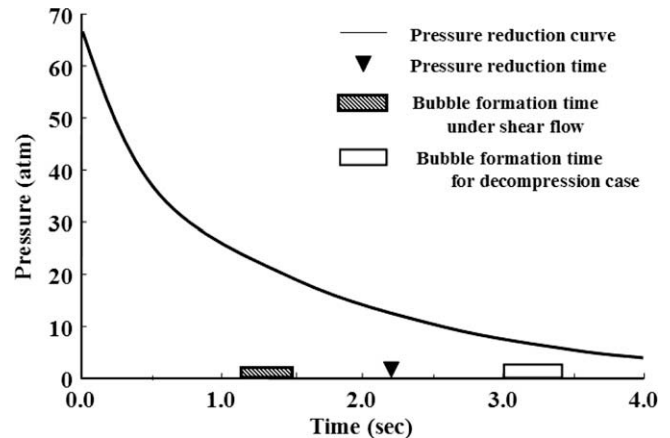


Fig. 3. Time dependent gas pressure inside the test chamber with an orifice diameter of 0.81-mm.

wiggly pattern of the Taylor vortex was seen in another test visualizing the flow pattern by using aluminum powder. This secondary flow is superimposed upon the main shear flow but is very weak in most instances. The time we imposed the shear flow field was 5 min before to 1 min after the decompression.

The decompression process was started by opening a ball valve (6) equipped with a fast-action, automatic, compressed air operator, located above the top of the test chamber. A high speed camera (Fairchild, Model HS 401) was started just before the decompression process. The film speed employed was about 200–400 frames/s. A timing light with 100 cycles per second was used to indicate the time at the edge of the film. The rate at which the pressure in the test section dropped was controlled by the size of the orifice on the outlet side of the ball valve. In this experiment an 0.81-mm diameter orifice was used. A piezoelectric pressure transducer installed at the wall of the test chamber measured the pressure reduction rate in the test section. A typical decompression rate in the test section is shown in Fig. 3.

After the decompression experiment finished, an attempt was made to measure the final concentration of the dissolved gas using gas chromatography (Beckman) with some external modifications. This modification consisted of some equipment to separate the water from the gas before it entered the diffusion column in the gas chromatography setup. Reliable results were usually achieved if the concentration was less than about 10 times the saturated concentration equilibrated at atmospheric pressure. The mole fraction of methane gas in water solution was estimated by Henry's law, $P = Hx$, where P is equilibrium pressure in atm unit. The value of Henry's constant for water–methane solution at 25 °C is about 4.13×10^4 atm [25].

4. Experimental results and discussion

4.1. Decompression experiment

As shown in Fig. 2, the pressure–time decay curve in the test chamber was of an exponential type from which an exponential time constant (t_e) can be obtained. The pressure reduction time (t_p) is defined as twice as the exponential time, or $t_p = 2t_e$. A bubble formation time (t_b) is defined as the time required to detecting a group of bubble in the solution after initiation of the decompression. Bubble nucleation in the supersaturated solution developed from the solution with the equilibrium pressure of 68 atm scarcely occurred by decompression only so that the final concentration of the dissolved gas was hardly measured. In this case the bubble formation time is about 2.97 s. As shown in Fig. 4a, a countable num-

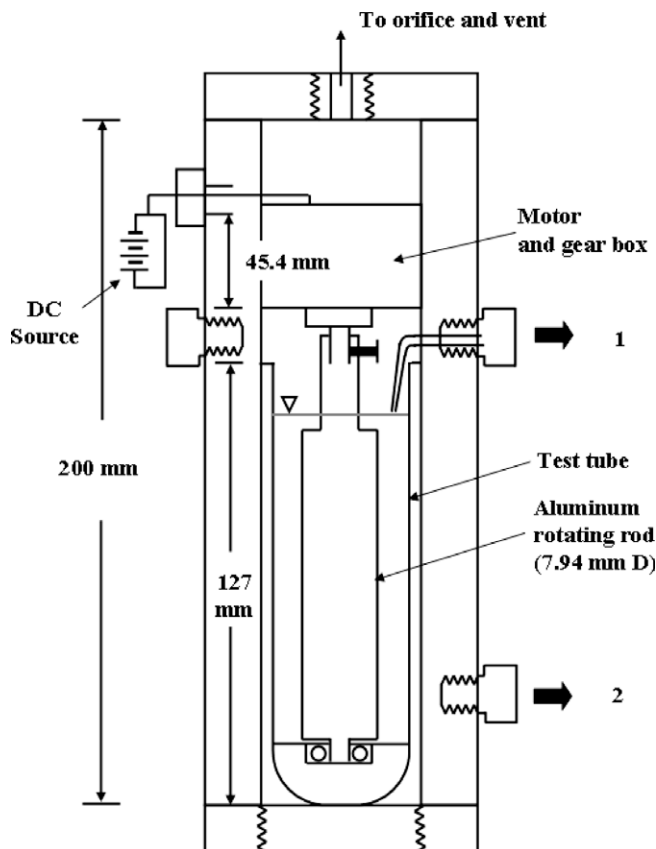


Fig. 2. Arrangement for shear flow experiments.

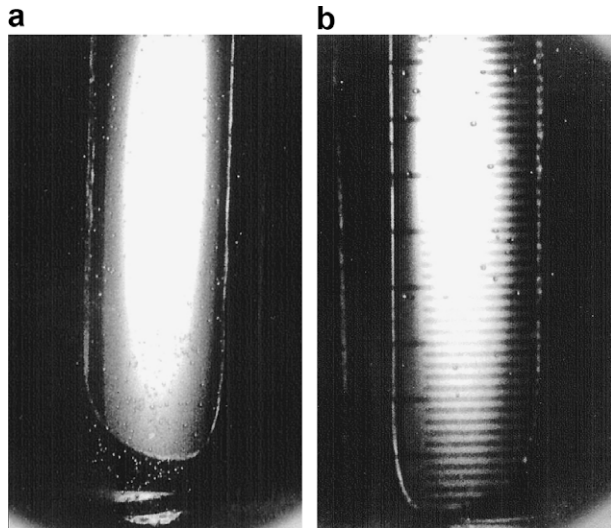


Fig. 4. Initial bubble formation stage for pure water at $t = 2.40$ s after decompression and for water mixed with a surfactant at $t = 3.60$ s after decompression. The bubble formation time in this case is $t_b = 1.83$ s.

ber of bubbles might be formed from the cavities on the surface of the test tube heterogeneously [26]. As is well known, gas cavities on the surface provide sites for bubble nucleation with lower energy barrier than that for homogeneous nucleation. In all these decompression tests, heterogeneous bubble formation occurred only a short period of time and the solution remained highly supersaturated.

4.2. Surfactant effect on gaseous bubble nucleation

In another series of tests, a surfactant (sodium-dodecyl-benzene-sulfonate) was added to the water–methane solution. For a very dilute surfactant concentration (1.5×10^{-4} g mol/l) a number of bubbles formed on the test tube surface as can be seen in Fig. 4b and the bubble growing process was inhibited. A further increase in the surfactant concentration hindered the nucleation process of the bubbles, and only 2–3 bubbles formed on the glass surface. With a surfactant concentration of 1.1×10^{-3} g mol/l which reduces the interfacial tension of water as much as 28 dyne/cm, no

Table 1

Shear flow experiments; initial saturation gas pressure is 68 atm where mole fraction of methane gas saturated with atmospheric pressure in water solution at 25 °C, x_o is 2.42×10^{-5} .

Test description	Rotation speed (RPM)	Bubble formation time, t_b (s)	$x_f \times 10^5$ final mole fraction	Level of concentration $\delta = x/x_o$	Remarks
Shear flow $t_p = 2.64$ s pure water	No rotation	2.97	50.4	20.8	Bubbles form on metal rotor surface only. One can hardly measure the residual concentration in this case
	300	1.46	12.6	5.21	Homogeneous bubble
	600	1.30	7.8	3.22	formation;
	900	1.19	7.2	2.98	bubbles can be seen inside tube
	1200	1.13	5.2	2.15	

bubble formed even on the glass surface. This might be due to the fact that a surface active agent plays a role stabilizing the bubble nucleus [27]. The surfactant molecules surround the bubble nuclei to form a micelle and block the diffusion of the dissolved gas molecules to the bubble nuclei by which the nuclei grow. Similar result was observed for the CO bubble formation in iron melts: no bubble formation occurs provided that the surface of embryo is fully covered by surface active atoms [21]. This observed results indicate that aggregation of the dissolved gas molecules in the solution is the very first process for bubble formation [5,17]. This finding suggests that the classical theory with the macroscopic surface tension value [28] cannot explain the gaseous bubble nucleation events in solution. In fact, Briggs [29] observed that the tensile strength of water reduced very much near melting point where the surface tension becomes large.

4.3. Gaseous bubble nucleation under shear flow

The shear flow effect on bubble formation was found to be very effective. Bubble formation under the shear flow occurred earlier

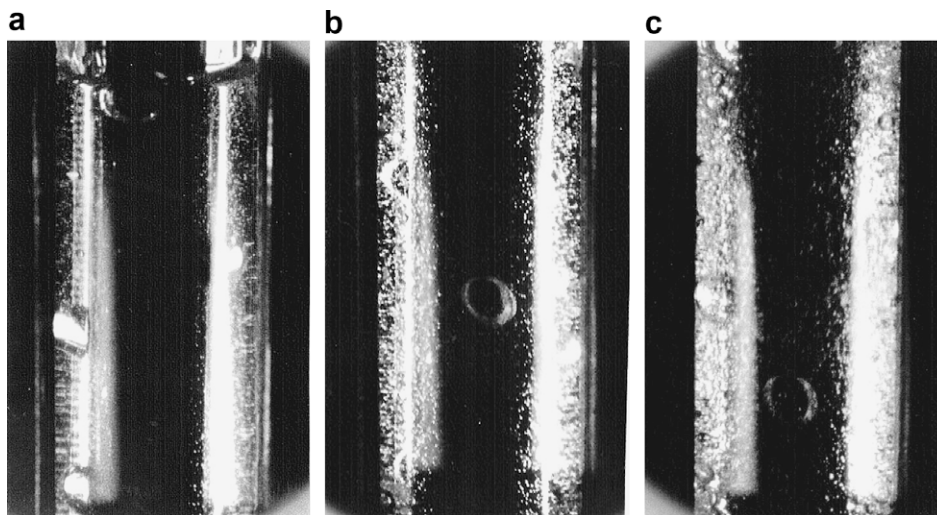


Fig. 5. Bubble nucleation and growing stage under shear flow at time (a) 2.16 s, (b) 3.16 s and (c) 4.66 s after decompression. In this case, the bubble formation time is $t_b = 1.46$ s.

than the decompression time, as shown in Fig. 3. Also the bubble formation time decreased as the rotation speed was increased as noted in Table 1. Active bubble formation always occurred and the final gas concentration in the solution reduced substantially even at the lowest speed of 300 rpm. A picture of the bubble formation at this speed is shown in Fig. 5. Many tiny bubbles move around the tube. A couple of large bubbles due to coalescence are also seen. The final supersaturation values decrease as the rotation speed increases from 300 to 1200 rpm, as confirmed in Table 1. The test results for the bubble formation in a shear flow field accompanying the decompression process are summarized in Table 1. The local heating due to the shearing action is certainly negligible for the speed ranges tested.

The decompression amount for massive bubble formation from a water–methane gas solution at 25 °C, calculated from Eqs. (4)–(6) with $J_{nc} = 10^6/\text{cm}^3$, is about 120 atm [5]. This value is the exactly same as the observed value by Gerth and Hemmingsen [30]. The number of molecules inside a critical cluster is about 560 in this case. A molecular dynamics study yielded that the shearing action changed the liquid structure to stratify along the line of shear [31] so that the molecules are reordered to be staggered in the normal to the velocity gradient, as shown in Fig. 6. Such a structure rearrangement enhances the self-diffusion coefficient of the dissolved molecules and increases the dissolved gas volume occupied in the solution so that the decompression amount for bubble formation reduces correspondingly.

With a 20% increase in the effective diameter of the dissolved molecules, the decompression amount for massive bubble formation in the water–methane gas solution reduces to 70 atm from 120 atm, as verified in this experiment. In Table 2, given amount of decompression of 67 atm, the number of molecules constituting the critical cluster and the corresponding nucleation rate dependent on the applied shear rate are listed. A proper nucleation rate

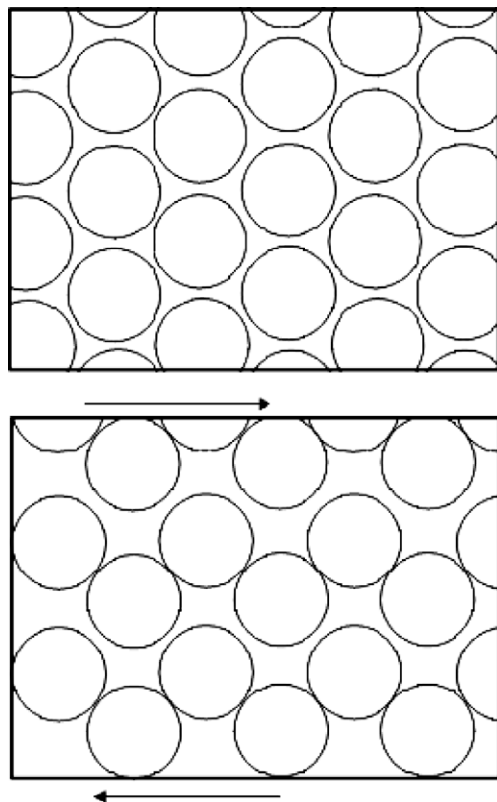


Fig. 6. A pictorial representation of the structural change of liquid molecules under shear flow by Heyes et al. (Ref. [31]).

Table 2

Possible fractions of volume changes and the corresponding number of molecules inside the critical clusters and their nucleation rates which are matched to the measured number of degassed methane molecules dependent on shear rates.

Shear rate (/s)	Fraction of volume change of dissolved molecule	Number of molecules inside the critical cluster, n_c	Nucleation rate of the critical cluster, J_{nc}	Number of molecules degassed per unit volume calculated from Eq. (9)
25	0.21475	951.7	5.07×10^3	5.08×10^{19}
50	0.21490	951.0	5.19×10^3	5.24×10^{19}
75	0.21499	950.6	5.27×10^3	5.26×10^{19}
100	0.21505	950.3	5.31×10^3	5.29×10^{19}

J_{nc} at given shear rate may be estimated from the measured number of degassed molecules per unit volume, which can be calculated by the RHS in the following equation.

$$J_{nc} n_b t_{nu} = (x_i - x_f) N_w \quad (13)$$

where n_b is the number of molecules inside a 120- μm radius bubble which is developed from the critical cluster [22,23] and t_{nu} is nucleation duration of 60 s. With the estimated nucleation rate value, one may calculate the effective molecular volume of the dissolved gas in shear flow. As can be seen in Table 2, about 21.5% increase in the molecular volume of dissolved gas in shear flow. In the above equation x_i and x_f are the mole fractions of dissolved methane molecules at initial state saturated with 68 atm and at final state after the nucleation process, respectively. The bubble radius of 0.12 mm is just average bubble radius observed in the experiments. It is noted that narrow range of size distribution in bubble radius was observed in the bubble formation in polymer solution [23,32].

Even though the final mole fraction of methane gas is discernable depending on the amount of shear rate, the nucleation events are almost similar as confirmed in Table 2. This is because only a few percent difference in the number of degassed molecules exists between the low and high shear rates. Furthermore, the calculation results shown in Table 2 indicate that homogeneous nucleation might occur under shear flow because degassing of large amount of molecules from the solution cannot be possible through countable number of bubble formation on surface, or heterogeneous bubble nucleation. Certainly, the homogeneous bubble nucleation under shear flow cannot be explained by the classical nucleation theory because the interfacial tension remains constant under the flow.

4.4. Temperature dependence on bubble nucleation

As can be seen in Table 1, it is very hard to degassing the water–methane solution to the saturated condition at the ambient pressure. At high solution temperature up to 100 °C, the decompression experiment for the water–gas solution was done for possible complete degassing. Such high temperature of the test chamber was achieved by irradiation of power lamp. For steady state condition of the test chamber at a prescribed temperature was obtained after 3–5 h of irradiation.

One may calculate the temperature dependence of the decompression amount for bubble formation. Assume that the surface tension for the formation of the cluster, σ_g in Eq. (3), depends on the temperature according to an empirical power law [33] such as

$$\sigma_g = A \left(1 - \frac{T}{T_c} \right)^\alpha \quad (14)$$

where α is some power and A is some constant. With the above relation, the temperature dependence of the stability condition of the critical cluster becomes

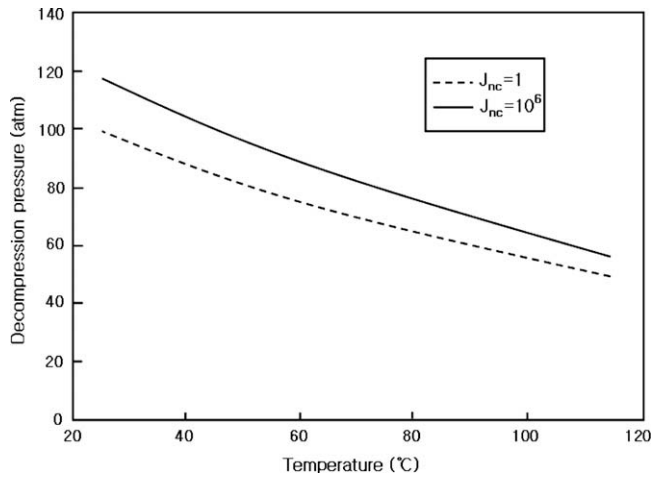


Fig. 7. Decompression pressure amount for bubble nucleation in water–methane solution depending solution temperature.

$$(P_i - P_f)n_c^{1/3} = \left(\frac{k_B T_{ref}}{V_{g,ref}} \right) \left(\frac{T_{ref}}{T} \right) \left(\frac{T_c - T}{T_c - T_{ref}} \right)^{6\alpha/5} \quad (15)$$

where $V_{g,ref}$ is the molecular volume of the dissolved molecule at a reference temperature T_{ref} , say 25 °C. With a value of $\alpha = 11/9$, the decompression amount with nucleation rate values of $J_{nc} = 1$ and $J_{nc} = 10^6$ are shown in Fig. 7. This figure indicates that massive bubble formation may occur around 80 °C with the decompression amount of 70 atm. Indeed, explosive bubble nucleation was observed at 80 °C at which vapor bubble nucleation hardly occurs as shown in Fig. 8. This observation shows vividly how the dissolved gas contents affect the bubble nucleation behavior in supersaturated solution at high temperature. However, such explosive bubble nucleation was not occurred at the solution temperature of 50 °C at which more heterogeneous nucleation occurred as shown in Fig. 9. In fact, previous study has revealed that the superheat limit of water 303 °C cannot be achieved experimentally due to the dissolved gases in solution [17]. The final concentration of the dissolved gases after decompression test at 80 °C is about $\delta = 2.55$.

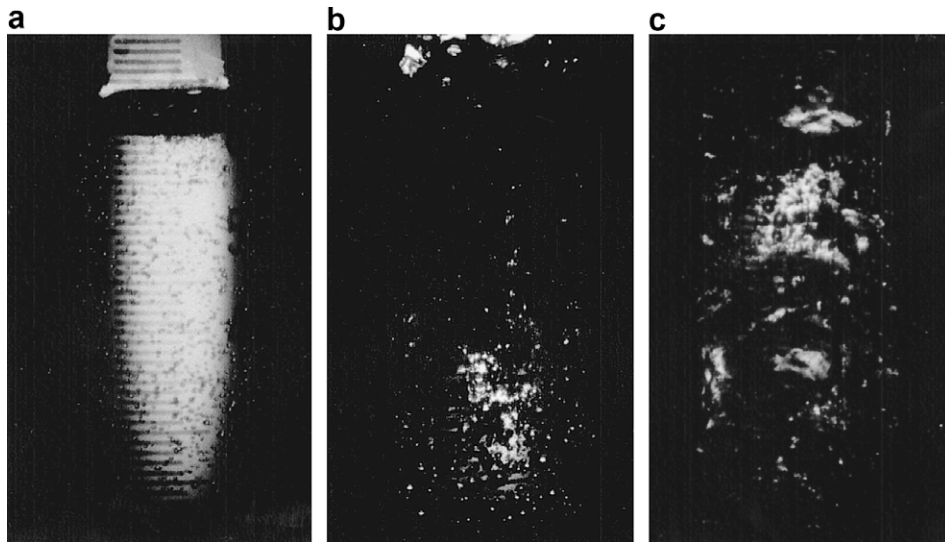


Fig. 8. Bubble nucleation and growing behavior in water–methane solution of temperature, 80 °C at time (a) 2.40 s, (b) 3.60 s and (c) 4.30 s after decompression from 68 atm. The bubble formation time in this case is $t_b = 1.83$ s.

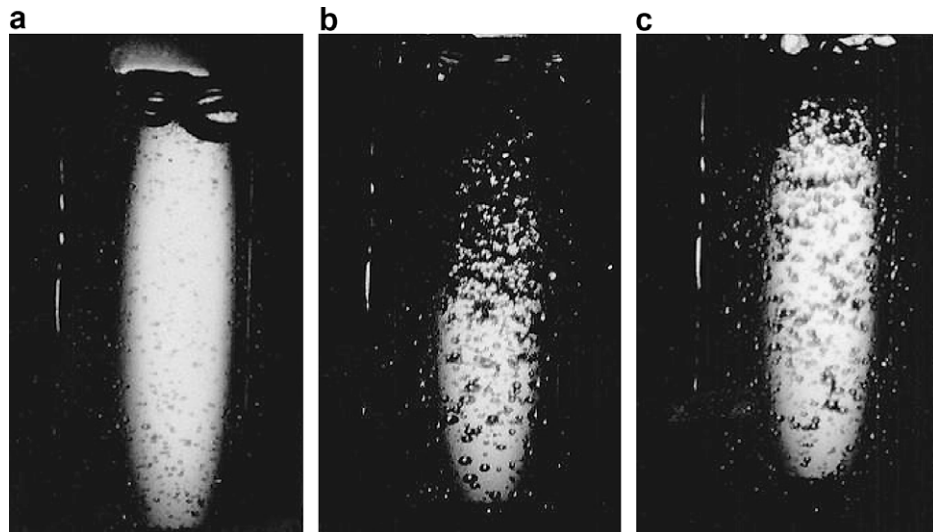


Fig. 9. Bubble nucleation and growing behavior in water–methane solution of temperature, 50 °C at time (a) 3.10 s, (b) 4.10 s and (c) 6.00 s after decompression from 68 atm. The bubble formation time is this case is $t_b = 2.44$ s.

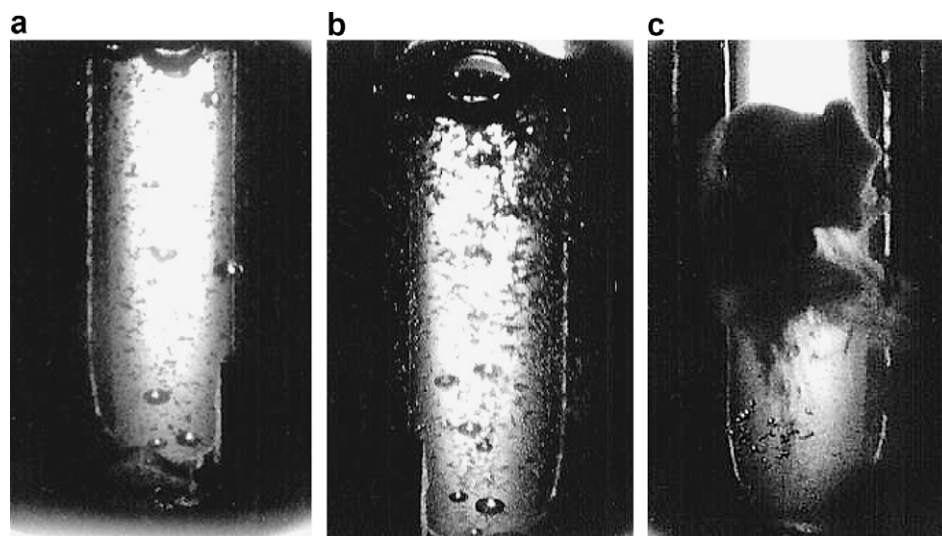


Fig. 10. Bubble nucleation process under ultrasonic field at time (a) 2.48 s, (b) 3.48 s with ultrasound frequency of 2.35 MHz and with 0.5 W power input and (c) 0.27 s ultrasound frequency of 1.65 MHz and with 4 W power input with 4 W input.

However, the level of the concentration saturated with atmospheric pressure ($\delta = 1.0$) was obtained for decompression test at 100 °C.

4.5. Decompression accompanying with ultrasonic fields

For complete degassing from the saturated water–methane solution at 68 atm, a decompression experiment accompanying with ultrasonic wave was also done. A disc type ultrasonic transducer (Channel Industries Inc., USA) was installed at the bottom of the test tube. Two different transducers with resonant frequencies of 2.35 MHz (0.89 mm thickness and 9.53 mm diameter) and 1.65 MHz (1.27 mm thickness and 9.53 mm diameter) were used. A function generator which was connected to a broadband power amplifier was used to operate the transducers.

When the ultrasonic power was relatively weak, below 0.5 W at 2.35 MHz, the bubble formation started slowly inside the solution as shown in Fig. 10a and b. The fine bubbles appeared in small irregularly shaped groups and the number of these groups gradually to darken the tube almost uniformly. At this low power input, the bubble formation time which was 1.26 s, was still well below the decompression time as shown in Fig. 3. The final mole fraction value of methane is about 2.43×10^{-4} in this case. Stronger ultrasonic power showed a strikingly different bubble formation behavior. A very short time after the decompression, a stream of fine bubbles was observed to flow from the bottom of the test tube. The bubble cloud expanded as it rose. Upon the reaching the top section of the test tube the cloud bend back and the upper part of the test tube would become dark with fine bubbles while a couple of cm of relatively clear liquid existed at the bottom. In most instances the entire test tube would eventually become dark with bubbles. Fig. 10c shows early stage of the bubble cloud. In this particular case of 4 W input power with 1.68 MHz frequency application after decompression, the level of concentration to the atmospheric pressure is about 0.94 or $\delta = 0.94$. Less explosive behavior of bubble formation was observed for the solution with addition of surfactant even though strong power of ultrasound was applied.

5. Conclusion

A decompression experiment of water–methane gas solution was done to investigate gas bubble formation under shear flow.

The shearing action which changes the liquid structure stratifying along the line of shear promotes the bubble nucleation process quite a bit. It is understood that the dissolved gas molecules can occupy more volume in the shear layer where the interaction of solvent molecules is loosened. In another test, a concentration of 1.1×10^{-3} g mol/l of sodium-dodecyl-benzene-sulfonate, which can reduce the interfacial tension of water as much as 28 dynes/cm in the solution stopped the bubble nucleation process completely. This result indicates that aggregation of the dissolved molecules in the solution is the very first process for bubble nucleation of dissolved gases. For complete degassing below the saturation with the atmospheric pressure, high power ultrasound input to the solution is required.

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Heterogeneous bubble nucleation on ideally-smooth horizontal heated surface



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ABSTRACT

Our experiments and analyses of the bubble incipient on ideally-smooth, horizontal heated surface confirm the observed low superheat and the weak surface-wettability dependence. These are contrary to the previous heterogeneous nucleation predictions, so to clarify this difference and the experimental results not explained by previous nucleation theories we adapt a new model based the thermal boundary layer. The model includes the kinetic dynamics of the superheated liquid and the thermodynamic stability of the generated vapors. The fluid particle transfer rate is estimated with the Smoluchowski equation. Consequently, the incipient bubble nucleation on the ideally-smooth horizontal surface, with different wettability, is described and the predictions match the experiments fairly well.

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1. Introduction

The early stages of nucleation theory, referred to as classic nucleation theory (CNT), are based on the Gibbs theory of new phase formation, ideal gas kinetics, and the energy barrier required for nucleus generation [1–5]. The energy barrier is mainly determined by the energy required for generating the new interface and the energy consumed by the phase change of the metastable initial phase to a stable state. In other way, kinetic nucleation theory (KNT) was also developed as a theoretical nucleation theory [6–12]. The main difference between CNT and KNT is how the model calculates the evaporation rate and condensation rate. In CNT, the nucleation rate is derived from the evaporation and condensation rates with an equilibrium distribution. In KNT, however, instead of using the equilibrium distribution, the evaporation and condensation fluxes and their corresponding transfer rates are calculated separately by considering kinetics and the potential field as a driving source. In recent studies, the rate of nucleation in the KNT model was characterized by the mean first passage time by solving the Smoluchowski equation [9–12]. According to previous nucleation theories, saturated water under atmospheric conditions could produce a newly generated bubble at ~ 300 °C.

The heterogeneous bubble nucleation occurs under transient or steady heating. In transient experiments the classical homogeneous

high-superheat limit is observed, since the associated high heating rates prevent growth of vapor bubbles from the surface imperfections [13]. Steady-state results show reduced superheat, since (a) the surface is rarely smooth at the scale of the critical nucleus, and (b) the surface energy heterogeneities such as local hydrophobicity. Corty and Foust [14] and Bankoff [15] suggested that the widely accepted trapped-vapor theory, which states that cavities on commercial heating surfaces can trap vapors and then it act as nuclei, is the most likely theory for explaining the origin of a boiling bubble. In other words, if the surface cavity is larger than the critical nucleus, the cavity traps vapor and becoming nucleus for heterogeneous nucleation at low superheat. Furthermore, the local surface hydrophobicity also induces heterogeneous nucleation at a reduced superheat, since the nanobubbles existing on the hydrophobic sites become activated and form nucleus seed [16,17]. Qi and Klausner [18] hypothesized the occurrence of nanobubbles for heterogeneous nucleation and Nam and Ju [19] analyzed the incipience of nanobubbles at low superheat on Teflon patterned surface. However, the presence of the nanobubbles could be detached via degassing procedure [20]. Thus, there is a continuing debate on the mechanism of bubble nucleation on a hydrophobic surface without surface cavities at low superheat.

Recently, studies regarding bubble nucleation have entered a new phase with the introduction of advanced surface treatment techniques. The most interesting experimental result is heterogeneous boiling bubble nucleation at low superheats (with a superheat for bubble inception of only ~ 10 K under atmospheric

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Nomenclature

c	concentration of particles in one dimension (m^{-1})
D	diffusivity ($\text{m}^2 \text{s}^{-1}$)
f	distribution function (–)
Gr	Grashof number (–)
g	acceleration of gravity [$9.81 (\text{m s}^{-2})$]
h	latent heat (J kg^{-1})
J	transfer rate (s m^3) ^{–1}
k_B	Boltzmann constant (J K^{-1})
L	the length from edge to center of heating surface (m)
n_B	number density of embryos (m^{-3})
P	pressure (N m^{-2})
Pr	Prandtl number (–)
Q	survival probability (–)
R_{ideal}	ideal gas constant [$8.314 (\text{J (K mol)}^{-1})$]
r	radius of nucleus (m)
s	entropy (J (K kg)^{-1})
T	temperature (K)
t	time (s)
u	internal energy (J kg^{-1})
$\vec{u}, \vec{v}$	x - and y -component velocities (m s^{-1})
v	specific volume ($\text{m}^3 \text{kg}^{-1}$)
x	horizontal position
y	vertical position

Greek symbols

β	volumetric thermal expansion coefficient (K^{-1})
θ	contact angle ($^\circ$)
δ_t	thermal boundary layer (m)
Φ	dimensionless temperature (–)
φ	potential free energy (J kg^{-1})
η	similarity variable (–)
μ	dynamic viscosity (kg (m s)^{-1})
ρ	density (kg m^{-3})
σ	surface tension (N/m)
τ	passage time (s kg)
ν	kinematic viscosity ($\text{m}^2 \text{s}^{-1}$)
ψ	stream function (–)

Subscripts

av	average
B	domain B
lv	interface between liquid and vapor phase
sat	saturated state
top	the top of bubble
y	vertical coordinate
0	initial state
∞	bulk state

water-saturated conditions) on a smooth hydrophilic surface that does not have any microstructures to trap a vapor as the seed for the bubble nucleus [21–25]. Using microelectromechanical system (MEMS) techniques for sub-nanometer roughness heating surfaces, researchers have confirmed the phenomenon on a variety of surfaces. Furthermore, researchers report, heterogeneous nucleation at low superheat on hydrophilic nanostructured heated surface, with no microstructure or hydrophobicity to trap vapor for the bubble nucleation [25–28]. These results are contradictory to those predicted by the heterogeneous nucleation theories.

In this study, we explain recent observations of heterogeneous nucleation at reduced superheat on horizontal heated surface free from trapped vapor and under steady-state condition. These contrast the heterogeneous nucleation theories and to clarify this we use a model based on the thermal boundary layer. This combined with the kinetics and dynamics of the superheated liquid and the thermodynamic stability of the generated vapor, leads to prediction of heterogeneous nucleation condition in absence of micro cavities. This model can also be used for hydrophobic heating surfaces.

2. Experiments

To verify the reported nucleation phenomena without surface cavities and at low superheats, we conducted pool boiling experiments with distilled water under atmospheric saturated condition. The electric Joule heating method was employed, using a power supply. The main pool was an aluminum bath and was maintained at a saturated condition by a PID temperature controller. A thin-film (platinum) heater was embedded on one side of the silicon wafer, and smooth surfaces were fabricated on the other side of the wafer via micro-electromechanical system techniques. The complete platinum film heater was H-shaped due to the configuration of the electrode and the main heating components. The central region of the H-shape ($10 \times 10 \text{ mm}$) was the main heating area. Based on the measured resistance of heater and the correlation

developed between resistance and wall temperature, the wall temperature was determined. Taking all instrument errors into account, the maximum uncertainty in the wall superheat is less than 1.2°C over the measured range of the ONB [24,25].

To analyze the heterogeneous nucleation temperature for different wetting surfaces, we used two different wetting smooth surfaces: silicon and heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane (HDFS) coated surface. The plain silicon wafer possesses a very smooth surface with sub-nanometer surface roughness. The HDFS was coated on silicon surface as a very thin layer using self-assembled monolayer (SAM) technique. As Fig. 1 shows, the plain silicon had a 72° static contact angle, while the static contact angle was 106° for the HDFS coated silicon surface.

To avoid the effect of trapped vapors on the surface cavity, the roughness of each surface should be smaller than the critical radius of the nucleus. The critical radius of the newly generated nucleus can be obtained by differentiating the energy barrier equation based on the Gibbs–Duhem equation (because there exists a maximum energy barrier for the nucleus at the critical condition), i.e.,

$$r_c = \frac{2\sigma_{lv}}{P_{sat}(T_l) \exp \left[\frac{v_l(P_l - P_{sat}(T_l))}{R_{ideal}T_l} \right] - P_l} \quad (1)$$

According to the result, the critical radius of the nucleus is of the order of $1 \mu\text{m}$ (Fig. 2). However, the measured roughness of all surfaces were in the nanometer range, as shown in Table 1. This supports that the roughness of these surfaces could not trap vapor as the seed for the nucleation.

All experiments were conducted after degassing procedure for 2 h. With the system open to ambient air pressure through the reflux condenser, the degassed air was expelled while the steam condensed and returned back to the vessel. The tests were carried out by increasing the electrical input in small steps, until the ONB was reached.

Repeatable results for each surface were obtained up and including the ONB. The required superheats for the silicon and HDFS coated surface at the ONB were 10.7 and 4.4 K, respectively.

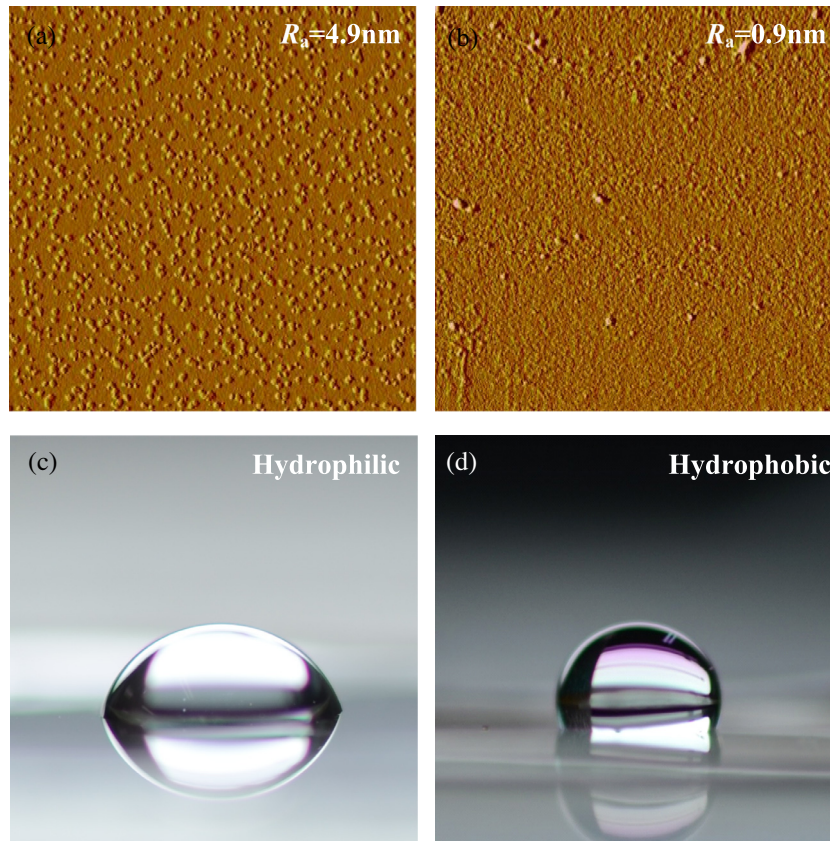


Fig. 1. The heated surfaces used in experiments: (a) AFM image of the silicon surface, and (b) HDFS coated surface. Both actual areas are $5 \times 5 \mu\text{m}$. (c) A $3 \mu\text{l}$ water droplet and its contact angle on the silicon surface (as a hydrophilic surface), and (d) HDFS coated surface coated surface (as a hydrophobic surface). The roughness statistics and contact angles are listed in Table 1.

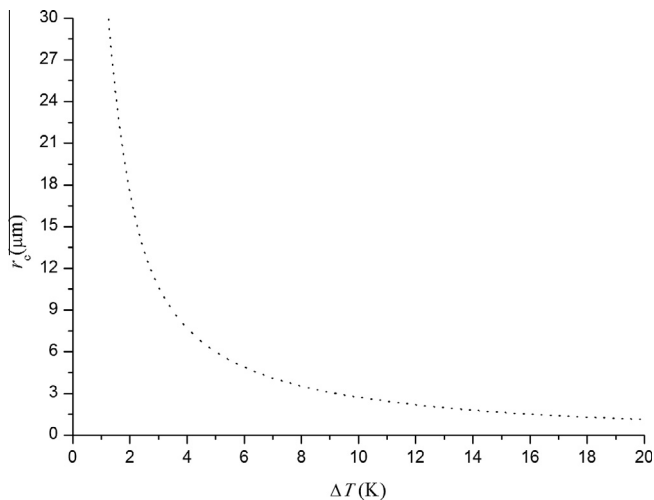


Fig. 2. Dependence of the critical radius of distilled water on wall temperature for atmospheric saturated water.

Table 1
Roughness parameters and water contact angle for the silicon and HDFS coated surfaces used this study. Roughness parameters were measured by AFM.

	R_a (nm)	R_q (nm)	R_{max} (nm)	Contact angle ($^\circ$)
Silicon	4.9	6.6	50.8	72
HDFS coated	0.9	1.9	51.7	106

The most important observation is that the ONBs for all smooth heating surfaces were definitely lower than the predicted values (280–300 $^\circ\text{C}$) by the classic heterogeneous nucleation models

without surface cavities, whether the heating surface was hydrophilic or hydrophobic. This is consistent with the previously reported results for several smooth and nanostructured surfaces [21–28].

3. Theory

To theoretically investigate the heterogeneous bubble nucleation without cavities, we use the potential gradient in the thermal boundary layer adjacent to heated surface for an ideally smooth heated surface. An ideal smooth heated surface has defects that are smaller than the critical size required for the stability of vapor existence on the heated surface; i.e., the vapor cannot be trapped on the surface. The total potential of the system is dependent on the temperature and pressure conditions, which can be represented as the Gibbs free energy:

$$d\phi = du + Pd v + v dP - T ds - s dT. \quad (2)$$

In previous models, the internal energy, volume, pressure, entropy, and temperature difference were not considered for nucleation, because the supplied heat effect and induced flow in the fluid phase were not adopted. However, in real boiling on heated surfaces, there is a definite temperature distribution, due to the supplied heat through the heated surface, as well as a pressure difference (represented by the vertical flow rate) on the heated surface. In this study, for describing the real potential distribution adjacent to the heated surface, the temperature and pressure of the fluid at or just before boiling bubble nucleation are evaluated using similarity analysis for natural convection on a horizontal flat hot surface, with an approximated thermal boundary layer thickness [29,30].

3.1. Evaluating potential gradient on a horizontal heating surface

To evaluate the potential gradient, for thermobuoyant flow over semi-infinite horizontal surface, the temperature and pressure distributions are evaluated. The continuity, momentum, and energy equation are expressed by the Boussinesq relation, under two-dimensional, boundary-layer approximations (x and y are for horizontal and vertical axes) are

$$\frac{\partial \bar{u}}{\partial x} + \frac{\partial \bar{v}}{\partial y} = 0 \quad (3)$$

$$\bar{u} \frac{\partial \bar{u}}{\partial x} + \bar{v} \frac{\partial \bar{u}}{\partial y} = -\frac{1}{\rho} \frac{\partial P}{\partial x} + \bar{v} \frac{\partial^2 \bar{u}}{\partial y^2} \quad (4)$$

$$0 = -\frac{1}{\rho} \frac{\partial P}{\partial y} + g\beta(T - T_\infty) \quad (5)$$

$$\bar{u} \frac{\partial T}{\partial x} + \bar{v} \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2}. \quad (6)$$

It should be noted that P used in these governing equations is the dynamic pressure difference induced by the buoyancy force. The governing equations are reduced using the Grashof number and a similarity variable $\eta(x, y)$

$$Gr_x = \frac{g\beta(\Delta T)x^3}{\nu^2}. \quad (7)$$

$$\eta(x, y) = \frac{y}{x} \left(\frac{Gr}{5} \right)^{1/5} = \frac{y}{x} \left(\frac{g\beta(\Delta T)x^3}{5\nu^2} \right)^{1/5} = \left(\frac{g\beta(\Delta T)}{5\nu^2} \right)^{1/5} yx^{-2/5}. \quad (8)$$

Based on this variable, the stream function ψ and dimensionless temperature are defined as

$$\psi(x, y) = \frac{y}{x} \left(\frac{Gr}{5} \right)^{1/5} f(\eta) = \frac{y}{x} \left(\frac{g\beta(\Delta T)x^3}{5\nu^2} \right)^{1/5} f(\eta). \quad (9)$$

$$T^*(x, y) = \frac{T - T_\infty}{\Delta T} = \Phi(\eta). \quad (10)$$

Owing to the temperature distribution along the heating surface, ΔT could change with the heating surface and liquid condition. Therefore, ΔT is assumed with some positive constant N depending on x as Nx^n ($\Delta T = Nx^n$). The constant for presenting the temperature variation (n) along the x direction is fixed as $1/3$ for the constant heat flux condition [29]. If the center temperature is known, N could be represented with the length from the center to the end of heating surface as

$$N = \frac{\Delta T_{x=L}}{L^n}. \quad (11)$$

$$\Delta T = \Delta T_{x=L} \left(\frac{x}{L} \right)^n. \quad (12)$$

where L denotes the length from edge to center of heating surface. In here, L will be 5 mm.

