

PROVING OF BREAD DOUGH: MODELLING THE GROWTH OF INDIVIDUAL BUBBLES

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Proving of bread dough was modelled using classical one-component diffusion theory, to describe the rate of growth of bubbles surrounded by liquid dough containing dissolved carbon dioxide. The resulting differential equation was integrated numerically to predict the effect of initial bubble size and system parameters (carbon dioxide concentration, surface tension at the bubble interface, temperature) on bubble growth. Two situations exist, potentially; the dough could be either supersaturated or subsaturated with carbon dioxide. When the dough is supersaturated, the model predicts a critical bubble size above which bubbles grow indefinitely, while below the critical bubble size bubbles reach a limiting size and stop growing. The critical bubble size decreases with increasing carbon dioxide concentration and increases with increasing surface tension. Below saturation, all bubbles reach an upper size limit proportional to their initial size. The final bubble size increases with carbon dioxide concentration and decreases with increasing surface tension. Higher temperatures increase the rate of bubble growth and reduce the critical bubble size for supersaturated doughs, by increasing the value of Henry's Law constant. Higher temperatures also increase the final bubble size for subsaturated systems. The model could be extended to include yeast kinetics and entire bubble size distributions, to develop a full simulation of the proving operation.

Keywords: diffusion; bubble growth; bread dough proving

INTRODUCTION

Breadmaking can be viewed as a series of aeration stages, in which bubbles are incorporated during mixing, inflated with carbon dioxide gas during proving, and the aerated structure modified and set by baking¹. This view of breadmaking emphasizes the physics of the process, in contrast to the emphasis on cereal chemistry which dominates most baking research. This offers a different perspective on breadmaking which encourages new approaches to studying and improving this unique food.

In modern processes such as the Chorleywood Bread-making Process (CBP), the state of aeration at the end of mixing is critical to baked loaf structure and texture¹. However, although mixing is arguably the most critical stage in Mechanical Dough Development (MDD) processes, affecting dough development and aeration, the proving stage is still the heart of all processes to make raised bread. Proving is the link between the state of the dough ex-mixer, and the final baked loaf quality. Understanding how aeration during mixing affects bread quality requires a knowledge therefore of how the bubbles in the dough grow and change during proving.

Proving expands the original bubble structure to give a dough mass which is predominantly gas. Baking then converts the foam structure (containing discrete bubbles) into a sponge structure (containing a continuous porous network of interconnected gas cells). See Bloksma^{2,3}

for reviews of mixing, proving and baking. Bubble growth during proving is influenced by four factors:

- (1) the rate of carbon dioxide production by yeast;
- (2) the extent to which the carbon dioxide is retained within the dough piece;
- (3) the rate of carbon dioxide diffusion from the (saturated) liquid phase into the nitrogen nuclei; and
- (4) the rate of bubble coalescence.

The first two of these factors are concerned with the gross, macroscopic gas behaviour, while the latter two focus on individual bubbles. The rate of carbon dioxide production by yeast has been studied extensively^{4,5,6}, along with the extent of gas retention⁵⁻¹¹; the latter depends on flour quality and is affected by ingredients such as emulsifiers. Bubble coalescence is difficult to observe and quantify in opaque doughs and has remained essentially unstudied.

Diffusion of gas into bubbles, the third factor listed above, is a classical chemical engineering problem. Using diffusion theory to model the changing bubble size distribution during proving can provide insights into this process and its relation to aeration during mixing. Earlier workers have modelled the shrinkage (due to gas dissolution) and growth (due to temperature rise) of bubbles in water and unyeasted doughs^{12,13}, and bubble growth during baking² and in starchy systems during extrudate expansion¹⁴. Gan *et al*¹⁵, reviewing gas cell stabilization in bread doughs, described qualitatively the physical system of

bubble growth during proving due to CO₂ diffusion. During proving, gas cells are stabilized by the gluten network and by the surface-active materials in the thin liquid film at the gas-dough interface (which include proteins, polar lipids and synthetic surfactants)¹⁵. Fat crystals also aid gas retention during proving, and more particularly during baking^{15–17}.

The current study applies diffusion theory to the growth of individual bubbles in bread doughs, in order to investigate the influence of initial diameter and system conditions on subsequent growth. The model is applicable to the early stages of proving i.e. while bubbles are still sufficiently small not to be distorted by the presence of other bubbles. The model also applies to slow bubble growth, as is the case during proving; in this case the viscoelastic nature of the dough rheology is incidental, at least during the early stages of proving before the gluten network is stretched significantly, as the dough is able to undergo viscous flow in response to bubble growth over the time scales involved. In this respect the model differs from models of rapid bubble growth resulting from thermal expansion or evaporation of water into steam during baking or extrusion, as modelled by other workers^{2,13,14}. The model developed below could also be applied to chemical leavening of cakes, although in this case rising takes place simultaneously with baking, and the timescales involved are shorter.

