Proceedings of the World Congress on Engineering 2011 Vol I
WCE 2011, July 6 - 8, 2011, London, U.K.

Mathematical Modelling of Bubble Nucleation in Stout Beers and Experimental Verification

M. G. Devereux and W. T. Lee

***Abstract*—Bubble nucleation is a phenomenon observed in many different physical situations from decompression sickness (DCS) to champagne research. It is of vital importance to the formation of a creamy head that is distinctive to stout beers. As stouts contain a lower quantity of dissolved carbon dioxide than other beers, nitrogen is also dissolved in the beer. This is necessary to produce the smaller bubbles required for a creamier head and the relatively lower quantity of dissolved carbon dioxide prevents the slightly sharp acidic taste present in other beers which contain more carbon dioxide. The problem with using less carbon dioxide is that the stout beers need to be initiated (the process of gas coming out of solution to form bubbles) as this does not happen as easily for other beverages which are solely carbonated. Canned stout beers are currently initiated using a device know as a widget. A widget is simply a hollow plastic sphere with a small hole in it. The widget initiates the stout by releasing a jet of gas into the liquid when the can is opened. Widgets, while effective, have a number of drawbacks including cost and the need for decontamination before it is placed in the sealed can. A cellulose fibre array is investigated as an alternative to the widget for canned stout beers. We demonstrate experimentally that these fibres can initiate the stout and develop a mathematical model to describe the growth of gas pockets within these fibres.**

***Index Terms*—Bubble-Nucleation, Stout, Widget, Nucleation, Cellulose-Fibres**

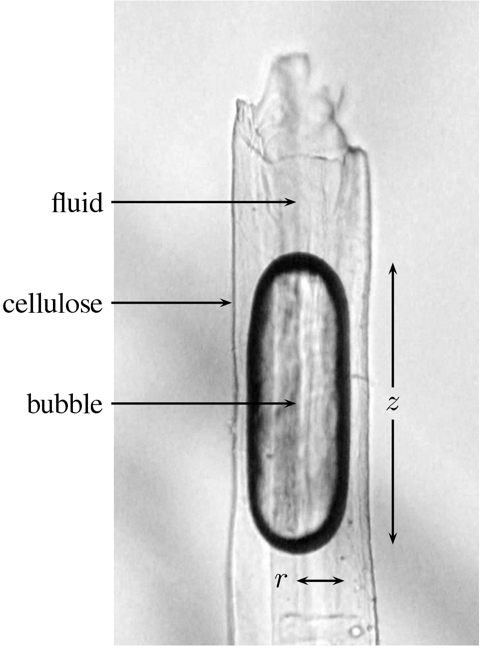

Fig. 1. Cellulose fibre containing bubble composed of nitrogen and carbon dioxide.

I. INTRODUCTION

A large amount of research has been done on the subject of bubble nucleation in champagnes [1], [2], [3]. It has been observed that cellulose fibres are one of the primary nucleation agents for champagne and other carbonated beverages. This is also a topic of interest for stout beers as a relatively cheaper alternative may be found to the widgets currently used to initiate stout beers. A can of stout beer is a sealed container with both nitrogen and carbon dioxide dissolved in the beer and contained inside the widget. The purpose of these gases is to give the creamy head that is distinctive to stout beers. A mixture of both nitrogen and carbon dioxide is used as this is the only mixture that will produce bubbles of an adequate radius for the desired head. An additional benefit of using nitrogen in the place of some of the carbon dioxide commonly found in other beers is that this prevents the formation of carbonic acid which gives a sharp or bitter taste to other beers and solely carbonated beverages.

The main problem with the use of nitrogen is that it is much more difficult to initiate (create bubbles in) nitrogenated beers than regular beers which are solely carbonated. This is due to the low solubility of nitrogen relative to carbon dioxide. By referring to Table I, it can be seen from the values of the Henry's Law constants that nitrogen is approximately 50 times less soluble than carbon dioxide. In fact just the motion of pouring a carbonated drink and the presence of a few stray cellulose fibres (from drying the glass with a towel etc) in a glass is enough to initiate it.