Chen et al. [29] and Pera and Gebhart [30] presented numerical simulation results for the temperature profile on a horizontal hot surface using governing equations and similarity variables. Evaluating the exact solution for the temperature and pressure profiles with natural convection flow is difficult. However, the complicated profile could be approximated as the proper functional expression with constrained boundary conditions in the thin range adjacent to the heating surface. In this study, the thin region is related to the critical size of nucleation. ($1 \gg \eta$)

Based on reported numerical simulation results, the trend lines of the general dimensionless temperature profile in the thermal boundary layer on a horizontal heating layer could be approximated to the exponential function [$a \exp(-b\eta)$] as shown in Fig. 3 (a and b are arbitrary constants for the given system). Although the arbitrary constants depend on other parameters, the form of the general function is kept. Therefore, we adopt the exponential function as the approximated dimensionless temperature profile in the thermal boundary layer:

$$T^*(x, y) = a \exp(-b\eta) = a \exp \left(-b \left(\frac{g\beta\Delta T_{x=L}}{5\nu^2 L^n} \right)^{1/5} yx^{(n-2)/5} \right). \quad (13)$$

$$T^*(x, 0) = 1, \quad T^*(x, 1) = 0 \quad \text{and} \quad T^*(x, \delta_t) = 0.01. \quad \text{Boundary condition of } T^* \quad (14)$$

Because of the initial condition, the constant a is determined to be unity. Among the boundary conditions, $T^*(x, \delta_t) = 0.01$ arises from the definition of the thermal boundary layer. Let the thickness of the thermal boundary at the center of the heater surface be $\delta_{t,x=L}$. With the boundary conditions and the distance from the edge to the center of the heating surface (L) [$T^*(L, 0) = 1$ and $T^*(L, \delta_{t,x=L}) = 0.01$], the temperature profile is specified as

$$0.01 = \exp \left(-b \left(\frac{g\beta\Delta T_{x=L}}{5\nu^2 L^n} \right)^{1/5} \delta_{t,x=L} L^{(n-2)/5} \right). \quad (15)$$

$$b = \frac{(\ln 100)}{\left(\frac{g\beta\Delta T_{x=L}}{5\nu^2 L^n} \right)^{1/5} \delta_{t,x=L} L^{(n-2)/5}}. \quad (16)$$

Substituting equation Eq. (17) into Eq. (13), one obtains the following dimensionless temperature profile

$$T^*(x, y) = \frac{T - T_\infty}{T_0 - T_\infty} = \exp \left(-\frac{\ln 100}{\delta_{t,x=L}} y \left(\frac{x}{L} \right)^{(n-2)/5} \right). \quad (17)$$

Eq. (18) is the approximated solution in a certain domain from the surface to δ_t by analyzing the trend line of the numerical solution for natural convection on a horizontal heating surface. However, even though the equation is not theoretically derived, the accuracy of the calculated temperature profile will be high near the boundary condition because the accuracy is calibrated by the boundary condition at zero and δ_t height (c.f. $\delta_{t,x=L}$ is approximated to be $210 \mu\text{m}$ based on the pool boiling experimental results with Fourier's law $\delta_t = k \frac{T - T_w}{q''}$; this is similar to value ($100 \mu\text{m}$) used in

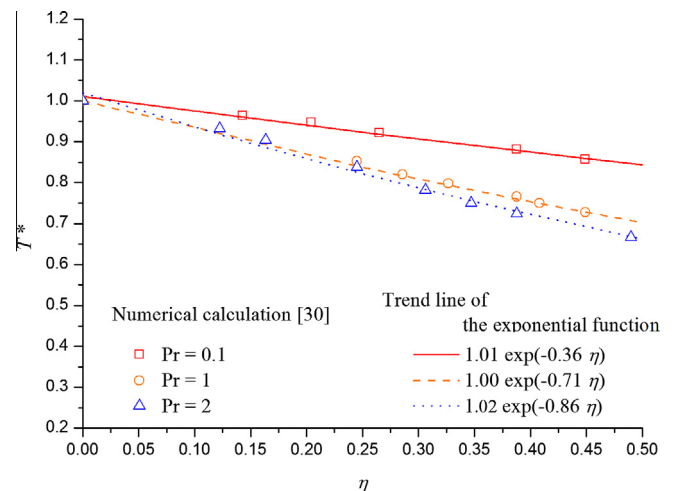


Fig. 3. Dimensionless temperature distributions from the numerical simulations [30], and from the trend-line approximated by the exponential function.

other classic literature for water boiling systems [31]). Furthermore, the domain of interest for nucleation is very small, and the evaluated solution, Eq. (18), could be reasonably applied to the nucleation phenomena. The dynamic pressure was estimated by the relation between the pressure function and the dimensionless temperature [29,30].

Finally, the potential gradient distribution of the superheated liquid on the horizontal heating surface could be investigated by incorporating the temperature profile with the appropriate boundary conditions and the pressure profile. (Although the temperature profile is approximated to the exponential function, because the interesting domain is very thin, we can see the linear trend in Fig. 4.)

3.2. Superheated liquid particles transfer in potential gradient

The evaluated potential profile on the horizontal heated surface is represented using the Smoluchowski's equation to obtain an appropriate fluid particle transfer rate on the ideal smooth horizontal heated surface. In general, the physical random motion of molecules is governed by the Fokker–Planck equation [32,33]. However, because the relaxation time for the velocity distribution is extremely short and negligible, the Fokker–Planck equation for a liquid can be reduced to the Smoluchowski equation. The Smoluchowski equation, with diffusion and convection terms, can be expressed as

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c - vc) \cong \nabla \cdot \left(-\frac{D}{k_B T} \nabla \phi c \right), \quad (18)$$

where c indicates the particle concentration (or the probability of a molecule being in a certain region at time t). The movement of particles in the thermal boundary layer can be expressed by substituting the evaluated potential distribution of the horizontal heated surface for the convection mass-flux term in Eq. (18). In this study, we assume that the convection mass-flux term is dominant. This approximation is reasonable for the potential gradient model, because there is the macroscopic flow induced by the temperature distribution and density difference; the diffusion term on the right-hand side of Eq. (18) is negligible.

With the evaluated potential profile and the Smoluchowski equation, the mean first-passage time is estimated for characterizing the nucleation rate on the horizontal heated surface. The mean first-passage time for boiling specifies the average time required for the particles of the working fluid to move from the certain bubble region to the outside. By setting the calculation domain (do-

main B) to be the critical state of newly generated nuclei, the mean first-passage time could represent the evaporation rate of real boiling on the horizontal heated surface as shown in Fig. 5.

To determine the mean first-passage time, the survival probability $Q(t)$, i.e., how many molecules will remain in the domain after time t , is defined as

$$Q(t|y_o) = \int_B c(y, t|y_o) dy \quad \text{Survival probability in domain B after time } t \quad (19-a)$$

$$Q(t \rightarrow \infty|y_o) = 0 \quad \text{and} \quad Q(t=0|y_o) = 1 \quad \text{Initial conditions of } Q. \quad (19-b)$$

The initial conditions of survival probability indicate that all of the molecules initially located in the domain will escape from the domain after an infinite time by molecule transfer dynamics. The survival probability can be transformed to the probability of escaping from the domain as $1 - Q(t)$. The mean first-passage time is expressed by the mean average of the survival probability integrated with respect to time as

$$\tau(y_o) = \int_0^\infty t dt \frac{\partial}{\partial t} [1 - Q(t|y_o)] = \int_0^\infty dt \cdot Q(t|y_o). \quad (20)$$

If Eq. (18) is integrated with respect to position y over the domain from time $t = 0$ to ∞ , then we obtain

$$\int_0^\infty \int_B \frac{\partial c}{\partial t} dy dt = \int_0^\infty \int_B \nabla \cdot \left(-\frac{D}{k_B T} \nabla \phi c \right) dy dt. \quad (21)$$

Integrating with respect to y transforms the probability of the molecules being in a certain bubble region at time t into the survival probability, Q , in the domain:

$$\int_0^\infty \frac{\partial Q(t|y_o)}{\partial t} dt = \int_0^\infty \nabla \cdot \left[-\frac{D}{k_B T} \nabla \phi Q(t|y_o) \right] dt. \quad (22)$$

The survival probability can be described in terms of the mean average of the escape probability by the initial condition of Q (Eq. (19-b)):

$$\tau(y_o) = \int_0^{y_o} 1 / \left(\frac{D}{k_B T} \nabla \phi \right) dy. \quad (23)$$

The escape time, τ , of a certain domain can be developed with the evaluated potential distribution on the horizontal heated surface in the thermal boundary layer, given by Eq. (2), and the Stokes–Einstein equation for the diffusivity:

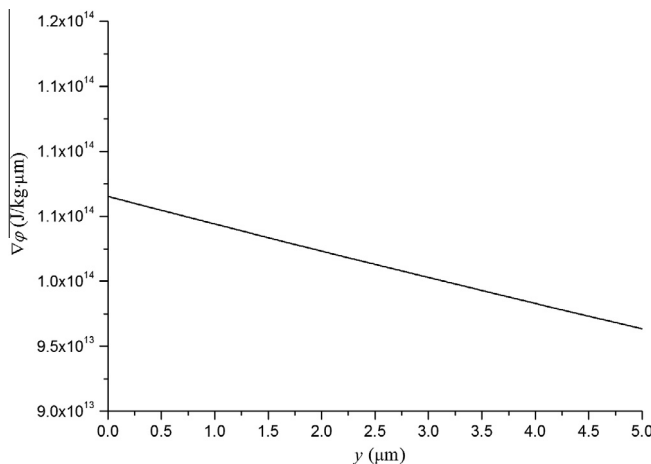


Fig. 4. Potential gradient distributions along the vertical direction, at the center of heated region ($\theta = 60^\circ$, $\Delta T = 5$ K and $\delta_t = 210$ μm).

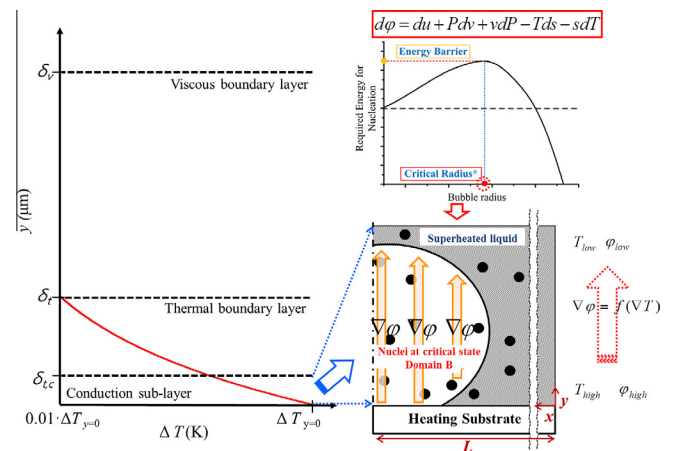


Fig. 5. Schematics of the temperature distribution, thermal boundary layer, total energy as function of bubble radius, and the bubble nucleation.

$$\tau(y_o) = \int_0^{y_o} 1 / \left[\frac{1}{6\pi\mu r_o} \left(\frac{\partial u}{\partial y} + P \frac{\partial v}{\partial y} + v \frac{\partial P}{\partial y} - T \frac{\partial s}{\partial y} - s \frac{\partial T}{\partial y} \right) \right] dy. \quad (24)$$

where r_o is the radius of fluid particle. The final average escape time for all possible initial positions in the domain, weighted by the Boltzmann factor with an equilibrium distribution of particles (or molecules), is given by

$$\tau_{av} = \frac{\int^B \tau(y_o) \exp\left(\frac{-\Delta\phi}{k_B T}\right) dy}{\int^B \exp\left(\frac{-\Delta\phi}{k_B T}\right) dy}. \quad (25)$$

Consequently, the transfer rate of superheated liquid particles in the domain can be defined by n , the number of molecules in the domain, as

$$J = \rho \frac{n_B}{\tau_{av}}. \quad (26)$$

To include the spatial variation of transfer rates, each calculated flux is averaged for the bubble regime. For the averaging procedure, the bubble domain from the center of the nucleus to the

end of the bubble nucleus was divided into 100 small sections. Then, the transfer rate was estimated with the number of particles and the average escape time along the y axes at each position. Finally, by normalizing the sum of the transfer rate at each local position by the number of divided sections (100), the average transfer rate of the nucleus (J_{av}) can be obtained.

Figs. 6 and 7 show the evaluated each evaporation rate for each small sections and average evaporation rate for the domain on the horizontal heated surface. These results are calculated for atmospheric saturated water boiling with superheated surfaces. Basically, in the calculation thermal boundary layer was assumed as $210 \mu\text{m}$ based on experimental results. However, because we could not know the exact thickness of thermal boundary layer, we calculated average evaporation rates for different thickness cases. According to the results, we can confirm very high transfer rates in the $10^2 \mu\text{m}$ order of thermal boundary thickness. It indicates that the liquid particles in the potential gradient (the thermal boundary layer) move out with a very high transfer rate from the domain to the outside, where the potential is lower than that in the previous location, even though the exact transfer rate is slightly dependent on the surface characteristics and the superheated condition.

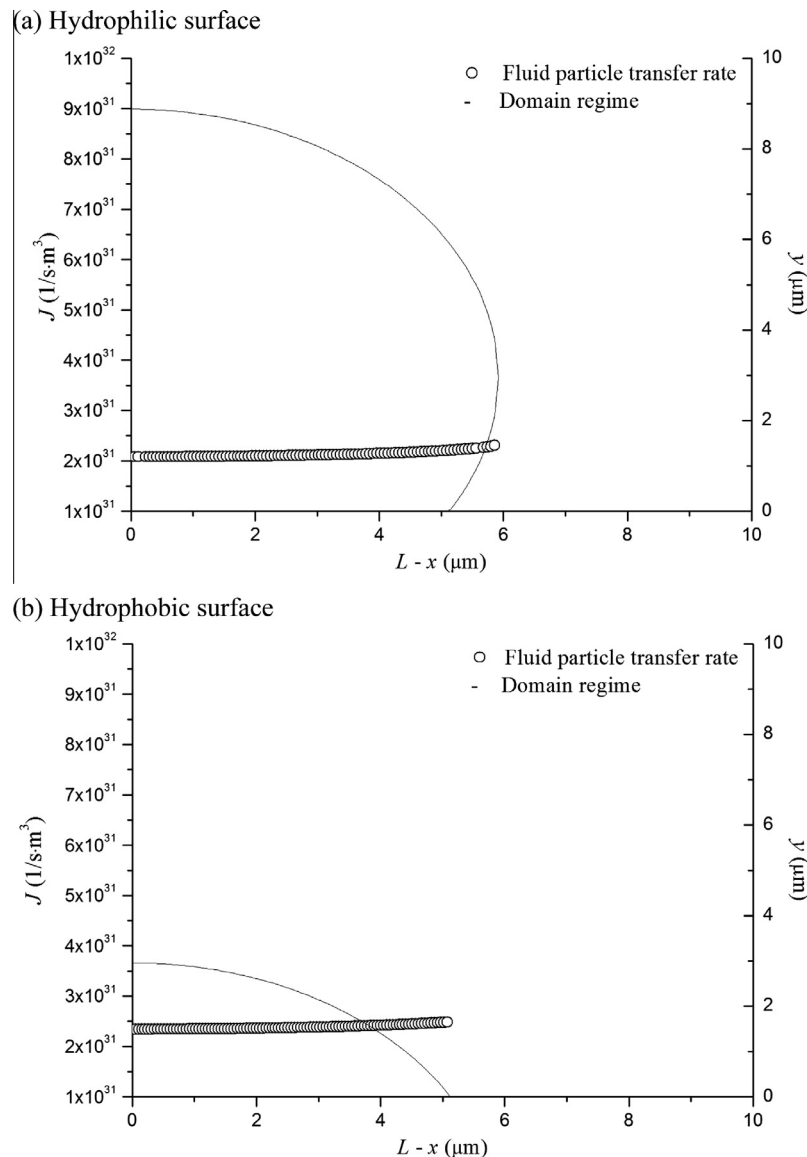


Fig. 6. Lateral distribution of the fluid particle transfer rate and bubble contour for, (a) $\theta = 60^\circ$, and (b) $\theta = 120^\circ$, for the critical nucleus condition and $\Delta T = 5 \text{ K}$ under atmospheric saturated water condition. $L - x = 0$ is at the center of surface.

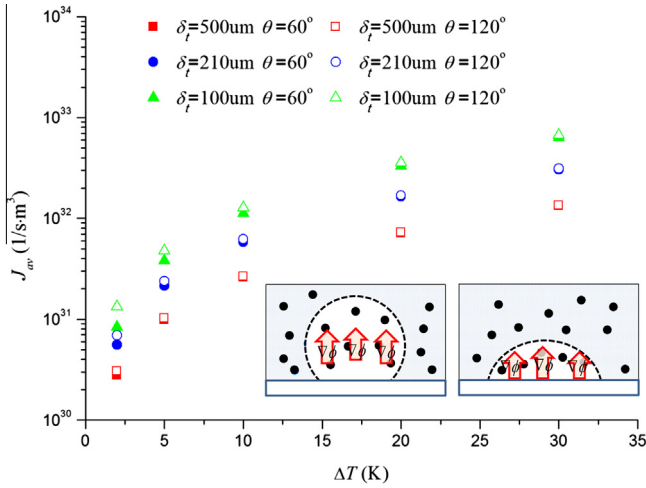


Fig. 7. Variations of the average fluid particle transfer rate for critical nucleus formation as function of wall superheat for two different contact angles under atmospheric saturated water condition with different thermal boundary layer thicknesses.

By such high liquid molecules transfer rate, a spontaneous decrease in the number of particles in the domain occurs, which may promote the initiation of bubble generation, because to initiate a phase change from liquid to vapor, a large density decrease is required. Interestingly, the order of evaluated nucleation rates is as high as the calculated nucleation rates for the moment of heterogeneous nucleation using PFT (phase field theory) [34] and MD (molecular dynamics) simulation tool [35]. This supports that the calculated transfer rate for the new nuclei is sufficiently high to lead to ebullition. From this, we can conclude that the induced potential gradient on the ideally smooth horizontal heated surface, due to the supplied heat, causes large enough particle transfer to generate vapor.

Such high transfer rates of liquid particles adjacent to the heated surface are directly related to energy gradient in the thermal boundary layer. To clarify the thermal boundary layer effect, we also calculated what would happen if the thermal boundary layer was very thin compared with the critical nucleus (calculation domain B). When the thermal boundary layer is very thin compared with the critical nucleus, we can neglect the effect of potential gradient, such as previous nucleation models. The critical nucleus is 2.7 μm for water at $T = 110^\circ\text{C}$. So a submicron thermal boundary layer thickness of 0.21 μm is assumed here to investigate the fluid particle transfer rate with negligible potential gradient, to investigate the superheat for incipient heterogeneous nucleation. With this boundary layer thickness ($1000 \times$ smaller than the thickness used in previous studies), the transfer rate is nearly uniform and approximately $10^{-35} (\text{m}^3 \text{s})^{-1}$. Such a low transfer rate with a very thin thermal boundary condition could not induce bubble nucleation and it corresponds well with the classic nucleation predictions that were derived without the potential gradient. It implies that the representation of bubble nucleation discussed in this study is compatible with the results of previous classical nucleation models.

3.3. Thermo dynamical equilibrium for nucleation

We confirm the high evaporation rates of fluid particle in the potential gradient on the heated horizontal surface by considering the kinetic motion of fluid particle. However, although there are very high transfer rates of fluid particle, the imbalance of particle transfer for the domain cannot be maintained for long if the do-

main is not in an equilibrium state for a new bubble at the same time. So, we also consider the thermo-equilibrium state of the generated bubble by the high evaporation rate for determining the condition of bubble nucleation. The equilibrium condition is determined by comparing the required temperature of the vapor for equilibrium with the surrounding liquid temperature at the top of the bubble. The temperature profile of working fluid is calculated from the similarity analysis for natural convection on a horizontal flat hot surface, as mentioned before. The required superheat of the vapor for equilibrium is evaluated by the Clausius–Clapeyron equation. If the environmental temperature is lower than the required temperature for equilibrium, the generated vapor will disappear for an instant. Therefore, the criterion for thermal stability of the vapor clusters is given as

$$\Delta T_{top} \geq \left(\frac{T_{sat}}{h_{lv}} v_{lv} \Delta P \right). \quad (27)$$

where ΔT_{top} is the superheat of working fluid at the top of bubble. v_{lv} and ΔP indicate the volume and pressure change of the phase transition, respectively. For comparison, the thermo stability is determined by dividing the superheat of working fluid at the top of bubble by the required superheat for equilibrium, $\Delta T_{top} / \left(\frac{T_{sat}}{h_{lv}} v_{lv} \Delta P \right)$. (Owing to the variation of the height of the formed vapor, the temperature required for stability is dependent on the wettability of the surface as shown in Fig. 8.) We already confirm that the kinetic transfer rates of fluid particle are sufficiently high to promote bubble nucleation in the potential gradient on the horizontal heated surface. It indicates that the bubble initiation condition could be predicted when the thermo-equilibrium of the generated bubble is satisfied. Consequently, if the normalized equilibrium parameter is larger than or equal 1 with the high evaporation rate, the bubble could be nucleated.

Fig. 9(a) and (b) show the thermal stability and the predicted bubble nucleation region for several wetting surfaces. As shown in Fig. 9(a), the heterogeneous bubble nucleation is predicted over 9 K superheat for any smooth heating surfaces when the thickness of thermal boundary layer is 210 μm. Even if the thermal boundary layer thickness is 100 μm, the heterogeneous bubble could be nucleated below the superheat of 13 K.

Fig. 9(b) shows the result of comparison with experimental data with smooth heating surface conducted in this study and previous reports. The theoretically predicted superheats for bubble nucleation within 210 μm thermal boundary layer are 5.3 K for a heating

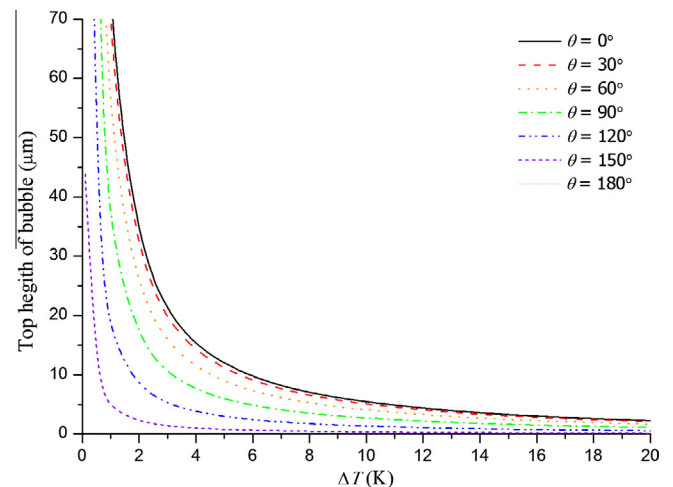


Fig. 8. The height of virtual bubble at the critical condition for nucleation on different wettability characteristics under atmospheric saturated condition.

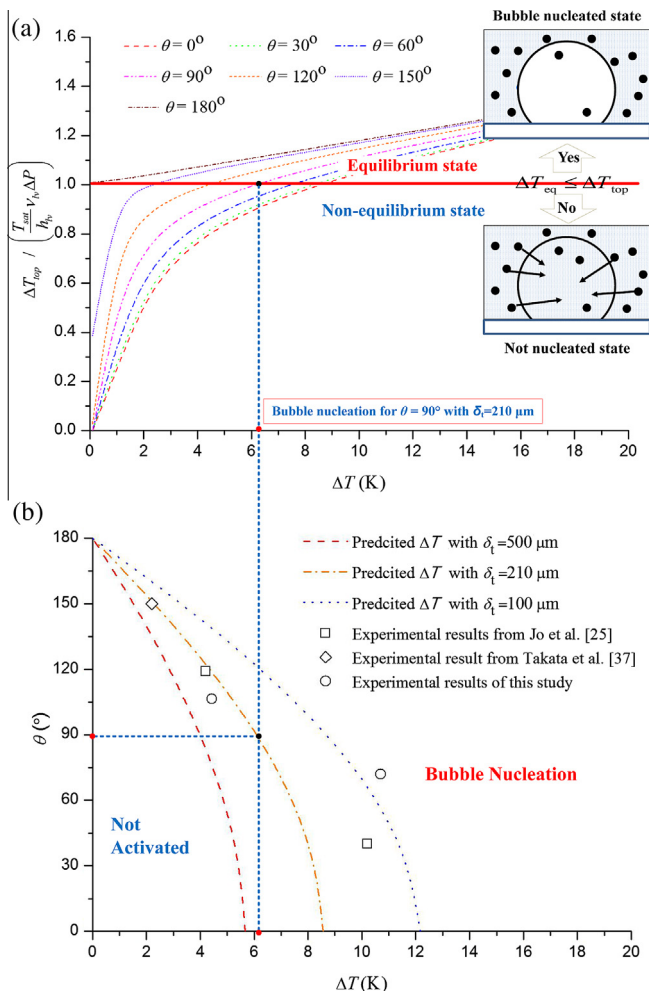


Fig. 9. (a) Required superheat for the thermal stability for various contact angles ($\delta_t = 210 \mu\text{m}$) and (b) comparison of predicted superheats as a function of contact angle for different thermal boundary layer thicknesses with experiments. The results are for atmospheric saturated water condition.

surface with a 106° contact angle and 7 K for 72° contact angle heating surface. In this study, experimentally reported ONBs for hydrophobic ($\theta = 106^\circ$) and hydrophilic ($\theta = 72^\circ$) surfaces are 4.4 and 10.7 K, respectively. The predicted superheat for nucleation varies from 4.4 to 8.1 K; the contact angles ranges from 120° to 40° . These results are in good agreement with the experimental results of Jo et al., whose study showed that on a Teflon-coated surface and a oxidized silicon surface, the first bubble was observed at 4.2 and 10.2 K superheat, respectively [25]. For a heated surface with a 150° contact angle, the predicted superheat of new bubble ebullition was 2.3 K. This prediction also agrees well with the experimental results of Takata et al. of 2.2 K [36].

The present model predicts 2–10 K superheats for bubble nucleation without trapped vapor. It is a more precise prediction compared than the previous nucleation models for a smooth heating surface. Furthermore, the model correctly depicts the trend that is increasing superheat for bubble nucleation as the contact angle decreases. Even though the agreement between the data and the model is quite good, the present model will be extended for other working fluids as further research.

4. Conclusions

To better understand bubble nucleation on smooth surfaces with different wettabilities, experimental and theoretical investi-

gations are conducted. In our nucleation model, the potential gradient is used to describe the bubble nucleation, adopting the kinetics of superheated liquid within thermal boundary layer and the thermodynamic stability of the generated vapor. The evaporation rate in the thermal boundary layer is estimated and as expected it is high in order to activate the nucleation phenomenon. The thermal non-equilibrium of the instantly generated bubble nucleus by this high evaporation rate is also evaluated via comparison of the equilibrium temperature of the generated vapor with the temperature of the surrounding liquid. Consequently, we can predict the bubble nucleation condition under thermal equilibrium of the generated bubble and satisfying the high evaporation rate within the thermal boundary layer. Our analysis of the bubble incipient on ideally-smooth horizontal surfaces, supports the observed low incipient nucleate boiling superheat under different wetting surfaces. The results from this study provide fundamental understanding of the incipient boiling.

Acknowledgments

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Bubble nucleation and growth in fluids

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Abstract

The nucleation and growth of CO₂ bubbles in non-Newtonian and Newtonian fluids that were initially supersaturated under different pressures are investigated in the present work. Quantitative information by means of two cameras reveals that at an immobile nucleation site the bubble grows rapidly followed by a linear increase in bubble diameter with time. After reaching a critical size, the bubble detaches from the stagnant site to rise in liquids with an exponential temporary increase for both the diameter and distance. A simple physical reasoning was proposed to qualitatively explain these observed phenomena. Recently, the growth rate and flow fields around a CO₂ micro-bubble were measured in a microdevice by a micro-Particle Image Velocimetry in water. This information at microscale gives new insight into the complex mechanism of bubble nucleation and growth in fluids and could help to develop a rigorous theoretical modelling and numerical simulation such as the Lattice Boltzmann approach.

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Keywords: Bubble; Nucleation; Growth; Non-Newtonian fluids; Visualisation; Micro-PIV

1. Introduction

In numerous industrial applications such as polymer devolatilisation process (Yang et al., 1997), generation of biogas bubbles by anaerobic sludge granules in a bioreactor (Wu et al., 2006), polymeric foam production during blow moulding (Amon and Denson, 1984), silicon oil purification (Wienecke et al., 2005), elaboration of microcellular plastics (Xu et al., 2005), carbonated drinks (Liger-Belair et al., 2002; Barker et al., 2002), etc., the mechanism related to the nucleation and subsequent growth of bubbles should be fully understood for engineering analysis of processes (Chhabra, 1992). Similar knowledge is also required in other disciplines like decompression sickness (Kungle and Beckman, 1983), gas-driven eruption including explosive volcanic eruptions driven by the exsolution of H₂O from a magma such as the 79 A.D. eruption of Vesuvius or by the exsolution of the CO₂ from water like the eruption of the Lake Nyos in 1986 (Zhang, 1998).

The classical nucleation theory assumes that bubble nucleation is initiated by the formation of the critical size nuclei

with required energy from the thermodynamical point of view (Abraham, 1974; Blander, 1975; Jones et al., 1999). After the nucleation, the bubble growth is a complex process involving interactions between mass, momentum and heat transfer and is governed by many characteristic parameters. Usually, the classical equations governing these interactions are numerically resolved as a bubble formation problem (Street et al., 1971; Patel, 1980; Shafi and Flumerfelt, 1997). Until now, there are very few experimental investigations in the literature. The existing works on growth process are often limited to an immobile bubble at a stagnant point in liquid. In an industrial devolatilisation installation, the elimination of gas phase is realised by the ascension of bubbles towards a complete separation from liquid. Due to the inherent complex nature of the dynamical coupling between the hydrodynamic and mass transfer aspects, the fundamental mechanisms related to the nucleation and growth of bubbles at microscale in viscous and non-Newtonian fluids remain unclear up to day.

The present work aims at investigating the nucleation and growth of CO₂ bubbles in both non-Newtonian and Newtonian fluids that are initially supersaturated under different pressures. We examine the nucleation and growth of bubbles not only at a stagnant point in liquids, but also the dynamical growth process

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during the ascension after the detachment from the nucleation site. Quantitative information concerning these different growth steps along with fine and local measurements at microscale by a micro-Particle Image Velocimetry (micro-PIV) could lead to an increased understanding of these complex phenomena and improvements in our ability to perform a more rigorous modelling and numerical simulation. In particular, the Lattice Boltzmann (LB) approach that we developed successfully for multiphase flows (Frank and Li, 2005, 2006, Frank et al., 2006) can be a good alternative to classical simulations.

2. Experimental

The experimental facilities include a 0.20×0.20 m square glass visualisation chamber of thin depth (0.01 m) to avoid too many bubbles in front of the objective of the camera (Fig. 1). At the bottom of the chamber a cylindrical tube of bored wall was used to inject CO_2 gas in the liquid. It was possible to change the initial saturation in liquids by applying various relative pressures of CO_2 . The whole set-up was installed on a mechanical vibrating system so that the dissolution of gas was accelerated to reach a desired saturation degree according to the applied gas pressure. The CO_2 was employed as volatile component owing to its adequate dissolution in various liquids. After stopping the vibration of the visualisation chamber, an electronic valve was commanded by a PC to ensure a sudden opening to provoke a depressurisation. The nucleation took place in the liquid due to the supersaturation of CO_2 under atmospheric conditions and was followed by the growth of bubbles. It is worthy noting that both the homogeneous and heterogeneous nucleation was observed respectively in the bulk liquid and at chamber's wall. In the present study, emphasis was given to the homogeneous nucleation. Moreover, the

degree of supersaturation within the explored experimental conditions ensured the nucleation of limited number of bubbles so that the interactions between bubbles like coalescence did not exist. The investigation was then focused on a single bubble in the bulk liquid in two distinguished steps. Firstly at the beginning of the nucleation, a fixed high-speed digital camera with a great magnification lens was employed to visualise locally a small growing nuclei that stayed still. After reaching a critical size according to fluid's nature and pursuing continuously the growth, the bubble began to leave the nucleation site towards the free surface. A second camera equipped with a less magnification lens was necessary to follow the ascension phase in the liquid over a wide field. Both the size and position of a bubble were determined by the image analysis.

Four non-Newtonian fluids were used in this work: 1% and 2% (wt) carboxymethylcellulose (CMC) in water, 0.5% (wt) polyacrylamide (PAAm) in water and 0.5% (wt) xanthan in water. A Rheometrics Fluid Spectrometer RFS II (Rheometrics Inc., USA) was employed to measure the rheological properties of these solutions which behaved as shear-thinning fluids. The CMC and xanthan solutions were inelastic with no measurable normal forces whereas the PAAm solution was elastic. In the range of shear rates corresponding to the bubble formation and moving in this study ($\dot{\gamma} = 1\text{--}30 \text{ s}^{-1}$), the power law model could fit the rheological behaviour of these fluids:

$$\tau = K \dot{\gamma}^n, \quad (1)$$

Table 1
Rheological properties of the fluids used.

	1% CMC	2% CMC	0.5 PAAm	0.5% xanthan
$K (\text{Pa s}^n)$	0.04	0.70	1.90	6.16
n	0.90	0.90	0.37	0.11

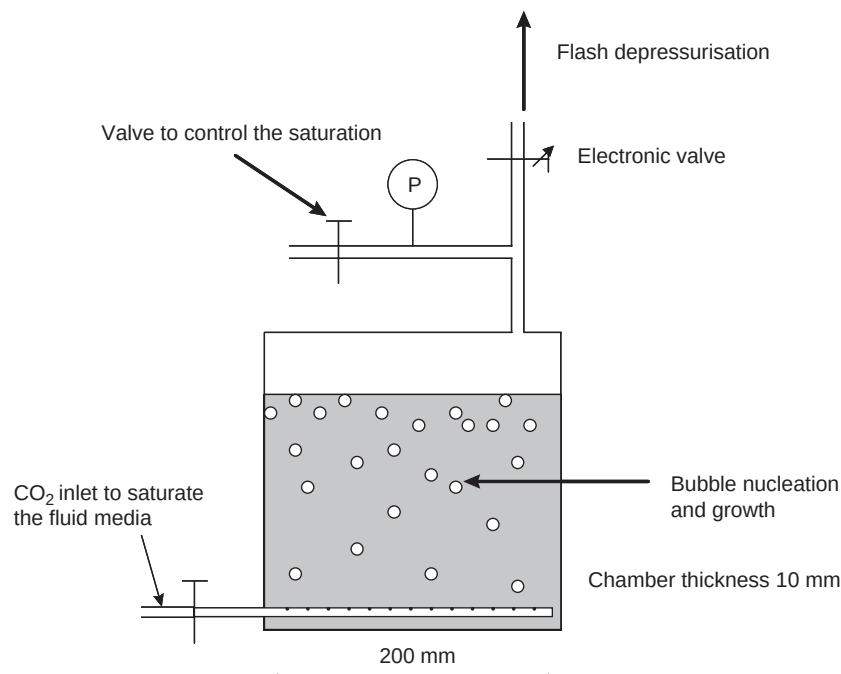


Fig. 1. Transparent visualisation chamber for the bubble nucleation and growth.

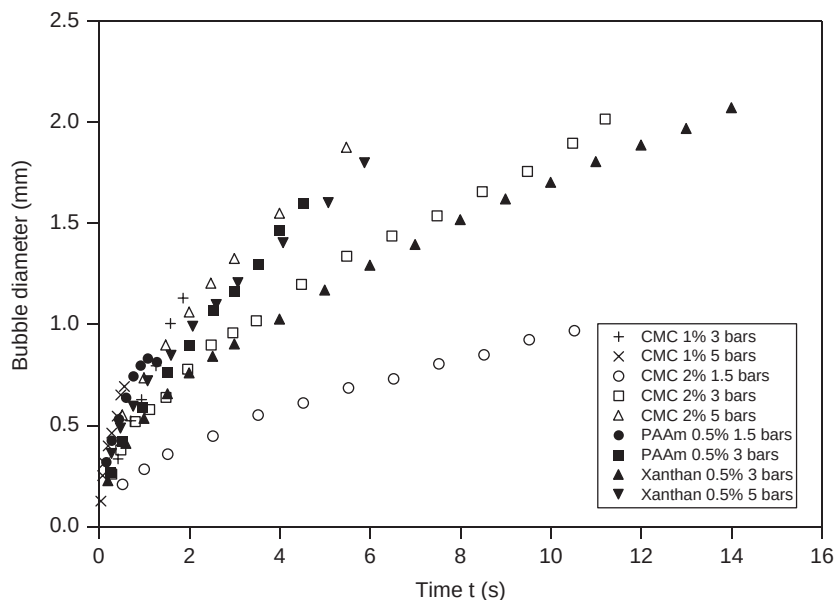


Fig. 2. Nucleation and growth of a CO₂ bubble at a nucleation site in non-Newtonian fluids under various relative pressures.

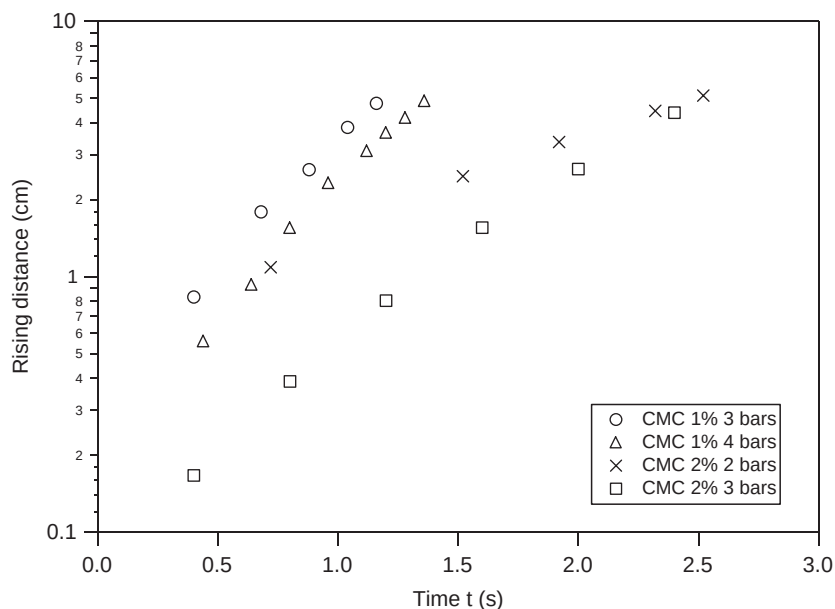


Fig. 3. Rising distance of a CO₂ bubble after the detachment from a nucleation site. Time zero corresponds to the beginning of the departure.

where K is the consistency and n the flow index. Their values for the above-mentioned fluids are gathered in Table 1.

The growth of an immobile bubble at a nucleation site was firstly studied in these different fluids under various applied relative pressures to control the initial CO₂ saturation. The variation of the bubble diameter with time is shown in Fig. 2. The bubble diameter was determined on the basis of an average value of 20 bubbles. Thanks to the great magnification lens mounted to the high-speed digital camera, the measurement accuracy was high enough with typically a relative error less than 2%. For a given fluid, the bubble size increases with

the applied pressure: a higher degree of initial supersaturation produces bigger bubbles. Qualitatively, a more important concentration gradient results in an efficient mass transfer for a fast growth of bubbles' size. In these viscous non-Newtonian fluids, the bubble growth at a nucleation site begins by a very fast period during a short time interval about 2 s, followed by a linear increase until the departure of the bubble. Clearly, the slope of the linear growth is proportional to the initial applied pressure.

When the critical size depending on the fluid's rheology is reached, typically around 1–2 mm, the bubble begins the departure from the nucleation site and the ascension takes place

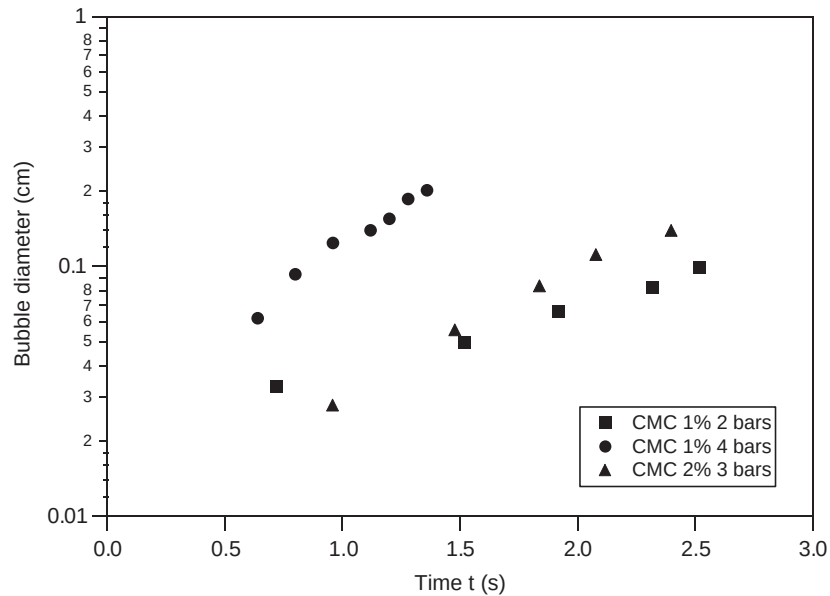


Fig. 4. After the detachment from a nucleation site, diameter increase of a CO₂ bubble during the ascension (at the beginning of the departure, $t = 0$).

in the liquid. A second camera was necessary to follow the displacement of the bubble with a less magnification lens to cover a larger observation field. On the contrary, the image resolution was also affected for the accurate determination of the bubble size. In this case, the main parameter to be measured was then the rising distance from the nucleation site (Fig. 3). The second camera had a lens of less magnification, the measurement error varied ranging from 3% to 4%. The time origin was determined when an observable motion of the bubble began in fluid. Globally, the rising distance increases exponentially with time whatever the experimental conditions may be. When the bubble approaches the free surface, the rise velocity is slowed down so that some deviation is observed for the final rising stage with respect to the exponential law. The relationship between the rise dynamics, the fluid rheology and the initial pressure does not seem to be straightforward. For example, the slope indicates a dependence on the initial relative pressure in 2% CMC whereas this is not the case for 1% CMC. Further experiments are still required to clarify this point.