MATHEMATICAL MODELLING

Model of the Growth of a Bubble in Dough

Dough mixing entrains bubbles which act as nucleation sites into which CO₂ diffuses during proving¹⁸. Consider a single bubble in a continuous dough phase containing dissolved CO₂, as shown in Figure 1. The bubble is assumed to be spherical with diameter D and at a total pressure P_b . The total pressure in the dough is P_∞ , which is less than the pressure in the bubble because of surface tension^{2,15,19}. The dissolved solute (CO₂) concentration in the dough is C_∞ , which is assumed to be uniform. The mass transfer resistance within the bubble is assumed to be negligible, so that C^* is the solute concentration that would be in equilibrium with the solute partial pressure in the bubble.

Initially, when $D = D_0$, there is nitrogen but no CO₂ in the bubble, so a concentration driving force for mass transfer exists allowing CO₂ to diffuse into the bubble, causing the bubble to grow. The following model describes the rate of growth, by considering the rate of mass transfer into the bubble, Q , in two ways. Firstly, the rate of mass transfer is described in terms of its effect on the number of moles of gas present, n , and thus bubble size:

$$Q = \frac{dn}{dt} = f\left(\frac{dD}{dt}\right) \quad (1)$$

Secondly, Q is described in terms of the mass transfer coefficient and concentration driving force for mass transfer using classical diffusion theory. These two equations for Q are then equated, and rearranged to give an expression for the rate of change of bubble size, dD/dt , in terms of CO₂ concentration and other system parameters.

The total pressure inside the bubble of diameter D is P_b and the surface tension is γ . The surface tension causes the internal bubble pressure to be raised above the pressure in

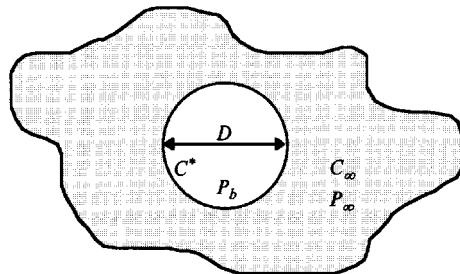


Figure 1. A bubble surrounded by dough containing dissolved carbon dioxide.

the liquid, as given by the Young-Laplace equation:

$$P_b = P_\infty + \frac{4\gamma}{D} \quad (2)$$

(A term to account for the yield stress of the dough could be included; however the major contribution to the excess pressure in the bubbles is surface tension².)

The bubble has grown from a nitrogen nucleus of diameter D_0 , which contains n_0 moles of nitrogen. From the ideal gas law:

$$n_0 = \frac{P_{b_0} V_0}{RT} = \frac{(P_\infty + 4\gamma/D_0)\pi D_0^3}{6RT} \quad (3)$$

since

$$P_{b_0} = P_\infty + \frac{4\gamma}{D_0} \quad (4)$$

Nitrogen is assumed not to diffuse into the dough phase, so that the bubble always contains n_0 moles of nitrogen. For a bubble of diameter D containing a total of n moles of gas:

$$n = \frac{(P_\infty + 4\gamma/D)\pi D^3}{6RT} \quad (5)$$

The molar rate of mass transfer can also be expressed as the rate of change of the number of moles with time, dn/dt :

$$Q = \frac{dn}{dt} = \frac{\pi D^2}{6RT} \left(3P_\infty + \frac{8\gamma}{D} \right) \frac{dD}{dt} \quad (6)$$

This gives the first expression for the mass transfer rate, Q , in terms of the rate of change of bubble size, dD/dt .

The mass transfer rate, Q , into a single bubble can now also be described in terms of the standard mass transfer equation:

$$Q = K_L(\pi D^2)(C_\infty - C^*) \quad (7)$$

where C^* is the concentration of carbon dioxide in the dough that would be in equilibrium with the partial pressure of carbon dioxide in the bubble, K_L is the overall mass transfer coefficient and (πD^2) is the surface area of a sphere of diameter D .