The widget overcomes this problem by introducing a jet of both nitrogen and carbon dioxide gas into the stout which creates many small bubbles which rise to the top to give a foamy head. However, the widget design has a number of problems associated with it including cost and the need to deoxygenate it to prevent spoilage of the beer. In this paper we present the possibility of a cellulose fibre array as an alternative to the widget.

It is easily observed that cellulose fibres in a carbonated beverage produces a steady stream of bubbles [1]. When the fibres are first submerged in the stout beer, pockets of air are trapped inside the fibres. These preexisting gas pockets (seed bubbles) within the fibres, as shown in Fig. 1, are required for type IV non-classical nucleation to occur [4]. This is the only type of nucleation that can happen at the relatively low partial pressures of the nitrogen and carbon dioxide dissolved in stout beers. Both nitrogen and carbon dioxide diffuse through the walls of the cellulose fibres into the seed bubble which grows in volume. When the bubble reaches a certain length or when a certain detachment requirement is met, a spherical

---

Manuscript received April 04, 2011; revised April 16, 2011. We acknowledge support of the Mathematics Applications Consortium for Science and Industry (www.macsi.ul.ie) funded by the Science Foundation Ireland Mathematics Initiative Grant 06/MI/005.

M. G. Devereux's postgraduate fellowship is funded by the Irish Research Council for Science, Engineering and Technology, IRCSET.

M. G. Devereux and W. T. Lee are with MACSI, Department of Mathematics and Statistics, University of Limerick, Limerick, Ireland. e-mail: michael.devereux@ul.ie

TABLE I
PARAMETERS USED IN SIMULATIONS

Parameter	Value	Reference
r	$22.00 \times 10^{-6}\,\mathrm{m}$	
λ	$14.00 \times 10^{-6}\,\mathrm{m}$	[1]
σ	$47.00 \times 10^{-3}\,\mathrm{N\,m^{-1}}$	[5]
$D_1(\mathrm{CO_2})$	$1.40 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$	
$D_2\ (\mathrm{N_2})$	$2.00 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$	
$H_1\ (\mathrm{CO_2})$	$3.4 \times 10^{-4}\,\mathrm{mol\,m^{-1}\,N^{-1}}$	
$H_2\ (\mathrm{N_2})$	$6.1 \times 10^{-6}\,\mathrm{mol\,m^{-1}\,N^{-1}}$	
T	$278\,\mathrm{K}$	
P_0	$1.00 \times 10^{5}\,\mathrm{Pa}$	
$P_1\ (\mathrm{CO_2})$	$0.80 \times 10^{5}\,\mathrm{Pa}$	[6]
$P_2\ (\mathrm{N_2})$	$3.00 \times 10^{5}\,\mathrm{Pa}$	[6]

bubble breaks off from the main body of the gas pocket. This bubble then floats up to the top surface of the liquid. As not all the gas in the pocket leaves the fibre, a seed bubble is retained and the process can repeat as long as there is sufficient gas left dissolved in the stout. Liger-Belair et al [1] describe the conditions required for a cellulose fibre to retain a gas pocket within the lumen (the cavity within the cellulose fibre) of the fibre for the case that the fibre is in a container the carbonated liquid is being poured into.

Our proposed alternative to the widget would consist of an array of cellulose fibres of approximately three square centimetres. Our research suggests stout could be initiated (create gas bubbles) using such an array of fibres in the 30 seconds it typically takes to pour a glass of stout. We present a mathematical model which predicts that cellulose fibres will produce the bubbles for the unique mixture of gases found in stouts. The production of these bubbles is verified experimentally. Details of the experimental setup are given, discussed and several of its advantages outlined. We also propose an alternative means for investigating bubble nucleation in fibres for carbonated drinks, such as champagne, which can be very difficult to observe due to the speed of the bubbling process and the large number of bubbles produced.