Similar exponential increase was roughly observed for the bubble size during the ascension. However, the bubble diameter was difficult to be measured accurately as the second camera covered a large visualisation field. As an indication, some results are given in Fig. 4.

3. Mathematical model

Within the framework of a simplified film model with δ the film thickness around the bubble, D the diffusion coefficient of CO₂ in the liquid, C the concentration of CO₂ in the bulk liquid and C^* the concentration of CO₂ at the bubble interface on liquid side, the gas diffusion flux into the bubble is then

$$\varphi = \frac{D}{\delta} (C - C^*) S = \frac{D}{\delta} (C - C^*) (\pi d_B^2). \quad (2)$$

The bubble continues to growth as long as the thermodynamical equilibrium is not reached between the liquid phase and the gas–liquid interface. As a first approach, the uniform pressure inside the bubble and the Henry's law are supposed. With P_0 as the atmospheric pressure, the Laplace's law gives the pressure inside the bubble: $P_B = P_0 + \frac{2\sigma}{R}$. This leads then to a concentration at the interface on the liquid side: $C^* = \frac{1}{H} (P_0 + \frac{2\sigma}{R})$. Far from the bubble, the dissolved CO₂ concentration C should be superior to C^* so that the bubble can growth due to the mass transfer across the bubble interface. Always according to the Henry's law, it could be possible to express this supersaturation by means of an over pressure in the liquid ΔP : $C = \frac{1}{H} (P_0 + \Delta P)$. The mass transfer flux is computed as follows:

$$\varphi = \frac{D}{\delta H} \left(\Delta P - \frac{2\sigma}{R} \right) (\pi d_B^2). \quad (3)$$

The experimental curve shown in Fig. 2 for an immobile bubble at the nucleation site has two different growth steps: a rapid growth of bubble diameter followed by a linear increase in time before the departure. This first rapid growth period, typically around 2 s, is nearly independent on the fluid's rheology. If the film thickness δ does not change much, the first rapid increase step could be mainly explained by both a high initial value of local supersaturation ΔP ($\sim 10^5$ Pa) and a significant decrease of the surface tension term due to the size increase $\frac{2\sigma}{R}$ ($\sim 10^2$ Pa) towards an asymptotically negligible value Eq. (3). The diffusivity of CO₂ in a non-Newtonian fluid ($D \sim 10^{-9}$ m² s⁻¹ in water) was difficult to be estimated due to its dependence on the fluid viscosity.

After 2 s, the establishment of a linear growth implies a certain equilibrium between the gas entering the bubble and mass transfer flux by diffusion from the bulk liquid. The experimental visualisation confirms a spherical shape of bubbles not only at a nucleation site but also during the ascension. The volume of a bubble is then: $V = \frac{\pi}{6} d_B^3$. The temporal volume variation

can be expressed as $\frac{dV}{dt} = \frac{\pi}{2} d_B^2 \frac{d(d_B)}{dt} = \frac{\pi}{2} a d_B^2$. As the increase rate of the bubble's diameter $a = \frac{d(d_B)}{dt}$ is a constant for the second growth step at the nucleation site as shown in Fig. 2, the mass transfer flux Eq. (3) towards the bubble is then linearly proportional to the volume increase rate: $\varphi \sim \frac{dV}{dt}$. This corresponds then to an equilibrium regime between the bubble volume growth and the mass transfer. However, the attribution of a predominant role is still difficult among three coupling parameters involved in Eq. (3): the film thickness δ , surface tension $\frac{2\sigma}{R}$ and local supersaturation term ΔP . A plausible assumption could be a constant film thickness, a negligible surface tension when the bubble size is sufficiently great and then a relative constant local supersaturation ΔP . There could be an equilibrium between the mass transfer to the bubble and diffusion flux from the bulk liquid. However, this supersaturation term was difficult to be quantified due to the pressurised chamber used. Some pH measurements in liquids by means of a pH probe implemented at the chamber's wall were tested under various applied gas pressures. However, the accuracy was not sufficient enough to give a satisfactory quantification. Further efforts are still required for measuring this parameter, in particular before the depressurisation.

To explain the exponential increase for both the bubble's diameter growth and rising distance after the detachment from a nucleation site, an analytical approach was developed for the shear-thinning fluids such as CMC and xanthan solutions.

The different forces acting on a bubble are mainly:

- the buoyancy: $\vec{F}_a = -(\rho_L - \rho_G)V\vec{g} \cong -\rho_L V\vec{g}$,
- the viscous drag: $\vec{F}_t = -\frac{1}{2}\rho_L C_d \frac{\pi d_B^2}{4} u^2 \frac{\vec{u}}{\|\vec{u}\|}$ with the drag coefficient $C_d = \frac{16}{Re}$, generalised

Reynolds number $Re = \frac{\rho_L d_B u}{\mu}$ and apparent viscosity $\mu = K \dot{\gamma}^{n-1} = K \left(\frac{u}{d_B}\right)^{n-1}$ (Frank et al., 2003),

- the inertial force due to not only the rising acceleration but also the volume increase: $\frac{d(m\vec{u})}{dt} = \frac{11}{16}\rho_L \left(\frac{dV}{dt}\vec{u} + V\frac{d\vec{u}}{dt}\right)$ with a classical added mass $m = (\rho_G + \frac{11}{16}\rho_L)V \cong \frac{11}{16}\rho_L V$ (Milne-Thomson, 1960; Li et al., 2002),
- the bubble having a spherical shape, the resulting surface tension force in the vertical direction is then zero.

The force balance is as follows:

$$\frac{d\vec{u}}{dt} = \frac{16}{11\rho_L V} (\vec{F}_a + \vec{F}_t) - \frac{1}{V} \frac{dV}{dt} \vec{u}. \quad (4)$$

This is an ordinary differential equation. However, the relationship between the bubble volume V and the volume variation rate dV/dt is not straightforward and cannot be derived by an analytical approach to our best knowledge. From the experimental data concerning the temporal variation of respectively bubble's diameter and rising distance after the detachment from a nucleation site, it could be possible to examine the relationship between these two experimentally measured parameters. For example, the exponential diameter growth curve shown in

Fig. 4 gives the following numerical fitting in 1% CMC with $P = 2$ bars:

$$\frac{d(d_B)}{dt} = 0.68 d_B. \quad (5)$$

This is equivalent to the relationship in form of the bubble volume:

$$\frac{dV}{dt} = \lambda V, \quad (6)$$

where the parameter $\lambda = 3 \times 0.68 = 2.04 \text{ s}^{-1}$. Effectively, it is not possible to compute the mass transfer coefficient as the CO_2 concentration was difficult to be experimentally measured in liquid. However, the fact that the mass transfer flux towards the bubble is linearly proportional to the volume increase rate $\varphi \sim \frac{dV}{dt}$ as shown above justifies to some extent Eq. (6). It will be envisaged in the future to use the laser holographic method to investigate the concentration field around the bubble.

Eqs. (4)–(6) can then be numerically integrated by a 4th order Runge–Kutta method to compute the rising distance with respect to the nucleation site. Fig. 5 shows a satisfactory agreement between the prediction of this simple model and the experimental measurements. This indicates that an exponential growth of the bubble volume (or diameter) leads consecutively to an exponential increase of the rising distance. Both parameters are intrinsically coupled indeed. In other words, the force balance is mainly governed by two principal forces that are buoyancy and drag. Although the bubble growth do introduce some inertial effects, they are not dominant. Based on this consideration, the asymptotic rise velocity can be obtained by simplifying Eq. (4):

$$\rho_L g V - \frac{1}{2} \rho_L C_d \frac{\pi d_B^2}{4} u^2 = 0, \quad (7)$$

$$u = \left(\frac{1}{12} \frac{\rho_L g}{K} \right)^{1/n} d_B^{n+1/n}. \quad (8)$$

This analytical expression confirms clearly that it is logical to obtain an exponential increase of the rising distance with an exponential growing bubble. Of course, this conclusion is based on the experimental observation of an exponential bubble diameter growth. Back to the above-mentioned film assumption for the mass transfer around a bubble, Eq. (3) contains a parameter related to hydrodynamic conditions: the film thickness δ . When the rise velocity is accelerated during the bubble ascension, the diminution of the film thickness brings about an acceleration of the mass transfer flux towards the bubble. In its turn, the accelerated volume increase leads to the faster augmentation of the rise velocity, a typically positive retroaction mechanism. Moreover, the thinning behaviour of the non-Newtonian fluids induces a diminution of the apparent viscosity, then a less drag for the bubble rise and a higher diffusion coefficient of CO_2 in liquids (Li et al., 2001; Kemiha et al., 2006). This contributes simultaneously to the intensification of the mass transfer. The complex flow fields around a bubble rising in non-Newtonian fluids, in particular in PAAM solutions (Funfschilling and Li, 2001), could also play a role in the mass transfer through a

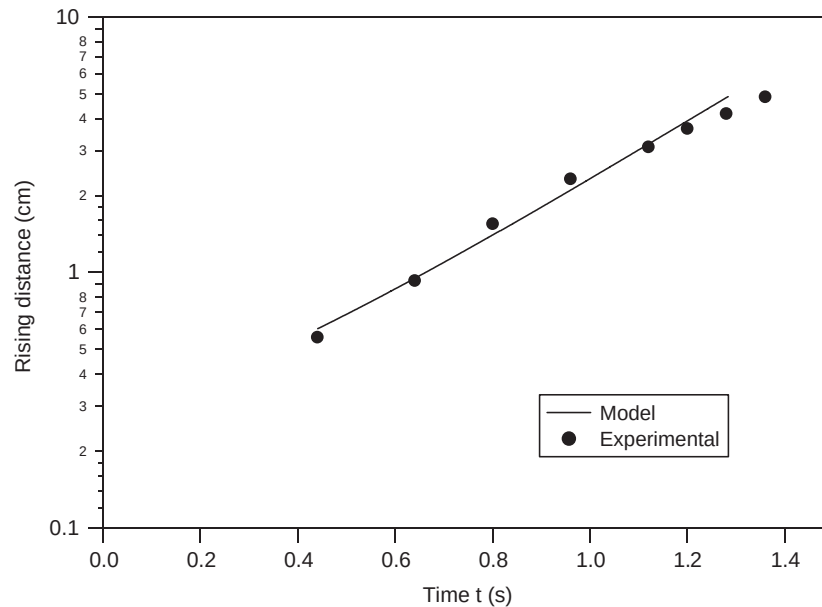


Fig. 5. Comparison of the rising distance of a CO_2 bubble between the model prediction and experimental measurement in 1% CMC solution with an initial relative pressure $P = 2$ bars.

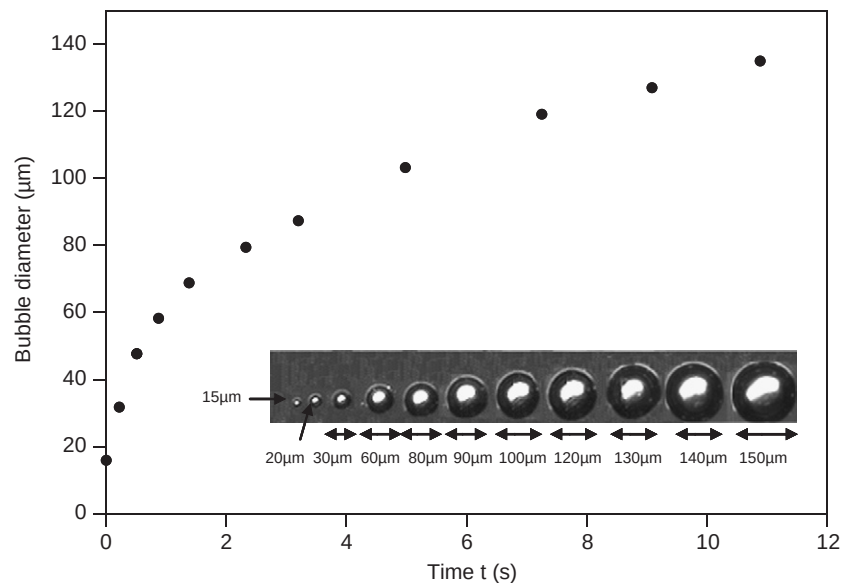


Fig. 6. A CO_2 bubble growth at a nucleation site in water under an initial relative pressure of 1 bar: visualisation by the micro-PIV device with 250 images s^{-1} .

largely extended wake in space. In the face of such a tremendous complexity involving hydrodynamics, mass transfer, interfacial phenomena and rheology, a classical numerical approach is certainly beyond the reach. Based on our previous work of the LB applied to multiphase systems (Frank and Li, 2005, 2006, Frank et al., 2006), we are currently trying to take up this challenge within the framework of the LB method.

4. Results at microscale

The recent development of advanced metrology such as the PIV allows quantifying the flow features around bubbles in non-Newtonian fluids (Funfschilling and Li, 2001; Li et al., 2001).

By means of a newly acquired micro-PIV system (Dantec Dynamics), we tried to follow in time the nucleation and the growth process for a bubble attached to the nucleation site as well as the determination of the local flow field due to the expansion of bubble size in liquid within a microdevice similar to the above-mentioned macroscale set up. This 0.01×0.01 m square visualisation chamber made of transparent PMMA (Poly-MethylMethAcrylate) had a very thin depth (0.001 m). As it was still difficult to work with higher pressure, the CO_2 saturation was realised under a relative pressure of 1 bar. Preliminary tests were carried out in demineralised water. The depressurisation was provoked by opening of a manual valve.

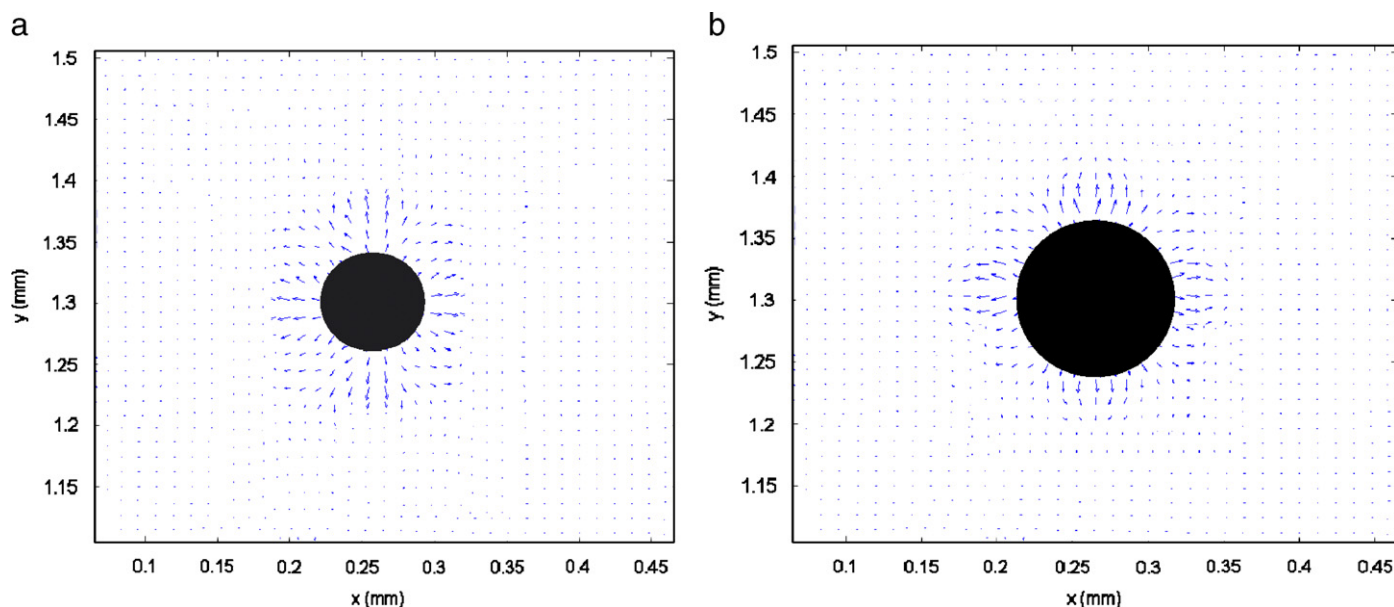


Fig. 7. Flow field around a growing CO_2 bubble at a nucleation site in water measured by the micro-PIV device with $1000 \text{ images s}^{-1}$ and a spatial resolution of 2048×2048 : (a) $t = 1.6 \text{ s}$ and $d_B = 70 \mu\text{m}$; (b) $t = 4.8 \text{ s}$ and $d_B = 100 \mu\text{m}$.

This microdevice was horizontally loaded onto an inverted Leica microscope used for the micro-PIV. Thanks to this technique, it was possible to obtain the flow field of the continuous water phase with the help of seeding particles around a growing bubble after the depressurisation as well as the bubble size variation in time. The micro-PIV system was constituted of a Flowsense Dantec Camera with a 2048×2048 pixel array. The microscope was equipped with different objectives ranging from $\times 5$ to $\times 100$. The microdevice under investigation faced the microscope and was illuminated from the back by a microstrobe emitting at 530 nm . Hydrophilic latex microspheres (Merck Estapor) with a density of 1056 kg m^{-3} and a mean diameter of $0.88 \mu\text{m}$ were used as seeding particles. These particles were small enough to follow the fluid and large enough to avoid the effects of Brownian motion.

The size growing in function of time is illustrated in Fig. 6 with a perfect spherical shape. Although the minimum nuclei size reported in this figure is limited to $15 \mu\text{m}$, we expect to decrease this size to 600 nm in further studies by means of a better illumination system. The bubble ascension was not observed in the microdevice due to its horizontal position. In Fig. 7, the flow fields were measured around two small bubbles of, respectively, 70 and $100 \mu\text{m}$. It is worth noting that the measurements of both nuclei size and flow fields at this scale were never reported yet in the literature to the best of our knowledge. In spite of some experimental perfection to gain, these original results can provide new insight into a theoretical modelling and numerical simulation at microscale that we envisage with the help of the LB approach.

5. Conclusion and discussion

The bubbles' nucleation and growth experiments were carried out in two transparent visualisation chambers at both macro- and microscale and under various operating conditions

such as liquid's nature and initial supersaturation. The emphasis was given to the homogeneous nucleation in the bulk liquid. Two different mechanisms were identified as central to the nucleation and growth of a bubble: immobile at a stagnant nucleation site and an exponential increase for both the bubble diameter and rising distance after the detachment from the nucleation site.

For the stagnant nucleation at a site, the bubble growth has a first rapid period of about 2 s whatever the fluid's rheology. A linear increase following this fast period indicates the establishment of a permanent mass transfer regime before the detachment from the nucleation site. The first rapid increase could be mainly explained by both a high initial value of local supersaturation just after the depressurisation and a significant decrease of the surface tension force due to the bubble's size increase. However, accurate measurements of the degree of supersaturation of dissolved CO_2 gas in a non-Newtonian fluid are still required to go ahead for a possible modelling.

A simple physical reasoning based on the coupling between a force balance, rheology and experimental data of the bubble size in function of time shows that it is logical to obtain an exponential increase of the rising distance with an exponential growing bubble size. Among the mass transfer efficiency, shear dependant viscosity, surface tension, bubble size and rise velocity, there is a positive retroaction mechanism. To a certain extent, a fractal scaling could be applied to this exponential variation for both the bubble size and rising distance. Clearly, the complex coupling nature of these different mechanisms cannot be handled yet by a classical Computational Fluid Dynamics (CFD) approach. In particular, physical understandings at microscale are seriously missing for the closure conditions at the interface between the bubble and surrounding fluid phase.

To gain insight into this extraordinary complexity involving hydrodynamics, mass transfer and interfacial phenomena,

some preliminary results were obtained within a microdevice by means of a micro-PIV device Particle Image Velocimetry (PIV) device. The dynamical bubble growth at a nucleation site and corresponding flow fields around the bubble were quantified at microscale for the first time. We have shown the particular suitability of a Lattice Boltzmann (LB) approach for complex multiphase flows in our previous works (Frank and Li, 2005, 2006, Frank et al., 2006). For a gas–liquid interface, some classical physical laws at macroscale are no longer valid at microscale. This is typically the case of the surface tension $\frac{2\sigma}{R}$ when the radius tends to infinitively small. These new experimental results by the micro-PIV lead to foresee some possibilities to develop and validate an LB scheme for modelling and simulating the nucleation and growth of bubbles in fluids. In a general way, it could be possible to gain insight into the interface behaviour at microscale.

Notation

C	gas concentration in liquid, mol m^{-3}
C^*	gas concentration in liquid at the bubble interface, mol m^{-3}
C_d	drag coefficient
d_B	bubble diameter, m
D	gas diffusion coefficient in liquid, $\text{m}^2 \text{s}^{-1}$
H	Henry's constant, J mol^{-1}
K	fluid consistency, Pa s^n
m	added mass, kg
n	flow index
P	relative gas pressure, Pa
P_0	atmospheric pressure, Pa
P_B	pressure in the bubble, Pa
R	bubble radius, m
u	bubble rise velocity, m s^{-1}
V	bubble volume, m^3

Greek letters

$\dot{\gamma}$	shear rate, s^{-1}
δ	film thickness, m
μ	generalised fluid viscosity, Pa s
ρ_G	gas density, kg m^{-3}
ρ_L	fluid density, kg m^{-3}
σ	surface tension, N m^{-1}
τ	stress, Pa
φ	mass transfer flux, mol s^{-1}

Acknowledgement

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The cycle of bubble production from a gas cavity in a supersaturated solution

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Abstract

Bubble nucleation, classified according to the review by Jones et al. (Adv. Colloid Interface Sci. 80 (1999) 27–50) as type IV non-classical, was examined in this study. Trains of bubbles were produced in carbonated water solutions at low levels of supersaturation, typically less than about 2, at specific sites on the surface of the vessel in contact with the liquid. Closer examination at a given site revealed a cycle of bubble formation, growth and detachment, defined by the growth time, t_g , required for the bubble to grow to its detachment diameter, and the nucleation time, t_n , required for a new bubble to appear following detachment. A relationship, representing the cycle of bubble production, was obtained by combining the bubble growth time, calculated using Scriven's model (Scriven, Chem. Eng. Sci. 10(1/2) (1959) 1–13), with the bubble nucleation time. That is,

$$\frac{1}{t_g} = \frac{N}{t_n} + \frac{1}{t_g^*}$$

where N is a dimensionless number characterising the bubble nucleation time, and t_g^* is the growth time of the last possible bubble. Experiments conducted at a number of sites, and at different temperatures, produced results consistent with the above relationship. Most of the experiments were conducted with the contact angle at 65° , and these generally resulted in a bubble detachment diameter of about $600 \mu\text{m}$, and a value of $N \sim 0.3$. It was concluded that the nucleation time was dependent on the diameter of the detaching bubble. This dependence was explained by considering the volume of liquid, partially depleted of carbon dioxide, in the boundary layer of the bubble. Some of this partially depleted liquid should

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leave with the departing bubble, and the rest should remain above the gas cavity, thus slowing down the rate of bubble growth in the cavity. A consideration of the critical condition for bubble detachment indicated that the bubble remained rooted at the cavity mouth during its growth. It was shown, using the growth time of the last possible bubble, that the critical radius of curvature of the meniscus in the cavity was about $3.3\ \mu\text{m}$ at 16°C . The radius was also found to increase significantly with temperature, suggesting that the position of the meniscus inside the cavity moved when the system temperature was changed, and that the cavity was essentially conical. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Nucleation; Bubbles; Mass transfer; Growth

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1. Introduction

It is common to observe bubble production in solutions containing dissolved gas, often when the level of supersaturation is relatively low, at less than 5. In carbonated beverages, for example, bubbles are often produced long after the solution is made supersaturated, following the opening of the bottle. These bubbles are usually produced on the container wall, at specific sites, where they form, grow, and then detach. The process may continue until the supersaturation is nearly depleted. These observations are contrary to expectations based on the classical view of nucleation, in which supersaturations in excess of 100 are needed [3].

In a preceding review [1] we classified the subject of bubble nucleation into four areas, covering (i) classical homogeneous nucleation, (ii) classical heterogeneous nucleation, (iii) pseudo classical nucleation, and (iv) non-classical nucleation. The first two types involve systems which are completely free of existing gas cavities just prior to the system being made supersaturated. The third type is concerned with systems which contain pre-existing gas cavities. When the system is made supersaturated, the radius of curvature of the meniscus of an existing gas cavity is smaller than the critical nucleation radius. In this case, the energy barrier associated with generating a bubble is therefore lower than required for a classical event. The fourth type, the subject of this paper, is associated with pre-existing gas cavities that have a radius of curvature greater than the critical size. Here, the probability of the cavity generating a full bubble is 1.0, as there is no nucleation energy barrier.

This paper expands upon a preliminary communication [4] on the type IV non-classical nucleation referred to above. The focus of the work was on the cycle of bubble production that occurs at fixed gas filled cavities on the base of a glass container. The physics of bubble growth, and the processes involved in the type IV nucleation were examined. Two characteristic times were also identified and correlated under isothermal conditions. These were the growth time needed for the bubble to reach its detachment diameter, and the nucleation time needed for a new bubble to appear following the detachment of a bubble from the substrate. This analysis provided an understanding of the type IV nucleation process.

2. Theoretical description of bubble production

The theoretical development begins with a simple analytical description for the growth of a bubble in a supersaturated solution, and its comparison with the solution produced by Scriven [2]. An expression for the theoretical bubble growth time is obtained based on both approaches, as well as an analogous expression for the bubble nucleation time. These expressions are then combined to yield a description of the bubble production cycle, expressed in terms of a single unknown dimensionless number, N . A further expression is developed for the nucleation time in order to obtain a physical insight into the factors that govern the magnitude of N .

2.1. Description of bubble growth

Consider a system consisting of ultra-pure water saturated with high purity carbon dioxide by sparging at atmospheric pressure, P . The system is jacketed at a temperature $T_0 = 1^\circ\text{C}$ resulting in an equilibrium mole fraction of carbon dioxide gas in the liquid at the level X_{i0} . This thermodynamic state [5] is indicated in Fig. 1 and is defined using Henry's law as,

$$P = H_0 X_{i0} \quad (1)$$

where H_0 is the Henry's law constant at T_0 .

The system is then heated to a temperature, T , at constant pressure, P , resulting in a supersaturated state, and the slow production of bubbles from just a few sites. Carbon dioxide gas is transferred out of the solution, via the surface of the liquid, and by the gas in the bubbles that rise to the surface. Because the vessel is not sealed, the mole fraction of the carbon dioxide in the bulk, X_b , decreases gradually towards the new equilibrium level, X_i . The Henry's law constant, H , under these conditions is given by,

$$P = HX_i \quad (2)$$

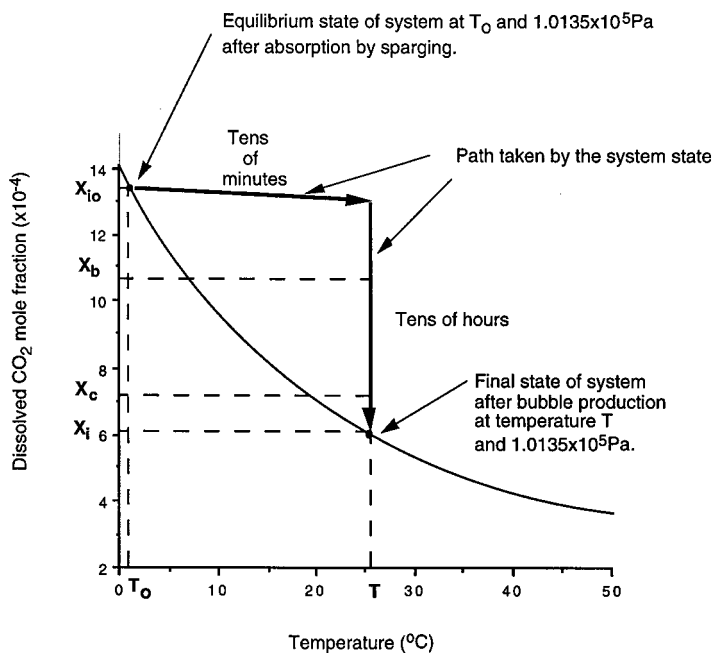


Fig. 1. Thermodynamic states of the system, showing the equilibrium mole fraction of carbon dioxide in water at $P = 1.013 \times 10^5 \text{ Pa}$ as a function of temperature [5].

where X_i is the saturation mole fraction at the temperature T and pressure P .

2.1.1. General assumptions

A number of simplifying assumptions are made in order to produce a first order physical description of the bubble growth process.

1. It is assumed that the bubble growth is controlled by the molecular diffusion of carbon dioxide through the liquid to the liquid–gas interface.
2. Convective transport, associated with the movement of the liquid–gas interface, is accounted for indirectly by producing a generalised solution based on a mass transfer boundary layer thickness of $Z = \kappa D$. In the limit of a zero growth rate, the Sherwood number is 2, and hence $\kappa = 0.5$. The density of the liquid phase is assumed to be independent of the gas concentration, and hence there is no density driven convection.
3. It is further assumed that the system is surfactant-free, and hence free of dynamic surface tension effects.
4. Evaporation of water is neglected. Although the vapour pressure of water increases exponentially with temperature, it remains relatively low at temperatures less than 35°C. At 35°C the vapour pressure is about 6 kPa, and hence for every 95 moles of carbon dioxide transferred into the bubble at atmospheric pressure, about 6 moles of water molecules are transferred.
5. It is also assumed that the effect of the latent heat of vaporisation of water on the local temperature is negligible, and hence the system may be assumed to be isothermal. This issue is considered in Appendix B.
6. It is usual practice to assume a negligible mass transfer resistance inside the bubble where rapid circulation is known to occur. Arguably, there should be no resistance in the gas phase if it is 100% carbon dioxide, as no concentration gradient can form.
7. The bulk concentration of dissolved carbon dioxide, C_b , is constant during the short time required for a bubble to grow.
8. Finally, the pressure inside the bubble is assumed to be constant for the majority of the growth. Hence the pressure elevation due to bubble curvature, which is significant initially, is neglected.

2.1.2. Mass transfer equations

Consider the bubble of diameter D , with a contact angle θ , growing on a solid substrate at a system temperature T and pressure P , as shown in Fig. 2. Assuming spherical cap geometry, the bubble surface area is $S = f_1 D^2$, where

$$f_1 = (\pi/2)(1 + \cos \theta) \quad (3)$$

and the volume, $V = f_2 D^3$, where

$$f_2 = (\pi/24)(2 + 3\cos \theta - \cos^3 \theta) \quad (4)$$

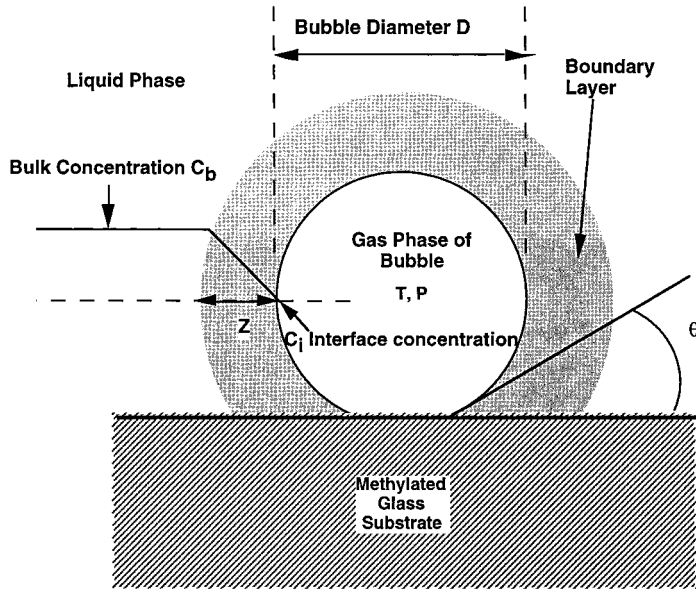


Fig. 2. Schematic representation of a bubble with a contact angle θ growing on a substrate in a supersaturated solution of carbon dioxide.

The molar rate of molecular diffusion, dn/dt , through the liquid–gas interface of the bubble is given by,

$$\frac{dn}{dt} = SkC_T(X_b - X_i) = Sk(C_b - C_i) \quad (5)$$

where C_T is the total number of moles in the liquid phase per unit volume, C_b the bulk molar concentration of carbon dioxide in the liquid, and C_i the saturation molar concentration of carbon dioxide in the liquid. The mass transfer coefficient, k , is given by the ratio of the liquid phase diffusivity of carbon dioxide, D , and the thickness of the boundary layer, $Z = \kappa D$. That is,

$$k = \frac{D}{Z} \quad (6)$$

and hence the Sherwood number is,

$$\text{Sh} = \frac{kD}{D} = \frac{1}{\kappa} \quad (7)$$

The ideal gas equation, $PV = nrT$, is now used to relate the molar transfer rate,

dn/dt , to the rate of change of volume of the growing bubble, dV/dt . That is,

$$\frac{dn}{dt} = \frac{P}{rT} \frac{dV}{dt} + \frac{V}{rT} \frac{dP}{dt} \quad (8)$$

where r is the ideal gas constant.

The bubbles examined in this study are considered to be sufficiently small for the spherical cap geometry to be applied. Distortion due to gravity becomes significant when the hydrostatic head across the bubble is comparable to the Laplace pressure, which occurs for water when the bubble radius is about $3000 \mu\text{m}$ [1]. Given that the bubble radius in this study is less than about $500 \mu\text{m}$, the spherical-cap geometry applies. It also follows that the Laplace pressure is non-zero and, hence, for a growing bubble dP/dt is finite and negative. However, the magnitude of dP/dt in this study is only significant early on, at a time when V is exceedingly small. As shown later, the growth rate dD/dt , is very high initially, and decreases significantly as the bubble diameter increases. So, the value of dP/dt is significant for only a small fraction of the total growth time. For example, as shown in Fig. 7, the bubble diameter increases to about $200 \mu\text{m}$ in the first 15% of the growth time, and to $600 \mu\text{m}$ in the final 85% of the growth time. At a diameter of $200 \mu\text{m}$, the Laplace pressure is less than 2% of the total system pressure. Therefore, in describing the majority of the bubble growth, it is reasonable to assume $dP/dt = 0$.

Following the simplifying assumption that changes in the bubble curvature have a negligible effect on the bubble pressure, P , for the bubble sizes considered, it follows that $dP/dt = 0$. Combining the equations above, and then integrating, gives

$$D^2 = K(C_b - C_i)t \quad (9)$$

where

$$K = \frac{2}{3} \frac{rT}{P} \frac{f_1}{f_2} \frac{1}{\kappa} D \quad (10)$$

Eq. (9) indicates that the bubble diameter squared should vary linearly with time, a result consistent with that obtained by Scriven [2]. The ratio, f_1/f_2 , ranges from about 5.3 at a contact angle $\theta = 65^\circ$ to exactly 6 at $\theta = 0^\circ$ and 90° . Scriven's analysis, which is based on a full sphere, and hence a contact angle of 0° , requires $f_1/f_2 = 6$.

2.1.3. Comparison of Eq. (9) and Scriven's equation

Scriven's solution [2], which is detailed briefly in Appendix A, is given by

$$D^2 = 16\beta^2 Dt \quad (11)$$

In his paper, the growth parameter, β , is tabulated numerically with correspond-

ing values of the concentration driving force, ϕ . The driving force is approximated here as,

$$\phi = \frac{rT}{P}(C_b - C_i) \quad (12)$$

Eq. (12) is a simplification based on the assumption that the gas phase density and the carbon dioxide contribution to the density of the liquid are negligible compared to the liquid density.

Combining our model for bubble growth (Eqs. (9) and (10)) with Scriven's model [Eqs. (11) and (12)] produces an equation for calculating the effective boundary layer thickness, $Z = \kappa D$, around the bubble. That is,

$$\frac{1}{\kappa} = \text{Sh} = \frac{24\beta^2}{\phi} \frac{f_2}{f_1} \quad (13)$$

For the purpose of this study, corresponding values of β and ϕ were obtained from Scriven's paper and substituted into Eq. (13), with $f_1/f_2 = 6.0$. The resulting Sherwood numbers, Sh, were then plotted as a function of the corresponding values of the dimensionless growth parameter, β , as shown in Fig. 3. Curiously, we found that the plot agreed very well with the following correlation,

$$\text{Sh} = 2.0 + 4.0\beta \quad (14)$$

Combining Eqs. (13) and (14) leads to the additional correlation between the

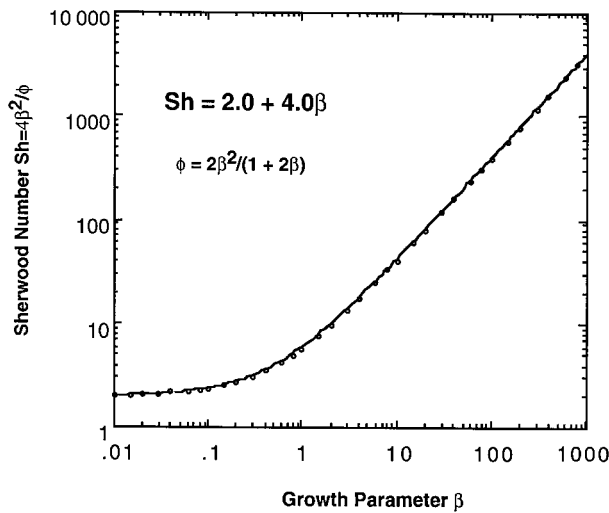


Fig. 3. A new representation of Scriven's solution in terms of a Sherwood number. The discrete points correspond to Scriven's data for $\varepsilon = 1$, and the curve is $\text{Sh} = 2.0 + 4.0\beta$.

driving force, ϕ , and the growth parameter, β . That is,

$$\phi = \frac{2\beta^2}{1 + 2\beta} \quad (15)$$

As expected, the analysis leads to the expected result of a Sherwood number of 2 in the limit of a zero rate of growth with $\beta = 0$. As the value of β increases, the Sherwood number and, hence, the mass transfer coefficient increases. In turn, the thickness of the boundary layer, as defined using κ , decreases. In this study, the Sherwood number is typically 4.0, and hence $\beta \sim 0.5$, and $\kappa \sim 0.25$. Given that κ is less than the pure diffusion value of 0.50, the contribution due to the convective movement of the liquid–gas interface is significant.

Eq. (14) can also be written as,

$$\text{Sh} = 2.0 + (2.0\text{ReSc})^{0.5} \quad (16)$$

where the velocity in the Reynolds number, Re , is dD/dt , obtained using Eq. (11), and Sc is the Schmidt number. The equation can also be interpreted using the following summation of resistances,

$$\frac{1}{\kappa} = \frac{1}{\kappa_d} + \frac{1}{\kappa_c} \quad (17)$$

where the dimensionless boundary layer thickness is composed of a contribution, $\kappa_d = 0.5$, for molecular diffusion only, and $\kappa_c = 1/(4.0\beta)$ for the convective movement of the liquid–gas interface. Combining κ_c with Scriven's law yields,

$$\kappa_c = \left(\frac{D}{D^2/t} \right)^{0.5} \quad (18)$$

demonstrating that at high growth rates, the thickness of the boundary layer is governed directly by the relative significance of the diffusivity and the convective surface velocity, D^2/t . For example, a ratio of 1:100 results in a thinning of the layer to $\kappa \sim \kappa_c = 0.1$.

2.2. The physics of the cycle of bubble production — the attractor

The term, attractor, has been coined to describe the preferred domain of a given system. The attractor for simple systems, like a pendulum swinging in a vacuum, is not particularly useful, given that an explicit analytical model is available here. However, for complex and even chaotic systems the attractor provides a useful representation and simplification of the system. A set of readily measurable variables are selected and used to construct a phase space, a coordinate system based on the chosen variables. The system is examined, and the state of the system, defined by the values of the chosen variables is plotted. The attractor is then the

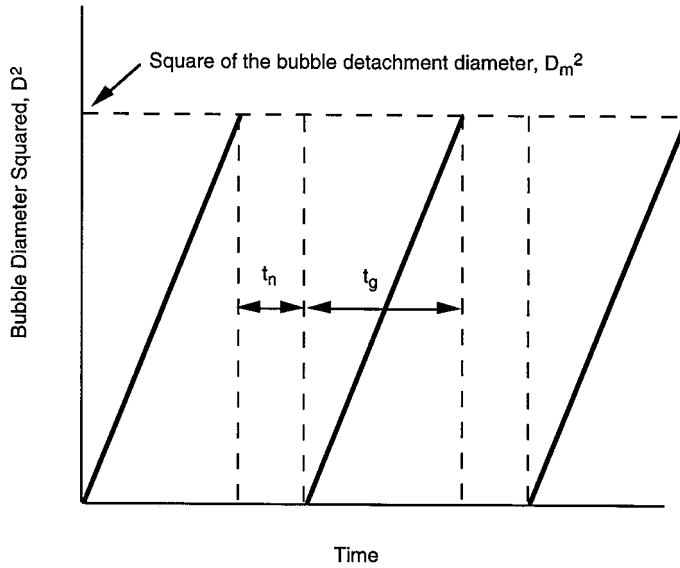


Fig. 4. Cycle of bubble production, consisting of a growth time, t_g , followed by a nucleation time, t_n . The cycle is represented by a plot of the bubble diameter squared vs. the time.

set of all states occupied by the system at different times, and is normally a sub-set of the whole phase space. In describing steady state dynamic systems, absolute time is not used as a variable, and hence the attractor embodies the physics of the system itself.

In this study there is an intimate link between the bubble nucleation, growth, and detachment processes. These are examined and used to obtain the attractor for the whole cycle. Two phase space parameters are used. The first is the growth time, t_g , which is the time a bubble takes to grow to its detachment size, and the second is the nucleation time, t_n , which is defined as the time lapse between the moment a bubble detaches from a site and the moment a new bubble reappears at the same site. Fig. 4, which demonstrates the cycle of bubble production in terms of the appropriate plot of the bubble diameter squared versus the time, provides a further definition of t_g and t_n .

2.2.1. Growth time

According to Eq. (9), it follows that the growth time required for a bubble to reach its maximum diameter, D_m , before detaching from the substrate, is

$$t_g = \frac{D_m^2}{K(C_b - C_i)} \quad (19)$$

Although the value, C_b , decreases significantly over time, the value is considered to be essentially constant during the brief time required to produce a given bubble.

The value of C_i , however, remains constant at all times if the system temperature and pressure remain fixed. The value of K , as defined by Eq. (10), depends on the value of κ and hence on the level of supersaturation. It is noted, however, that the variation in the value of κ for a given cycle is invariably small, especially at the low levels of supersaturation used in this study. The main reason for this is that the bubble production at a given cavity ceases well in advance of the bulk concentration reaching the saturation value. Even if the saturation condition were reached, the value of κ would not fall below 0.50. So, if the maximum bubble diameter remains constant throughout the cycle, the quantity D_m^2/K is essentially a system constant at a given temperature, T .