From the two film theory of mass transfer at a gas-liquid interface²⁰:

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{RT}{Hk_G} \quad (8)$$

where k_L and k_G are the individual mass transfer coefficients for the liquid and gas phases, respectively. Assuming mass

transfer is liquid side controlled (i.e. H is relatively large), then

$$K_L \approx k_L \quad (9)$$

For pure diffusion²⁰:

$$Sh = \frac{k_L D}{\mathcal{D}} = 2 \quad (10)$$

where Sh is the Sherwood number and \mathcal{D} the diffusivity of carbon dioxide in dough. Therefore equation (7) becomes:

$$Q \approx 2\mathcal{D}(\pi D)(C_\infty - C^*) \quad (11)$$

Before equating this expression with equation (6) an expression for C^* is needed. This may be found by considering the partial pressure of carbon dioxide in the bubble, $P_b^{\text{CO}_2}$. From equations (3) and (5):

$$P_b^{\text{CO}_2} = \left(\frac{n - n_o}{n}\right)P_o = \frac{P_\infty(D^3 - D_o^3) + 4\gamma(D^2 - D_o^2)}{D^3} \quad (12)$$

Assuming Henry's Law for dilute concentrations of solute:

$$C^* = \frac{P_b^{\text{CO}_2}}{H} = \frac{P_\infty}{H} \left[1 - \left(\frac{D_o}{D}\right)^3 \right] + \frac{4\gamma}{HD} \left[1 - \left(\frac{D_o}{D}\right)^2 \right] \quad (13)$$

Equating equations (6) and (11) for Q and rearranging gives the final expression for the rate of change of bubble diameter, dD/dt :

$$\frac{dD}{dt} = \frac{12RT\mathcal{D}_L(C_\infty - C^*)}{3P_\infty D + 8\gamma} \quad (14)$$

where C^* is given by equation (13).

This model predicts the rate of change of bubble diameter for a single spherical bubble into which carbon dioxide is diffusing from the surrounding dough. The model assumes that the values of C_∞ , P_∞ and H are constant over time, and that the dough phase behaves as an infinitely large region of constant CO_2 concentration. The model does not need to consider dough rheology, as surface tension predominates over rheology in affecting the pressure in bubbles during proving², and bubbles will grow as described above if a suitable mass transfer driving force exists (the dough will simply move in response to the bubble growth).

Values for Physical Constants

The values used for the physical constants required to integrate equation (14) are given in Table 1. Proving occurs

typically at 40°C for around 45 minutes, and dough typically contains around 40% water.

The constant in Henry's law was taken for a carbon dioxide-in-dough system². The value for surface tension and solute concentration in dough were also taken from the literature. The mass diffusivity coefficients were calculated after the method of de Cindio and Corra²¹ who assumed that carbon dioxide diffuses through the water present in dough and approximated the diffusion coefficient through the dough phase as a fraction of the diffusion coefficient of carbon dioxide in water:

$$\mathcal{D} = 1.77 \times 10^{-9} X_W \left(\frac{T}{298} \right) \quad (15)$$

Assuming that the mass fraction of water, $X_W = 0.4$ and that proving takes place at 313 K (40°C) gives $\mathcal{D} = 7.44 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

In the initial studies presented below, the value for the carbon dioxide concentration in the dough was chosen to be $C_\infty = 0.031 \text{ kmol m}^{-3}$, indicating a slightly supersaturated solution (in a real dough this situation could occur once the dough phase becomes saturated if CO_2 production exceeds diffusion into bubbles and loss of CO_2 to atmosphere). Saturation occurs when $C_\infty = P_\infty/H = 0.0303 \text{ kmol m}^{-3}$. The effect of CO_2 concentration on bubble growth is discussed below. For this modelling, bubble sizes in the range 0 to 300 μm were considered (the number average bubble size in a dough ex-mixer is around 100 μm ^{1,23}, with a range from below 40 μm to above 400 μm ²³).

RESULTS AND DISCUSSION

Modelling the Growth of Single Bubbles in Dough Supersaturated with Carbon Dioxide

From this model of the growth of a single bubble in yeasted dough, a FORTRAN 77 program was written to predict the growth of a bubble with a given initial diameter. The program used a 5th-order Runge-Kutta algorithm²⁴ with adaptive step-size control to integrate equation (14) over time for different initial bubble diameters, for the conditions defined in Table 1.

Figure 2 shows the predicted bubble growth over a 50 minute proving time for the conditions given in Table 1. Under these conditions of slight supersaturation, a critical bubble size exists below which bubbles stop growing; bubbles of 9.0 μm cease growing when they reach about 32 μm , while 10 μm bubbles continue to grow indefinitely.

Table 1. Values for physical parameters used in modelling growth of bubbles in dough.