II. MATHEMATICAL MODEL

Lee et al [7] develop a two gas model for the number of moles of gas molecules present in a bubble based on a model for champagne by Liger-Belair et al [1]. In this model, the rate of change of the numbers of carbon dioxide (N_1) and nitrogen (N_2) molecules in the gas pocket are given by

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = 4\pi r^2 D_1 \frac{\Delta c_1}{\lambda} + 2\pi r z D_{1\perp} \frac{\Delta c_1}{\lambda}, \tag{1}$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = 4\pi r^2 D_2 \frac{\Delta c_2}{\lambda} + 2\pi r z D_{2\perp} \frac{\Delta c_2}{\lambda}, \tag{2}$$

as the gases diffuse both through the cellulose fibre walls and through the hemispherical caps of the bubbles. Using Henry's law, Laplace's law and the ideal gas equation:

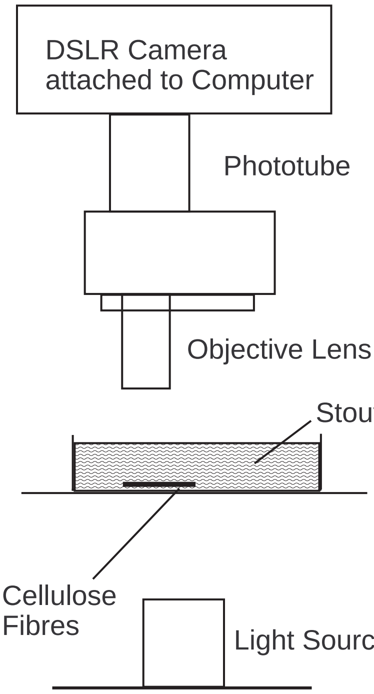

Fig. 2. Schematic diagram of experimental setup.

$$\Delta c_1 = H_1 \left(P_1 - \frac{P_\mathrm{B} N_1}{N_1 + N_2} \right), \tag{3}$$

$$\Delta c_2 = H_2 \left(P_2 - \frac{P_\mathrm{B} N_2}{N_1 + N_2} \right), \tag{4}$$

$$P_\mathrm{B} = P_0 + \frac{2\sigma}{r}, \tag{5}$$

$$z = \frac{(N_1 + N_2)\,RT}{\pi r^2 P_\mathrm{B}}, \tag{6}$$

where P_1 is the partial pressure of dissolved carbon dioxide, P_2 is partial pressure of dissolved nitrogen, P_B is the pressure in the gas pocket given by the Laplace law, P_0 is atmospheric pressure and σ is surface tension and r is the radius of the fibre. Using these equations (1) and (2) can be rewritten as

$$\frac{dN_1}{dt} = \left(\frac{4\pi r^2 D_1}{\lambda} + \frac{2(N_1+N_2)RTD_{1\perp}}{rP_B\lambda} \right) \times H_1 \left(P_1 - \frac{P_B N_1}{N_1 + N_2} \right) \tag{7}$$

$$\frac{dN_2}{dt} = \left(\frac{4\pi r^2 D_2}{\lambda} + \frac{2(N_1+N_2)RTD_{2\perp}}{rP_B\lambda} \right) \times H_2 \left(P_2 - \frac{P_B N_2}{N_1 + N_2} \right) \tag{8}$$

III. EXPERIMENTAL METHODS

The formation of bubbles in stout beers was verified experimentally using the setup shown in Fig. 2. A standard biological compound trinocular microscope was used to observe the fibres. A trinocular microscope was used as this gave the option of attaching a single-lens reflex (SLR) camera by means of a specially fitted phototube.

A Canon 550D Digital single-lens reflex (DSLR) camera was used for these experiments. Not only does this give us the advantages of a standard digital camera but this particular model allows the recording of the 1080p standard of video at $25\,\mathrm{FPS}$ or 720p at $50\,\mathrm{FPS}$. 1080p video is composed of stills of 1920×1080 pixels. These videos can be decomposed for analysis using MATLAB. This camera can be attached to a computer and the fibre can be observed in realtime using a computer monitor and recorded where necessary. A scale is obtained by imaging a standard length.

An array of fibres is secured to the base of a transparent biological specimen observation container and this is placed on the stage. Uninitiated stout is gently placed into the container using a dropper and a fibre suitable for observation is recorded. The method for obtaining uninitiated stout is now described.

As all cans of stout contain widgets if we were to simply open one as a person normally would, the stout would be initiated and the gas lost from solution. Therefore, a means of opening the can while retaining as much of the gas in solution as possible is necessary. This is achieved by piercing the can with a pin and allowing the gas to exit the widget at a rate which does not initiate the stout. For safety purposes and to aid in regulating the rate at which the gases leave the can, a putty-like adhesive (such as Blu-Tack) is first placed over the area to be pierced. Once the pressure inside the widget and can is the same as the ambient pressure, it is possible to open the can while retaining most of the nitrogen and carbon dioxide dissolved in the liquid.