As the concentration of dissolved carbon dioxide, C_b , decreases, the rate of bubble growth decreases. Eventually, at a critical bulk concentration, C_c , the bubble formation should end at the site in question, as a consequence of the curvature and hence the Laplace pressure elevation of the meniscus in the cavity. At this stage of the cycle, the growth time for the last bubble, t_g^* , is

$$t_g^* = \frac{D_m^2}{K(C_c - C_i)} \quad (20)$$

Also at this point, the critical nucleation radius, R'^* , equals the value of the meniscus radius, R' , in the cavity. The equilibrium state is defined using Henry's law as,

$$P_c = HX_c \quad (21)$$

where $P_c = P + 2\gamma/R'$, H is the Henry's law constant at the temperature T , and X_c is the mole fraction of carbon dioxide in the liquid bulk. It follows that,

$$2\gamma/R' = P_c - P = H(X_c - X_i) = \frac{H}{C_T}(C_c - C_i) \quad (22)$$

So, by measuring the bubble growth and hence the ratio of D_m^2/t_g , it is possible to calculate β using Eq. (11), and in turn calculate, ϕ , from Eq. (15). It is then straightforward to calculate the driving force, $C_b - C_i$, using Eq. (12), and hence the value of the bulk concentration, C_b , using the saturation condition from the literature. In the case of the last possible bubble, $C_b = C_c$, and hence from Eqs. (2) and (22), the critical radius of curvature of the meniscus in the cavity is readily obtained. That is,

$$R' = \frac{2\gamma}{P\left(\frac{C_c}{C_i} - 1\right)} \quad (23)$$

Substituting values of γ , P , C_c , and C_i into Eq. (23) provides a measure of the minimum radius of curvature in the cavity, R' . An estimate of the radius of the

wetting line in the site can then be obtained using the contact angle, θ , assuming a cylindrical cavity geometry. That is,

$$R_{\text{site}} = R' \cos \theta \quad (24)$$

2.2.2. Bubble nucleation time

Given that mass transfer is always directly proportional to the concentration driving force, it is reasonable to expect the nucleation time, t_n , to vary inversely with the concentration driving force, $C_b - C_c$, above the meniscus. A possible relationship which describes such dependence is,

$$t_n = \frac{ND_m^2}{K(C_b - C_c)} \quad (25)$$

where N is an unknown constant of proportionality, and the ratio, D_m^2/K , is included simply to make the parameter, N , dimensionless.

2.2.3. The attractor

The bubble growth time depends upon the driving force, $C_b - C_i$, and the bubble nucleation time depends upon the driving force, $C_b - C_c$. These characteristic times can therefore be related using the growth time of the last possible bubble in terms of its driving force, $C_c - C_i$. The attractor for the cycle of bubble production, therefore, is obtained by inverting Eqs. (19),(20),(25) and then combining.

$$\frac{1}{t_g} = \frac{N}{t_n} + \frac{1}{t_g^*} \quad (26)$$

A plot of $1/t_g$ vs. $1/t_n$ should produce a straight line of slope N and intercept $1/t_g^*$. In conjunction with the value of D_m , the growth time, t_g , provides a measure of the level of supersaturation at a given instant, and the inverse of the intercept, t_g^* , is the theoretical growth time of the last bubble, and depends on the critical radius of curvature of the liquid gas interface in the cavity, and hence the size of the cavity.

2.3. Analysis of the dimensionless parameter N

As noted earlier, the thickness of the boundary layer around a growing bubble is $Z = \kappa D$. The concentration of carbon dioxide in this layer can be considered to vary linearly from the bulk value, C_b , down to the saturation value, C_i , at the surface of the bubble. Clearly, a significant zone, partially depleted of carbon dioxide, exists around a growing bubble.

When the bubble reaches its maximum size and detaches from the substrate, a fraction of the boundary layer should be entrained with the rising bubble, and the

remainder should then reside above the gas cavity. A portion of this liquid, partially depleted of carbon dioxide, should rush toward the cavity and penetrate to a certain depth h , as shown in Fig. 5. An estimate of the liquid volume involved can be made by considering the added mass effect [6]. For an accelerating sphere, the volume of liquid that departs with the bubble should be about half of the bubble volume. The bubble just prior to detachment has a diameter equal to D_m and is surrounded by a boundary layer with a width of $\kappa_1 D_m$ partially depleted of carbon dioxide. Hence the volume of liquid partially depleted of carbon dioxide is,

$$v = \frac{\pi}{6} (D_m^3 (1 + 2\kappa_1)^3 - D_m^3) \quad (27)$$

and after detachment, the volume of liquid remaining above the site, which is partially depleted of carbon dioxide is,

$$\frac{\pi}{6} D_m^3 ((1 + 2\kappa_1)^3 - 1) - 0.5 \frac{\pi}{6} D_m^3 = \frac{\pi}{6} (\kappa_2 D_m)^3 \quad (28)$$

A linear concentration field ranging from the bulk concentration, C_b , to the equilibrium cavity concentration C_c , is assumed to form in the zone of liquid above the nucleation cavity after the bubble departs. According to Eq. (28), the diameter of the zone is $Z = \kappa_2 D_m$. Assuming $\kappa_1 = 0.25$, then $\kappa_2 = 1.23$. Therefore, the height of the zone is of a scale comparable to the diameter of the departing bubble. This is an important point because it follows that the nucleation time is influenced by a mass transfer resistance associated with a length scale far greater than the scale of the cavity. These ideas are similar to the view of Westwater [7] that the time for the boundary layer to be restored following detachment governs the nucleation process.

It is worth deriving an approximate expression for the nucleation time, t_n , in order to account for the magnitude of the dimensionless parameter N . Again, it is necessary to simplify the physical circumstances in order to arrive at a first order solution. The pressure inside the meniscus is assumed to remain constant and equal to P_c . This assumption is reasonable for a cylindrical cavity prior to when the bubble emerges from the cavity. The volumetric rate of growth inside the cavity is obtained by rearranging Eq. (8) with $dP/dt = 0$.

$$\frac{dV}{dt} = \frac{rT}{P_c} \frac{dn}{dt} \quad (29)$$

The concentration gradient of carbon dioxide in the zone above the cavity is assumed to be constant and linear. If a boundary layer of liquid of height Z is located just above the active nucleation site, as shown in Fig. 5, the gradient is equal to $(C_b - C_c)/Z$.

The geometry of the gas cavity is assumed to be cylindrical, with a wetting depth h , and area A , and the meniscus inside the cavity is assumed to be a hemisphere with an area $2A$. The velocity of the meniscus up through the cavity is obtained

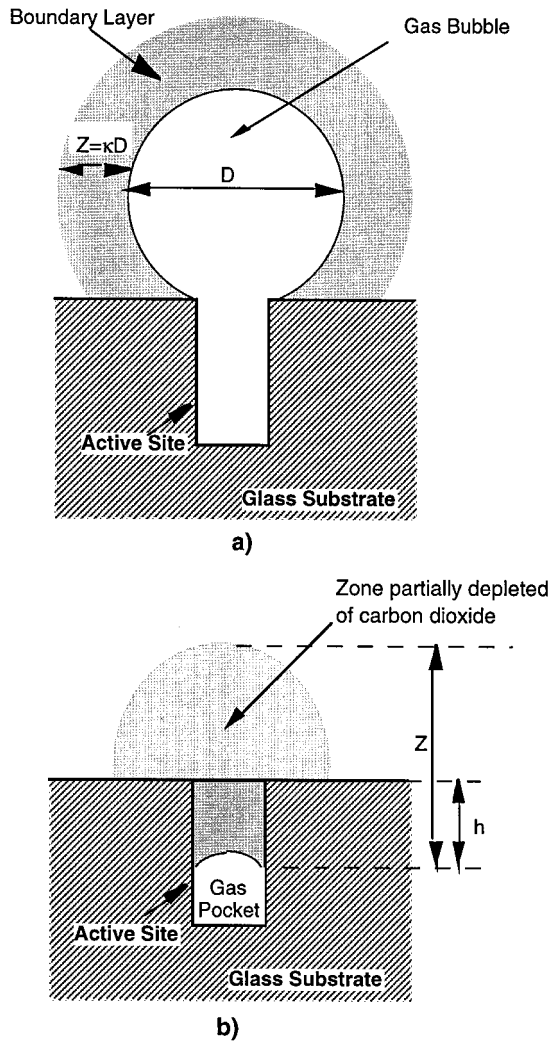


Fig. 5. Schematic representation of concentration field in the vicinity of the cavity before and after bubble detachment.

using Eqs. (5),(29) with $dV/dt = Adh/dt$. That is,

$$\frac{dh}{dt} = 2 \frac{rT}{P_c} \frac{D}{Z} (C_b - C_c) \quad (30)$$

Integration gives a nucleation time of,

$$t_n = \frac{1}{2} \frac{P_c}{rT} \frac{hZ}{D(C_b - C_c)} \quad (31)$$

Combining this result with Eqs. (25) and (10) gives,

$$N = \frac{2}{\kappa} \frac{P_c}{P} \frac{hZ}{D_m^2} \quad (32)$$

Assuming $\kappa \sim 0.25$, $P_c/P \sim 1.3$, and $Z \sim 1.23D_m$, typical of the values in this study, it follows that,

$$N = \frac{10h}{D_m} \quad (33)$$

Eq. (33) should be examined in conjunction with Eq. (25). It is then apparent that the nucleation time is proportional to the product, hD_m . So, a larger departing bubble results in a longer nucleation time.

2.4. Bubble detachment

An integral part of the cycle of bubble production is the critical moment when the bubble detaches from the substrate. There are two probable states for the bubble at detachment. In one case, the bubble maintains its designated contact angle with the substrate at all times, and in the second case, the bubble remains rooted to the mouth of the cavity, with an apparent contact angle that depends upon the size of the bubble. As noted in the review by Jones et al. [1], the critical condition of a bubble attached to the cavity mouth can be approximated by the equation,

$$2R_d\gamma\sin\alpha = \Delta\rho g \frac{4}{3}R^3 \quad (34)$$

where R_d is the radius of the cavity mouth, α the apparent contact angle, R the radius of the bubble, as a sphere, γ the interfacial tension, $\Delta\rho$ the density difference between the liquid and the gas, and g the acceleration due to gravity. A modified version of Eq. (34) was also presented by Jones et al. [1] for the case involving a spherical cap bubble on the substrate, of contact angle θ .

3. Experimental methodology

3.1. Preparation of glassware

The cleaning of the glassware involved a combination of a strong chromic acid treatment for 20 min, several rinses with ultra pure water from a Millipore Milli Q system, followed by a strong alkali treatment over several days (soaking), using a diluted solution of Extran 300 supplied by BDH. Just prior to conducting the experiment, the glassware underwent repeated rinses with the ultra pure water, a rinse with a 50% BDH Analar nitric acid solution, and final rinses with the ultra

pure water. The acids had an oxidising action and the alkali ensured the removal of the surface layer to which organic contaminants are often attached [8].

In order to promote the type IV non-classical nucleation, and hence preserve the existence of gas filled cavities in the constant pressure cell (see Section 3.2), a methylation treatment was applied to the glass substrate. Methylation with trimethylchlorosilane (TMCS) is a common practice in studies of flotation when it is necessary to render model hydrophilic particles hydrophobic [9,10]. Methyl groups are then firmly attached by covalent bonds to the glass substrate.

Methylation of the glass substrate was carried out using solutions of TMCS (BDH Chemicals) in cyclohexane obtained from Univar-Ajax Chemicals. In order to relate bubble nucleation and growth rate data to the substrate condition, the contact angle of a droplet of water on a similarly prepared glass substrate (microscope slide) was measured. An initial droplet of water was located onto the test substrate, and then several small droplets were added to the main droplet. When mechanical equilibrium was achieved, the contact angle was measured.

In seeking to obtain a given contact angle, the effects of concentration and time of contact of the TMCS solution with the substrate were examined. As a result of preliminary experiments, a standard method of substrate preparation was ultimately adopted. A solution with a concentration of 0.06% by volume was selected and was applied to the glass cell substrate for a specific period of 20 min. The contact angles obtained were generally $65^\circ \pm 5^\circ$. After coating with the TMCS solution, the cell was rinsed with copious quantities of purified water, drained, and then thoroughly dried using carbon dioxide gas prior to adding the test water.

3.2. Constant pressure experimental system

A schematic representation of the experimental set-up is given in Fig. 6. A cylindrical constant pressure cell, made from glass with a smooth glass window at the base, was jacketed around the sides and the base for temperature control. Inlet and outlet tubes were used for bubbling carbon dioxide through the test water within the cell to achieve the desired level of saturation. A CCD video camera with a microscope objective, positioned below the cell using two micrometer stages, was used to record the bubble growth. A light source focused from above was used to produce sharp images of the bubbles.

The temperature of the system was controlled by pumping water at 6 l/min from a water-bath (Grant LTD6G, accuracy $\pm 0.1^\circ\text{C}$) and through the external jacket of the cell. The temperature of the contents, and the jacketed water, were measured using a thermocouple and were found to agree well with the temperature set point of the water-bath. After the TMCS treatment, ultra pure water was added to the cell and sparged using carbon dioxide (anaerobic grade, 99.8% pure) at a fixed gas flow rate of 0.4 l/min, using a GEC rotameter (Series 1100 with a 2-A-150 tube and a B2R float), for 17 h at atmospheric pressure. The system temperature was maintained at 1°C . The system was not sealed after saturation, and hence remained at atmospheric pressure. According to Fogg and Gerrard [5] the equilibrium mole fraction of carbon dioxide in water at 1°C and 1.013×10^5 Pa is 13.35×10^{-4} .

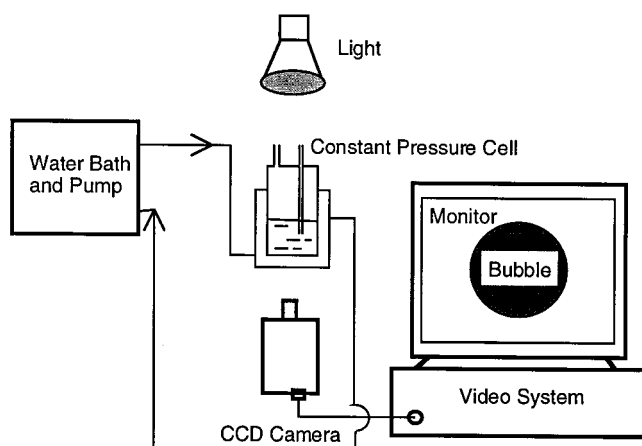


Fig. 6. Schematic representation of experimental setup for bubble observation in the constant pressure cell.

3.2.1. Preliminary nucleation experiments on clean glass

The very first experiments involved the use of the ultra clean constant pressure cell, free of the TMCS treatment. Bubbles failed to form, even when the cell was heated to as high as 50°C and hence to a supersaturation of 2.7. Numerous experiments were conducted without success. Clearly, the water was able to wet all of the potential nucleation sites because the contact angle was zero. The wetting of the sites was a further consequence of saturating in-situ over a period of 17 h. Under these conditions all nucleation is effectively homogeneous, and therefore nearly impossible to achieve, unless the level of supersaturation is more than about 100 [11,12].

3.2.2. Preliminary nucleation experiments with TMCS treatment

In order to generate bubbles, the wettability of the substrate was modified using the TMCS treatment described above, resulting in a contact angle greater than 0°. This treatment prevented the cavities in the surface of the glass from becoming wetted after pouring and after the in-situ saturation in the constant pressure cell.

Again, ultra-pure water was placed in the cell and sparged at 1°C and atmospheric pressure with carbon dioxide until saturation was achieved. The saturated solution was then heated in a stepwise fashion to the temperature at which a bubble appeared on the glass substrate at the base of the vessel. At this critical temperature, the supersaturation was just sufficient to produce nucleation. The variation of the critical temperature with the wettability used, as defined by the contact angle, is shown in Table 1. The critical radius of curvature of the meniscus was calculated using Eq. (23) by assuming the critical bulk concentration was equal to the 1°C saturation value. According to Eq. (24), the radius of curvature can be corrected for the contact angle to obtain an estimate for the radius of the wetting

Table 1
Conditions necessary to establish bubble production

Contact angle	Minimum temperature (°C)	Supersaturation $\sigma = (C_c/C_i - 1)$	$R' (\mu\text{m})$	$R_{\text{site}} (\mu\text{m})$
0	> 50	> 2.7	—	—
15	23	1.1	1.3	1.3
47	18	0.8	1.8	1.2
64	13	0.5	2.9	1.3
89	9	0.3	4.9	0.1

line in the gas cavity. The estimate for the radius of the wetting line was nominally $1.3 \mu\text{m}$ in each case, except when the contact angle was almost 90° , at which point there is significant relative error in the value of $\cos\theta$.

Although, over time, some desorption of the TMCS must occur, the experimental observations indicated that the contact angle and the surface tension of the liquid remained constant. Bubbles produced over a 2-day period from the one site were found to detach at the same size.

3.3. Measurement of carbon dioxide concentration

Because of the difficulty of measuring the carbon dioxide concentration without disturbing the system, the bubble growth time, t_g , was actually used as a convenient and sensitive probe of the small concentration difference, $C_b - C_i$. These data were converted using saturation data to obtain the bulk concentrations.

However, in order to establish the virtues of this approach, the bulk concentration was also measured in some experiments by titration [13]. The concentration of carbon dioxide was determined by adding an excess of a standard solution of sodium hydroxide and barium chloride to a measured sample of the test solution and back-titrating carefully with standardised hydrochloric acid and thymol blue as an indicator [14,15]. The concentration determined by this method is the total dissolved carbon dioxide concentration in all its forms including HCO_3^- and H_2CO_3 . Fogg and Gerrard [5] point out, though, that only about 0.35% of carbon dioxide exists in the form of carbonic acid at 298.2 K and a partial pressure of carbon dioxide of $1.013 \times 10^5 \text{ Pa}$.

Because the system was disturbed by the removal of a sample for titration analysis, titrations were not conducted routinely. Rather, in a select number of experiments they were conducted to verify (i) the saturation condition and (ii) the suitability of using the bubble growth time as a measure of the bulk concentration. The carbon dioxide mole fraction of saturated solutions was determined for different temperatures to firstly determine the equilibrium curve. The results are plotted with the data of Fogg and Gerrard [5] in Fig. 12, together with other experimental data. As the agreement between the saturation results of the titrations and the data available in the literature were reasonable, except for a few

cases, it was concluded that saturation was achieved after 17 h of sparging. The accuracy of some titrations was poor because the excess of BaCl_2 was too large.

Bisperink and Prins [16] made use of a carbon dioxide specific probe as a qualitative indication that the saturation of the carbon dioxide was complete, as indicated by a constant reading. They considered it unsuitable for measurement of the saturation concentration however, relying instead on the literature value.

3.4. Examination of the cycle of bubble production

The test solution was sparged at 1°C and at atmospheric pressure for 17 h to reach saturation. Upon raising the temperature, the solution became supersaturated to a level sufficient for bubbles to start to form at a few sites on the bottom surface and walls of the glass vessel. The required temperature was typically 16°C for the TMCS treated glass. To obtain satisfactory images of a bubble closer to the centre of the glass the temperature was sometimes raised to 20°C . Bubbles with diameters larger than about $15\text{ }\mu\text{m}$ were just detectable but the nucleation sites themselves could not be seen. The formation and the growth of bubbles were recorded on video tapes which were later time coded.

A bubble appeared at a given site, grew in a time period, t_g , to a particular size, D_m , and then detached, leaving a blank screen on the recording monitor. After a nucleation time, t_n , a new bubble appeared at the same site, and then repeated the growth of its predecessor, detaching at a diameter, D_m in the same time period, t_g . This pattern of formation, growth and detachment often continued for hours with only a very gradual increase occurring in the nucleation time, t_n , and reduction in the bubble growth rate, and hence an increase in the growth time, t_g .

Generally it was concluded that the site was inactive and that the supersaturation was too low for nucleation when t_n exceeded 10 min. The temperature was then raised, usually by another 4°C , to regenerate the site. After a short period of time, during which the temperature became uniform, the site produced a new series of bubbles. The growth and nucleation was again recorded, and the system temperature increased when the site became inactive. Hence, within a single run, the bubble growth was observed at the one site, and under isothermal conditions at a series of temperatures.

3.5. Summary of experimental conditions

Table 2 lists the conditions for the experiments performed using the constant pressure cell. It indicates the conditions at which the solution was saturated, the contact angle, and the temperatures at which the bubble growth data were obtained. Runs A, B and C were conducted according to the standard method described in Section 3.4.

Run D was performed by first raising the temperature to 16°C to select an active site, then raising the system temperature straight to 35°C . This experiment was conducted to determine whether the results at a relatively high temperature were dependent on the path followed in raising the temperature.

Table 2

Experimental conditions used in the constant pressure cell

Run	A	B	C	D	E	F
Date	30/1/96	2/4/96	12/4/96	27/4/96	12/12/95	23/1/96
Saturation conditions	1°C 1 atm	1°C 1 atm	1°C 1 atm	1°C 1 atm	1°C 1 atm	16°C 10 atm
TMCS treatment	0.06% v/v 20 min	0.06% v/v 20 min	0.06% v/v 20 min	0.06% v/v 20 min	3.36% v/v 20 min	No TMCS
Contact angle	65	65	65	65	90	0
Temperatures (°C)	16, 20, 24, 28, 32	22, 26, 30, 34	16, 20, 24,	16, 35 32,40	12, 16, 20, 24,	16, 20, 24 28,32,36

Runs E and F were performed at contact angles of 90° and 0°, respectively. The 90° contact angle was obtained by applying a stronger TMCS treatment, while the 0° contact angle was obtained by eliminating the TMCS treatment step. In order to achieve bubble production at a contact angle of 0°, an auxiliary pressure vessel was used to saturate at 16°C and 10 atm for 48 h. The solution was then poured into the clean constant pressure cell. By avoiding in-situ saturation, it was possible to prevent the full wetting of cavities in the glass substrate.

4. Results and discussion

In general, trains of bubbles were observed to form from a given site. Their growth was recorded and analyzed, as shown by the selection of data in Fig. 7. Firstly, it is evident that the bubble diameter squared varied linearly with time. This linearity occurred in virtually every experiment, and at all times [17]. Each bubble grew in a time period, t_g , to a specific size, D_m , and then detached. After the nucleation time, t_n , a new bubble reappeared at the same site, reproducing almost exactly the growth of its predecessor. This process often lasted for hours. However as time passed, the concentration of carbon dioxide in the liquid phase decreased due to bubble production from all the active sites and diffusion from the upper surface. Therefore, during the course of the experiment the growth and nucleation time values increased.

The overall data consisting of the nucleation time and the growth time for almost every single bubble from Run C are plotted in Fig. 8 as a function of the experimental time. The results are also divided into regions for each temperature condition. The exponential increases in the nucleation times are evident for each of the temperatures, as shown in Fig. 8a. At the same time, the growth times increased gradually and almost linearly with the time, as shown in Fig. 8b.

4.1. The attractor

This study is principally concerned with the isothermal correlation between the

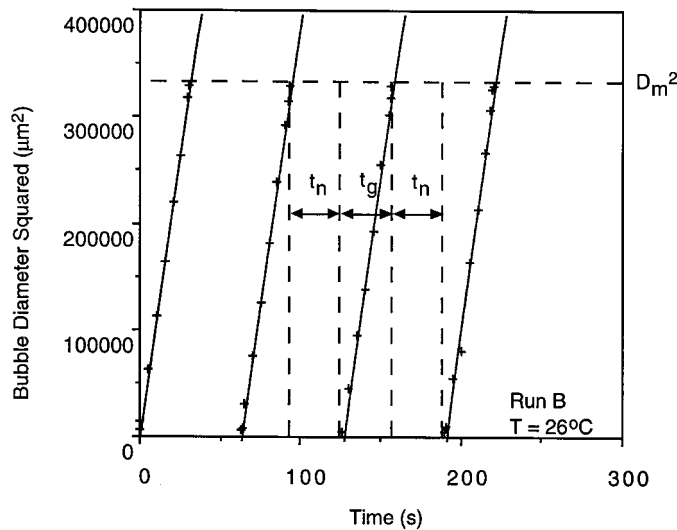


Fig. 7. Successive bubbles from one site, represented by linear plots of the diameter squared vs. time. The figure shows successive growth and nucleation times, obtained by extrapolation of the growth data to zero diameter. The nucleation times are very large relative to the time period associated with the extrapolation of the growth curves to $D = 0$. Hence, the potential extrapolation error is small.

bubble growth time, t_g , and the bubble nucleation time, t_n . Hence, the obvious transient responses associated with segments of the data following a temperature change were disregarded. It should be noted however, that much of the scatter during a transition exhibits a form of correlation because a temperature shift produces a similar effect on the growth time as it does on the nucleation time. Other scatter may be explained by changes in the wetting position in the cavity during an experiment.

In Section 2 it was shown that the inverse of the growth time should vary linearly with the inverse of the nucleation time. Fig. 9 shows the relationship between the growth time t_g and the nucleation time t_n for Run C at $T = 24^\circ\text{C}$. The data on the growth time, t_g , and the nucleation time, t_n , are consistent with the relationship given by Eq. (26). That is,

$$\frac{1}{t_g} = \frac{N}{t_n} + \frac{1}{t_g^*}$$

Eq. (26) mathematically describes the underlying attractor of the bubble production cycle. The journey time from right to left along the line in Fig. 9, as effervescence proceeds, may range from tens of hours to a few minutes because the rate of decrease in the value of the dissolved carbon dioxide bulk concentration varies significantly, depending on the number of sites in the system, and the volume of the liquid. Irrespective of these factors, the t_g and t_n data adheres to the attractor, provided the temperature remains constant. Although the growth time of

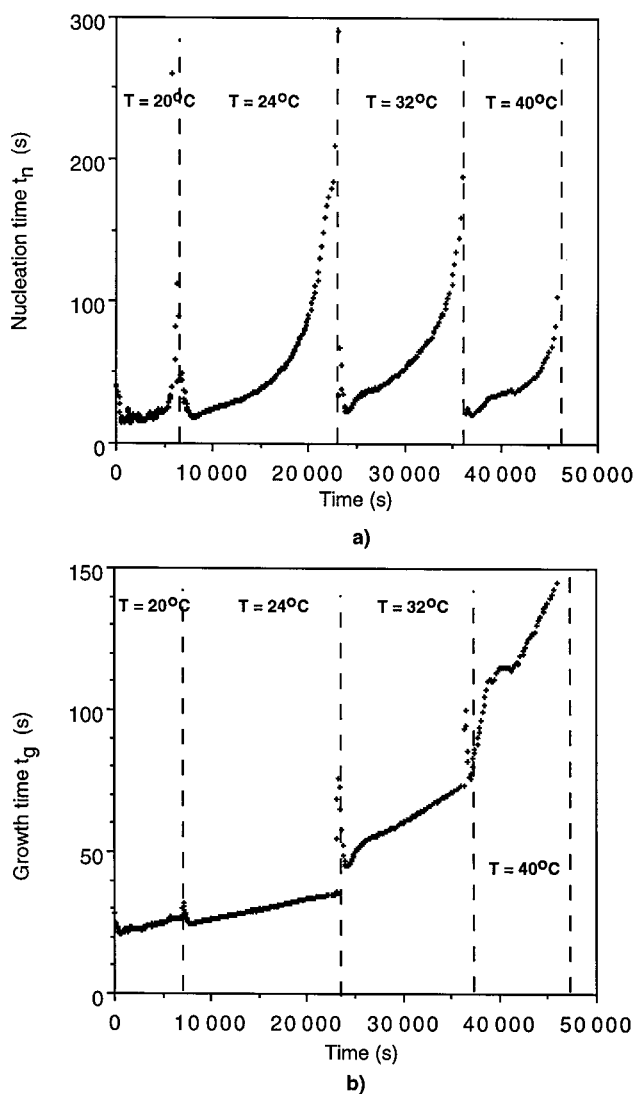


Fig. 8. Bubble evolution from a given site in Run C.

the last bubble was about 36 s, the intercept value indicates a theoretical growth time for the last possible bubble of 37 s. The bubble production generally ceases ahead of the theoretical limit, suggesting the gas cavity requires a minimum level of supersaturation to generate a bubble. Similar plots for all of the cycles in Runs A–C are shown in Fig. 10a–c.

4.2. Influence of temperature

It is evident from the experimental results that the values of the slope, N ,

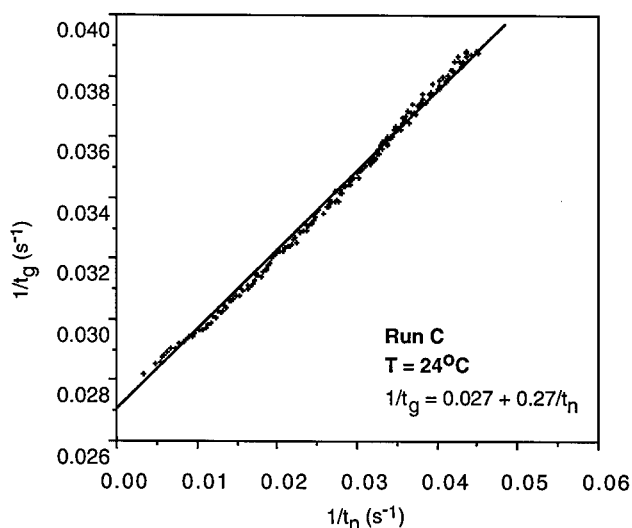


Fig. 9. Inverse of the bubble growth time vs. inverse of the bubble nucleation time for Run C at 24°C.

obtained do not vary significantly with temperature for a given run. Therefore, a common slope was used to generate the curves through the data of a given run, for each temperature. Between runs, N varied from 0.27 to 0.35. The intercepts, however, decreased significantly with temperature. Fig. 11 shows the relationship between the intercept of the attractor and the temperature for each of the runs. As can be seen, the inverse of the theoretical time for the growth of the last possible bubble, $1/t_g^*$, decreases linearly as the temperature increases. Although different sites were used in each run, it appears that the active nucleation sites were of similar geometry.

Cycles at a given temperature were permitted to run to completion up until the production of the last possible bubble. The growth curve of the final bubble was used to determine the bulk concentration at cessation, using Eqs. (11), (12) and (15). In an additional series of experiments, not listed in Table 2, cessation concentrations were measured at a series of temperatures by titration. Concentrations, based on bubble growth measurements and those based on the titrations, are compared in Fig. 12 as a function of the system temperature. The good agreement demonstrates the virtue of relying on the bubble growth time as a measure of concentration. This figure also shows the titration measurements referred to earlier for the saturated systems, as well as the literature saturation values [2].

Fig. 13 shows the critical concentrations, C_c , based on the actual intercept, $1/t_g^*$. The value of $1/t_g^*$ is useful because it is directly related to the concentration, C_c , in Eq. (20), which in turn is related to the radius of curvature of the meniscus inside the gas cavity, according to Eq. (23). The intercept-related concentrations decreased significantly as the temperature increased.

The radius of curvature of the meniscus, based on the data in Fig. 13 and Eq. (23), is shown as a function of temperature in Fig. 14. Surprisingly, the radius

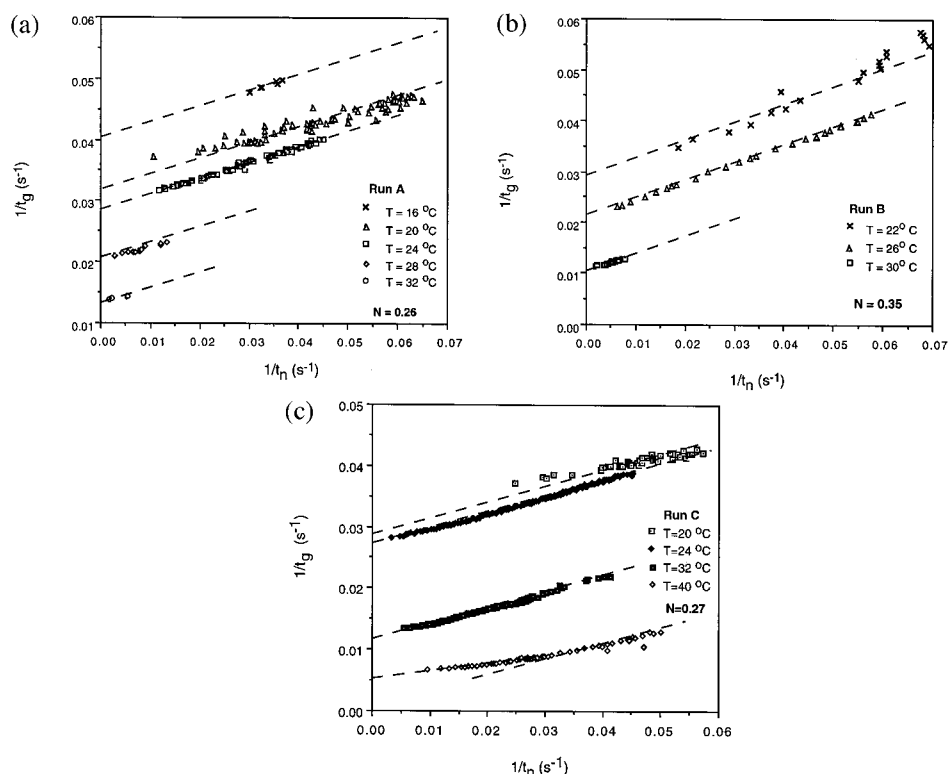


Fig. 10. Attractors representing bubble production cycles in Runs A–C at various temperatures. Generally, the slopes are similar, and the intercepts vary significantly with temperature.

increases significantly with temperature. This result was unexpected because a single site and contact angle were used to examine the effect of temperature. We have no actual knowledge of the cavity geometry, and hence any statements made on the geometry can only be inferred from related information, such as that shown in Fig. 14. The first question to consider is, how can a single cavity produce different radii of curvature? The second is, are the radii shown in Fig. 14 unique to the temperature concerned? The results of Run D should help here.

In Run D, a nucleation cavity was located in the usual way by raising the temperature to 16°C. However, in this case the system temperature was then raised straight to 35°C. In Runs A–C it was very difficult to generate bubbles at temperatures higher than 32°C, perhaps because the initial supersaturation at such temperatures was too low. In Run D, however, there was no such problem, and hence the data forming the attractor shown in Fig. 15 covered a much broader range than usual. The slope, $N = 0.37$, of the data is consistent with that obtained in Runs A–C. However, the intercept, 0.027, is very much higher than the value of 0.005 expected on the basis of the data in Fig. 11. In fact, the entire attractor for

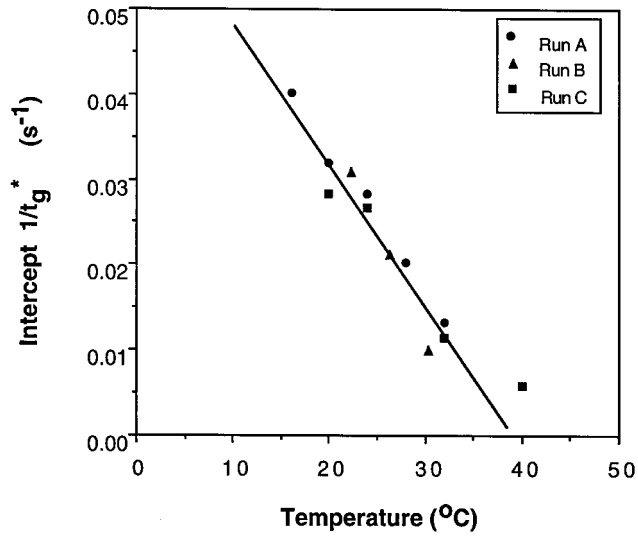


Fig. 11. Dependence of the growth time intercept, $1/t_g^*$, on the temperature.

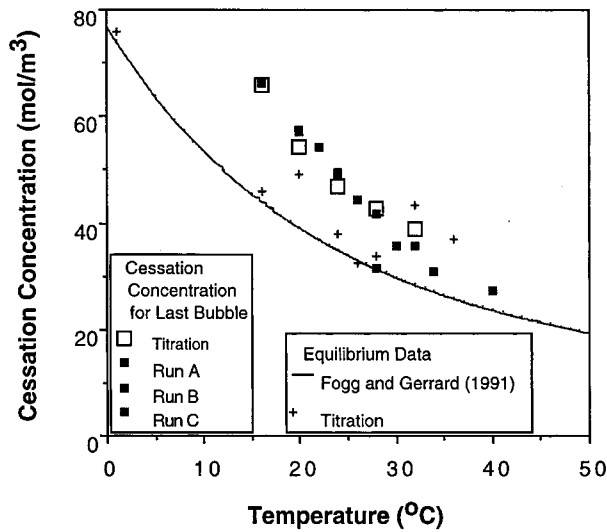


Fig. 12. The bulk concentration of carbon dioxide in the liquid at the cessation of bubble production, as a function of the system temperature. Good agreement was obtained between the titration results and those obtained using the bubble growth data of the last bubble and Scriven's Eq. (2). Also shown are the equilibrium data of Fogg and Gerrard [5] and titration results obtained in this study at saturation.

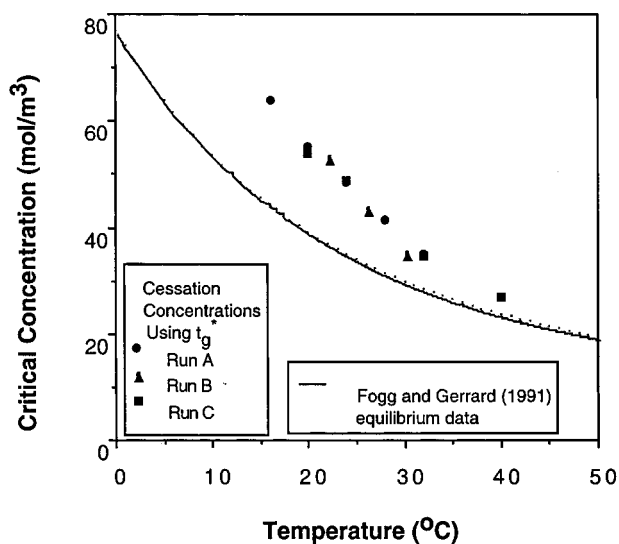


Fig. 13. The critical concentrations determined using the inverse of the intercept, t_g^* , and Scriven's equation. The difference between the critical and equilibrium concentration is related to the meniscus radius of curvature in the cavity.

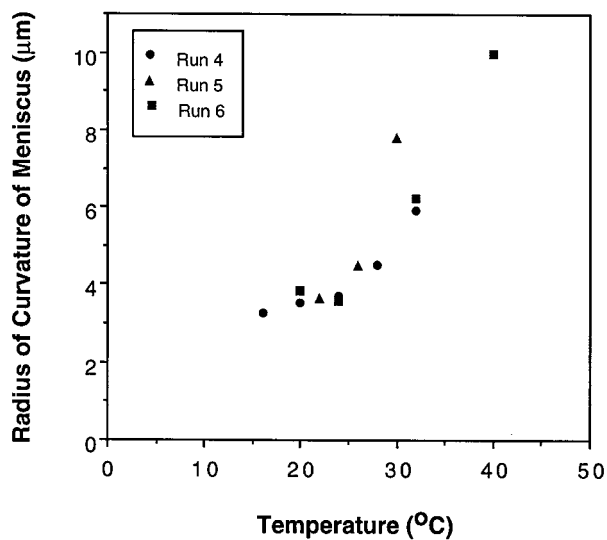


Fig. 14. The estimated radius of curvature of the meniscus in the cavity, as a function of the system temperature.

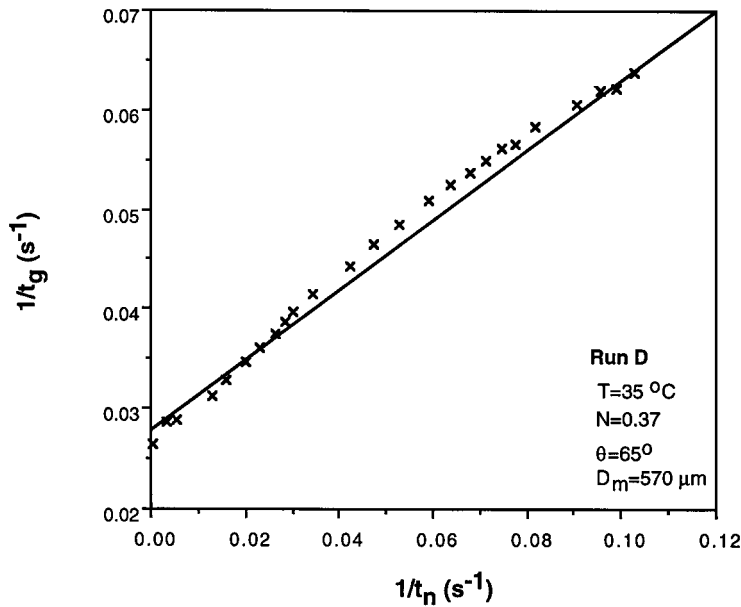


Fig. 15. Attractor obtained for Run D. In this case the system temperature was increased directly from 16°C to 35°C. This resulted in bubble production over several days and hence a broad range of results.

Run D at 35°C is similar to that obtained for Run B at 22°C. So, the stepwise procedure used to increase the temperature in Runs A–C may have caused the increase in the critical radius of curvature with temperature. Presumably, when a new cycle of bubble production commences, the critical position of the wetting line in the cavity is positioned in a way that depends upon the level of supersaturation. The precise reason, however, is unclear. This wetting line position is then maintained throughout the cycle.

It is possible that the cavity geometry was conical. This geometry permits a broad range of possible meniscus curvatures, depending on the position of the wetting line in the cavity. In Runs A–C, in which the temperature was raised over long periods in a stepwise fashion, the levels of supersaturation at the commencement of each cycle was relatively low. In response, the wetting line at the start of the cycle may have positioned itself at a higher level, thus producing a larger radius of curvature and hence a lower value of C_c and permitting the cycle to proceed. By chance, bubbles were generated in Run C at a temperature of 40°C. Interestingly, there was a shift in the attractor with the slope decreasing in value towards the end. Perhaps, in this case, the critical position of the wetting line was near the cavity mouth. However, in Run D, there was no need for the critical wetting line to undergo a shift, given that the supersaturation was significant.

Application of Eq. (34), based on the conditions for the detachment of the bubbles ($D_m \sim 600 \mu\text{m}$), gives $R_d \sin \alpha = 2.5 \mu\text{m}$. This value suggests that the

bubble remained anchored to the cavity mouth during its growth, and that the radius of the mouth was relatively small. If we consider a meniscus inside a conical cavity, with one contact angle, then the radius of curvature will increase as the wetting line rises toward the mouth. Then, at the mouth, the radius decreases in value as the bubble emerges, reaching a minimum when the radius of curvature matches the radius of the mouth. The radius then increases in value. Given that the maximum critical radius of curvature obtained was $10\ \mu\text{m}$ in Run C at a temperature of 40°C , it is proposed that the radius of the cavity mouth was also $10\ \mu\text{m}$. For $R_d = 10\ \mu\text{m}$, the apparent contact angle of the detaching bubble should be about 14° .

So, in most cases, the meniscus must have sat deep within the cavity producing a radius of curvature of just over $3\ \mu\text{m}$. If we assume a cavity depth of $20\ \mu\text{m}$, not unreasonable for a mouth radius of $10\ \mu\text{m}$, and use $D_m = 600\ \mu\text{m}$, it follows from Eq. (33) that $N = 10 \times 20 / 600 = 0.33$, a result which is in excellent agreement with the slopes in Fig. 10a–c.