Parameter	Value	Reference
Carbon dioxide concentration in dough, C_∞	Varied: 0.029–0.033 kmol m^{-3}	
Diffusivity of carbon dioxide in dough, \mathcal{D}	$7.44 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$	de Cindio and Corra ²¹
Henry's Law constant, H	$3.30 \times 10^6 \text{ J kmol}^{-1}$	Bloksma ²
Ambient pressure in dough, P_∞ (ignoring hydrostatic pressures)	100,000 Pa	
Universal gas constant, R	$8314 \text{ J kmol}^{-1} \text{ K}^{-1}$	
Proving temperature, T	313 K	
Surface tension, γ	0.04 N m^{-1}	Kokelaar and Prins ²²

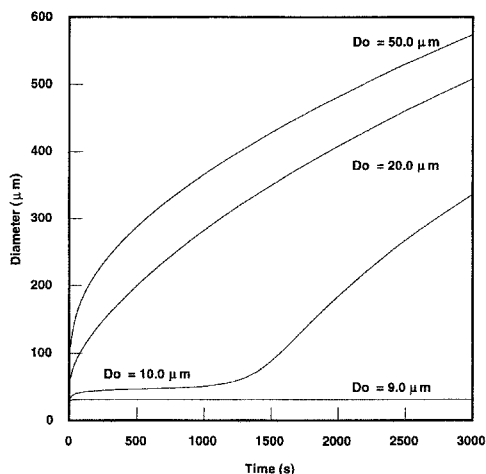


Figure 2. Influence of the initial diameter (D_o) on subsequent bubble growth, as predicted by integrating equation (14), showing how a small change in bubble size from 9 to 10 μm affects long term growth. $P_\infty = 100 \text{ kPa}$, $\gamma = 0.04 \text{ N m}^{-1}$, $C_\infty = 0.031 \text{ kmol m}^{-3}$ (slightly super-saturated).

Calculation of the Critical Bubble Size

Bubbles stop growing because the partial pressure of carbon dioxide inside the bubble balances the carbon dioxide concentration in the dough i.e. $C^* = C_\infty$. Large bubbles never stop growing; this means C^* never reaches C_∞ . As bubbles grow, C^* increases initially (it must do, as CO_2 is entering the bubble), then it decreases again later (again, it must do, as C^* is proportional to $P_b^{\text{CO}_2}$, which decreases at large diameter as diameter increases, according to equation (12)). Therefore, as bubbles grow, C^* and $P_b^{\text{CO}_2}$ pass through a maximum. But if C^* reaches C_∞ , then the bubble will stop growing. So the initial bubble size for which this maximum corresponds to $C^* = C_\infty$ is the critical bubble size; this is the bubble size which is *just* small enough for C^* to reach C_∞ and stop growing. This can be calculated by differentiating equation (12) and setting the differential to zero, and solving to find the diameter at which the partial pressure of CO_2 is at a maximum. From this C_{max}^* can be calculated; the critical bubble size occurs when C_{max}^* and C_∞ are equal. The derivation is as follows:

$$\frac{dP_b^{\text{CO}_2}}{dD} = \frac{3P_\infty D_o^3 - 4\gamma D^2 + 12\gamma D_o^2}{D^4} = 0 \quad (16)$$

Therefore, setting D_o^* as the critical initial bubble size and D^* as the corresponding final diameter, gives:

$$P_\infty D_o^{*2} + 4\gamma D_o^{*2} - \frac{4}{3}\gamma D^{*2} = 0 \quad (17)$$

This gives one equation and two unknowns; another equation relating the initial and final bubble diameters is needed. This is provided by equation (13), as when the bubble initially of diameter D_o^* reaches D^* and stops growing, then $C^* = C_{\text{max}}^* = C_\infty$:

$$C_{\text{max}}^* = \frac{P_\infty}{H} \left[1 - \left(\frac{D_o^*}{D^*} \right)^3 \right] + \frac{4\gamma}{HD^*} \left[1 - \left(\frac{D_o^*}{D^*} \right)^2 \right] = C_\infty \quad (18)$$

Rearranging equation (18) gives:

$$P_\infty D_o^{*3} + 4\gamma D_o^{*2} - [P_\infty - HC_\infty] D^{*3} - 4\gamma D^{*2} = 0 \quad (19)$$