We have also tried to reproduce this experiment for carbonated soft drinks but found it very difficult for a number of reasons. Carbonated drinks are very easily initiated so even the task of transferring the liquid to a fibre array can be difficult without premature bubble formation. Also, due to the large number of bubbles produced when the carbonated beverage comes in contact with the fibres, it is nearly impossible to observe bubble formation from individual fibres. There is also the problem of bubbles splashing onto the objective of the microscope due to bubbles floating on the surface of the liquid.

If one was to attempt this experiment with champagne it would be nearly impossible due to the relatively high pressure of approximately $5\,\mathrm{bar}$ [8] of dissolved carbon dioxide. The bubble production rate would be far too high and individual fibres could not be observed due to foam and bubbles on the surface. From all this we conclude that it is easier to study nucleation in stouts than it is in champagne and other carbonated liquids because of the slow growth rates of the bubbles. Stout beers may prove to be a useful model system in which to study nucleation in carbonated liquids.

IV. RESULTS

A. Experimental Results

Fig. 3 shows eight selected stills from a video showing the entire cycle of a bubble inside the lumen of a fibre. The bubble grows from a seed bubble and detaches while leaving a new seed bubble behind. The newly formed bubble outside the fibre will float to the top of the stout and the cycle repeats with the remaining seed bubble.

B. Video Analysis

Fig. 4 is a plot showing the length of the bubble contained in the lumen of the fibre shown in Fig. 3. The length of bubble is measured frame by frame using MATLAB. Initially the video must be decomposed into stills. Then each image is individually read in by MATLAB and converted to a binary image (to aid in edge detection). The length of the bubble in each frame is then measured in pixels which is then converted to metres using the scale calculated earlier.

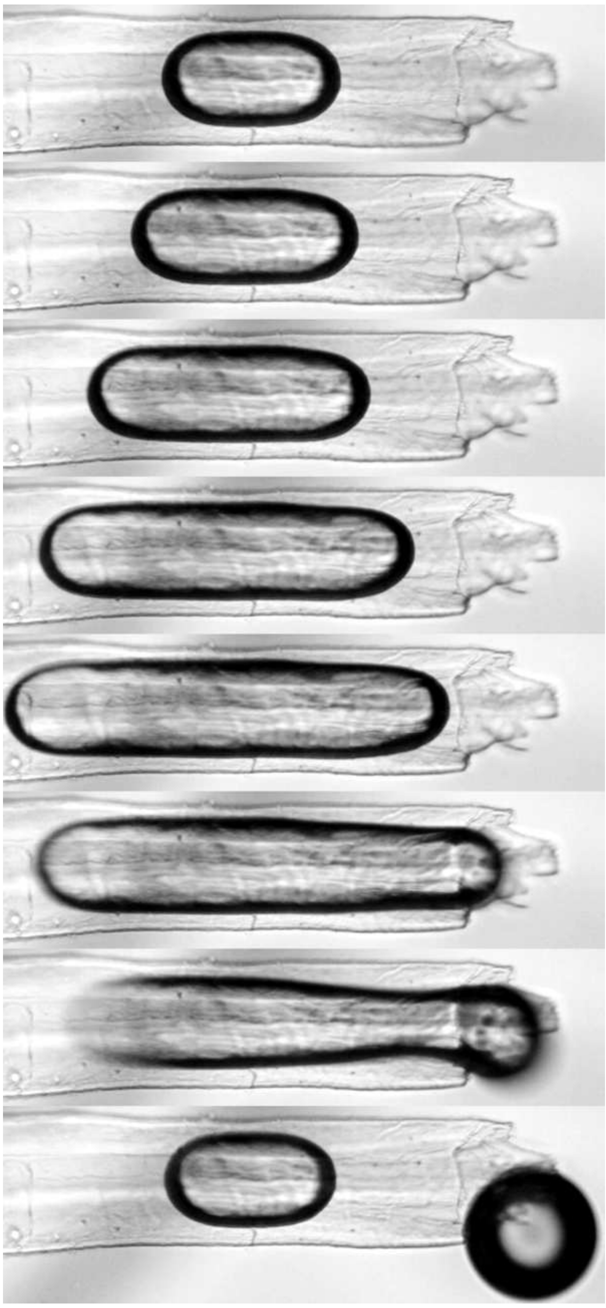

Fig. 3. Selected stills showing bubble growing inside the lumen of the fibre and detaching when it reaches a critical length. The width of the entire frame is approximately $270\,\mu\mathrm{m}$.