4.3. Effect of contact angle

Further experiments were conducted to demonstrate that an attractor could be produced at different contact angles. The effect of the contact angle was investigated in Run E with $\theta = 90^\circ$, and Run F with $\theta = 0^\circ$. A higher level of supersaturation was used in Run F by placing the test solution in an auxiliary pressure vessel

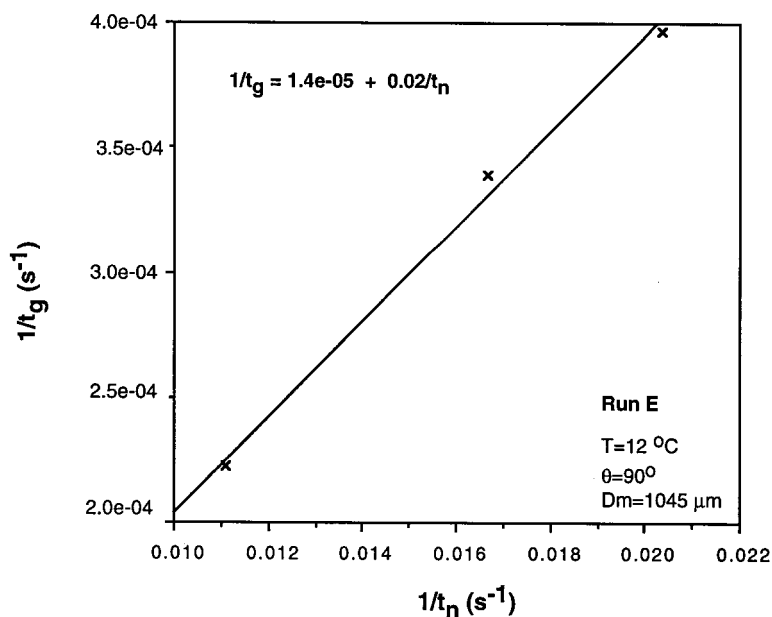


Fig. 16. Attractor obtained for Run E with the contact angle nominally 90° . Note that the growth time values should not be compared directly with those from Runs A–D because D_m is larger.

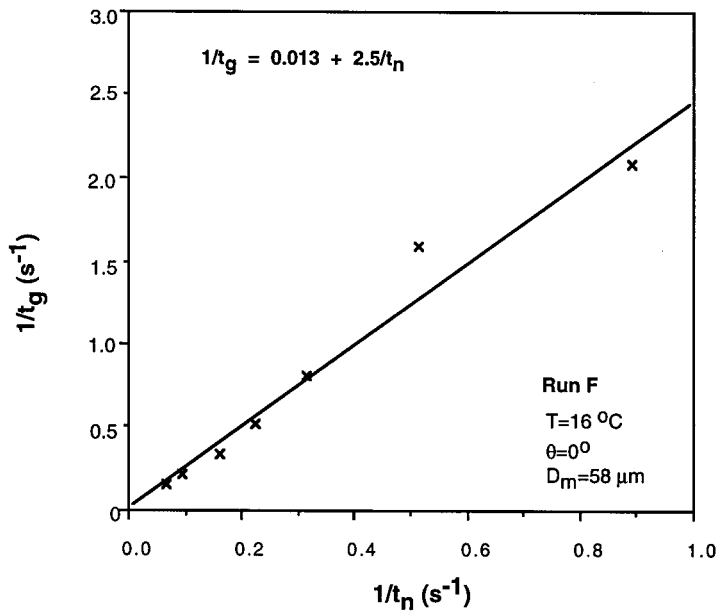


Fig. 17. Attractor obtained for Run F with the contact angle nominally 0° . Note that the growth time values should not be compared directly with those from Runs A–D because D_m is much smaller.

under 10 atm of carbon dioxide at 16°C , for 48 h. The results obtained for Runs E and F are presented in Figs. 16 and 17, respectively. At $\theta = 90^\circ$, the values of $1/t_g$ and $1/t_n$ for the last bubble were extremely small. On such a hydrophobic substrate, relatively large cavities fail to wet, resulting in the existence of gas filled cavities with relatively large radii of curvature. These, therefore, remain active at lower levels of supersaturation with $C_b \sim C_i$. This is confirmed by the extremely small value of $1/t_g^*$ of the order of 1.4×10^{-5} . At these low levels of supersaturation, the bubble growth times are relatively long, and are also made longer because the bubble volume at detachment is very much greater. Conversely, at $\theta = 0^\circ$, the growth times are relatively small, given the bubble detachment size is small, and the supersaturations relatively high.

Table 3 provides a summary of the results obtained in the study. The value of the bubble diameter at detachment, D_m , varies significantly with the contact angle. For all runs with $\theta = 65^\circ$, except one, the value of D_m was approximately equal to $600 \mu\text{m}$. For $\theta = 0^\circ$, $D_m = 58 \mu\text{m}$ and for $\theta = 90^\circ$ $D_m = 1050 \mu\text{m}$. A significant variation in N is also observed. For $\theta = 90^\circ$ $N = 0.02$, for $\theta = 65^\circ$ $N = 0.27\text{--}0.37$, whereas, for $\theta = 0^\circ$ $N = 2.5$.

5. Conclusions

In this study of type IV non-classical nucleation, it was shown that the time a

Table 3

Values of N and D_m as a function of the contact angle

Run	Contact angle	N	D_m (μm)
E	90	0.02	1050
A–D	65	0.27–0.37	~ 600
F	0	2.5	58

bubble takes to reappear at a nucleation site, t_n , is related to the time, t_g , the bubble takes to grow to its detachment diameter, D_m . This correlation, referred to as the attractor, is given by Eq. (26). It was concluded that the nucleation time was proportional to the product, hD_m , where h is the height of the wetting depth in the cavity, and D_m the diameter of the detaching bubble. The dependence on D_m was thought to be due to the relationship between the boundary layer thickness and the bubble diameter. Some of the liquid comprising the boundary layer probably remains above the gas cavity when the bubble detaches. Hence, the lower concentrations above the gas cavity result in longer nucleation times.

According to the review by Jones et al. [1], most studies have been concerned with the conditions necessary for the first nucleation event to occur, and hence the minimum supersaturation required for bubbles to form. This study, however, focused on the conditions governing the last nucleation event. Although analogous, these critical states were different, probably because in a cycle of bubble production the position of the wetting line is influenced by the detachment process and the flow of liquid back into the gas cavity. Indeed, we found that the critical radius of curvature increased from about $3.3 \mu\text{m}$ to $7 \mu\text{m}$ as the temperature increased from 16 to 30°C .

6. Nomenclature

f_1	defined by Eq. (3)
f_2	defined by Eq. (4)
h	depth of critical wetting line (m)
h	heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
k	mass transfer coefficient (m s^{-1})
k_w	thermal conductivity of water ($\text{W m}^{-1} \text{K}^{-1}$)
n	number of moles (mol)
r	ideal gas constant
t	time (s)
t_g	bubble growth time (s)
t_g^*	growth time of the last possible bubble (s)
t_n	bubble nucleation time (s)
C_b	bulk concentration of carbon dioxide in the water (mol m^{-3})
C_c	equilibrium concentration of carbon dioxide in the water at a pressure P_c (mol m^{-3})

C_i	equilibrium concentration of carbon dioxide in the water at pressure P (mol m ⁻³)
C_T	molar concentration of water (mol m ⁻³)
D	bubble diameter (m)
D	diffusivity of carbon dioxide in water (m ² s ⁻¹)
D_m	bubble diameter just prior to detachment (m)
F	fraction of molecules in bubble that are water
H	Henry's law constant, Pa per mole fraction
K	defined by Eq. (10)
N	dimensionless number for describing nucleation time, defined by Eq. (25)
P	nominal system pressure (Pa)
P_c	pressure inside the meniscus when the radius of curvature is R' (Pa)
ΔP	pressure elevation due to curvature (Pa)
Q	rate of heat transfer (W)
R	radius of bubble (m)
R'	radius of curvature of bubble in nucleation site (m)
R_d	radius of contact line when bubble detaches (m)
Re	Reynolds number
R_{site}	radius of site (m)
Sc	Schmidt number
Sh	Sherwood number
T	system temperature (K)
ΔT	temperature difference (K)
V	bubble volume (m ³)
X_c	mole fraction of carbon dioxide in water when the last bubble is produced
X_i	equilibrium mole fraction of carbon dioxide in water
Z	length scale of the depletion zone and boundary layer thickness (m)
α	apparent contact angle, at detachment
β	dimensionless growth parameter [2]
ϕ	dimensionless concentration driving force [2]
γ	gas–liquid interfacial tension
κ	dimensionless boundary layer thickness
κ_d	dimensionless boundary layer thickness due to diffusion
κ_c	dimensionless boundary layer thickness due to convection
κ_1	dimensionless boundary layer thickness around bubble at detachment
κ_2	dimensionless diameter of depletion zone after detachment
λ	latent heat of vaporisation (J mol ⁻¹)
$\Delta\rho$	density difference between water and gas (kg m ⁻³)

Acknowledgements

The authors wish to thank the Research Management Committee of the University of Newcastle and the Australian Research Council for supporting this work.

Appendix A: Scriven's solution

Scriven [2] obtained the general result,

$$R = 2\beta(Dt)^{0.5} \quad (\text{A1})$$

The dimensionless concentration driving force, ϕ , was related to the dimensionless growth coefficient, β , and a dimensionless density factor, ε . These are defined as:

$$\phi = \phi\{\varepsilon, \beta\} = \frac{\rho_L(C_b' - C_i')}{\rho_G(\rho_L - C_i')} \quad (\text{A2})$$

$$\varepsilon = 1 - \frac{\rho_G}{\rho_L} \quad (\text{A3})$$

where C_b' is the bulk concentration of dissolved gas, C_i' is the equilibrium saturation concentration, both expressed in kg/m^3 . ρ_L and ρ_G are the densities in kg/m^3 of the liquid and the gas, respectively.

For the system consisting of water and carbon dioxide, under the conditions used in this study, $\rho_L \gg \rho_G$ and hence $\varepsilon \sim 1$. Similarly, $\rho_L \gg C_i'$. Therefore,

$$\phi = \frac{(C_b' - C_i')}{\rho_G} \quad (\text{A4})$$

Using the ideal gas law,

$$\rho_G = \frac{MP}{rT} \quad (\text{A5})$$

where M is the molecular weight in kg/kmol . Similarly, $C_b' = MC_b$ and $C_i' = MC_i$. Hence, it follows that,

$$\phi = \frac{rT}{P}(C_b - C_i) \quad (\text{A6})$$

where C_b and C_i are the bulk and interfacial molar concentrations of carbon dioxide in the liquid.

Appendix B: Conduction of latent heat

The purpose of this appendix is to demonstrate that the effect of water evaporation on the temperature of the liquid–vapour interface is negligible, and hence that isothermal conditions can be assumed.

The rate of evaporative cooling is,

$$Q = F\lambda dn/dt \quad (\text{B1})$$

where, F is the proportion of molecules in the bubble that are water, λ is the latent heat of vaporisation of the water on a molar basis, and dn/dt is the total molar rate of carbon dioxide into the bubble, which is approximately the total molar rate. The rate of heat conduction away from the bubble is,

$$Q = hS\Delta T \quad (\text{B2})$$

where S is the bubble surface area, and ΔT is the temperature difference between the bulk and the interface. For a Nusselt number of 2, the heat transfer coefficient, h , is

$$h = 2k_w/D \quad (\text{B3})$$

where k_w is the thermal conductivity of water, and D the bubble diameter. When the rate of evaporative cooling is matched by the rate of heat conduction, the temperature difference, ΔT , becomes constant. Equating Eq. (B1) and Eq. (B2), and substituting in Eq. (B3) and Eq. (5) and Eq. (6), with $\kappa = 0.5$, gives

$$\Delta T = F\lambda D(C_b - C_i)/k_w \quad (\text{B4})$$

where $(C_b - C_i)$ is the concentration driving force. The temperature difference, ΔT , estimated using $F = 0.05$, $k_w = 0.6 \text{ W m}^{-1} \text{ K}^{-1}$, $\lambda = 43\,668 \text{ J/mol}$, $D = 1.5 \times 10^{-9} \text{ m}^2/\text{s}$, and $(C_b - C_i) = 5 \text{ mol/m}^3$ gives $\Delta T = 3 \times 10^{-5}^\circ\text{C}$. Therefore, the evaporation of water produces a negligible decrease in the temperature of the liquid–vapour interface.

Appendix C: Physical property data used in calculations

Table C1

T ($^\circ\text{C}$)	T (K)	D ($\text{m}^2 \text{ s}^{-1}$)	C_T (mol m^{-3})	γ_w (N m^{-1})	C_i (mol m^{-3})	H ($\text{Pa (mol frac)}^{-1}$)
16	289	$1.58\text{e} - 09$	55 650	0.0736	44.2	$1.27\text{e} + 08$
20	293	$1.77\text{e} - 09$	55 580	0.0728	39.2	$1.44\text{e} + 08$
24	297	$1.97\text{e} - 09$	55 514	0.0720	35.0	$1.61\text{e} + 08$
28	301	$2.18\text{e} - 09$	55 450	0.0712	31.5	$1.79\text{e} + 08$
32	305	$2.40\text{e} - 09$	55 380	0.0703	28.5	$1.97\text{e} + 08$
36	309	$2.64\text{e} - 09$	55 320	0.0695	25.9	$2.16\text{e} + 08$

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Analisis de Variables de las Burbujas producidas usando Nucleacion Homogenea y Nucleacion Heterogenea

Propiedades de las burbujas generadas usando materiales de nucleación M1, M2 y M3

Este documento muestra de manera resumida las diferencias presentadas en las propiedades de las microburbujas generadas segun los procedimientos usados mediante los materiales de nucleacion heterogenea M1, M2 y M3. Se evalúan las variables de mayor importancia tales como número de burbujas producidas por unidad de volumen y el tamaño de estas en cada uno de los estados experimentales.

Analisis de Variables de las Burbujas producidas usando Nucleacion Homogenea y Nucleacion Heterogenea

Allianza SAS

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[Edición 1, volumen 1]

Comparativo de la eficiencia de burbujas generadas en cuatro diferentes escenarios

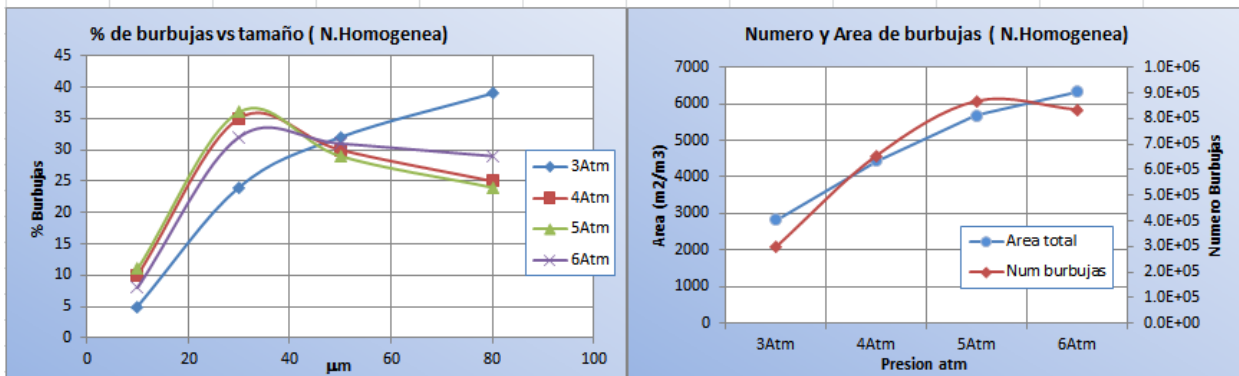
Los escenarios que se evaluación son los siguientes:

1. Las condiciones de evaluación son agua corriente, a 30 °C
2. Las condiciones de presión son 3, 4, 5 y 6 Atmosferas
3. Sistema de generación sin nucleación Heterogénea
4. Sistema de generación usando le material **M1** activado para nucleación Heterogénea
5. Sistema de generación usando le material **M2** activado para nucleación Heterogénea
6. Sistema de generación usando le material **M3** activado para nucleación Heterogénea

Es importante hacer notar que se buscan condiciones de generación de burbujas que cumplan con las siguientes características, las cuales son las deseables para los procesos de tratamiento de aguas, según las recomendaciones de la literatura técnica disponible sobre el tema.

1. Tamaño promedio entre 20 y 40 micras
2. Alta densidad de generación (preferiblemente mayor a 6 millones por centímetro cubico MM/cm³)
3. Alta área de contacto. (preferiblemente mayor a 5000 m²/m³)
4. Menor presión de generación

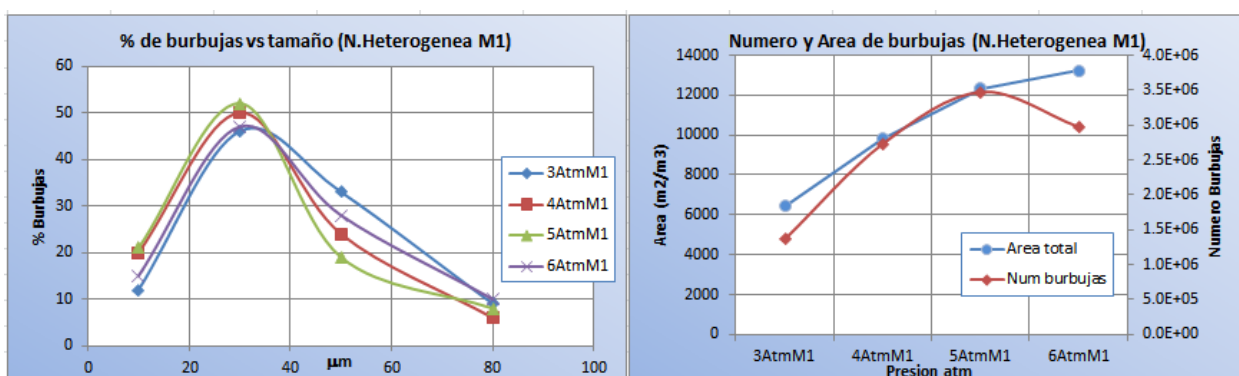
E0. Generacion de burbujas SIN Nucleacion Heterogenea Vs Presion



Se observa que la presión es una variable que incide de manera importante en la calidad de la microburbujas, según los datos de las graficas se concluye que:

1. La distribución de diámetro de burbuja es muy dispersa a 3 atmosferas, ,mientras que a 4 y 5 atmosferas esta dispersión es menor, ampliándose nuevamente a 6 atmosferas.
2. El tamaño promedio de las burbujas es menor a 4 y 5 atmosferas , mientras que a 3 atmosferas es mucho mayor.
3. El Área total de las burbujas se incrementa con la presión, aunque se presenta una relación de incremento menor después de 5 atmosferas.
4. El número de burbujas es máximo a 5 atmosferas.
5. Aunque a 6 atmosferas tanto el área como el numero de las burbujas es mator que a 4 atm, se prefiera las generadas a 4 atm, debido a que la presión es menor y su tamaño es mas adecuado según las condiciones requeridas.

E1. Generacion de burbujas CON Nucleacion Heterogenea Vs Presion (usando Material M1)

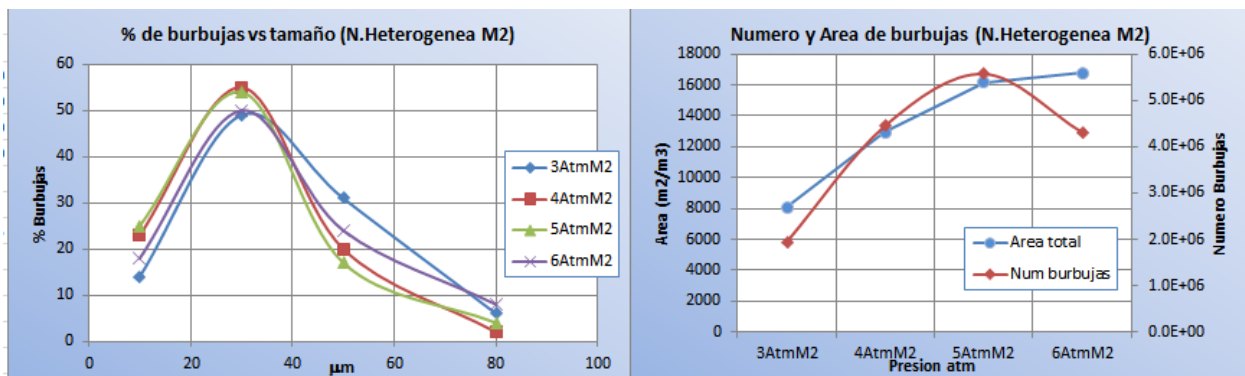


Se observa nuevamente que la presión es una variable que incide de manera importante en la calidad de la microburbujas, según los datos de las graficas se concluye que:

1. La distribución de diámetro de burbuja es mas dispersa a 3 atmosferas, ,mientras que a 4 y 5 atmosferas esta dispersión es menor, ampliándose nuevamente a 6 atmosferas. Similar a lo presentado cuando no se usan materiales de Nulceacion Heterogenea.
2. El tamaño promedio de las burbujas es menor a 4 y 5 atmosferas , mientras que a 3 y 6 atmosferas es mayor. Sin embargo no es tan alto como cuando no se usa materiales de nucleación Heterogenea.

3. El Área total de las burbujas se incrementa con la presión, aunque se presenta una relación de incremento menor después de 5 atmosferas. Similar al caso sin nucleación Heterogenea.
4. El número de burbujas es máximo a 5 atmosferas.
5. Aunque a 6 atmosferas tanto el área como el numero de las burbujas es mayor que a 4 atm, se prefiera las generadas a 4 atm, debido a que la presión es menor y su tamaño es mas adecuado según las condiciones requeridas.
6. El numero de burbujas se incrementa en mas del 300% e en todas las presiones de la prueba, respecto a las generadas sin Nucleacion Heterogenea.
7. El material M1 genera un incremento de generación de microburbujas en todas las presiones evaluadas, y adicionalmente se presenta una reducción del tamaño de las burbujas, lo cual es favorable para el tratamiento de aguas.
8. El área de la burbujas producidas se incrementa de manera apreciable respecto a la generación sin Nucleacion Heterogenea, lo cual es favorable para el tratamiento de fluidos.

E2. Generacion de burbujas CON Nucleacion Heterogenea Vs Presion (usando Material M2)

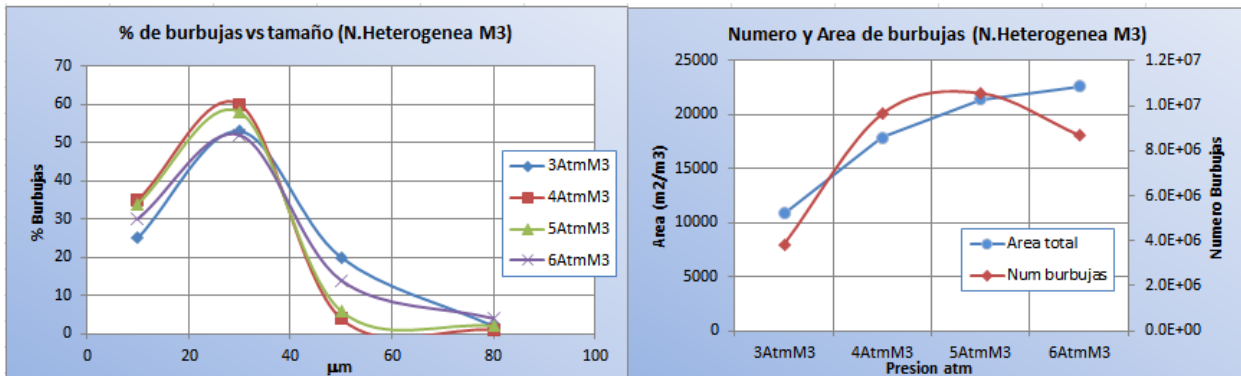


Se observa nuevamente que la presión es una variable que incide de manera importante en la calidad de la microburbujas, según los datos de las graficas se concluye que:

1. La distribución de diámetro de burbuja es mas dispersa a 3 atmosferas, mientras que a 4 y 5 atmosferas esta dispersión es menor, ampliándose nuevamente a 6 atmosferas. Similar a lo presentado en las pruebas E0 y E1.
2. El tamaño promedio de las burbujas es menor a 4 y 5 atmosferas, mientras que a 3 y 6 atmosferas es mayor. Sin embargo no es tan alto como cuando no se usa materiales de nucleación Heterogenea.
3. El tamaño de las burbujas y su dispersión es mucho menor que los presentados en las pruebas E0 y E1.
4. El Área total de las burbujas se incrementa con la presión, aunque se presenta una relación de incremento menor después de 5 atmosferas. Similar a los casos E0 y E1.
5. El número de burbujas es máximo a 5 atmosferas.
6. Aunque a 6 atmosferas el área de las burbujas es mayor que a 4 atm, se prefiera las generadas a 4 atm, debido a que la presión es menor y su tamaño es mas adecuado según las condiciones requeridas.
7. A a 6 atmosferas el numero de las burbujas es similar que a 4 atm, a diferencia de los pruebas E0 y E1.
8. El numero de burbujas se incrementa en mas del 500% en todas las presiones de la prueba, respecto a las generadas sin Nucleacion Heterogenea, y tambien cuando se usa el material de nucleación M1.
9. El material M2 genera un incremento de generación de microburbujas en todas las presiones evaluadas, y adicionalmente se presenta una reducción del tamaño de las burbujas, lo cual es favorable para el tratamiento de aguas.

10. El área de la burbujas producidas se incrementa de manera apreciable respecto a la generación en E0, lo cual es favorable para el tratamiento de fluidos, y también respecto a la prueba E1.

E3. Generacion de burbujas CON Nucleacion Heterogenea Vs Presion (usando Material M3)



Se mantiene el comportamiento ya observado en el cual la presión es una variable que incide de manera importante en la calidad de la microburbujas, según los datos de las graficas se concluye que:

1. La distribución de diámetro de burbuja es mas dispersa a 3 atmosferas, mientras que a 4 y 5 atmosferas esta dispersión es menor, ampliándose nuevamente a 6 atmosferas. Similar a lo presentado en las pruebas E0, E1 y E2.
2. El tamaño promedio de las burbujas es menor a 4 y 5 atmosferas, mientras que a 3 y 6 atmosferas es mayor. Sin embargo no es tan alto como cuando no se usa materiales de nucleación Heterogenea.
3. El tamaño de las burbujas y su dispersión es mucho menor que los presentados en las pruebas E0, E1 y E2.
4. El Área total de las burbujas se incrementa con la presión, aunque se presenta una relación de incremento menor después de 5 atmosferas. Similar a los casos E0, E1 y E2..
5. El número de burbujas es máximo a 5 atmosferas.
6. A diferencia de las pruebas E0, E1 y E2., a 6 atmosferas el área de las burbujas no es mayor que a 4 atm, por tanto las condiciones de generación a 4 atm son preferidas porque ademas de requerir menos energía también su tamaño es mas adecuado según las condiciones requeridas.
7. A a 6 atmosferas el numero de las burbujas es menor que a 4 atm, a diferencia de los pruebas E0, E1 y E2..
8. El numero de burbujas se incrementa en mas del 1000% en todas las presiones de la prueba, respecto a las generadas sin Nucleacion Heterogenea, y también cuando se usa el material de nucleación M1 y M2..
9. El material M3 genera un incremento de generación de microburbujas en todas las presiones evaluadas, y adicionalmente se presenta una reducción del tamaño de las burbujas, lo cual es favorable para el tratamiento de aguas.
10. El área de la burbujas producidas se incrementa de manera apreciable respecto a la generación en E0, lo cual es favorable para el tratamiento de fluidos, y también respecto a la prueba E1 y E2.
11. Según estos resultados el Material M3 es el de mayor eficiencia en la generación de microburbujas debido a que genera mayor cantidad de estas, así como de menor tamaño.

Tabla 1. Cambio Relativo de Numero , Tamaño y Area de las burbujas generadas Vs Presion de operación para las pruebas E0, E1, E2 y E3.

Tabla de Cambio Relativo de Numero de Burbujas Vs Presion				
	Nucleacion Homogenea	Nucleacion Heterogenea Material 1	Nucleacion Heterogenea Material 2	Nucleacion Heterogenea Material 3
3 Atmosferas	100%	457%	652%	1287%
4 Atmosferas	100%	417%	680%	1471%
5 Atmosferas	100%	400%	641%	1215%
6 Atmosferas	100%	356%	516%	1041%
Tabla de Cambio Relativo de Area de Burbujas Vs Presion				
	Nucleacion Homogenea	Nucleacion Heterogenea Material 1	Nucleacion Heterogenea Material 2	Nucleacion Heterogenea Material 3
3 Atmosferas	100%	227%	287%	384%
4 Atmosferas	100%	220%	291%	402%
5 Atmosferas	100%	217%	285%	377%
6 Atmosferas	100%	209%	265%	358%
Tabla de Cambio Relativo de Diametro de burbuja Vs Presion				
	Nucleacion Homogenea	Nucleacion Heterogenea Material 1	Nucleacion Heterogenea Material 2	Nucleacion Heterogenea Material 3
3 Atmosferas	100%	70%	66%	55%
4 Atmosferas	100%	73%	65%	52%
5 Atmosferas	100%	74%	67%	56%
6 Atmosferas	100%	77%	72%	59%

1. En la tabla 1 de muestran los cambios de las propiedades de las microburbujas generadas en las pruebas E1, E2 y E3 a las condiciones de presión ya mencionadas. De forma relativa a los resultados obtenidos en la prueba base E0.
2. Se observa que para todos las condiciones de las pruebas, las mejores condiciones de generación de burbujas están entre 4 y 6 atmosferas, con una media de 5 atmosferas. Esta condición es independiente el tipo de material de nucleación heterogénea usado.
3. En general el comportamiento del material M3 para generar burbujas es superior a los otros materiales usados. (M1 y M2)
4. El uso de estos materiales de nucleación heterogenea es altamente beneficioso debido a que en todos los casos se mejoran las condiciones ideales de las burbujas producidas para ser usadas en el tratamiento de aguas y otros procesos similares.
5. La reducción de costos por energía y operación es demostrada ya que la nucleación heterogenea siempre es mas favorable que las condiciones de generación de nucleación homogénea.(E0)

Conclusiones generales.

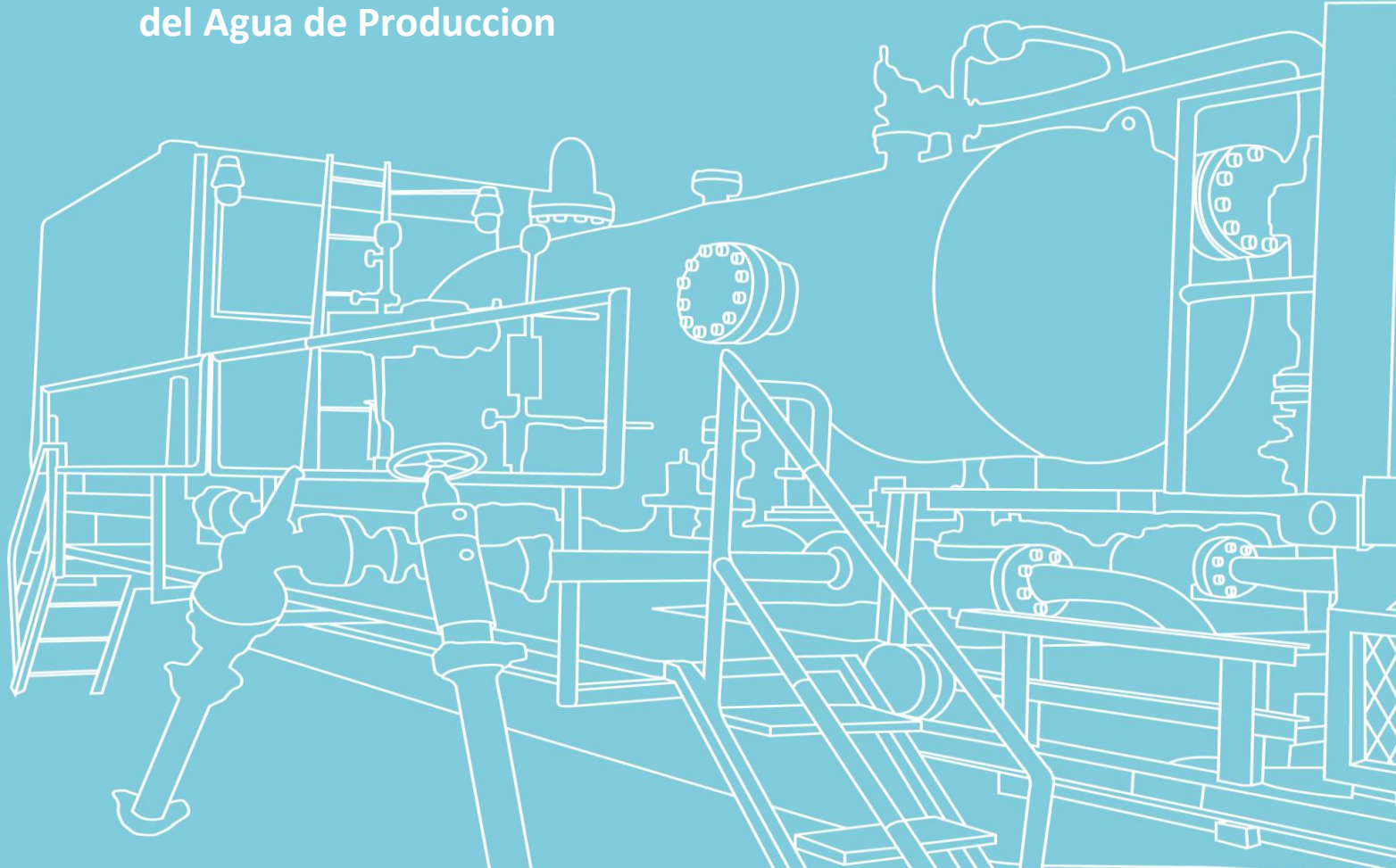
1. La nucleación heterogénea es muy favorable para generar burbujas para el tratamiento de aguas residuales ya que estas son de menor tamaño y con una distribución de diámetro de baja dispersión (recomendado por la literatura técnica)
2. EL mejor material evaluado es el M3 que puede generar burbujas en mas de 1000% respecto al las generadas por los sistemas DAF básicos.
3. Usando el material M3 es posible incrementar el área de las burbujas producidas en mas de 350% , respecto los sistemas de generación clásicos sin nucleación heterogenea.
4. El diámetro de las burbujas se reduce de manera notoria al usar la nucleación heterogenea y en especial el material M3, a niveles menores a 59%, lo cual es favorable para el tratamiento de aguas.
5. Los resultados presentados demuestran que los materiales usados en la generación de las microburbujas son apropiados para maximizar la eficiencia de este proceso respecto a los sistemas tradicionales.
- 6.



MICROBURBUJAS POR NUCLEACION HETEROGENEA

(VIDEOS REALES DE LA TECNOLOGIA QUE SOLICITA PATENTE Y
DE LA LITERATURA)

Fundamentos Innovadores en el Tratamiento Eficiente y de Bajo Costo del Agua de Produccion



Tratamiento de aguas industriales servidas/producidas

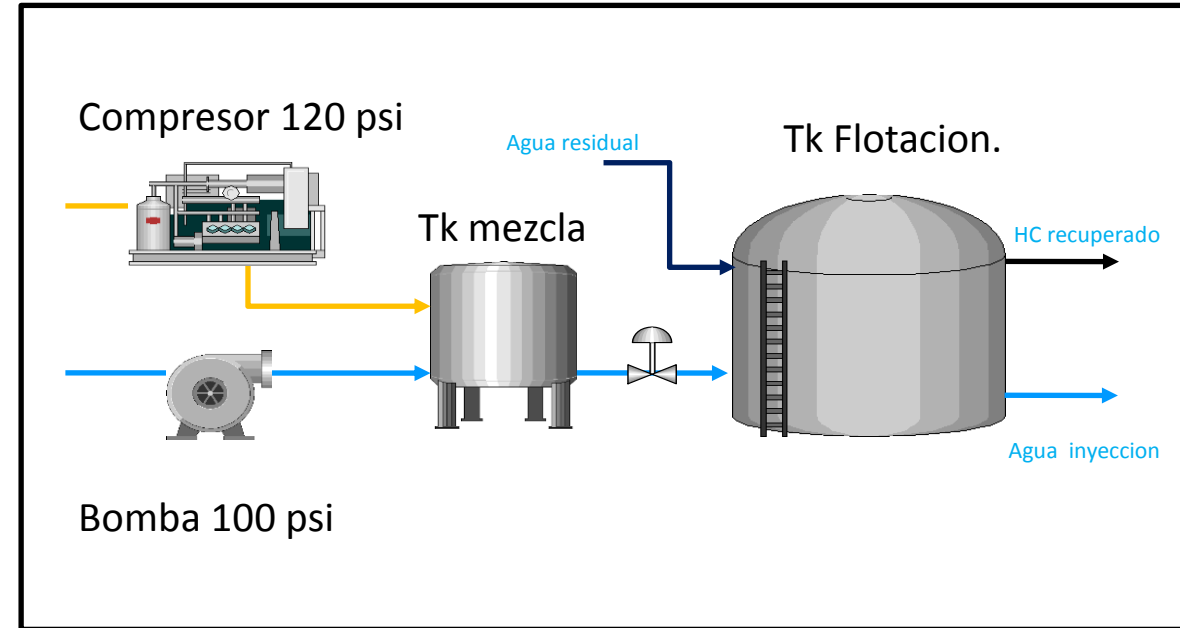
- Tecnologías de Flotacion con Microburbujas



- DAF clasico.
- Bombas de Cavitacion.
- Saturacion de liquidos.
- Electricos.
- Ultrasonido.
- Nucleacion
- Esfuerzos cortantes

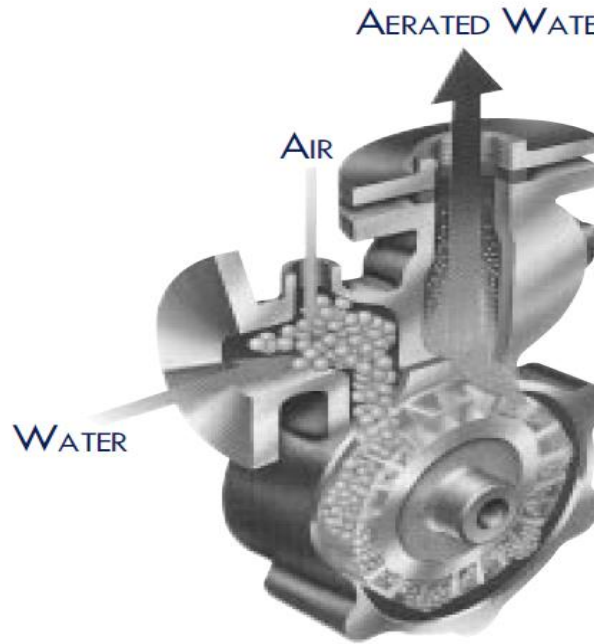
Tratamiento de aguas industriales servidas/producidas

- DAF CLASICO



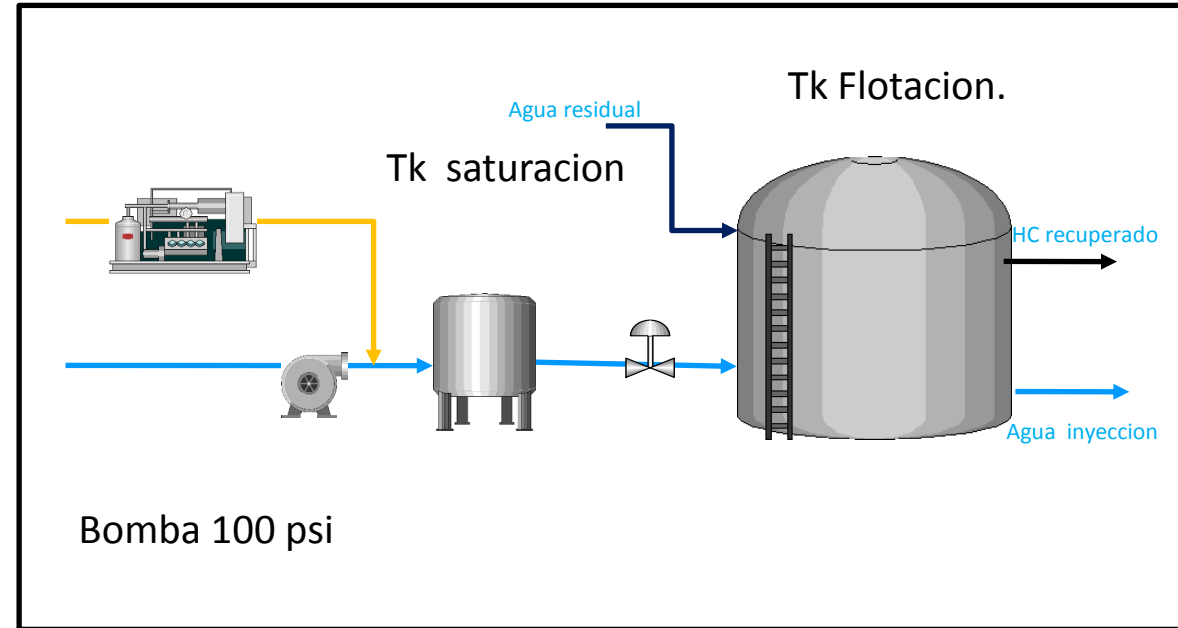
Tratamiento de aguas industriales servidas/producidas

- BOMBA DE CAVITACION



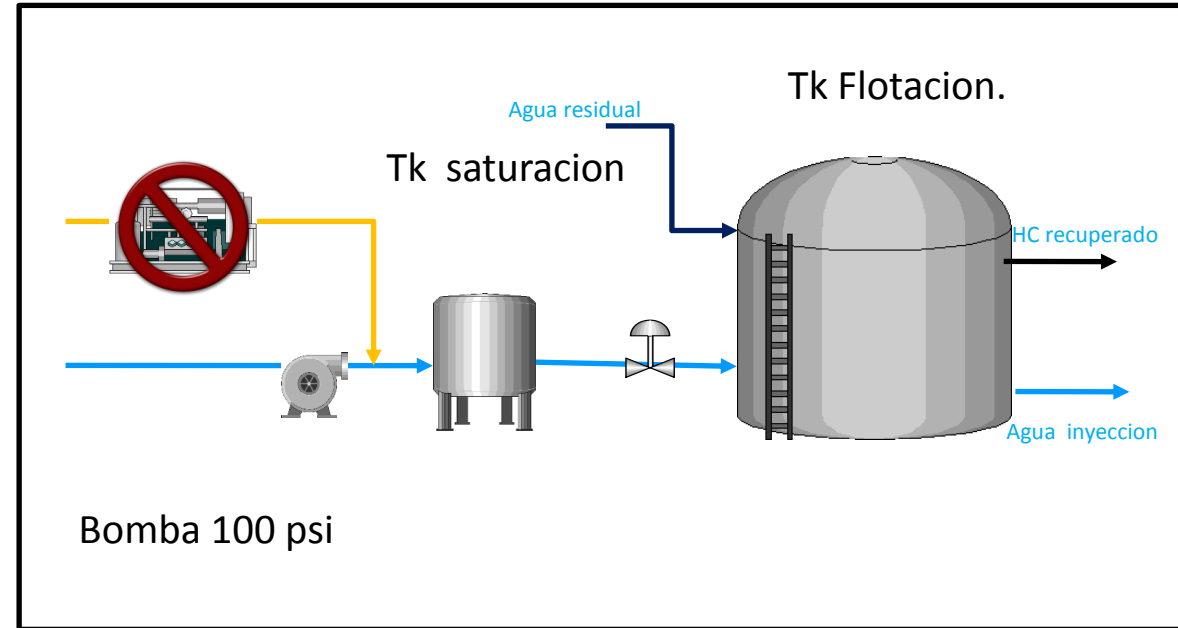
Tratamiento de aguas industriales servidas/producidas