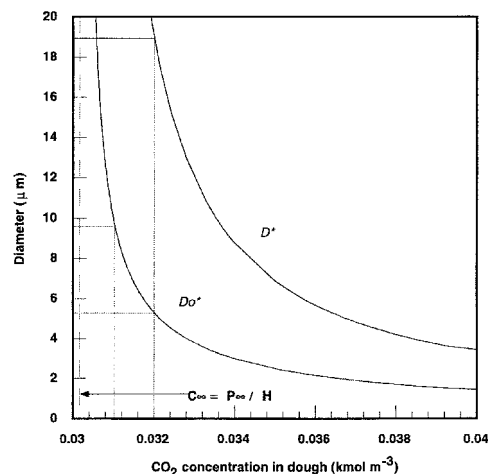


Figure 3. Critical initial bubble size, D_o^* for different solute concentrations in the dough. The corresponding final bubble size, D^* , is also shown. $P_\infty = 100 \text{ kPa}$, $\gamma = 0.04 \text{ N m}^{-1}$.

Equations (17) and (19) can be solved simultaneously to give the following equation for D^* :

$$D^* = \frac{8\gamma}{3[HC_\infty - P_\infty]} \quad (20)$$

which can be substituted back into equation (17) to solve for D_o^* . Figure 3 shows the relationship between D_o^* , D^* and C_∞ . For the conditions modelled above (CO_2 concentration = $0.031 \text{ kmol m}^{-3}$), $D_o^* = 9.6 \mu\text{m}$ and $D^* = 46.4 \mu\text{m}$. For a CO_2 concentration in the dough of $0.032 \text{ kmol m}^{-3}$, $D_o^* = 5.5 \mu\text{m}$ and $D^* = 19.0 \mu\text{m}$, i.e. at greater levels of supersaturation, smaller bubbles can be forced to grow.

Clearly, when $P_\infty = HC_\infty$, equation (20) has no solution, and when $P_\infty > HC_\infty$, a meaningless negative solution for D^* results. So a critical initial bubble size exists only when $P_\infty < HC_\infty$, i.e. when the dough is supersaturated with carbon dioxide. This is indicated on Figure 3 by the fact that the curve of D_o^* versus C_∞ approaches $C_\infty = P_\infty / H = 0.0303 \text{ kmol m}^{-3}$ asymptotically.

Potentially two situations exist; the dough could be

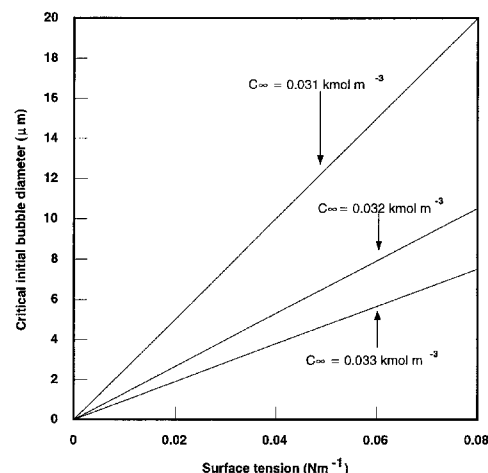


Figure 4. Effect of surface tension γ on the critical bubble size D_o^* for C_∞ above saturation.

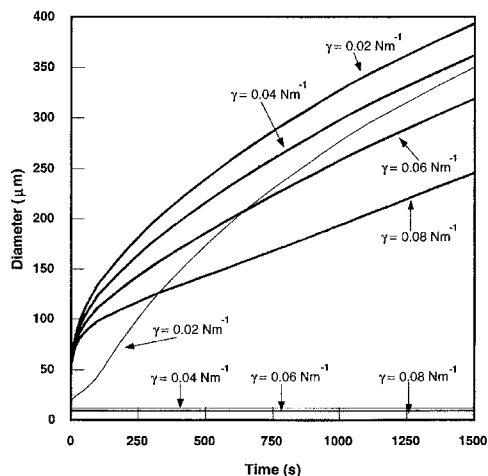


Figure 5. Effect of surface tension on the growth of bubbles and the critical bubble size. $C_{\infty} = 0.031 \text{ kmol m}^{-3}$, $P_{\infty} = 100000 \text{ Pa}$, — $D_o = 5 \mu\text{m}$, — $D_o = 25 \mu\text{m}$.

supersaturated or subsaturated with carbon dioxide. Subsaturations will occur in a dough at least during the early stages of proving. Supersaturation could arise when the rate of CO_2 production by yeast exceeds the rate of diffusion into gas bubbles and loss to atmosphere; whether this situation is reached within the 50 minutes of proving has not been established (see later discussion). Under conditions of supersaturation, a critical initial bubble size exists below which bubbles are unable to grow indefinitely. The greater the level of supersaturation, the smaller the critical bubble size, as illustrated in Figure 3. The growth of bubbles in dough not saturated with CO_2 is considered below. First, the effect of surface tension on the critical bubble size is considered.