At the end of each bubble cycle (detachment) there is no distinct boundary at the ends of the bubbles so this length is approximated by setting it to the initial value for the seed bubble in the next frame. This does not affect the overall results due to this happening for only one frame per bubble growth cycle. Fig. 4 shows this analysis performed on thirty seconds worth of video. This length of time was chosen as this is the typical amount of time allocated to allow a head to grow on a pint of stout.

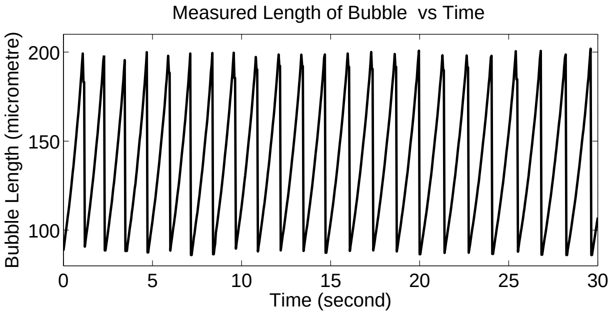

Fig. 4. Analysis performed on video showing the length of the bubble versus time for the first thirty seconds of bubble production from a fibre.

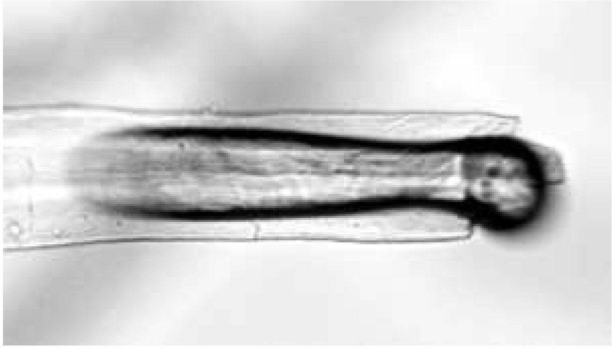

Fig. 5. Image showing Plateau Rayleigh instability type characteristic just before the bubble detaches.

C. Plateau Rayleigh Instability Before Detachment

Of particular interest is the shape of the bubble just before it detaches in Fig. 5. This image suggests the bubble undergoes a Plateau Rayleigh type instability just before it is about to detach. The Plateau Rayleigh instability is responsible for the breaking up of a stream of water (e.g, from a tap) into droplets due to the existence of tiny perturbations in the stream.

The exact means by which a bubble detaches from a cellulose fibre is still in question and the nature of the conditions to be met just before detachment unknown. This phenomenon will be investigated further in the future.

D. Numerical Solution of Mathematical Model

The parameters r and the initial quantity of gas are measured and calculated directly from the stills shown in Fig. 3. The system of ordinary differential equations (ODEs) given by equations (7) and (8) is solved numerically using the standard ODE solvers in MATLAB. The first subplot of Fig. 6 shows the length of the bubble as a function of time. As expected, the length grows. The solver is stopped when this length reaches the final length of the bubble shown in Fig. 3 as it detaches at this time. The second subplot of Fig. 6 shows the total number of moles of gas within the bubble and the third subplot shows the fraction of the volume occupied by carbon dioxide. There is no carbon dioxide present at the start due to the original bubble being formed from atmospheric gases which are composed of approximately 0.03% carbon dioxide.