- MICROBURBUJAS POR SATURACION



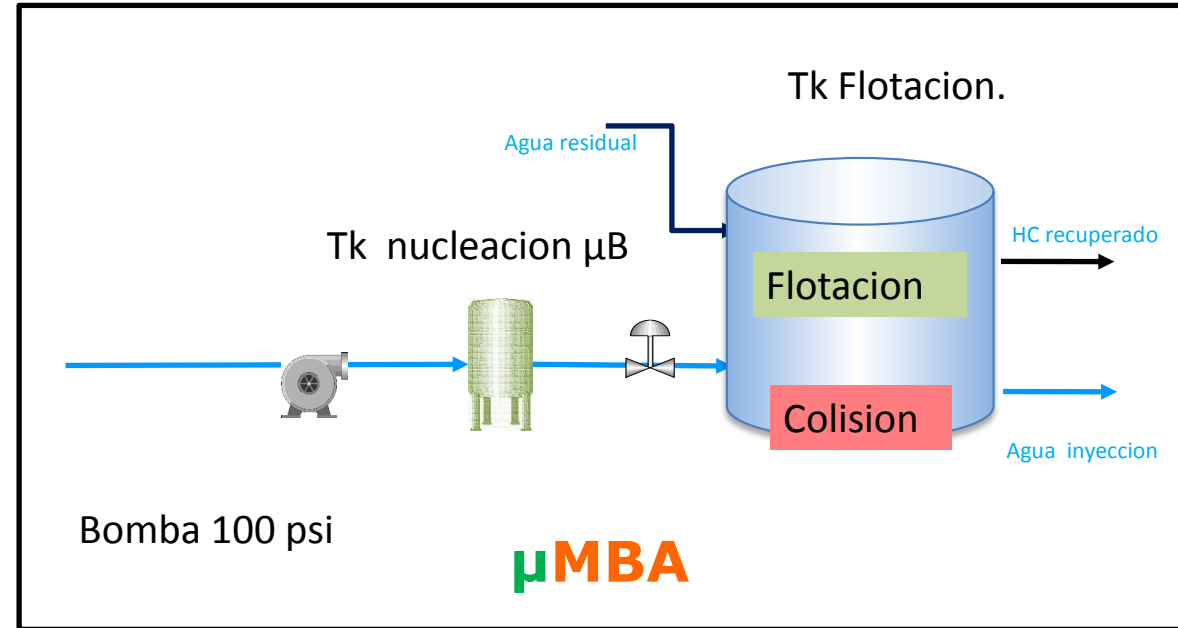
Tratamiento de aguas industriales servidas/producidas

- MICROBURBUJAS POR SATURACION



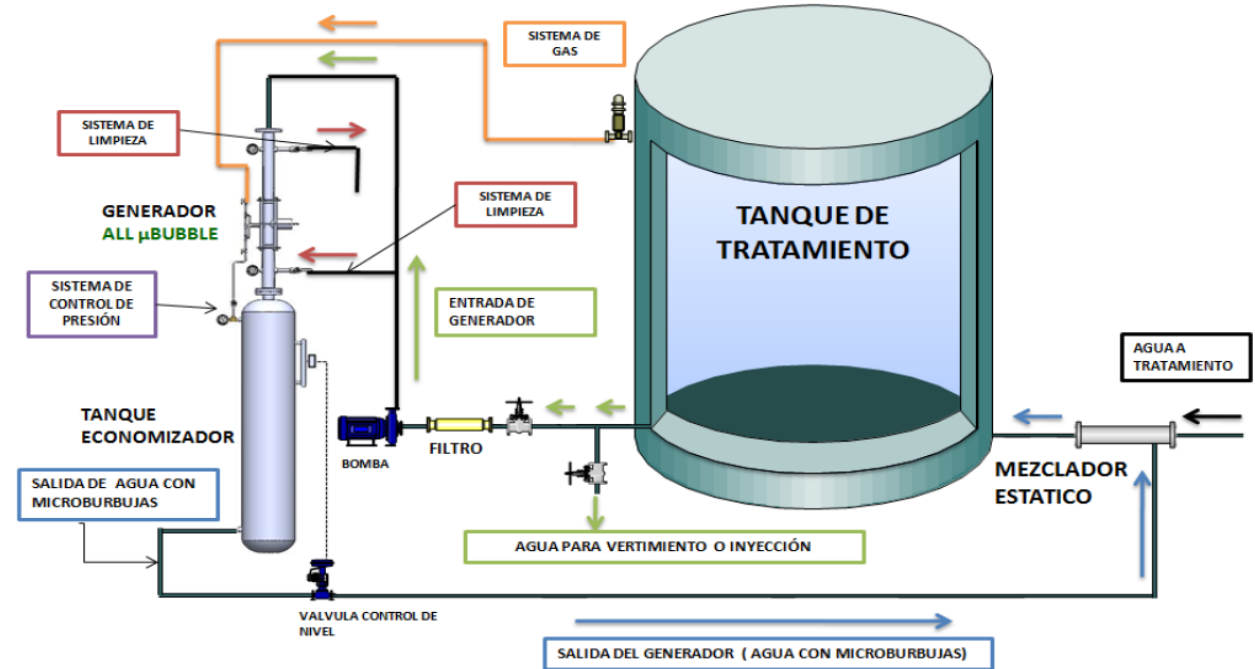
Tratamiento de aguas industriales servidas/producidas

- MICROBURBUJAS POR NUCLEACION AllμBubbles AMB (patente)



Tratamiento de aguas industriales servidas/producidas

Sistema de Flotación por Microburbujas de Gas



Tratamiento de aguas industriales servidas/producidas

- Tomado de youtube



Tendencias en el tratamiento de agua de Producción como actividad **RENTABLE** (Produced Water Management)

DAF. (Alto costo)



- Alto consumo **Energía**. (1-3 Hp/1000 bwpd).
- Requiere **gas comprimido** y compresores.
- Consumo de gas mayor a 1 Scf/bbl.
- Generalmente genera **aguas no compatibles**.
- **Cataliza Bacterias**
- **Limitado** para usar gases **húmedos** o **Acidos**.
- **Alta recirculación** (mayor 20-30%)
- **Baja calidad Microburbujas** (tamaño y densidad)
- Proceso **caótico** e **incontrolable**
- **Limitado** a altas **temperaturas** (45-50 °C)
- Sobrenadante de **baja calidad**
- Consumo **medio** de **Aditivos**
- **Altos tiempos** de **retención**
- **Modelos** de **Utilidad**

μFlotación (Minimiza costo)

- Bajo consumo **Energía**. (0.3–0.6 Hp/1000 bwpd)
- **No** Requiere **gas comprimido** ni compresores.
- Consumo de gas menor a 0.01 Scf/bbl. (1% DAF)
- Generalmente genera **aguas no compatibles**.
- **Inhibe Bacterias**
- **Uso ilimitado** de gases.
- **Baja recirculación** (menor 12%, 35% DAF)
- **Alta calidad Microburbujas** (tamaño y densidad)
- Proceso **controlable**
- **Ilimitado** a altas **temperaturas** (100 °C)
- Sobrenadante de **alta calidad**
- Consumo **muy bajo** o **nulo** de **Aditivos**
- **Bajos tiempos** de **retención**.
- **Patente** de **Invencción**

Tratamiento de aguas industriales servidas/producidas

- COMPARATIVO SISTEMA DE FLOTACION 1 AÑO



	Capex 1	Capex 2	Opex	Ener,Hp	Mantto	Peso, ton	Area, m2	Fac, Oper.	T.Costos
AllµBubble	100	100	100	100	100	100	100	100	100
Saturacion	130	100	150	180	130	200	200	98	130
Cavitacion	150	100	150	180	130	50	100	60	130
DAF	250	200	500	600	400	550	1000	95	250
Macroburbujas	300	400	1000	1000	400	550	3000	80	750

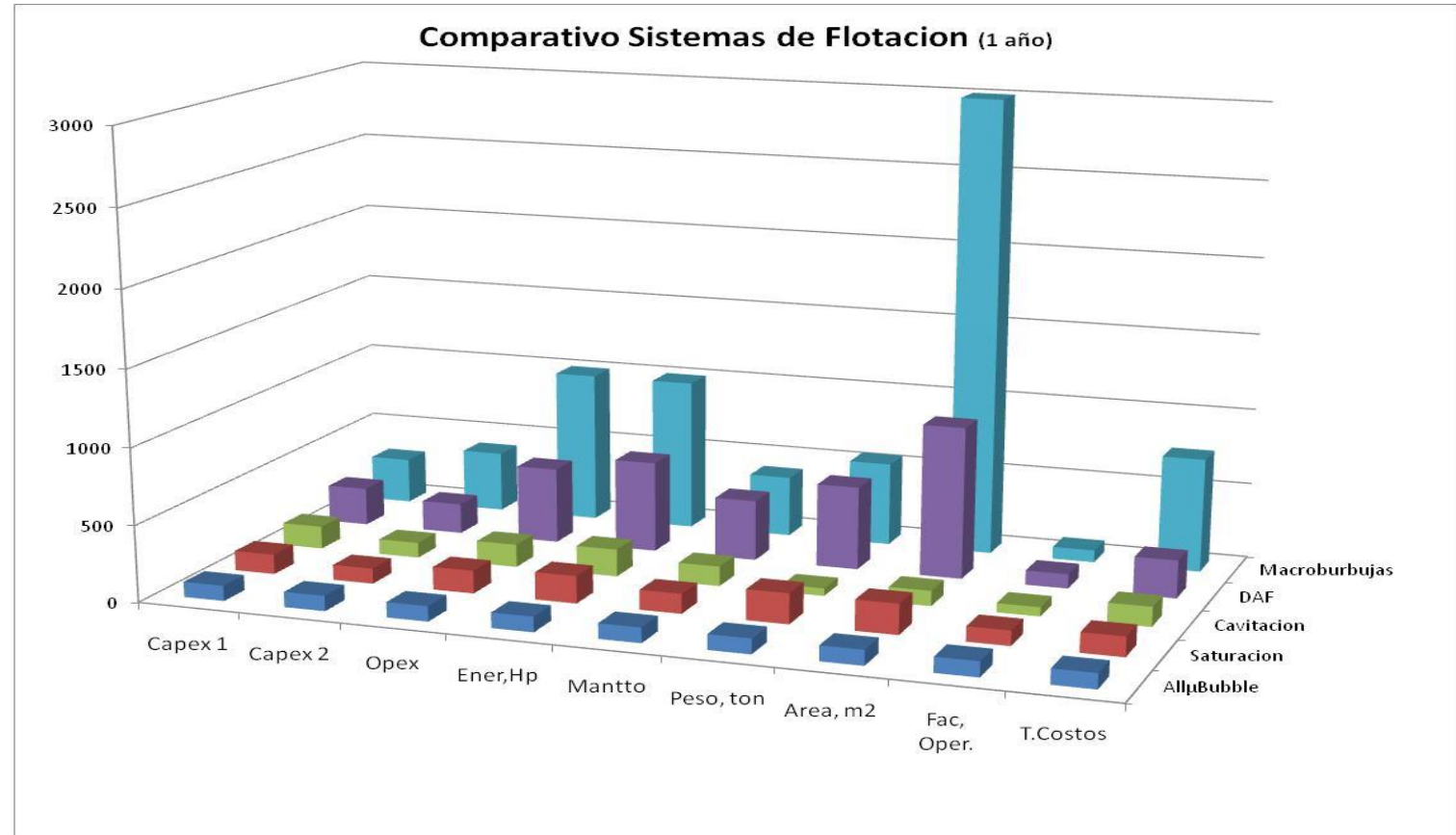
Tratamiento de aguas industriales servidas/producidas

- COMPARATIVO SISTEMA DE FLOTACION 5 AÑOS

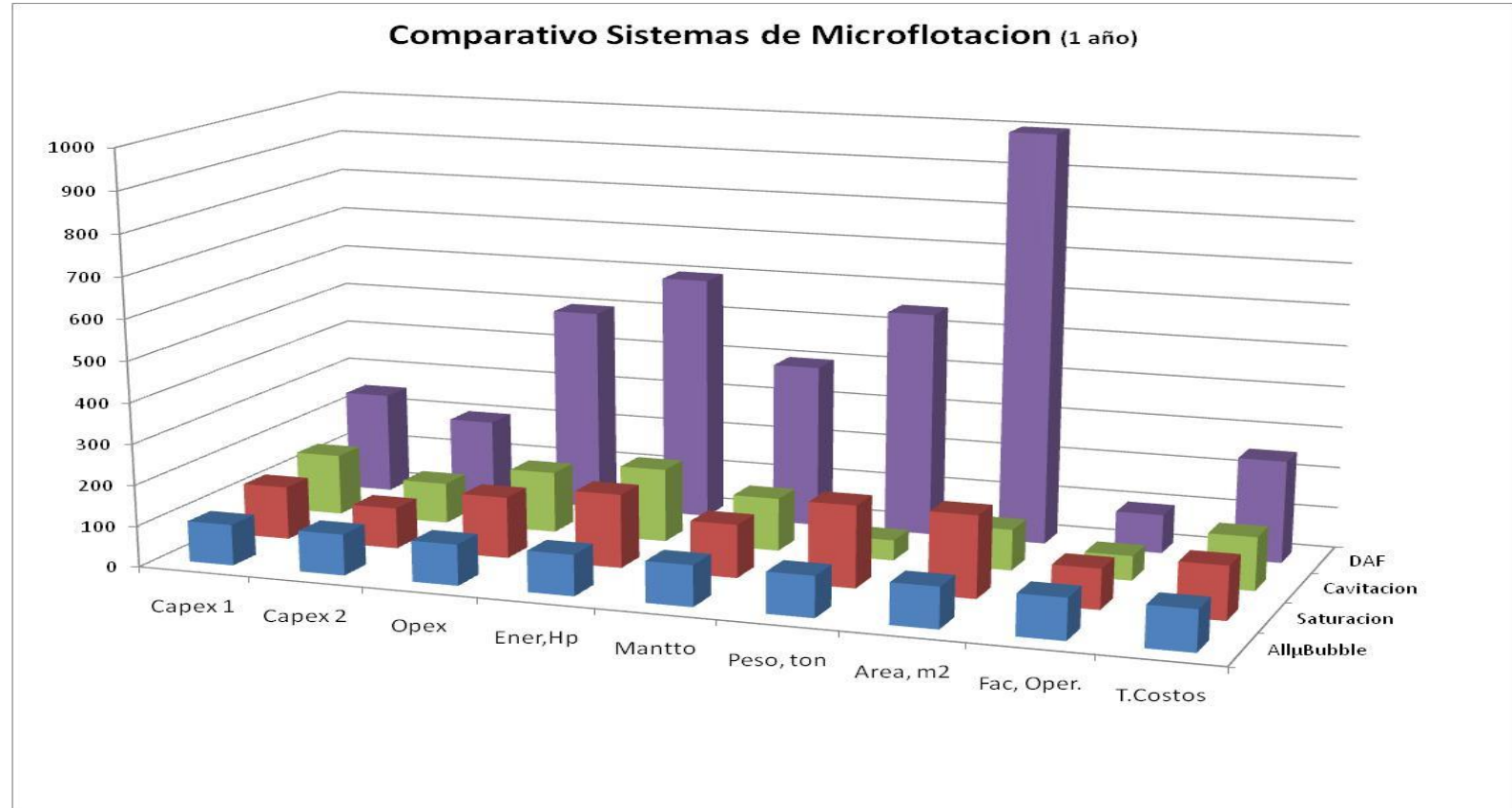


	Capex 1	Capex 2	Opex	Ener,Hp	Mantto	Peso, ton	Area, m2	Fac, Oper.	T.Costos
AllμBubble	100	100	100	100	100	100	100	100	100
Saturacion	130	100	150	180	150	200	200	98	150
Cavitacion	300	100	150	180	150	50	100	60	280
DAF	250	200	500	600	450	550	1000	95	280
Macroburbujas	300	400	1000	1000	450	550	3000	80	800

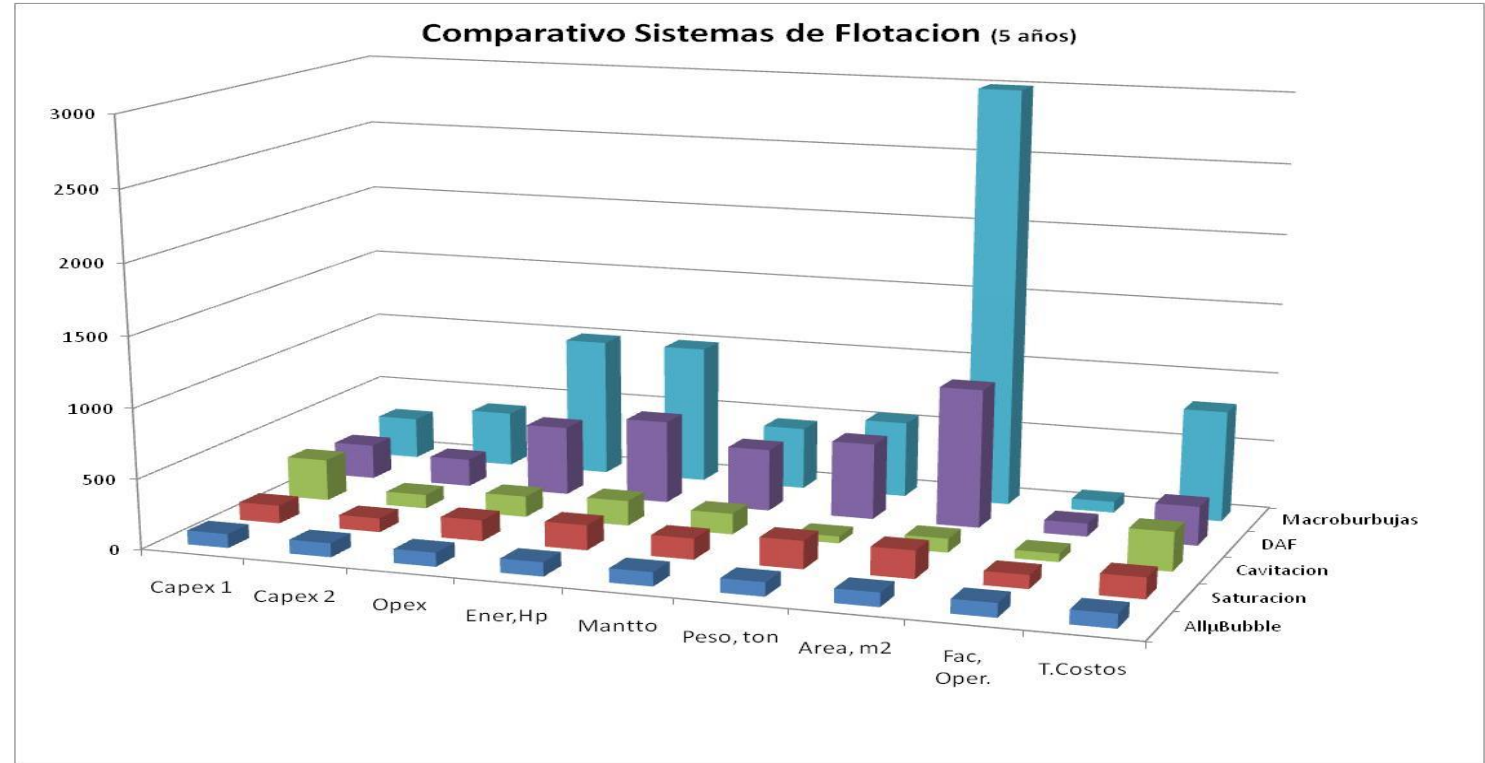
Tratamiento de aguas industriales servidas/producidas



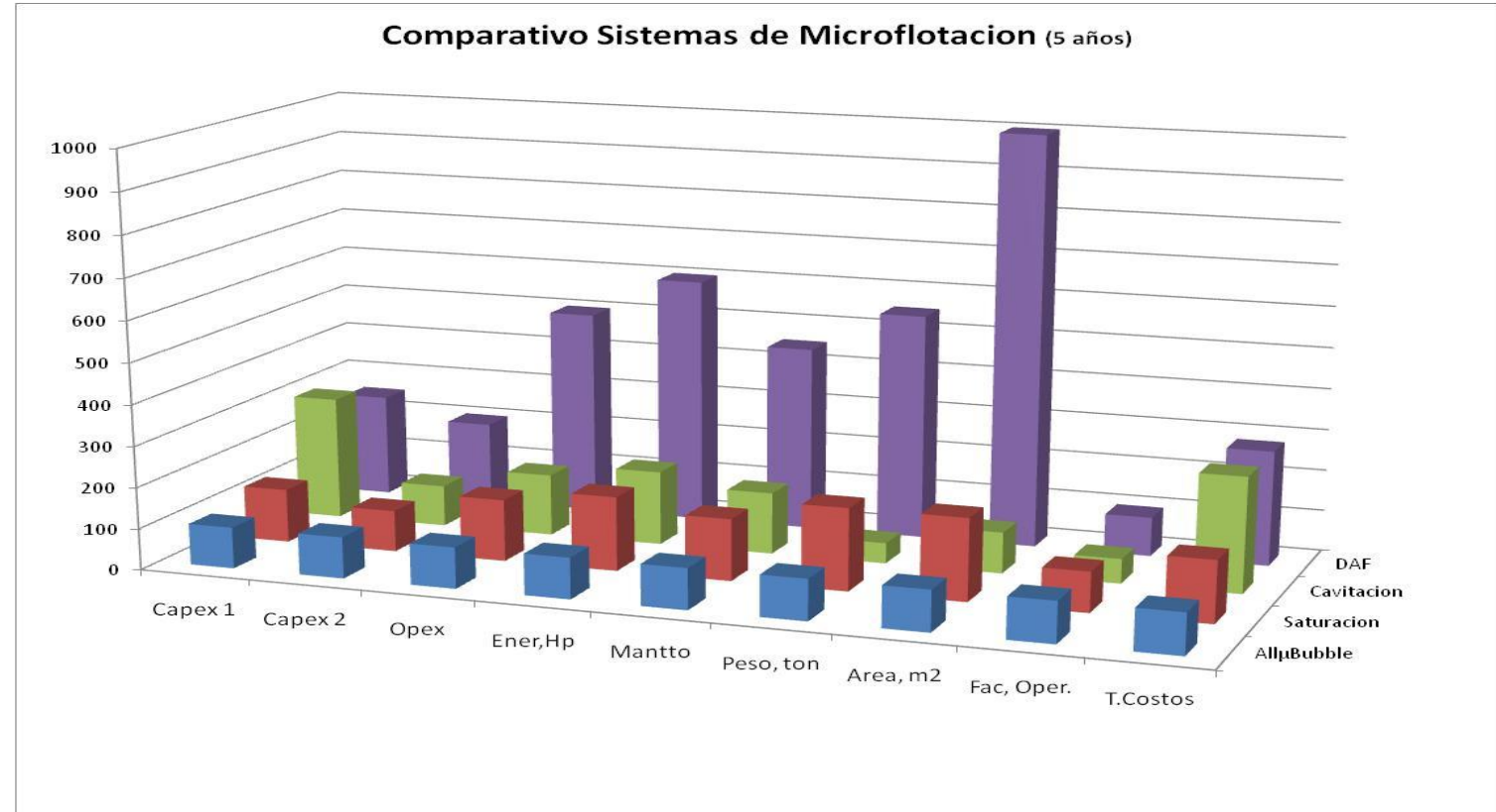
Tratamiento de aguas industriales servidas/producidas



Tratamiento de aguas industriales servidas/producidas



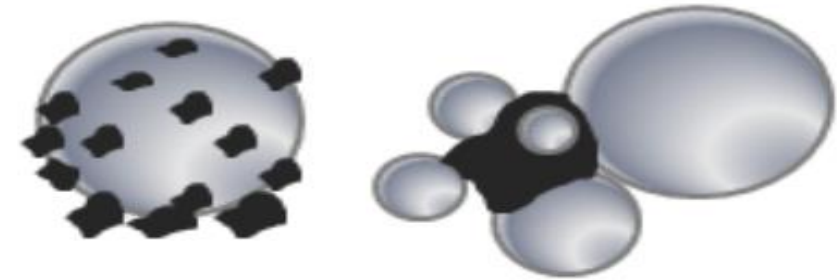
Tratamiento de aguas industriales servidas/producidas



Registro fotográfico de la microburbujas generadas con esta tecnologia



- **Burbujas vs. Microburbujas?**



Bubble-Particle Aggregates

**AN INVESTIGATION OF THE GAS DISPERSION PROPERTIES OF
MECHANICAL FLOTATION CELLS: AN IN-SITU APPROACH**

by

Sanja Miskovic



Control tamaño de microburbujas



Alta densidad y homogeneidad de microburbujas

Plantas operando con nuestra tecnologia.



Plantas operando con nuestra tecnologia.



MICROFLOTACION POR NUCLEACION LA INNOVACION PARA EL TRATAMIENTO DE AGUAS DE PRODUCCION DE BAJO COSTO



Señores
DELEGATURA PARA NUEVAS CREACIONES
Superintendencia de Industria y Comercio

Asunto: **Respuesta a observaciones Artículo 45 Decisión 486**
Expediente: **2013-25761**

JORGE ENRIQUE FORERO SANABRIA identificado como aparezco al pie de mi firma, mediante este escrito y en uso del término dispuesto por la ley de 60 días hábiles presento a ustedes la respuesta a las observaciones presentadas por esta delegatura de la siguiente manera:

La observación presentada por la Delegatura respecto de los requisitos de patentabilidad se efectuó mencionando los siguientes antecedentes:

Los requisitos de Patentabilidad de la presente solicitud están afectados así:

Ítem	Documento	Reivindicaciones afectadas	Requisito que afecta
D2	WO2008/147050	1, 2, 5	Nivel Inventivo
D3	US6054048	1, 2, 5	Nivel Inventivo

Consideramos respetuosamente que los documentos indicados por la delegatura no afectan el nivel inventivo de las reivindicaciones mencionadas por lo siguiente:

Manifestamos respetuosamente que el documento D2 es un sistema DAF la cual necesita succión de gas por medio de un elemento rotativo, en este caso una bomba especial, Con una bomba estándar D2 perdería un gran porcentaje de eficiencia o no podría operar, este factor que es inexistente en nuestra solicitud, ya que existe una sección (8) que es la cámara de inyección de agua y generación de vacío para la succión de gas que está formado por un contenedor, que puede ser cilíndrico, que dispone internamente de una o varias boquillas aerodinámicas, esta cámara de inyección de agua y generación de vacío para la succión de gas, puede ser formada por una o varias etapas de succión, En esta cámara se conforma también la primera etapa de mezcla entre el gas y el líquido.

El hecho de no requerir bombas especiales costosas sino bombas estándar de bajo costo hace que nuestra solicitud sea innovadora debido a que no se requiere de gases de baja corrosión, o inertes, como si se requiere si se usan elementos rotativos, que son altamente limitados por la calidad del gas, tanto que se pueden destruir muy fácilmente si este gas reactivo o es un gas corrosivo, situación que no afecta nuestro proceso, debido a que la bomba solo maneja líquidos.

En cuanto al documento D3, es un sistema que puede operar por succión inducida de gases, sin embargo existe una gran diferencia conceptual con nuestra solicitud, y es que D3 no tiene como objetivo saturar el líquido con gas y mantener un flujo en estado líquido para en una etapa posterior generar micro burbujas usando nucleación heterogénea, para hacer separación de partículas en el agua u otros fluidos (se consideran así las burbujas de diámetro menor a 100 micras), y menos aún si se usa múltiples etapas de mezcla para lograr generar gran cantidad de estas, así como tampoco podría usar cualquier tipo de gas solamente puede usar gases que contengan alto contenido de oxígeno, ya que según su operación, su objetivo no es separar fases sino que es aumentar el contenido de oxígeno en el agua, arrastrando gas para mejorar los procesos de oxidación, de impurezas solubles e insolubles, lo cual es conceptualmente diferente a nuestra solicitud, ya que podemos usar cualquier gas, preferiblemente aquel que sea mas recomendable para el agua, en el caso de la industria del petróleo no se deben usar gases ricos en oxígeno en la mayor proporción de casos de tratamiento.

Se debe mencionar que la formación de burbujas tanto en los documentos D2 y D3 se realiza casi totalmente por nucleación homogénea, que tiene como característica que requiere muy alta energía y las burbujas generadas tienen baja o nula concentración de micro burbujas (menores a 100 micras), su distribución de tamaño es muy disperso, su número es bajo, lo que quiere decir su aplicabilidad para separar pequeñas partículas de líquidos como el agua es baja, especialmente en aquellas generadas por D3.

En el caso de D1 esta eficiencia es mejor, pero en ningún caso las burbujas generadas por nucleación homogénea pueden superar la calidad y la cantidad, de aquellas generadas por nucleación heterogénea a las mismas condiciones de procesamiento y consumo de energía, Esta generación por nucleación heterogénea es tal vez la innovación mas grande en nuestra solicitud, ya que opera principalmente según el principio de generación de micro burbujas a partir de la obtención de un líquido metaestable (sobresaturado) que se pone en contacto con placas de superficie activa (nanotecnología) para la nucleación heterogénea, fija, controlada y simultáneamente con el fenómeno de aplicación de esfuerzos cortantes controlados. El desarrollo de estas placas es uno de las tareas que ha tomado mas recursos de investigación y desarrollo, ya que se requirió de muchas evaluaciones para lograr encontrar materiales y tratamientos que aseguraran alta calidad en este tipo de superficies, según el objetivo planeado (ver artículos anexos)

En D2 no existe línea de conducción de agua a presión, como en nuestra solicitud, allí existe un fluido mezclado de líquido y gas entrando a la bomba (fig 2, línea 4, 6,7,7a), esta particularidad de operar una bomba con líquidos y gases, genera un fenómeno que se conoce como cavitación, el cual es un fenómeno muy destructivo, aun si la bomba esta construida en materiales especiales y costosos, situación que seguramente es un requerimiento para la operación del sistema D2, ya que si se opera con una bomba estándar seguramente tendrá un vida útil muy corta (par de semanas o meses), Tambien es importante resaltar que la descripción de D2, es errónea, manifiesta que la línea 10 es un línea para conducción de agua, y lo real es que en esta línea se conduce agua y gas, generando inestabilidad en el flujo, que también afecta de manera notoria la generación de burbujas adecuadas para la separación.

En nuestra solicitud no se presentan estos fenómenos (cavitación e inestabilidad en el flujo) , debido a que la bomba es un equipo estándar y que a esta no llegan gases en su línea de succión, por lo tanto esta bomba podrá operar por tiempos prolongados sin ningún problema (años), esta diferencia conceptual es fundamental en estos dos procesos, por lo tanto demostramos que hay innovación en nuestra solicitud..

En D2 el contacto gas líquido se realiza especialmente en la bomba, (generando cavitación) y la segunda etapa se genera en el recipiente (20), mediante cambios de dirección, debidos a la presencia de tabiques y restricciones de flujo, lo que genera alto consumo de energía. En nuestra solicitud no hay presencia de gas a presión en la bomba, y el contacto se realiza en elementos estáticos, que no generan problemas de degradación de los materiales, lo que reduce muy significativamente el mantenimiento del equipo y el consumo de energía, y hace nuestro proceso innovador.

En D3 hay un contacto gas líquido en una sola etapa y se realiza en las tuberías de conexión del venturi, con el objetivo principal de succionar el gas rico en oxígeno y distribuirlo en el agua a tratar como fase gaseosa, en la solicitud se hace mezcla o contacto en multiples etapas, con el fin de saturar el líquido con el gas presente, sin que esta fase gaseosa pase a la zona de formación de microburbujas, ya que afectaría la calidad de estas para realizar el proceso de separación, para las cuales se requiere, condición que no existe en D3, que es un proceso de transferencia de masa esencialmente y **no** de generación de microburbujas para separación de partículas suspendidas, como lo es la solicitud en mención.

En nuestra solicitud existe una válvula (7) que es un elemento regulador de presión , el cual opera en caso de que el tanque contenedor (9) alcance una presión mayor a la definida, En el caso de D3 esta válvula no existe , porque el contenedor de este proceso no es hermético y no genera presiones que requieran este tipo de elementos, en el caso de D2 las válvulas que se presentan como reguladoras de presión, no son realmente sistemas de control de presión, las válvula 14 y 16 son válvulas de control de flujo hacia la bomba y de cheque, si estas válvulas fallan seguramente habrá limitaciones menores, que solo afectaran la eficiencia del equipo por flujos no apropiados, tarea que es muy diferente a la valvula (7) de la solicitud que tiene como función principal proteger la integridad del equipo generador específicamente.

El sistema de succión de D3, es un sistema de baja presión que tiene como objetivo inyectar gas (oxígeno) al agua que está en tratamiento y no a relacionar relaciones de flujo gas líquidos según se requiera, operan con bajos índices de recuperación de presión, generalmente solo pueden operar en una etapa y es un sistema ampliamente conocido como eyectores, de los cuales hay muchas marcas y modelos en el mercado, sin embargo el sistema de succión de la solicitud, tiene unos elementos específicos de operación selectiva, que operan en una o varias etapas a condiciones que permiten mantener presiones altas y mantener una relación gas líquido según diseño, con el fin de incrementar la producción de la burbujas, ya que exceso de gas o defecto de este limita la calidad y cantidad de la burbujas generadas, D2 no tiene este tipo de elementos, que hacen nuestra propuesta innovadora y eficiente.

En la solicitud se presenta un dispositivo (10) que controla la interface liquido-gas en el contenedor, factor clave para controlar la operación de generación de microburbujas de manera eficiente, sin embargo este elemento no existe en D2, la parte (18) que se menciona en la comunicación de la superintendencia no es un indicador de nivel de interfase de gas, realmente se refiere a un medidor de flujo, lo cual muestra nuevamente que nuestra solicitud es innovadora.

Asimismo, el documento D2 divulga las características de las reivindicaciones dependientes así:

- Reivindicación 2. Sistema de generación de micro burbujas que opera con una sola fuente de presión (10) (D2: Fig. 3; Pág. 50).
- Reivindicación 5. Contactor de placas (D2: Fig. 4; Párr. 58, 60, 64).

Por lo anterior, dichas reivindicaciones dependientes 2 y 5 no proporcionan al objeto de la reivindicación independiente 1 ningún efecto sorprendente, y en consecuencia no tienen nivel inventivo.

Se menciona que el documento D2 tiene placas de contacto, lo cual conceptualmente no es válido, las placas presentes en esta invención, son placas de contención, de división de zonas de diferente presión, tabiques de separación o de limitación de flujo, llamadas en el documento original *partitions*, lo cual traduce *partición, pared, muro, medianera, valla, tapia*. En nuestra invención las placas tienen como función principal actuar como zonas de reacción o contacto que incrementan la transferencia de masa entre los fluidos, hasta la metaestabilidad en el caso del contactor primario o de disponer de una zona activa (superficie modificada) para que se genera la nucleación heterogénea, por el contacto de un líquido metaestable con una superficie modificada y activa para generación de microburbujas. Para mejorar el contacto los fluidos viajan de manera paralela a las placas.

En el documento D2 estas placas que tienen como objetivos separar cámaras de condiciones de flujo diferente y de limitar el flujo por algunas zonas de la cámara de saturación. Además el flujo es normalmente ortogonal al eje de las placas causando choques y altas caídas de presión, que no se presenta en nuestras placas elementos de contacto.

Se menciona que el documento D2 tiene en su estructura un bloque de placas con puntos de nucleación en línea, lo cual no es cierto ni válido, las placas con puntos de nucleación en línea como objetivo principal incrementar la cinética de generación de las microburbujas, controlar su calidad y cantidad los fluidos viajan de manera paralela a las placas, sin embargo en el documento D2 las placas que existen son realmente tabiques de separación o de limitación de flujo, llamadas en el documento original *partitions*, lo cual traduce *partición, pared, muro, medianera, valla, tapia*.

En cuanto a la manifestación arriba mencionada y teniendo en cuenta las explicaciones y análisis anteriores, respetuosamente manifestamos, que la reivindicación 2, si es innovadora , porque tenemos “- (7) una válvula de seguridad y/o reguladora de presión, que mantiene el sistema a la presión deseada, según las condiciones de saturación deseadas de los fluidos (líquido y gas)”, la cual se demostró no esta contenida ni en el D2 ni en D3 y que es fundamental para el control de calidad de la microburbujas y para asegurar la integridad del equipo, que tiene como variable de control la presión de generación de microburbujas por nucleación heterogenea. Además En la reivindicación 2, se están comparando las bombas de Cavitación y flujo multifasico del documento D2, con una bomba centrifuga estándar que tiene como único objetivo aumentar la presión de un fluido monofásico (liquido) , las cual son conceptualmente totalmente diferentes.

En cuanto a la reivindicación 5, se menciona que hay un contactor de placas, sin embargo se demostró que estas placas no son contactores sino son realmente tabiques de separación o de limitación de flujo, llamadas en el documento original partitions , lo cual traduce partición, pared, muro, medianera, valla, tapia. , en nuestra solicitud, efectivamente existe un contactor-reactor, que tiene como principal objetivo, generar nucleos, por el contacto del liquido-sólido que ha pasado por dos etapas de mezcla y se ha sobresaturado , que son los precursores de las microburbujas, Esta placas tienen una selección y un dimensionamiento definido basado en las propiedades de los materiales con que se fabrican, y claramente se observa que este tipo de placas no existe ni en D2 ni en D3, por lo tanto respetuosamente solicitamos el reconocimiento de esta innovación y nivel inventivo de esta reivindicación (ver artículos anexos)

También quiero manifestar que mediante correo del día 6 de Julio del 2014, se dio repuesta a las argumentaciones de oposición dadas el 14 de agosto de 2013 por la empresa opositora Exterran Holdings, Inc.

De igual manera con ocasión al presente escrito presento una modificación a la descripción y el resumen y las reivindicaciones y de igual manera anexo encontraran material de referencia para permitir a los examinadores un estudio más adecuado de la solicitud de la referencia.

ANEXOS

1. Documento de reforma del resumen, de reforma de la descripción y de reforma de reivindicaciones
2. Bibliografía complementaria que consideramos relevante para un mejor examen de la solicitud de patente:
 - 2.1.E.J Langham and Bj Mason The heterogeneous and homogeneous nucleation of supercooled water, Imperial College, London
 - 2.2.Ho-Young Kwak, Ki Moon Kang; Gaseous Bubble Nucleation Under Shear Flow; International Journal of Heat and Mass Transfer 52(2009) 4929 a 4937

- 2.3. Hanglin jo, Massoud Kaviany, Seol Ha Kim, Moo Hwan Kim; Heterogeneous Bubble Nucleation on Ideally-Smooth Horizontal Heated Surface; International Journal of Heat and Mass Transfer 71(2014) 149-157
- 2.4. Xavier Frank, Nicholas Dietrich, Jing Wu, Renaud Barraud, Huai Z Li; Bubble Nucleation and Growth in Fluids; Chemical Engineering Science 62(2007) 7090-7097
- 2.5. SF Jones, GM Evans KP Galvin; The Cycle of Bubble Production from a Gas Cavity in a Supersaturated Solution; Advances in Colloid and Interface Science 80 (1999) 51-84
- 2.6. JE Forero, OP Ortiz, Analisis Nucleacion Homogenea y Nucleacion Heterogenea, Documento interno, confidencial.
- 2.7. JE Forero, OP Ortiz, Presentacion Microburbujas por Nucleacion Heterogenea, Documento interno, confidencial

Atentamente



JORGE ENRIQUE FORERO SANABRIA
C.C. 91.227.105 de Bucaramanga

PATENTE DE INVENCION (13-025761)

SISTEMA DE GENERACION DE MICROBURBUJAS PARA TRATAMIENTO DE LIQUIDOS Y/O AGUAS PRODUCIDAS O RESIDUALES.

SECTOR TECNOLÓGICO

La presente invención corresponde al área de tratamiento de líquidos en proceso, residuales industriales o domésticos, con el cual se mejora los procesos de separación de sólidos y fluidos inmiscibles presentes y dispersos como contaminantes en el líquido a tratar, además de generarse un proceso de despojo de gases contaminantes solubles en el líquido tratado y de alta transferencia de masa entre el gas y el líquido, si se desea saturar el líquido tratado con el gas o gases usados, similar al caso de oxigenación de agua para reducción de DBO y DQO si el gas usado en la generación es rico en Oxígeno.

ANTECEDENTES DE LA INVENCION

En el campo de los procesos de flotación, aireación y gasificación de líquidos se emplean diferentes equipos para generar burbujas con diferentes fines, tales como gasificación, agitación, homogenización, entre estos equipos se encuentran placas porosas, placas perforadas, tubos perforados, sistemas de disolución de gases en líquidos para generación de burbujas por cambios de presión, entre otros.

Existen varios procesos en los que se emplean gases en fluidos con diferentes fines tales como generar burbujas para eliminar sólidos suspendidos, basados en hacer reaccionar gases con fluidos o disolver gases en fluidos.

La anterioridad EP 0 692 999 B1 (A fluidized bed reactor system and a method of manufacturing the same, 1996) enseña un reactor de lecho fluidizado en el que un líquido reacciona con un gas en presencia de un catalizador. En dicho reactor el gas es burbujeado a través del líquido, el cual contiene el catalizador, por medio de una placa perforada en la base del reactor. Dicha placa se encuentra conectada a un sistema de tubos unidos a un compresor, el cual se encarga de forzar el gas a través del lecho fluidizado.

Por su parte, la anterioridad EP 0 829 534 B2 (Gas driven fermentation system, 2006) relacionada con un sistema de fermentación que emplea un conjunto de inyectores o boquillas para proporcionar aire a un tanque de fermentación, dicho sistema también incluye un sistema de aspersión de oxígeno que comprende 12 boquillas. Las dos corrientes de gas, tanto aire como oxígeno, deben ser inyectadas a presión en el caldo de cultivo para proporcionar simultáneamente una fuente de oxígeno y generar corrientes que ayudan a circular los gases en el tanque.