From equation (24), if the surface tension, γ , is zero, then the solution to the equation is $D^* = 0$ and no critical bubble size exists. Figure 4 shows the effect of surface tension and C_{∞} on the critical bubble size. As surface tension decreases, the pressure inside the bubble decreases. Therefore the partial pressure of CO_2 decreases, allowing smaller bubbles to grow for a given value of C_{∞} . Figure 4 also confirms the conclusion noted above, that larger values of C_{∞} produce smaller critical bubble sizes.

Figure 5 shows the effect of surface tension on bubble growth for two bubble sizes. For a bubble initially of $5.0 \mu\text{m}$, a change in γ from 0.04 to 0.02 Nm^{-1} has the effect of lowering the critical bubble size, allowing the bubble to grow indefinitely.

Modelling the Growth of Single Bubbles in Dough Not Saturated With Carbon Dioxide

If C_{∞} is below saturation, a critical bubble size does not exist; all bubbles grow, but none grows indefinitely. Figure 6 shows, for $C_{\infty} = 0.030 \text{ kmol m}^{-3}$, that all bubbles, regardless of their initial size, approach an upper size limit. The final bubble size, D^* , is only reached after very long time scales, in excess of 3 hours (*c.f.* typical proving times of 45 minutes).

The final bubble size depends on C_{∞} and γ , as shown in Figure 7, which summarizes the effects of C_{∞} and γ both above and below saturation. Below saturation, the final

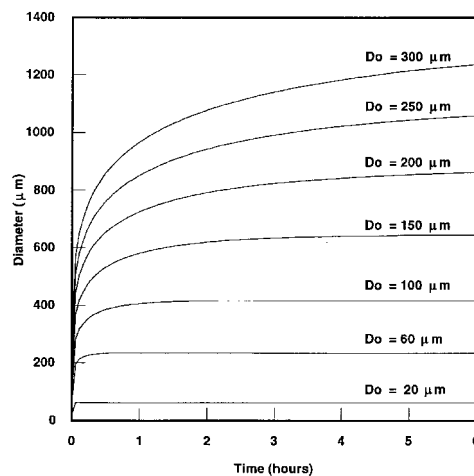


Figure 6. Bubble growth for different initial bubble sizes under subsaturated conditions. $C_{\infty} = 0.030 \text{ kmol m}^{-3}$, $P_{\infty} = 100 \text{ kPa}$, $\gamma = 0.04 \text{ Nm}^{-1}$.

bubble size, D^* , increases as C_{∞} increases. When C_{∞} exceeds saturation, no final bubble size exists, except for bubbles below the critical initial bubble size. Larger values of C_{∞} reduce the critical bubble size, as smaller bubbles can be forced to grow by the larger concentration driving force. Reducing surface tension increases the final bubble size when $C_{\infty} < C_{\text{sat}}$, and reduces the critical bubble size when $C_{\infty} < C_{\text{sat}}$, by reducing the pressure inside bubbles and therefore the partial pressure of carbon dioxide.

The final bubble size can be calculated for large initial bubble diameters by assuming the surface tension contribution to C^* is negligible. From equation (18), growth will cease when $C^* = C_{\infty}$:

$$C^* = \frac{P_{\infty}}{H} \left[1 - \left(\frac{D_o}{D} \right)^3 \right] + \frac{4\gamma}{HD} \left[1 - \left(\frac{D_o}{D} \right)^2 \right] \approx \frac{P_{\infty}}{H} \left[1 - \left(\frac{D_o}{D} \right)^3 \right] = C_{\infty} \quad (21)$$

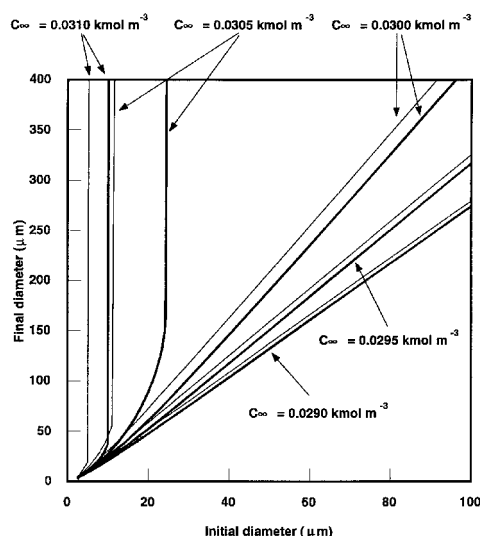


Figure 7. Effect of carbon dioxide concentration in the dough, C_{∞} , and surface tension, γ , on the final bubble diameter. — $\gamma = 0.02 \text{ Nm}^{-1}$, — $\gamma = 0.04 \text{ Nm}^{-1}$.