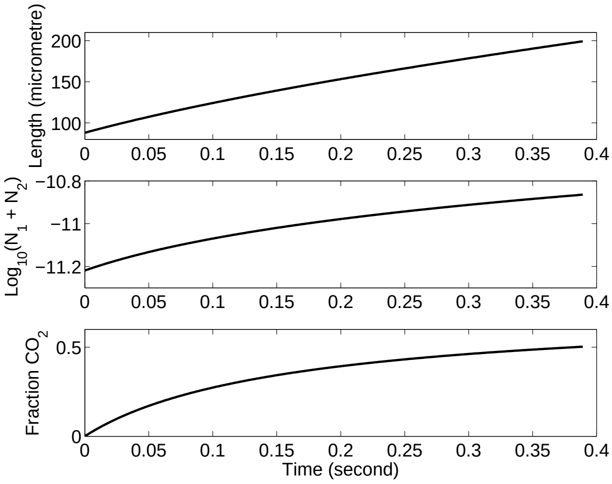

Fig. 6. Numerical solutions of equations (7) and (8).

As can be seen from Fig. 4, there are 23 maxima each corresponding to a bubble detaching. This gives a bubbling rate of 0.8 bubbles per second. The numerical results shown in Fig. 6 gives a bubbling rate of approximately 2 bubbles per second. The difference here may be due to a number of factors. Our simulations assume that the partial pressures of nitrogen and carbon dioxide are $3\,\mathrm{bar}$ and $0.8\,\mathrm{bar}$ respectively. In reality, the process of opening the can and allowing the stout to be exposed to the atmosphere suggests that the actual values of these parameters could be significantly less. Also in question is the parameter λ measured by [1] on a fibre of a much smaller radius using carbon dioxide. The width of the boundary layer λ around the fibre may be much larger then we have used here.

V. CONCLUSION

Using a mathematical model, it has been predicted that cellulose fibres can be used to nucleate bubbles in stout beers containing a mixture of carbon dioxide and nitrogen. This model can be used to predict the rate of bubbles produced for different parameters such as the radius of the fibre. The production of bubbles is also verified experimentally and the videos are analysed to give the bubble production rate. It is also observed from Fig. 5 that the bubble appears to undergo a Plateau Rayleigh type instability just before it detaches. This could be of use in more accurately modelling bubble detachment.

REFERENCES

[1] G. Liger-Belair, C. Voisin, and P. Jeandet, “Modeling nonclassical heterogeneous bubble nucleation from cellulose fibers: Application to bubbling in carbonated beverages,” *J. Phys. Chem. B*, vol. 109, pp. 14 573–14 580, 2005.

[2] G. Liger-Belair, M. Vignes-Adler, C. Voisin, B. Robillard, and P. Jeandet, “Kinetics of gas discharging in a glass of champagne: The role of nucleation sites,” *Langmuir*, vol. 18, pp. 1294–1301, 2002.

[3] G. Liger-Belair, D. Topgaard, C. Voisin, and P. Jeandet, “Is the wall of a cellulose fiber saturated with liquid whether or not permeable with CO2 dissolved molecules? Application to bubble nucleation in champagne wines,” *Langmuir*, vol. 20, pp. 4132–4138, 2004.

[4] S. Jones, G. Evans, and K. Galvin, “Bubble nucleation from gas cavities - a review,” *Advances In Colloid And Interface Science*, vol. 80, no. 1, pp. 27–50, FEB 28 1999.

[5] C. W. Bamforth, “The relative significance of physics and chemistry for beer foam excellence: Theory and practice,” *Journal of the Institute of Brewing*, vol. 110, pp. 259–266, 2004.

[6] O. A. Power, W. T. Lee, A. C. Fowler, P. J. Dellar, L. W. Schwartz, S. Lukaschuk, G. Lessells, A. F. Hegarty, M. O'Sullivan, and Y. Liu, "The initiation of Guinness," in *Proceedings of the Seventieth European Study Group with Industry*, S. B. G. O'Brien, M. O'Sullivan, P. Hanrahan, W. T. Lee, J. Mason, J. Charpin, M. Robinson, and A. Korobeinikov, Eds., 2009, pp. 141–182.

[7] W. T. Lee, J. S. McKechnie, and M. G. Devereux, "Bubble nucleation in stout beers," *arXiv:1103.0508 Accepted by Physical Review E*, 2011.

[8] G. Liger-Belair, G. Polidori, and P. Jeandet, "Recent advances in the science of champagne bubbles," *Chem Soc Rev*, vol. 37, pp. 2490–2511, 2008.