Un campo en el que se hace un uso extensivo de las burbujas de gas es el del tratamiento de aguas residuales. La patente US 6.875.351 (Methods and apparatus for oil demulsification and separation of oil and suspended solids from produced water, 2005) enseña un sistema para la flotación de sólidos suspendidos en un clarificador que hace uso de una serie de bombas y un

vénturi para inyectar aire a una corriente de agua recirculada del clarificador. El aire es inyectado a un lado del clarificador y fluye de manera paralela a la superficie, con un área de contacto muy pequeña. A su vez, la patente US 5.173.184 (Wastewater treatment apparatus, 1992) enseña un sistema de flotación que comprende una serie de tanques en los cuales, mediante una placa perforada ubicada en el fondo de los mismos, se inyecta aire al fluido que se va a tratar con el fin de ocasionar la flotación de los sólidos suspendidos o aglomerados mediante un floculante.

Las burbujas también pueden emplearse como un sistema de mezclado como lo evidencia la patente US 7.387.428 (Method for mixing slurry, 2008), la cual divulga un proceso para la mezcla de suspensiones acuosas espesas. Para este proceso se tiene un tanque lleno de una suspensión y en el fondo del tanque se ubica un inyector de gas y una placa acumuladora. El gas es inyectado a presión en el tanque y la placa acumuladora garantiza que la burbuja de gas tenga una forma y tamaño específicos. A medida que la burbuja asciende se generan corrientes que hacen circular la suspensión, resultando en una mezcla homogénea sin necesidad de emplear mezcladores mecánicos.

Finalmente se menciona la patente de un sistema precursor del proceso de la referencia, que fue desarrollada también por parte del equipo encargado del presente proceso. esta patente (WO 2010/067187 A1) Bubble Generation System Immersed in a Liquid-Processing Tank describe un sistema que consiste en recircular parte del agua por /tratar. Se debe utilizar un sistema de bombeo de baja presión para enviar el fluido a un vénturi abierto a la atmósfera. Al producirse el cambio de velocidad dentro del vénturi, se produce un vacío que induce el aire hacia la salida del mismo, mezclándolo con el agua en forma de microburbujas. Esta corriente puede entonces ser distribuida por un arreglo de tubería dentro del cuerpo de agua a tratar para producir la flotación. Mientras que las microburbujas como las que este proceso genera son fácilmente transportadas por tubería, facilitando su inyección en puntos específicos del proceso.

Todos los sistemas del arte previo involucran el uso de gases presurizados o sistemas de presurización de gases, tales como bombas y compresores, para lograr la formación de burbujas. Además, tales sistemas emplean inyectores, placas perforadas o materiales porosos *que no garantizan un tamaño de burbuja en el rango de la microburbujas y que sea constante*, como tampoco alta densidad de estas en el fluido usado como vehículo para las microburbujas.

En esta invención se resuelven la mayoría de estas limitaciones, dado que el sistema propuesto no requiere de gases presurizados para su operación, ni compresores, ni bombas especiales, ni ningún tipo de elementos móviles en el proceso de generación (excepto la bomba que es un equipo estándar), con esta propiedad los recursos dedicados a mantenimiento del sistema son muy bajos, casi nulos.

RESUMEN GENERAL DEL INVENTO

El sistema de la presente invención comprende un dispositivo primario de inyección de líquido , que consiste de un sistema de presionamiento y recirculación un sistema de tuberías de succión y descarga de esta agua al elemento contenedor de los fluidos , un sistema de

suministro de gas, preferiblemente desde la cámara de gas del sistema de tanques de contacto (ver Pat 12-100762) en donde se usaran las microburbujas para hacer la microflotacion, una cámara de succión, que puede ser de una a varias etapas de inyección de líquido (se anexa figura de cámara de succión de simple y doble etapa), la cual por cambios de velocidad asegura la succión de gas, y que realiza un contacto primario entre los fluidos, necesario para la generación de las microburbujas, un sistema de elementos en el cual se asegura el contacto secundario del líquido y el gas, un módulo de nucleación en el cual por cambios de velocidad, presión y por efectos de los puntos activos de nucleación heterogénea se generan las microburbujas, y un tanque contenedor en donde se contienen los fluidos requeridos y se realizan los procesos necesario para la generación de las microburbujas controladas por tamaño y densidad.

En el proceso de la presente invención las microburbujas se caracterizan por ser generadas por un sistema combinado de saturación, agitación y sobretodo de nucleación heterogénea en superficies activas, asegurando que

- la dispersión de tamaño de las microburbujas es baja, lo cual es deseable para los procesos de flotación en los que se usaran estas microburbujas. Para este proceso es posible tener alta eficiencia en la generación las microburbujas en un rango de $\pm 10\%$ del diámetro promedio. El cual es poco probable en procesos de generación diferentes al de nucleación heterogénea.
- El consumo de gas para la generación de las microburbujas es autocontrolado, de manera que no hay excedentes ni faltantes de este recurso de manera que tanto el número de microburbujas así como su tamaño es óptimo , (con adecuado relación de tamaño y fuerza de agarre, generalmente se logra con diámetros de burbuja entre 10 y 50 micras) respecto a los sistemas en donde el gas no está controlado, tal como los DAF convencionales de nucleación homogénea, que generan burbujas sin equilibrio entre la fuerza de agarre de la partícula y la velocidad de flotación, lo cual baja la eficiencia de separación e incrementa el consumo de energía.
- La probabilidad que se generen burbujas de tamaños mayores a los deseables (de 10 a 50 micras de diámetro) para microflotacion, es muy baja, lo cual es deseable para optimizar los sistemas de separación por microflotacion y tratamiento, ya que las burbujas de alta diámetro afectan la hidrodinámica del proceso de separación de partículas dada su alta velocidad de ascenso.
- Debido a que internamente el sistema no tiene partes móviles la integridad del equipo es muy alta a diferencias de sistemas que requieren equipos rotativos especializados.
- En este proceso no se requiere que el gas usado deba ser tratado de alguna manera para eliminar los líquidos o su carácter corrosivo, situación que en algunos casos es muy costosa o limita severamente otros procesos similares.
- El gas usado en este proceso en puede ser reusado en más del 95%, lo cual hace el proceso muy económico especialmente cuando se usan gases inertes o especiales.
- El área y peso del sistema de generación de microburbujas es muy bajo, lo cual los hace de gran utilidad en su aplicación en estaciones limitadas en estas variables como plataformas petroleras, campos o industrias de producción pequeñas, plantas de baja disponibilidad de área. Etc.

- Dado su tamaño es fácilmente adaptable a plantas de tratamiento ya existentes. Lo cual hace que la actualización de plantas con esquemas anteriores sea económicas.
- Adicionalmente, se propone un sistema con un *bajo consumo de energía*, en el que se incrementa de ampliamente la eficiencia de la flotación, debido a que se asegura un alto índice de colisión entre las microburbujas y las partículas suspendidas en el fluido, asegurando la formación de floculos de baja densidad, proceso que es fundamental para asegurar alta eficiencia en la separación por flotación.

Este sistema puede ser instalado en una o múltiples etapas según los diagramas adjuntos. Se recomienda el uso de múltiples etapas en casos en que las partículas suspendidas son muy estables, se incrementa el flujo a tratar, o se requiere mejor eficiencia de tratamiento. Estas múltiples etapas pueden estar contenidas en un único recipiente de flotación.

La generación de núcleos por interacción de fases, en este caso microburbujas, por nucleación heterogénea es energéticamente mucho más eficiente que la generación de núcleos o microburbujas por nucleación homogénea, debido a la interacción termodinámica de la interface liquido sólido, esto se resume en la figura 2-3. Tomada de la tesis doctoral "BUBBLE GROWTH BEHAVIOR IN SUPERSATURATED LIQUID SOLUTIONS" de la Universidad de Maine, 2001.

Se observa claramente que la nucleación homogénea requiere mayor energía que la nucleación heterogénea, y que dependiendo del tipo de nucleación heterogénea este consumo de energía puede ser mínimo.

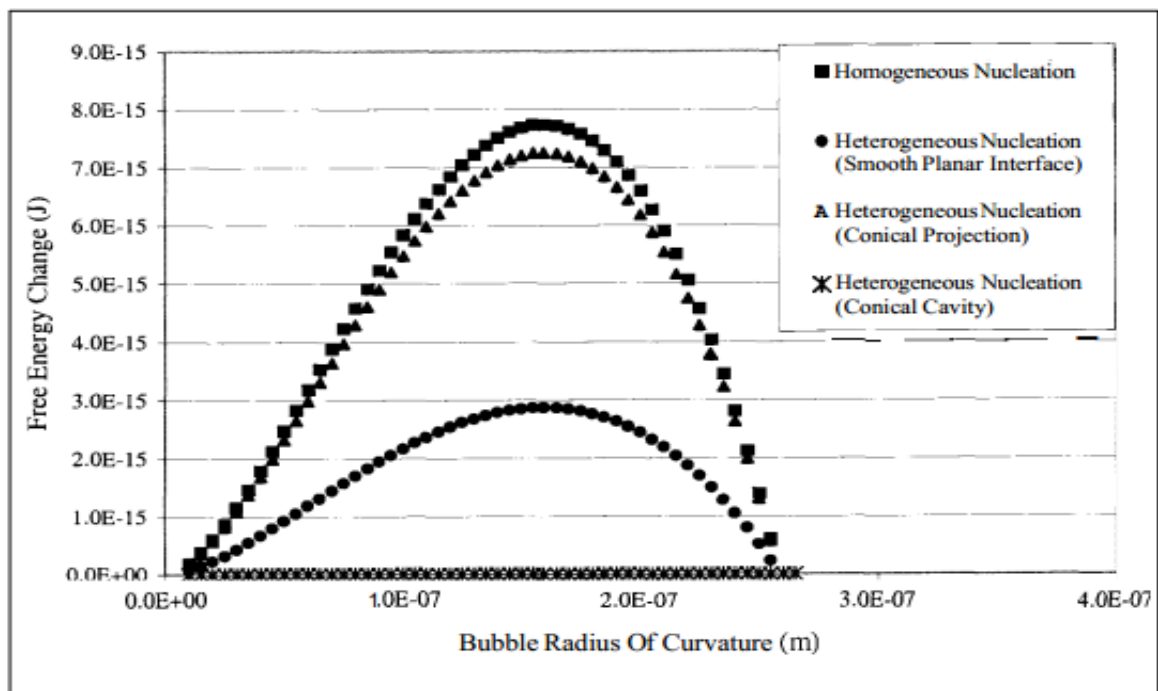


Figure 2-3. Free energy change as a function of the bubble radius of curvature for four cases of bubble nucleation.

DESCRIPCIÓN DE LAS FIGURAS

Figura 1. Esquema de los elementos que conforman el sistema de la invención en la modalidad de sistema único de bombeo

Figura 2. Esquema de los elementos que conforman el sistema de la invención en la modalidad de sistema dual de bombeo (de líquido fresco y líquido en proceso).

Figura 3. Esquema de los elementos que conforman el sistema de inyección de líquido y succión en la modalidad de etapa única.

Figura 4. Esquema de los elementos que conforman el sistema de inyección de líquido y succión la modalidad de múltiples etapas (dos en este esquema).

Figura 5. Esquema de los elementos que conforman el contacto secundario.

Figura 6. Esquema de los elementos que conforman el generador de microburbujas principal.

Figura 7. Esquema de los elementos que conforman el uso del generador en la modalidad de etapa única de microflotación.

Figura 8. Esquema de los elementos que conforman el uso del generador en la modalidad de etapa múltiple de microflotación. (tres para este diagrama)

DESCRIPCIÓN DETALLADA DE LA INVENCION

Conforme a lo ilustrado en la figura 1, en su versión de una solo etapa de presionamiento de líquidos , el sistema de la invención comprende (1) una línea de conducción de líquido de alimento de baja presión la cual debe ser previamente tratada por sedimentación y/o flotación o estar libre de solidos y/o líquidos sedimentables o de fácil separación por efecto de la gravedad, (2) (2a) una o varias fuentes de presión de líquido que incrementan la presión del líquido de alimento hasta una presión mayor o igual a 151.000 kPa (3) una línea de conducción de este líquido a presión proveniente de las fuentes de presión (2)(2a) , (4) una boquilla que conecta la línea de conducción de líquido a presión con (8) el generador de micro burbujas por el sistema de inyección-aceleración de líquido y succión de gas y/o contacto primario ,(11) un sistema de placas paralelas el flujo de contacto secundario gas-liquido, (5) una línea de conducción de líquido a presión que ingresa al generador de micro burbujas por el contacto secundario, que tiene como objetivo principal asegurar las condiciones de mezcla gas-liquido requeridos para asegurar condiciones para alcanzar el estado metaestable, (11), (2a) una fuente de presión alterna que recircula liquido del contenedor (9) en el sistema de contacto secundario (11) (6) una línea succión y de conducción de gas a alta presión, presión atmosférica o baja presión, (7) una válvula de seguridad y/o reguladora de presión, (8) sistema de inyección-aceleración de líquido y succión de gas, que comprende una o varias etapas (figura 3 y figura 4) (9) elemento contenedor en donde se contienen los fluidos requeridos para la generación de las microburbujas, (10) controlador indicador de nivel de interface liquido gas, (11) un sistema de placas paralelas el flujo de contacto secundario gas-liquido, para los fluidos (líquido y gas) provenientes del sistema de inyección-aceleración de líquido y succión de gas (12) elemento de

conducción de fluidos en fase líquida, que provienen del contactor–mezclador secundario (11) hasta el elemento de (13) contactor-reactor terciario líquido-sólido, conformado por una serie de superficies con elementos geométricos muy pequeños (menores a 10 micras) que son especialmente seleccionados o procesados de manera que en su superficie haya alta densidad de zonas con propiedades específicas para generar nucleación heterogénea, que entran en contacto con el líquido proveniente del contactor mezclador secundario (11) estas zonas activadas reaccionan generando núcleos que producen una gran cantidad de microburbujas, mucho mayor a cualquier sistema de generación tipo DAF tradicional que genera burbujas solamente cambios de presión, fenómeno controlado en gran medida por nucleación homogénea, además el (13) contactor-reactor terciario líquido-sólido consume muy poca energía, lo cual le da una gran ventaja sobre los sistemas de generación de burbujas tradicionales, también opera como dispersor de presión del fluido, y que puede estar en la parte interior o exterior del elemento (9)

El sistema de la invención, ilustrado en la figura 2, se refiere a la versión de dos etapas de incremento de presión de líquidos con bombas estándar, comprende a diferencia de la versión de una sola etapa de incremento de presión o bombeo solamente para la fase líquida, de una etapa de bombeo adicional (2a) que recircula líquido del sistema de contacto secundario, esta modalidad presenta como ventaja sobre la versión de una etapa, que la densidad de generación de microburbujas es mayor y permite manipular más fácilmente el diámetro de estas, lo cual es favorable en la eficiencia del proceso de separación por microflotación en las cuales se usan estas microburbujas.

En la Figura 3 se muestra el Esquema de los elementos que conforman el sistema de inyección de líquido y succión de gas en la modalidad de etapa única. El cual tiene como función principal asegurar la succión del gas, sin requerir de compresores, sopladores o gas a presión, y la mezcla inicial entre los fluidos usados (líquido-gas) generalmente agua ya tratada, y el gas usado para la formación de las microburbujas. Su operación tiene como principio usar la presión del fluido líquido para acelerar el gas a través de la cámara de dispersión, la cual asegura que haya un contacto entre los dos fluidos, de manera que la mezcla ideal de fluidos líquido y gaseoso sea llevada a los generadores de microburbujas y lograr que estas sean generadas en la calidad y cantidad requerida para optimizar el tratamiento de fluidos en las cuales se usan principalmente.

En la Figura 4 se muestra el Esquema de los elementos que conforman el sistema de inyección de líquido y succión de gas en la modalidad de múltiple etapa. El cual tiene como ventaja sobre el sistema de etapa única, que la mezcla de fluidos líquido y gaseoso es de mayor eficiencia y se recomienda para ser usado en sistemas en donde la mezcla está en condiciones no favorables, tales como altas temperaturas, gases de baja solubilidad, presión de gas muy baja, alta densidad de generación de microburbujas. En este esquema la etapa de mezcla y de dispersión se repiten sin requerir energía adicional al sistema de etapa única.

En la Figura 5 se muestra el Esquema de los elementos que conforman el contacto secundario. El cual está conformado por sistema de elementos en donde se circula la mezcla de fluidos líquidos y gaseosos provenientes del sistema de inyección de líquido y succión de gas, estos elementos disponen de un arreglo interno que son adecuado para asegurar velocidad y presión adecuadas para que se genere el fenómeno de saturación metaestable del líquidos requerido para preparar el fluido a condiciones ideales de saturación, presión y velocidad para el generador nucleación principal.

Figura 6. Esquema de los elementos que conforman el generador de microburbujas principal. El cual está conformado por sistema de elementos geométricos en donde se circula la mezcla de fluidos líquidos provenientes del generador primario, estas tuberías que contienen elementos geométricos internos que aseguran condiciones de velocidad y presión adecuadas para que se genere el fenómeno de nucleación de microburbujas, por contacto liquido-sólido en la superficie de los elementos activos, la cual está cubierta de gran número de centros de nucleación, en donde el fluido saturado, genera el proceso de nucleación heterogénea, homogénea, agitación y sobresaturación se generan un número alto de microburbujas incrementado la densidad de estas en el fluido final. Bajo estas condiciones se asegura que se producen microburbujas con diámetros bajos de $10\text{ }\mu\text{m}$ a $50\text{ }\mu\text{m}$ y una densidad de $0,6$ a $1,2 \times 10^7$ microburbujas por cm^3 . La calidad y cantidad de las microburbujas obtenidas por este método son significativamente mayores a las obtenidas por métodos mecánicos o de gas disuelto.

Figura 7. Esquema de los elementos que conforman el uso del generador en la modalidad de etapa única de microflotación. Representada por un solo tanque de microflotación

Figura 8. Esquema de los elementos que conforman el uso del generador en la modalidad de etapa múltiple de microflotación. Representada por varios tanques de microflotación los cuales están conectados a un solo generador de microburbujas. (tres para este diagrama).

El sistema o proceso de generación de microburbujas presenta las siguientes características a saber:

El generador de microburbujas de la presente invención, no requiere de partes móviles en su interior para operar, solo requiere de una sistema de presionamiento que tiene como objetivo elevar la presión de la corriente de líquido (1) al nivel de operación,

El generador de microburbujas de la presente invención puede operar con una sola bomba estándar (figura 1) o con doble bomba estándar (figura 2), en donde la corriente de fluido previamente inyectado al generador puede ser recirculado al contacto secundario, lo que permite que se logren mayores eficiencias en la generación y control del tamaño y densidad de las microburbujas.

El sistema de inyección de líquido y succión de gas está diseñado para que mediante la presión del fluido (1) genere una zona de baja presión por la cual se realiza la succión del gas, este sistema puede ser de una o dos etapas, lo cual mejor su eficiencia de succión de gas y permite que la relación gas líquido este en la relación apropiada para optimizar la generación de microburbujas.

El gas requerido para la generación de microburbujas no requiere de presión mayor a la atmosférica ni compresores de gas para incrementar esta presión.

El sistema de generación propuesto no requiere de sistema de compresión de gases, para la generación de microburbujas por lo tanto no está limitado a usar gases limpios o libres de líquidos, lo que le da gran flexibilidad de operación respecto a los sistemas similares que usan sistemas de compresión en su operación. Debido a que los sistemas de compresión requieren altos consumos de energía y que los gases deben ser pre tratados para eliminar líquidos y contaminantes que afecten el sistema de compresión.

El sistema de generación propuesto no tiene limitaciones en usar gases propios del proceso, los cuales pueden ser corrosivos, saturados o con partículas sólidas ya que esta sistema de succión no tiene partes móviles y puede construirse en materiales poliméricos o compuestos que no sean sensibles a la corrosión, en sistemas que usan sistemas de compresión rotativos estos factores son altamente nocivos para el proceso.

El contenedor en donde se contienen los fluidos requeridos para la generación de las microburbujas, puede ser construido en materiales poliméricos o en materiales compuestos permitiendo que el proceso sea poco sensible a ambientes corrosivos.

El sistema de contacto secundario está construido por un arreglo de elementos que garantiza las condiciones de velocidad y presión que aseguran un contacto óptimo entre el líquido y el gas de manera que se logre la adecuada mezcla y el estado metaestable de saturación, para generar las microburbujas El sistema de generación principal está conformado por un contactor terciario líquido sólido, conformado por una serie de elementos superficiales geométricos que son procesados o seleccionados de manera que en su superficie haya alta densidad de zonas con propiedades tales que generan nucleación heterogénea, estas zonas están definidas como áreas microscópicas que por sus propiedades termodinámicas y/o geométricas (Angulo de contacto, concavidad, tamaño, forma geométrica, etc.), minimizan la energía libre de la formación de la microburbujas, por lo cual se generan alta densidad de microburbujas entre 2 y 20 veces más que con sistemas de nucleación homogénea para las mismas condiciones termodinámicas, además estos elementos se disponen de manera específica y controlada, para que se generen altos esfuerzos de corte, que incrementa aún más la producción de microburbujas al entrar en contacto con el líquido sobresaturado o metaestable proveniente del contactor o mezclador secundario.

REIVINDICACIONES

1. El sistema de generación de micro burbujas que se caracteriza por comprender (1) una línea de conducción de líquido de alimento de baja presión (2) (2a) una o varias bombas estándar que incrementan la presión del líquido de alimento hasta una presión absoluta mayor o igual a 151.000 kPa (3) una línea de conducción de este líquido a presión proveniente de las bombas previas (2)(2a) hasta la (8) cámara de inyección de agua y generación de vacío para la succión de gas.
2. El sistema de generación de micro burbujas que se caracteriza por comprender también de (8) cámara de inyección de agua y generación de vacío para la succión de gas, es una cámara de succión, compresión y dispersión de gas de baja presión, puede no contar con partes móviles conformada por , (4) una boquilla de diseño aerodinámico específico, conformada por una sección de tubería, de área de flujo cambiante, que contiene laminas estabilizadoras de flujo, que acelera el líquido y una zona de área menor de flujo estable, que mediante láminas de limitación de flujo, genera una zona de muy baja presión , o presión negativa o de succión, este elemento convierte velocidad en presión negativa , según el principio de conservación de la energía, o ecuación de Bernoulli, por lo cual no se requiere presión del gas usado, (6) una línea succión y de conducción de gas que puede ser de presión mayor a la atmosférica, presión atmosférica o presión de vacío, que se conecta a la zona de baja presión de la (4) boquilla aerodinámica- (7) una válvula de seguridad y/o reguladora de presión, que mantiene el sistema a la presión deseada, según las condiciones de saturación deseadas de los fluidos (líquido y gas) (8) el cuerpo de la cámara de inyección de agua y generación de vacío para la succión de gas está formado por un contenedor , que puede ser cilíndrico , que dispone internamente de una o varias boquillas aerodinámicas, esta cámara de inyección de agua y generación de vacío para la succión de gas, puede ser formada por una o varias etapas de succión, En esta cámara se conforma también la primera etapa de mezcla entre el gas y el líquido.
3. El sistema de generación de micro burbujas que se caracteriza por comprender también, (11) un sistema de mezcla secundario para el gas y el líquido, conformado por un arreglo de placas paralelas o limitadores de flujo, dispuestos de manera que se garantiza el flujo uniforme a velocidad controlada, de la mezcla gas-líquido que proviene de (8) la cámara de inyección de agua y generación de vacío para la succión de gas (5) una línea de conducción de líquido a presión que ingresa al generador de micro burbujas por el contactor o mezclador secundario (11), (2a) una Bomba estándar alterna que recircula líquido del (9) contenedor del contactor o mezclador gas-liquido secundario (11) (6) una línea succión y de conducción de gas que puede ser de presión variable incluida presión alta, presión atmosférica o presión de vacío, (7) una válvula de seguridad y/o reguladora de presión, (9) elemento contenedor en donde se contienen los fluidos gas y líquido provenientes de (8) la cámara de inyección de agua y generación de vacío, un (10) controlador indicador de nivel de interface líquido gas, (12) elemento o elementos de conducción de líquidos que han pasado por las etapas primarias y secundarias de

mezcla, hasta el (13) contactor-reactor terciario liquido-solido, conformado por una serie de superficies con elementos geométricos muy pequeños (menores a 10 micras) que son especialmente seleccionados o procesados de manera que en su superficie haya alta densidad de zonas con propiedades específicas para generar nucleación heterogénea, que entran en contacto con el líquido proveniente del contactor mezclador secundario (11) , el contactor reactor terciario puede estar en la parte interior o exterior del elemento (9).

4. Sistema de generación de micro burbujas conforme a la reivindicación 1 caracterizado además por operar con una sola fuente de presión (2) o con un sistema doble fuente de presión (2,2a). y por contener un (13) contactor-reactor terciario liquido-solido, conformado por una serie de superficies con elementos geométricos muy pequeños (menores a 10 micras) que son especialmente seleccionados o procesados de manera que en su superficie haya alta densidad de zonas con propiedades específicas para generar nucleación heterogénea, que entran en contacto con el líquido proveniente del contactor mezclador secundario (11)
5. Sistema de generación de micro burbujas conforme a la reivindicación 1 y 2 caracterizado porque el (8) cámara de inyección de agua y generación de vacío para la succión de gas, que opera a alta velocidad y altos esfuerzos de corte, tiene un diseño de una o más etapas que generan una zona de baja presión que permite succionar gas al sistema aun a condiciones de presión por debajo de la presión atmosférica, sin que se requiera el uso de compresores, sopladores u otros sistemas rotativos.
6. Sistema de generación de micro burbujas conforme a la reivindicación 1, 2 y 3 que se caracteriza por comprender una serie de elementos que promueven e incrementan la mezcla de líquido-gas en un contactor mezclador secundario (11) que opera con bajos esfuerzos de corte y sin cambios fuertes de velocidad entre el gas y el líquido provenientes de la primera etapa de mezcla (8) denominada cámara de inyección de agua y generación de vacío para la succión de gas , que opera a alta velocidad y altos esfuerzos de corte, para que haya una nueva etapa de mezcla liquido-gas, y así incrementar la saturación entre los fluidos (liquido-gas)
7. Sistema de generación de micro burbujas conforme a la reivindicación 1 a 4 caracterizado porque, comprende un (13) contactor-reactor terciario liquido-solido, conformado por una serie de superficies con elementos geométricos muy pequeños (menores a 10 micras) que son especialmente seleccionados o procesados de manera que en su superficie haya alta densidad de zonas con propiedades específicas para generar nucleación heterogénea, que entran en contacto con el líquido proveniente del contactor mezclador secundario (11)

8. Sistema de generación de micro burbujas conforme a la reivindicación 1 a 5 caracterizado porque el ((13) contactor-reactor terciario líquido-sólido que puede operar con diferentes condiciones de flujo, (velocidad, caída de presión, tiempo de contacto) dando como resultado diferentes tipos de microburbujas tanto en tamaño como en número.

CONFIDENCIAL

RESUMEN

El sistema de la presente invención comprende un dispositivo primario de inyección de líquido , que consiste de (2)un sistema de bombeo estándar para subir la presión del líquido y/o de para recirculación de líquido, un sistema de tuberías (1,3,5)de succión y descarga de esta agua al tanque contenedor , (6)un sistema de suministro de gas, preferiblemente desde la cámara de gas del sistema de tanques de contacto (ver exp 12-100762) en donde se usaran las microburbujas para hacer la microflotacion, (4,8) (8) una la cámara de inyección de agua y generación de vacío para la succión de gas, que está formado por un contenedor , que puede ser cilíndrico , que dispone internamente de una o varias boquillas aerodinámicas, esta cámara de inyección de agua y generación de vacío para la succión de gas, puede ser formada por una o varias etapas de succión, En esta cámara se conforma también la primera etapa de mezcla entre el gas y el líquido. (se anexa figura de cámara de succión de doble etapa), la cual por cambios de velocidad asegura la succión de gas, necesario para la generación de las microburbujas, (11)un sistema de contacto-mezcla secundario en el cual se asegura una nueva etapa de contacto del líquido y el gas, (13) un módulo contactor-reactor terciario liquido-solido, conformado por una serie de superficies con elementos geométricos muy pequeños (menores a 10 micras) que son especialmente seleccionados o procesados de manera que en su superficie haya alta densidad de zonas con propiedades específicas para generar nucleación heterogénea, que entran en contacto con el líquido proveniente del (11) contactor mezclador secundario , (9) un tanque contenedor en donde se contienen los fluidos requeridos y se realizan los procesos necesario para la generación de las microburbujas controladas por tamaño y densidad.

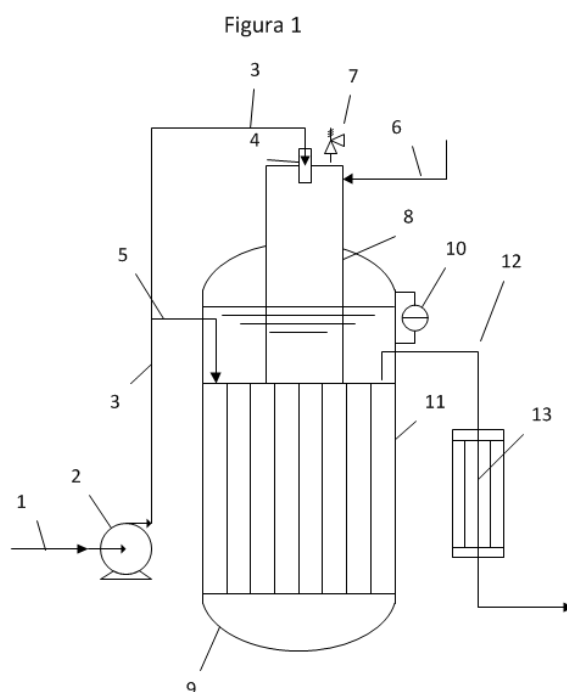


Figura 2

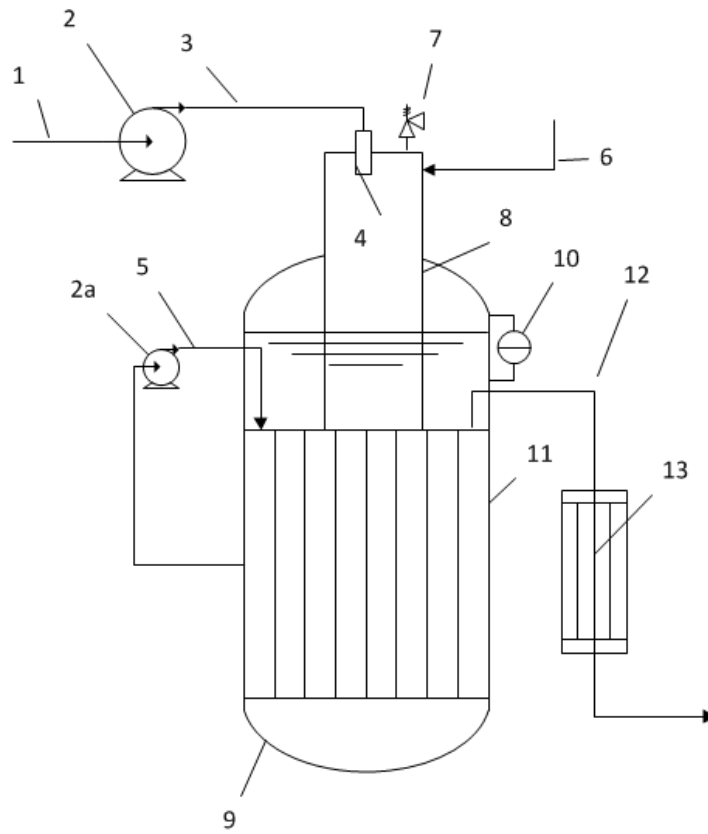


Figura 3

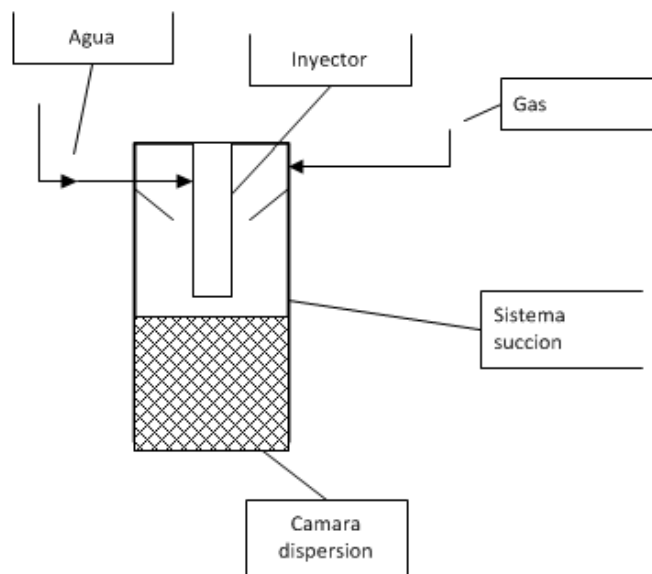


Figura 4

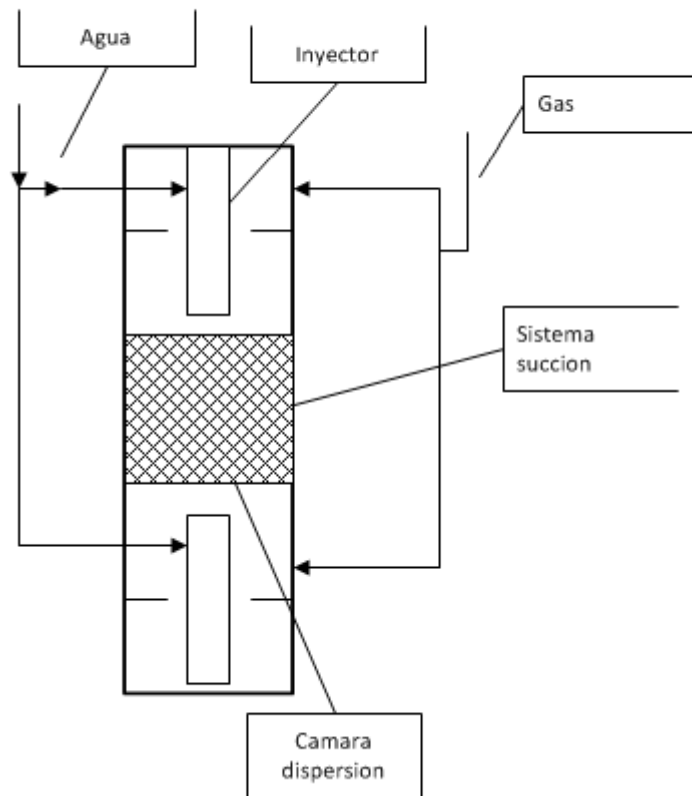


Figura 5

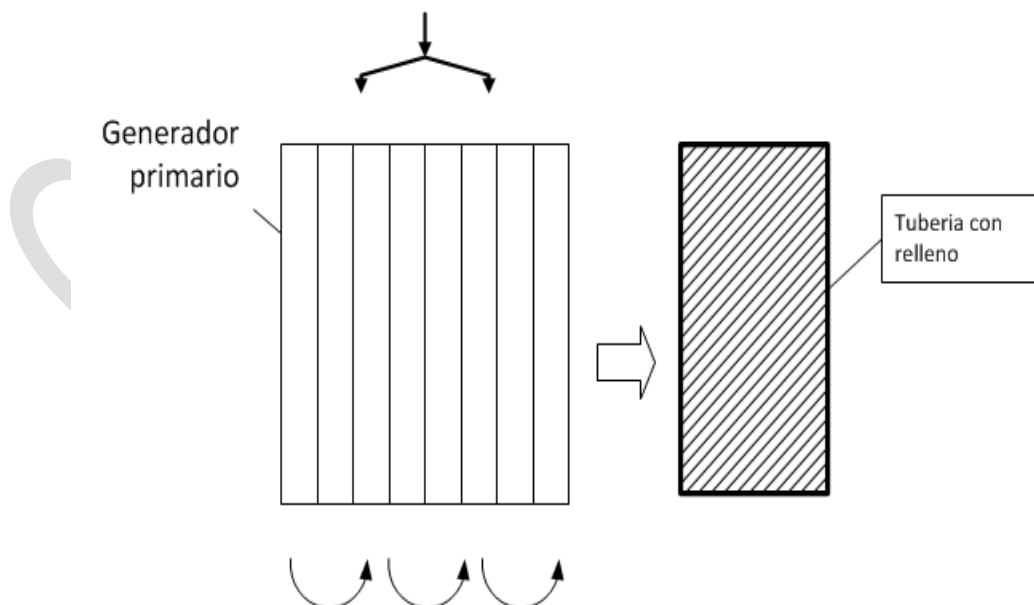


Figura 6

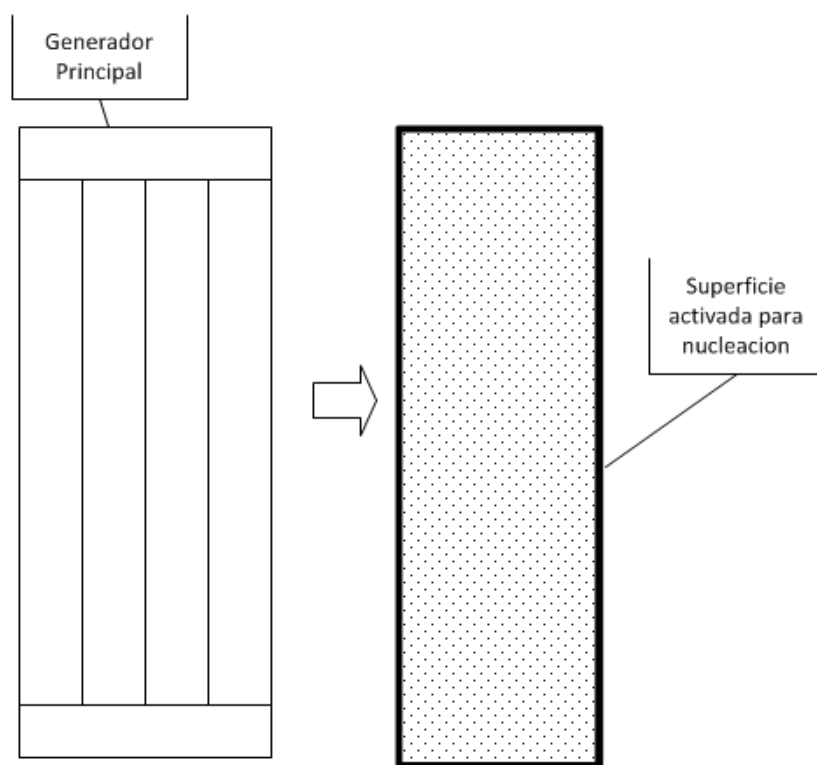
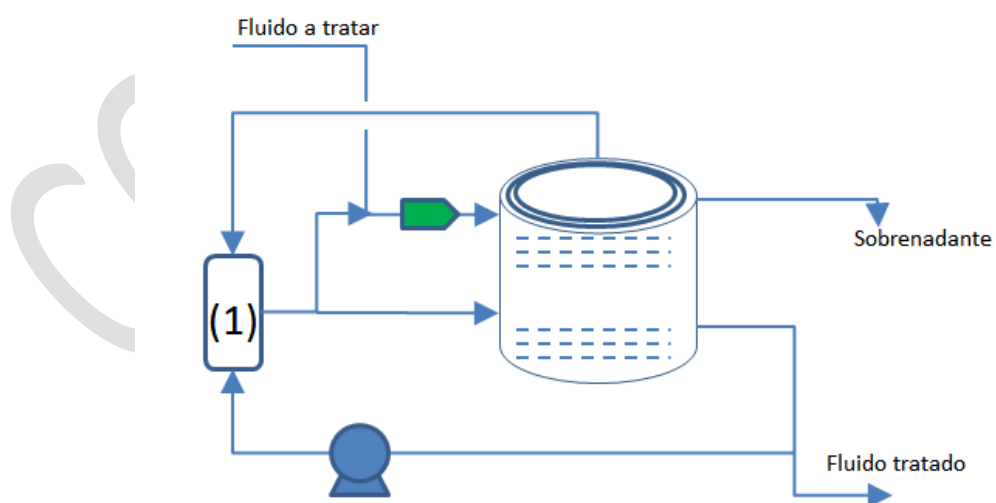
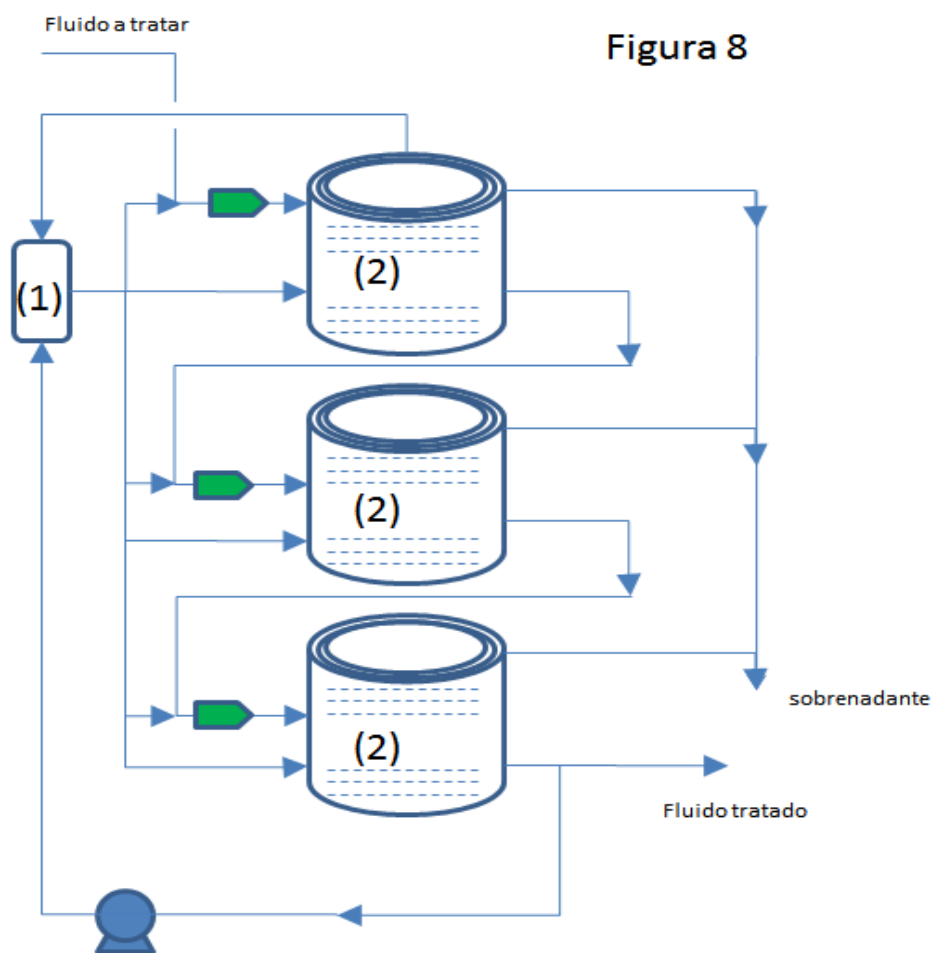


Figura 7





The heterogeneous and homogeneous nucleation of supercooled water

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[Plate 11]

In extension and confirmation of the work of Bigg, observations on the freezing of large numbers of drops of distilled water, ranging from $10\ \mu$ to 1 cm in diameter and suspended at the interface of two immiscible liquids in order to avoid the nucleating effects of solid surfaces, have established proportionality between the logarithm of the droplet volume and its freezing temperature for a constant rate of cooling. Such a relationship appears to characterize the heterogeneous nucleation of water droplets containing small foreign nuclei, and it is interpreted in terms of the droplets being infected with atmospheric aerosols whose ice-nucleating ability is known to increase roughly logarithmically with decreasing temperature. A technique has been developed for purifying water so that drops of up to 1 mm diameter may be supercooled to temperatures at which freezing occurs spontaneously without the aid of foreign nuclei. The empirical relationship between droplet volume and nucleation temperature, which differs from that representing heterogeneous nucleation, shows good agreement with theory.