when $D = D^*$. Therefore

$$D^* \approx 3 \sqrt{\frac{P_\infty}{P_\infty - HC_\infty}} D_0 \quad (22)$$

The slopes of the upper parts of the lines of D^* versus D_0 in Figure 7 are equal to:

$$3 \sqrt{\frac{P_\infty}{P_\infty - HC_\infty}},$$

for $C_\infty = 0.0290, 0.0295$ and $0.0300 \text{ kmol m}^{-3}$. When $P_\infty \leq HC_\infty$ (i.e. the solution is saturated or supersaturated), equation (22) has no positive real solution, and no final bubble size exists; bubbles continue to grow indefinitely. This is shown on Figure 7 by the slopes becoming infinite above the critical bubble size for $C_\infty > 0.0303 \text{ kmol m}^{-3}$.

Considering the range of initial bubble sizes reported by Campbell *et al.*²³, from below 40 to above 400 μm , all of these bubbles will grow, but not indefinitely if supersaturation is not achieved. If a final CO_2 concentration of $0.0300 \text{ kmol m}^{-3}$ were achieved, bubbles initially of 40 μm would reach around 150 μm , and bubbles of 400 μm initially would reach about 1800 μm .

Effect of Temperature On Bubble Growth

If proving were to take place at higher or lower temperatures than 313 K, then bubble growth would be affected. As T increases, H also increases², i.e. CO_2 is less soluble at higher temperatures, which has the effect of reducing C^* . Equation (14) shows that if T increases and $(C_\infty - C^*)$ increases, then dD/dt also increases; this is borne out by Figure 8. Furthermore, raising the temperature decreases D_0^* , since according to Henry's Law, increasing H reduces C^* . This increases the concentration driving force for diffusion, allowing even smaller bubbles to grow. Equation (22) shows that for systems below saturation, raising the temperature increases H and therefore $(P_\infty - HC_\infty)$ decreases. Thus the ratio $P_\infty / (P_\infty - HC_\infty)$ becomes larger, increasing D^* , so higher temperatures tend to produce larger final bubble sizes.

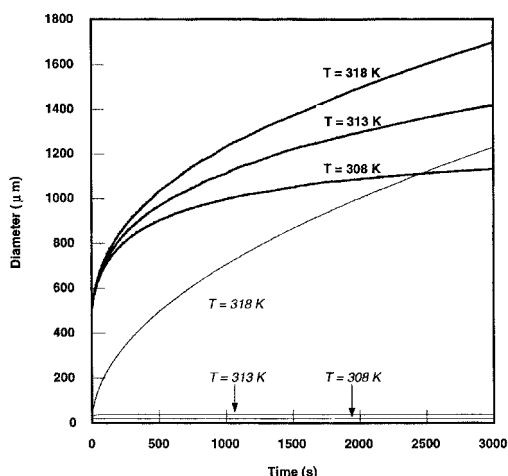


Figure 8. Effect of temperature, T , on bubble growth. $C_\infty = 0.031 \text{ kmol m}^{-3}$, $\gamma = 0.04 \text{ Nm}^{-1}$, — $D_0 = 10 \mu\text{m}$, — $D_0 = 500 \mu\text{m}$.

Qualitative Description of Proving

The above discussion gives useful indications about how initial bubble size and system parameters should affect bubble growth. The real situation during proving is that initially the dough is essentially free of dissolved carbon dioxide. The yeast produces carbon dioxide at a rate of around $2.5 \times 10^{-5} \text{ kmol gas per m}^3 \text{ liquid dough phase per second}^2$; to reach a saturated concentration of $0.0303 \text{ kmol m}^{-3}$ would therefore take around 20 minutes, ignoring transfer of CO_2 into bubbles or loss to atmosphere. So for at least the first half of proving, the dough is not saturated; all bubbles are below the critical bubble diameter during this time, and no bubbles are destined to grow indefinitely unless supersaturation is achieved. Whether or not supersaturation is ever achieved depends on whether the rate of CO_2 production by the yeast ultimately exceeds the rate of mass transfer into bubbles and to atmosphere. Resolution of this question will require a more fully developed application of the above model to consider the growth of entire bubble size distributions, along with yeast kinetics and losses of carbon dioxide to atmosphere.