Photographs taken of freezing droplets upwards of $50\ \mu$ in diameter reveal that, in some cases, solidification was accompanied by rupture of the ice surface and the liberation of a number of small ice splinters. This suggests a secondary mechanism of ice crystal formation in natural clouds.

1. INTRODUCTION

Although the supercooling and freezing of water have been studied by a large number of workers during the last 200 years, it has not been possible hitherto to answer such questions as how does the maximum attainable degree of supercooling depend upon the volume of the sample, its purity, and the rate of cooling. Examination of the extensive literature on the subject suggests that the earlier work may have failed to provide this information for three main reasons. First, the water samples used by different investigators varied greatly in purity; secondly, they were usually contained in glass tubes or supported as drops on variously treated metal surfaces so that nucleation may often have been induced by the solid boundaries; thirdly, in any one investigation, the volume of the sample was not usually varied sufficiently to establish clearly how this might be related to the degree of supercooling, particularly as there was usually a considerable spread in the freezing temperatures recorded for specimens of the same volume.

The great majority of the investigations reported in the literature have been concerned with *heterogeneous* nucleation in that the water used almost certainly contained foreign particles. But in recent years, cloud physicists have studied the supercooling of tiny fog droplets produced by condensation in very pure air. Droplets a few microns in diameter may readily be supercooled to about $-40\ ^\circ\text{C}$, but once the temperature falls slightly below this value they become rapidly transformed into ice crystals. This is a case of *homogeneous* nucleation in which foreign particles are not involved. Unfortunately, the problems of removing all such particles from an appreciable quantity of water makes it difficult to extend

these studies to much larger volumes. However, some progress has recently been made in this direction, and there follows a description of some new experimental work from which we deduce relationships which appear to characterize the heterogeneous and the homogeneous nucleation of supercooled water.

2. THE SUPERCOOLING OF WATER CONTAINING FOREIGN PARTICLES— HETEROGENEOUS NUCLEATION

A considerable improvement in the technique of investigating the supercooling of water was made in this laboratory by Bigg (1953), who eliminated the influence of solid supporting surfaces by suspending water drops at the interface of two liquids having different densities, where they were also protected from infection by airborne particles. He also investigated a wide range of droplet diameters—from about $20\ \mu$ to 2 cm—thus covering a volume range of 10^9 . The use of five pairs of supporting liquids, the members of a pair being practically immiscible with water and each other, established that the observed freezing temperatures of the droplets were a property of the water and not of the surrounding media.

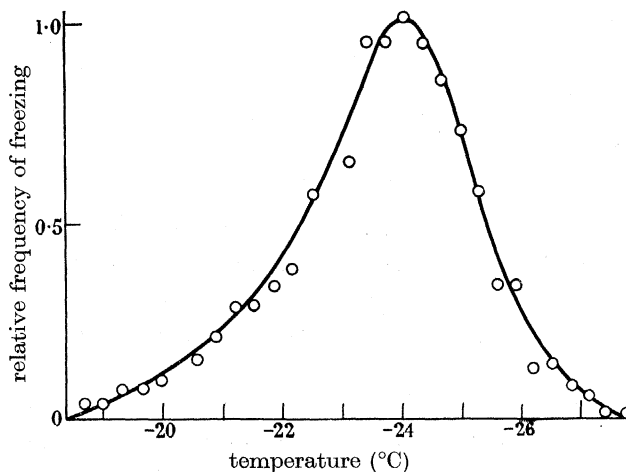


FIGURE 52. The distribution of freezing temperatures of 1127 water drops of 1 mm diameter (after Bigg).

Bigg determined the freezing temperatures of large numbers of drops of various sizes and divided them into groups according to drop diameter, each group containing not less than 100 individual observations. A curve showing a typical distribution of freezing temperatures of drops in a particular size group is shown in figure 52, which contains observations on 1127 drops of 1 mm diameter. The median freezing temperature for each group, i.e. the temperature below which half the drops froze, is plotted against the drop diameter, on a logarithmic scale, in figures 53 and 54. Bigg thus discovered a linear relationship between the logarithm of the drop diameter (or volume) and the degree of supercooling $T_s = (273 - T)$ °C, the line in figure 54 being represented by the relationship

$$\log_{10} V = A - BT_s, \quad \text{where } A \text{ and } B \text{ are constants.}$$

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The present authors have checked Bigg's results with a slightly improved version of his apparatus in which the water drops are suspended between carbon tetrachloride and liquid paraffin in a shallow metal dish and cooled in a refrigerated chamber at the rate of about $\frac{1}{3}$ °C/min. After careful mapping of the temperature field in the dish had revealed it to be everywhere uniform within $\frac{1}{2}$ °C, the temperature of the drops was measured by a fine thermocouple located at the interface of the two supporting liquids and half-way out along the radius of the circular dish.

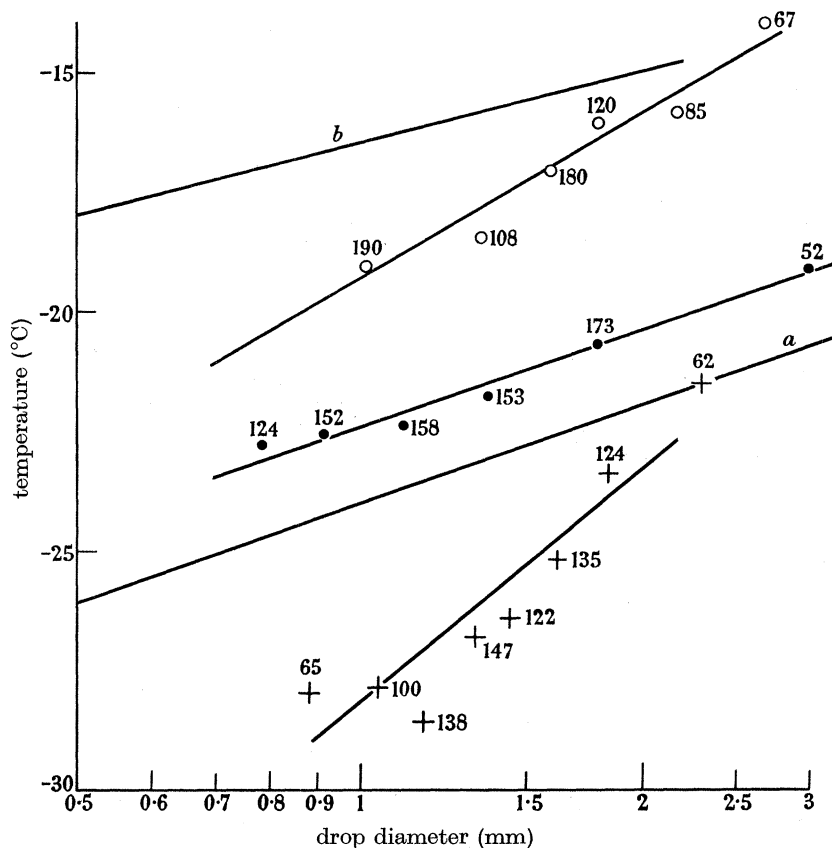


FIGURE 53. The median freezing temperatures of groups of water drops as a function of their diameter. The results of three experiments, each using water of a different degree of purity, are compared with those obtained by Bigg (*a*) and Dorsch & Hacker (*b*). The number of drops in each size group is shown.

The numbers of frozen and unfrozen drops appearing, against a squared scale, in the field of view of a telescope were mapped at temperature intervals of $\frac{1}{2}$ °C until all of them had frozen, and distribution curves like figure 52 were constructed from these maps. When studying drops less than $\frac{1}{2}$ mm in diameter, the metal dish was placed in a specially constructed cryostat. The drops were viewed through a microscope and the numbers freezing at various temperatures were determined from photomicrographs taken at regular temperature intervals of $\frac{1}{4}$ °C.

The results obtained with water varying in purity from that of rain water to that produced by repeated distillation showed the same general trend as those of Bigg;

plots of the median freezing temperatures of groups of drops against the logarithm of their diameters produced straight lines almost parallel to that of Bigg, but lying below or above it, depending upon whether the water used was more or less pure than that used by him (see figure 53). Further confirmation of the general validity of Bigg's relation was found by Mason (1956) in analyzing the results of some

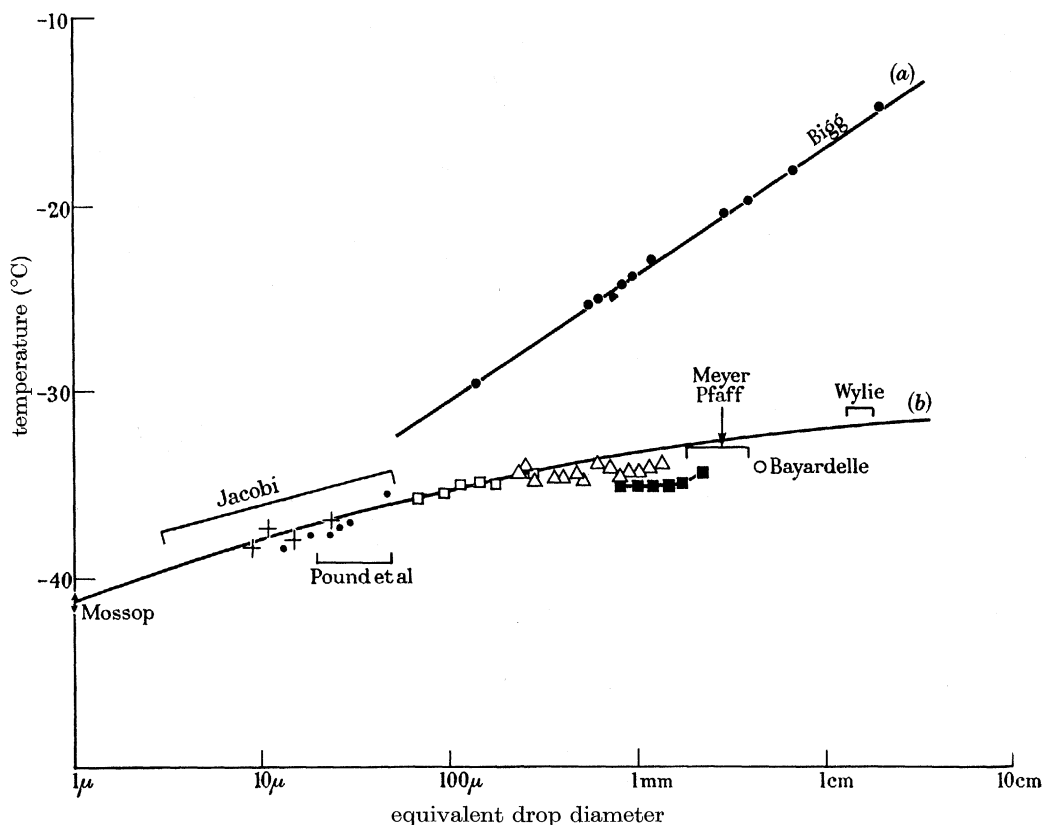


FIGURE 54. (a) Bigg's relationship between the median freezing temperatures and the diameters of water drops containing foreign nuclei (heterogeneous nucleation). (b) Median freezing temperatures for groups of droplets of very pure water having diameters < 0.5 mm, and the *lowest* freezing temperatures recorded for drops of diameter < 0.5 mm. These experimental data all lie close to the curve calculated from the theory of homogeneous nucleation. ●, Bigg; +, Carte; △, Mossop; □, Langham & Mason (medians); ■, Langham & Mason (lowest).

earlier work by Dorsch & Hacker (1950) in which 5000 water droplets, with diameters between 8.75μ and 1 mm, were frozen on a metal plate. The median freezing temperatures for the different size groups lay on a line exactly parallel to that of Bigg's, but displaced by 7°C towards higher temperatures, as shown in figure 53.

Although Bigg, no doubt, removed the grosser particles from his water samples by double distillation, his drops almost certainly contained large numbers of small particles which, as we now know, can be removed only by taking extreme measures. It is therefore reasonable to consider his $\log_{10} V - T_s$ relationship as representing nucleation by foreign particles (heterogeneous nucleation). This is

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also suggested by the fact that other workers, who have taken greater precautions to purify their water, have occasionally been able to supercool specimens to temperatures well below those indicated by Bigg's line—see §3 and figure 54.

We now suggest that his relationship between droplet volume and depth of supercooling may be explained on the assumption that his water was contaminated by particles which were originally airborne and whose ice-nucleating activity might be expected to vary with temperature in much the same way as for atmospheric aerosols.

The numbers of ice crystals appearing in a supercooled cloud, produced by condensation on atmospheric aerosols in cloud chambers, have been determined by a number of different workers; the results have been reviewed by Mason (1957). In the temperature range -10 to -35 °C [above which natural ice nuclei are very rare, and below which the effects of *homogeneous* nucleation become apparent, (Mason 1955)], the number of particles which initiate the freezing of supercooled droplets increases roughly logarithmically with decreasing temperature.

If we now assume that the bulk water used in our supercooling experiments contains a representative sample of what were originally atmospheric particles, then the activity of the contained freezing nuclei will also be represented by

$$n = n_0 e^{aT_s}, \quad (1)$$

where n is the concentration of nuclei which become effective at temperatures between 0 and $-T_s$ °C, and n_0 and a are constants. For drops of volume V being cooled to a temperature $-T_s$ °C, and containing a randomly distributed population of freezing nuclei, the probability P of a drop containing at least one effective nucleus on reaching this latter temperature is given by

$$P \simeq 1 - e^{-Vn}, \quad (2)$$

$$\text{or} \quad \ln(1 - P) \simeq -Vn = -Vn_0 e^{aT_s}. \quad (2a)$$

Now the empirical relationships of figure 53 show the values of T_s for which drops of different volumes have a 50 % chance of freezing, i.e. $P = \frac{1}{2}$, and for these equation (2a) becomes

$$Vn_0 e^{aT_s} = \text{const.}$$

$$\text{or} \quad \ln V = \ln C - aT_s, \quad (3)$$

which is Bigg's relationship. The value of the constant a fixes the shape of the freezing-nucleus distribution with respect to temperature, while the value of C depends upon the absolute concentration of nuclei, i.e. upon the purity of the water.

The fact that the plots of $\log_{10} V$ against T_s for other samples of water produced by repeated distillation lie parallel to Bigg's, but displaced to lower temperatures according to the degree of purity, may be explained as follows. When water is distilled with ebullition, the spray from bursting bubbles is likely to carry over nuclei into the condensate without changing the *relative* proportions of different classes, but the condensing vapour will dilute nuclei of *all* classes. Thus distillation of this type might be expected to lower the value of n_0 and to cause a displacement

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of the $\log_{10} V - T_s$ plot towards lower temperatures without greatly affecting its slope. If this argument is correct, in order to produce water containing very low concentrations of motes, it would seem necessary to suppress ebullition during distillation.

3. THE HOMOGENEOUS NUCLEATION OF SUPERCOOLED WATER

A number of experimenters have reported on the possibility of supercooling small droplets (radius $< 5\mu$) to about -40°C before freezing occurs. Cwilong (1947) and Fournier d'Albe (1949), by expanding atmospheric air in small cloud chambers, found that while at temperatures above -40°C a few ice crystals appeared among a much larger number of water droplets, below -41°C the fog was composed almost entirely of ice crystals. Mossop (1955), in a rather more careful study of the freezing of tiny droplets ($d \simeq 1\mu$), also found that the number of ice crystals increased rapidly as the temperature fell below -40°C , and all the droplets were estimated to have frozen after being maintained at $-41.2 \pm 0.4^\circ\text{C}$ for 0.6 s. Very similar results have been reported by Mason (1956) from observations on droplets formed on small ions in the clean air of a diffusion cloud chamber as they fall at the rate of about $\frac{1}{4}\text{ cm s}^{-1}$ through a vertical temperature gradient.

As solid particles are excluded from these tiny droplets formed in clean air, nucleation of the ice phase can occur only by small groups of water molecules becoming locked by chance into an ice-like configuration; such molecular aggregates will continually arise and disappear through thermal fluctuations. The lower the temperature, the greater their size and frequency of formation until, eventually, they attain a critical size above which they survive and continue to grow, forming nuclei for the ice phase. An expression for the rate of formation of such nuclei has been derived by Mason (1952, 1957) viz.

$$\log_{10} I = 32.84 + \log_{10} T - \frac{U}{2.303 kT} - \frac{1.11 \times 10^{17} \sigma_{SL}^3}{L_f^2 T \ln^2 T_0/T}, \quad (4)$$

where I is the rate of production of nuclei per cm^3 per sec, U is the activation energy for self-diffusion of a molecule in the liquid, k is Boltzmann's constant, σ_{SL} is the specific surface free energy of the crystal-liquid interface, L_f is the latent heat of fusion, T is the absolute temperature and T_0 ($= 273^\circ\text{K}$), the thermodynamic freezing point. Because the parameter σ_{SL} cannot be calculated with confidence, and because a 10% error would lead to an error of 10^6 in the calculated value of I , it does not appear profitable to make a close comparison between the nucleation rate calculated from equation (4) and that which may be deduced from experimental observations of freezing droplets. However, Mason, using Mossop's experimental data on 1μ droplets to calculate, from (4), a value for $\sigma_{SL} = 17.2\text{ erg cm}^{-2}$ at -41°C , used this to compute the temperature coefficient of nucleation, dI/dT , which is not very sensitive to the adopted value of σ_{SL} , and having then found quite good agreement between the computed value of dI/dT and that deduced from observation at temperatures close to -40°C , provided some check of the theory. Having evaluated σ_{SL} as just described, equation (4) can now be used to predict the temperatures at which water drops will crystallize spontaneously, in

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terms of their volume and the time. Thus the lower curve of figure 54, calculated on the basis of Mossop's data that $1\text{ }\mu$ -diameter droplets freeze after being held at $-41\text{ }^{\circ}\text{C}$ for 0.6 s , indicates the temperatures at which larger drops would freeze when cooled for a similar period. This curve, representing homogeneous nucleation, differs markedly in shape from that of Bigg's line which, we believe, represents heterogeneous nucleation.

Also in figure 54 are plotted the observations of a number of different workers who have been able to supercool small droplets (10 to $30\text{ }\mu$ diameter) down to temperatures approaching $-40\text{ }^{\circ}\text{C}$, and also a few exceptional cases, recorded in the literature, of much larger volumes being supercooled to unusually low temperatures. The essential information on these observations is set out in table 16.

The close grouping of these experimental observations about the theoretical curve (the shape and position of which is not materially affected by changing the time factor by an order of magnitude) strongly suggests that, in those cases listed in table 16, the nucleation of the water samples was spontaneous and that freezing nuclei were not involved. It is not possible to make an exact comparison between the observations and the theory because the cooling rates of all the various samples are not known but, in most cases, they did not deviate from those of Bigg and Mossop by more than tenfold so that the corresponding temperature correction would be less than one degree.

This result encouraged us to try and produce, in appreciable quantity, water entirely free from foreign particles, so that we could study systematically the homogeneous nucleation of large numbers of drops varying in diameter from about $10\text{ }\mu$ to 1 mm .

4. THE PRODUCTION OF VERY PURE WATER

Out of a number of unsuccessful attempts to produce water which could be regularly supercooled to temperatures indicated by the theory of homogeneous nucleation, a satisfactory technique was evolved, the final version of the apparatus being represented in figure 55.

The components of the all-Pyrex still were carefully cleaned with chromic acid and flushed with steam before being assembled. Starting with ordinary laboratory distilled water, this was passed, via a gravity feed, through an ion-exchange column which removed most of the dissolved ions and lowered the conductivity to about 10^{-6} mho. cm. It then dripped into flask *A* where it was redistilled, the condensate passing over into flask *B*. Before any water samples were taken from the still, it was flushed for several hours with steam produced in flask *A* and passed through the whole apparatus to emerge at the sampling jet *J*. This procedure was designed to drive out the particle-laden room air from the apparatus and to remove particles lodged on the glass walls. The bacteriological filter *F* was inserted to remove particles larger than $0.3\text{ }\mu$ from the room air which was sucked into the apparatus when this cooled down between periods of flushing. To prevent the smaller particles which would penetrate the filter from entering flask *B*, this was completely filled up to the level of tap T_2 with water distilled from *A* and condensed in C_1 , and the tap was closed before the final distillation from *B* commenced.

Periodic checks on the conductivity of the water in *B* were made by connecting a resistance-measuring circuit to two small platinum electrodes sealed into a side tube as shown in figure 55.

After the final distillation in flask *B*, the water, condensed in *C*₂, emerged under pressure in the form of drops from the glass jet *J*. The small metal dish, containing liquid paraffin floating on freshly distilled carbon tetrachloride, was brought up to the jet, and with its tip dipping into the liquids, water drops upwards of $\frac{1}{2}$ mm in diameter were forced out under a controllable excess pressure built up in the flask *B*. Thus the drops came to rest at the interface of the two supporting liquids without having come in contact with the atmosphere during their transfer.

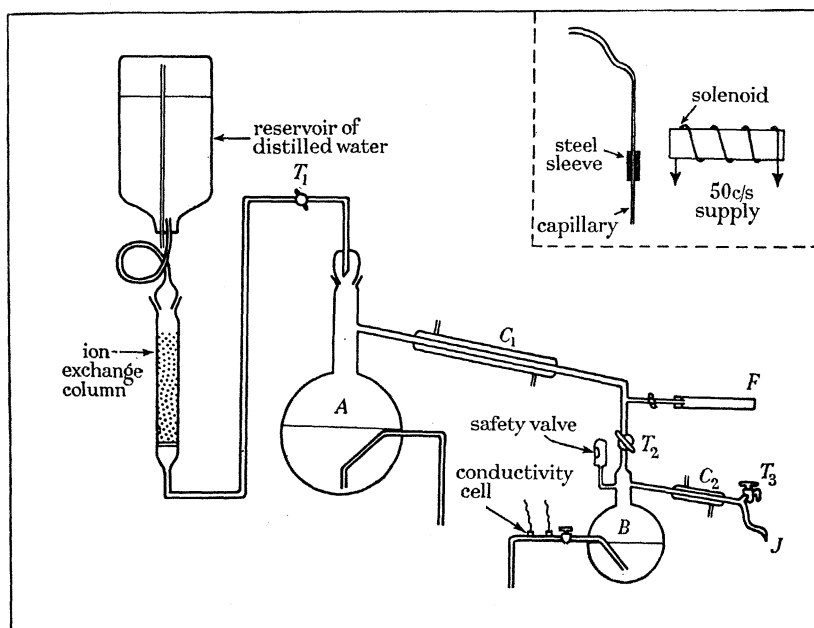


FIGURE 55. The apparatus used for producing very pure water.

The first samples taken in this way were disappointing in that their freezing temperatures were not very different from those obtained by Bigg for ordinary laboratory-distilled water. Further flushing of the apparatus with steam for several hours produced some improvement, but still the freezing points of the majority of the drops were higher than we expected. It was at this stage that we realized the possibility of some motes being carried over from one part of the apparatus to another in small spray droplets. To prevent this, the water in flask *A* was boiled only gently so that there was little chance of spray droplets produced by bursting bubbles being carried up the long, wide neck of the flask and over into the exit tube. For a similar reason, the water supply from the ion-exchange column to flask *A* was cut off during the distillation process in order to avoid the production of splash droplets. Finally, attempts were made to produce a high flux of vapour from flask *B* without boiling the water, simply by allowing distillation to take place under an excess pressure controlled by the safety valve. However, complete sup-

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pression of ebullition proved possible only after the apparatus had been flushed with steam for many days to remove particles lodged on the glass walls and which acted as nuclei for bubble formation.

When all these precautions were taken, the median freezing temperatures for groups of drops, a few mm^3 in volume, now lay some 5° below Bigg's line (see figure 53), while the lowest freezing points recorded were some 10° below. Smaller droplets, in the diameter range 50 to 500 μ , were produced by drawing out the jet J into a long, fine capillary tube and vibrating this at 50 c/s by means of a steel sleeve actuated by an a.c. solenoid. By adjusting the mode of vibration of the capillary, it was possible to vary the size of the drops produced over quite a wide range. These smaller droplets were collected in a dish containing the two freshly distilled supporting liquids by immersing the tip of the vibrating capillary just under the liquid surface. At the low temperatures required to freeze the smallest droplets, the liquid paraffin became partially opaque and was replaced by a silicone fluid after this had been shown not to affect the freezing of millimetre drops. The dish was transferred to a small cryostat, cooled at the rate of $1^\circ\text{C}/\text{min}$, and the droplets were photographed through a microscope at regular temperature intervals of $\frac{1}{4}^\circ\text{C}$.

5. RESULTS ON THE SUPERCOOLING OF HIGHLY PURIFIED WATER

The median freezing temperatures for homogeneous groups of drops covering a diameter range of 0.8 to 2.1 mm are plotted in figure 53, the total number of drops in each group being marked on the diagram.

These results also appear to conform to a linear relationship between $\log_{10} V$ and T_s , although the slope of the line of best fit is rather steeper than that of Bigg. These *median* freezing temperatures, though appreciably lower than those of Bigg, are appreciably higher than one would expect for homogeneous nucleation. It appears then, that even with the precautions described above, it was still not possible to produce water sufficiently free from foreign particles for a majority of such *large* drops to be entirely free from freezing nuclei. It may even be that some tiny particles suspended in the supporting liquids had some effect at this stage. However, the *lowest* freezing temperatures recorded in each size group, and which are plotted in figure 54, lie quite close to the calculated curve for homogeneous nucleation; about 10 % of these larger drops could be supercooled to within 1° of this limit.

The behaviour of droplets of diameter less than 250 μ was rather different; the spread of freezing temperatures for drops in a given size group (see figure 56) was considerably narrower than for the larger drops just described, and the *median* values lie very close to the curve for homogeneous nucleation, as shown in figure 54. In this respect, they also fit in very well with those obtained by other workers for much smaller droplets. Indeed, the agreement between the theoretical curve and the experimental results of the several different workers, each of which investigated only a small range of drop sizes, but altogether covered a range of more than 10^{12} in volume, is rather impressive.

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The work described in this paper, together with the results of other workers, provides a substantial body of experimental evidence from which we may deduce that Bigg's line in figure 54 (i.e. equation (3)), represents the relationship between the volume of a water drop and the maximum degree of supercooling for *heterogeneous* nucleation, and that the curve in figure 54 (i.e. equation (4)), represents the corresponding relationship for *homogeneous* nucleation.

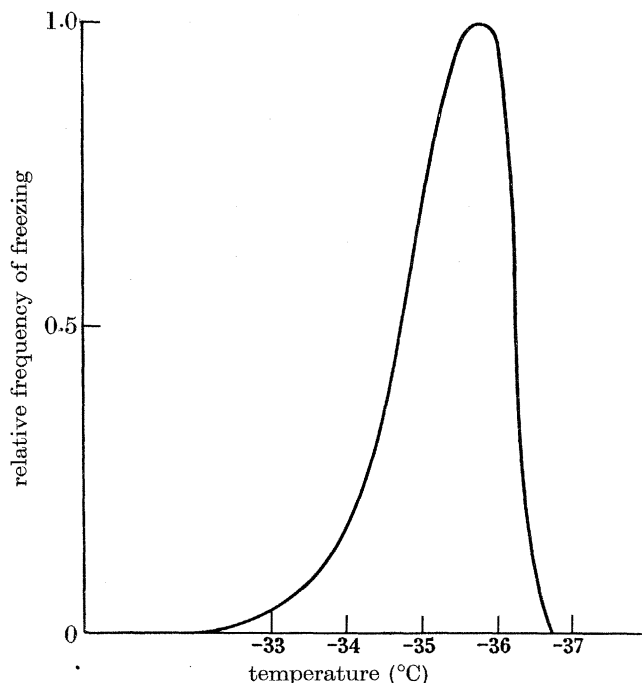


FIGURE 56. The distribution of freezing temperatures of 100 droplets of $90\ \mu$ diameter produced by the new still.

6. SOME OBSERVATIONS ON THE RUPTURE AND SPLINTERING OF FREEZING DROPS

Observations under the microscope reveal that an appreciable fraction of water droplets, suspended between two other liquids and varying in diameter from $50\ \mu$ to a millimetre, burst during freezing. Rapid cinematography shows that freezing often starts at the surface of the drop which solidifies very rapidly to surround the drop with a shell of ice. When freezing starts, release of the latent heat quickly raises the drop temperature to $0\ ^\circ\text{C}$ and allows only $T_s/80$ ths of its volume to freeze, T_s being the degree of supercooling. Subsequent freezing of the liquid interior occurs at a rate determined by the rate of dissipation of latent heat from the drop, and the consequent expansion may cause the ice shell to rupture.

Observations on millimetre-size drops suspended, from a fibre, in air indicate that the manner of the rupture depends largely upon the quantity of dissolved air in the water and the rate of freezing (i.e. on the degree of supercooling). Since, at $-10\ ^\circ\text{C}$, the maximum solubility of air in water is nearly 4% by volume while the solubility in ice is negligible, nearly all the air contained in the water forming the

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TABLE 16. SUMMARY OF EXPERIMENTAL DATA ON THE SUPERCOOLING OF WATER SAMPLES TO VERY LOW TEMPERATURES—PROBABLY TO THE THRESHOLD OF HOMOGENEOUS NUCLEATION

author	method of preparation of water	equivalent drop diameters	median freezing temp. (°C)	lowest freezing temp. (°C)	remarks
Meyer & Pfaff (1935)	multiple distillation and filtration through sintered glass and collodion filters; test sample contained in quartz tube	between 1.8 and 3.8 mm (estimated)	—	-33	only a very few samples were supercooled to this temperature
Wylie (1953)	water condensed from a moist, nucleus-free stream of oxygen into fairly large glass tubes	between 1.4 and 1.7 cm (estimated)	—	-30 ± 1	only one sample supercooled to this low temperature on two occasions
Bigg (1953)	doubly-distilled water dispersed as small droplets at the interface of two immiscible liquids	15 to 50 μ	-37.6 to -36.2	—	six groups covered this diameter range with more than 100 droplets in each
Pound <i>et al.</i> (1953)	water condensed as small droplets to form an emulsion in silicone oil	20 to 50 μ	-39	-42	no differentiation with respect to droplet size reported
Mossop (1955)	water condensed into glass, silica and silicone-treated glass capillaries	0.25 to 1.05 mm	—	-33.8 to -34.7	fifteen samples altogether supercooled to these low temperatures
	tiny droplets produced by condensation in an expansion chamber	1 μ	—	-41.2 ± 0.4	—
Jacobi (1955)	droplets condensed on collodion films supported by highly polished metal surfaces	3 to 50 μ	—	-37.4 to -34.2	—
Bayardelle (1954)	drops of doubly-distilled water suspended between mercury and a silicone liquid	4.6 mm	—	-34.1	—
Carte (1956)	droplets condensed on a metal surface and covered with silicone oil	9 to 30 μ	-38.2 to -37.3	-39 to -37.8	results of repeated freezings of three individual drops of 9, 15, 30 μ dia. and of a single freezing of 100 droplets of 10 μ dia.

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ice shell is released during freezing. If the freezing is rapid, the air bubbles become trapped in the ice and give the shell an opaque appearance. In this case, cracking of the shell may occur rather gradually and in several places.

If, on the other hand, the water contains little air and freezing occurs slowly, the small quantity of air released may have time to escape as bubbles to the surface rather than become trapped in the ice, and then the shell forms as a clear, transparent layer of ice. Expansion of the interior on freezing may now cause a violent rupture of the shell (which is less yielding than the opaque ice), perhaps at only one spot, through which the liquid is ejected to become frozen into a large spike. A spike may become extended in a number of stages as fresh liquid is ejected from the interior of the drop and ruptures the tip of the spike formed in an earlier stage (see figure 57, plate 11). The formation of these protuberances is usually associated with a clear ice shell and occurs only rarely when the shell is opaque.

Because it seemed likely that the fracture of the ice shell might be accompanied by the production of small ice splinters which would not be easily detected in the supporting liquids, separate experiments were designed to detect them. Droplets of 50 to 100 μ diameter were allowed to fall freely through a column of cold air in which the temperature fell from 0 °C to about -60 °C over a vertical distance of 20 cm. The falling droplets were illuminated intermittently at 50 c/s and photographed with a ciné camera. Figure 58, plate 11 shows the tracks of falling droplets which were made visible by condensation, and the ejection, at large angles to the vertical, of a few small ice splinters from a droplet which had frozen. Droplets of this size rarely produced more than five visible splinters, but in experiments with millimetre-size drops suspended on fibres about one drop in ten produced upwards of one hundred splinters, and occasional drops of more than a thousand.

This secondary production of ice crystals by the rupture of freezing drops may be a significant factor in the ice-nucleus economy of rain clouds.

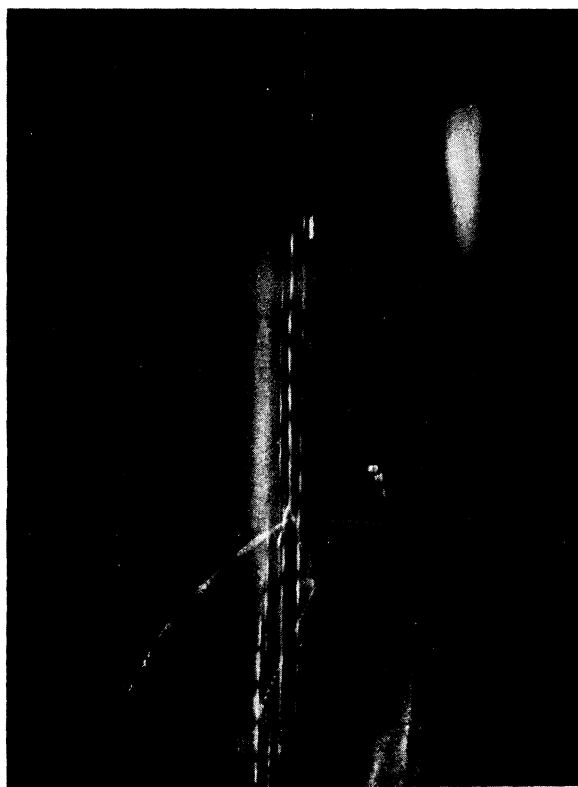
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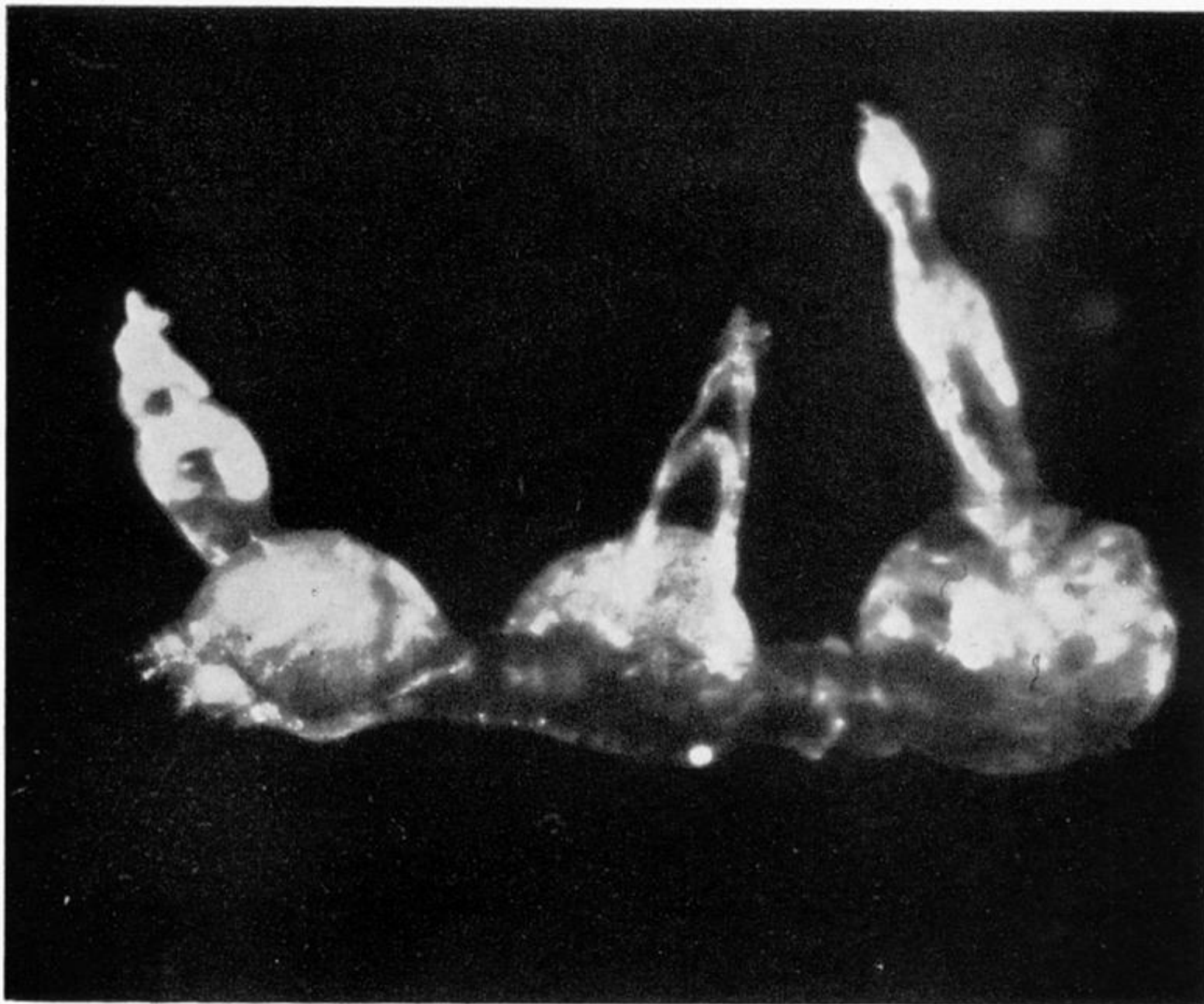


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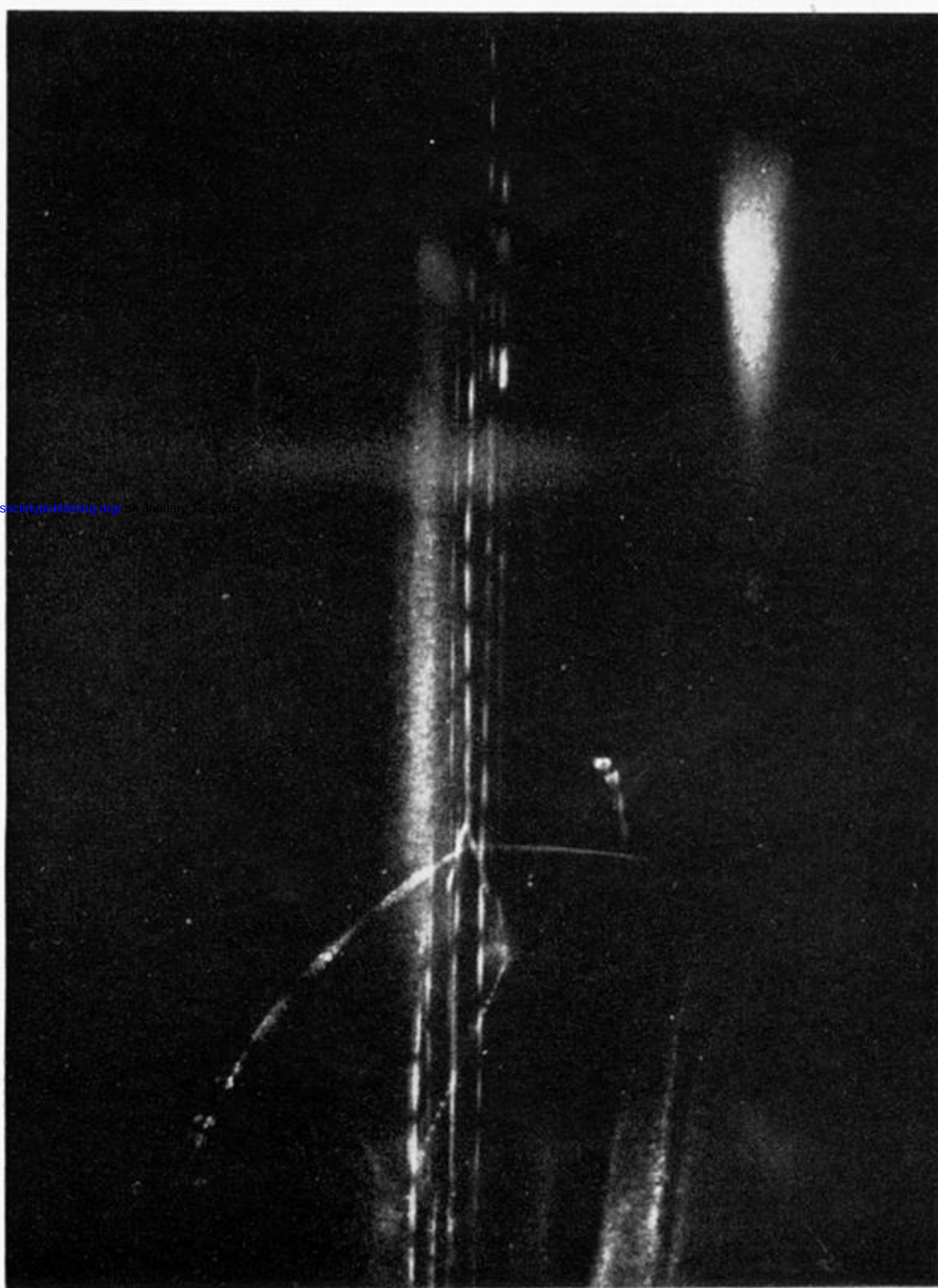
FIGURE 57. Photograph showing the appearance of large spikes in the ice shell of drops during freezing. (Drop diameter about 1 mm.)

FIGURE 58. Photograph showing the ejection of tiny ice splinters from a small droplet ($d \simeq 100 \mu$) which has just frozen while falling through a column of air with a steep temperature gradient.

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FIGURE 57. Photograph showing the appearance of large spikes in the ice shell of drops during freezing. (Drop diameter about 1 mm.)

FIGURE 58. Photograph showing the ejection of tiny ice splinters from a small droplet ($d \simeq 100 \mu$) which has just frozen while falling through a column of air with a steep temperature gradient.