In a dynamic system containing a distribution of bubbles, bubbles are competing for the available CO_2 . Large bubbles have the advantage that they have lower pressures and therefore a greater driving force for mass transfer, but smaller bubbles have greater mass transfer coefficients, as indicated by equations (9) and (10). Also, smaller bubbles tend to be more numerous. One can envisage a complex and interesting situation in which small bubbles initially grow quickly, with larger bubbles maintaining their growth over the longer term.

Mita and Matsumoto²⁵ studied bubble growth in fermenting doughs by photographing the exposed surfaces of freeze-dried dough samples. They found that the number of visible bubbles increased during the first 20 minutes of proving, but that their size increased only slowly during this time. Beyond 20 minutes, bubble growth accelerated, and bubbles started to coalesce after about 50 minutes. This may reflect the initial rapid growth of small bubble nuclei, such that these became visible, taking up much of the available CO_2 , while larger bubbles grew only slowly. Once the supply of nitrogen nuclei was exhausted, the pressure advantage of the larger bubbles dominated, so that these showed more rapid growth for the remaining time. Again, modelling of the growth of entire bubble size distributions should demonstrate this phenomenon.

CONCLUSIONS

Bubble growth during proving of bread dough can be modelled in terms of classical diffusion theory. The resulting differential equation can be integrated numerically to reveal insights into how bubble growth is likely to be affected by bubble size, surface tension and other system conditions.

Two situations can exist in theory; the dough can be supersaturated or subsaturated with carbon dioxide. When the dough is supersaturated, a critical bubble size exists; above the critical bubble size, bubbles continue to grow indefinitely, while below the critical bubble size bubbles stop growing due to the carbon dioxide concentration in the bubble and in the dough reaching equilibrium. The critical

bubble size depends on the degree of supersaturation and the value of the surface tension at the bubble interface.

At carbon dioxide concentrations below saturation, all bubbles eventually reach an upper limit, albeit over timescales, much longer than typical proving times. The final bubble size is approximately proportional to the initial bubble size. Higher dissolved carbon dioxide concentrations in the dough increase the final bubble size, while larger values of the surface tension decrease the final bubble size. Higher temperatures increase the rate of bubble growth and decrease the critical bubble size, due to the dependency of Henry's Law constant on temperature.

Real dough systems are not saturated with carbon dioxide for at least the first half of proving, and possibly never reach saturation. Bubbles compete for the available carbon dioxide, and the final bubble size distribution will depend on the degree of saturation of carbon dioxide achieved and the relative extent of mass transfer of carbon dioxide into bubbles of different sizes within the time available.

The model could be applied to entire bubble size distributions, and could be extended to incorporate yeast kinetics, loss of carbon dioxide to atmosphere and spatial variations throughout a proving dough. This is the subject of future work.

NOMENCLATURE

C^*	solute concentration at interface, kmol m^{-3}
C_{max}^*	maximum solute concentration at interface, kmol m^{-3}
C_{∞}	solute concentration in dough, kmol m^{-3}
D_o	initial bubble diameter, μm
D_o^*	critical initial bubble diameter, μm
D	bubble diameter, μm
D^*	final bubble diameter corresponding to critical initial bubble diameter, μm
\mathcal{D}	coefficient of diffusivity, $\text{m}^2 \text{s}^{-1}$
H	Henry's Law constant, J kmol^{-1}
k_G	gas phase mass transfer coefficient, $\text{m}^2 \text{s}^{-1}$
k_L	liquid phase mass transfer coefficient, $\text{m}^2 \text{s}^{-1}$
K_L	overall mass transfer coefficient, $\text{m}^2 \text{s}^{-1}$
n	number of moles of nitrogen in a bubble, kmol
n_o	initial number of moles of nitrogen in a bubble, kmol
P_b	solute pressure in bubble, Pa
$P_{b\text{CO}_2}$	initial solute pressure in bubble, Pa
P_b	partial pressure of carbon dioxide in bubble, Pa
P_{∞}	solute pressure in dough, Pa
Q	molar rate of transfer, kmol s^{-1}
R	universal gas constant, $\text{J kmol}^{-1} \text{K}^{-1}$
Sh	Sherwood number
t	time, s
T	absolute temperature, K
V_o	initial bubble volume, m^3
X_w	mass fraction of water in dough
γ	surface tension, N m^{-2}

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