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Bubble growth in a variable diffusion coefficient liquid

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Abstract

A model for the mass-transfer-controlled spherical bubble growth in a quiescent liquid is presented. The liquid is of variable diffusion coefficient, which depends exponentially on the concentration. Using the method presented in Scriven [L.E. Scriven, On the dynamics of phase growth, Chem. Eng. Sci. 10 (1959) 1–13], for a constant diffusion coefficient liquid, the differential binary mass balance was transformed into an ordinary differential equation, trough a similarity transformation, which was numerically solved. The final results were also compared with approximately analytical solutions, for slow and fast growth rates, developed by Polyanin and Dil'man [A.D. Polyanin, V.V. Dil'man, The method of the 'carry over' of integral transforms in non-linear mass and heat transfer problems, Int. J. Heat Mass Trans. 33 (1990) 175–181] and by the authors. © 1998 Elsevier Science S.A.

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1. Introduction

Polymer melt devolatilization is an industrial process in which low concentrations of volatile components (unreacted monomers, solvents, water) are removed from the polymer melt. This process, which is conducted at superheated conditions for the volatile components (high temperatures and low pressures), results in the formation and growth of bubbles [1,2].

The large number of models for bubble growth presented in the literature were developed for the case in which the liquid had a constant diffusion coefficient. However, it is well known that in a solvent–polymer system, the diffusion coefficient is not constant and it depends on the solvent concentration. Furthermore, at solvent concentrations lower than 10%, the diffusion coefficient may change by several orders of magnitude [3].

In previous works, the growth of a spherical bubble in a quiescent liquid has been theoretically studied [4,5]. In their work it was assumed that the process was controlled by mass (or heat) transfer, and a similarity solution was found out under the assumption that the bubble radius changes as the square root of time. The present paper extends those theoretical works, and treats the case in which the liquid has a variable diffusion coefficient. Another approach to this problem is discussed by Shulman and Levitskiy [6].

2. Theory

A differential mass balance in a binary system assuming spherical symmetry, constant density, Fickian diffusion, but variable diffusion coefficient (D) is of the form

$$\frac{\partial c}{\partial t}+v_r\frac{\partial c}{\partial r}=D\frac{\partial^2 c}{\partial r^2}+\frac{2}{r}D\frac{\partial c}{\partial r}+\frac{\partial D}{\partial r}\frac{\partial c}{\partial r} \tag{1}$$

where c is the molar concentration of the solvent, t is the time and v_r is the radial velocity of the liquid, which is given approximately by

$$v_r=\left(\frac{R}{r}\right)^2\frac{\mathrm{d}R}{\mathrm{d}t} \tag{2}$$

where R is the radius of the bubble. Eq. (2) is valid when the density of the liquid is much greater than that of the bubble. The last two equations will be solved with the following boundary and initial conditions.

$$c=c_s \text{ at } r=R(t) \tag{3}$$

$$c=c_\infty \text{ at } r=\infty \tag{4}$$

$$c=c_\infty \text{ at } t=0 \tag{5}$$

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In order to solve the problem, another boundary condition is required. Assuming that only the volatile component is present within the bubble, and that it acts as an ideal gas of constant density, then a mass balance over the volatile solvent in the bubble leads to

$$\frac{P_b}{R_g T}\frac{dR}{dt}=D_s\left(\frac{\partial c}{\partial r}\right)_{r=R} \tag{6}$$

where P_b is the constant pressure in the bubble, R_g is the universal gas constant, T is the absolute constant temperature in the bubble and D_s is the constant diffusion coefficient of the liquid at the bubble's surface.

We present here a solution based on Scriven's classical paper from 1959. First, it is assumed an expression for the change of the radius of the bubble with time

$$R(t)=2\beta\sqrt{D_s t} \tag{7}$$

where β is the dimensionless growth constant. Similarly to the case of constant diffusion coefficient, we are looking for a solution to Eqs. (1) and (2) of the form of $c^*=c^*(\eta)$, where c^* is a dimensionless concentration

$$c^*=\frac{c-c_s}{c_\infty-c_s} \tag{8}$$

and η is a dimensionless similarity variable given by

$$\eta=\frac{r}{2\sqrt{D_s t}} \tag{9}$$

The new variables transform Eq. (1) into an ordinary differential equation

$$\frac{d^2c^*}{d\eta^2}+\frac{1}{D^*}\frac{dD^*}{dc^*}\left(\frac{dc^*}{d\eta}\right)^2+2\left(\frac{\eta}{D^*}+\frac{1}{\eta}-\frac{\beta^3}{\eta^2 D^*}\right)\frac{dc^*}{d\eta}=0 \tag{10}$$

where $D^*=D/D_s$. It appears that the similarity variable, used for the case of constant diffusion coefficient, can also be used in the present case.

Diffusivity coefficients of a polymer–solvent system, at different solvent concentrations, were measured (for example) by Duda et al. [3]. For typical devolatilization systems (solvent concentrations < 10%), their results together with theoretical considerations can be approximated by

$$D^*=\exp(Ac^*) \tag{11}$$

where A is a dimensionless constant. According to the experiments and theory, the diffusivity coefficient increases with an increase in the solvent concentration. Therefore, for bubble growth ($c_\infty > c_s$), the dimensionless constant A should be positive. In general A depends on the solvent–polymer system and it is a strong function of the temperature [7]. Substituting Eq. (11) into Eq. (10) results in

$$\frac{d^2c^*}{d\eta^2}+A\left(\frac{dc^*}{d\eta}\right)^2+2\left[\frac{\eta}{\exp(Ac^*)}+\frac{1}{\eta}-\frac{\beta^3}{\eta^2\exp(Ac^*)}\right]\frac{dc^*}{d\eta}=0 \tag{12}$$

Eq. (12) has to be solved with the following conditions

$$c^*=0 \text{ at } \eta=\beta \tag{13}$$

$$c^*=1 \text{ at } \eta=\infty \tag{14}$$

Note that Eq. (3) transforms to Eq. (13), and Eqs. (4) and (5) transform to Eq. (14). The last boundary (Eq. (6)) may be written in a dimensionless form as

$$\beta=\frac{1}{2}\mathrm{Fm}\left(\frac{dc^*}{d\eta}\right)_\beta \tag{15}$$

where Fm is the 'foaming number' defined by

$$\mathrm{Fm}=\frac{R_g T(c_\infty-c_s)}{P_b} \tag{16}$$

Bubble growth is enhanced by increasing Fm, since large growth rates are obtained at high temperatures, low pressures and large concentrations differences.

A given system is characterized by two constant dimensionless numbers: Fm and A. After which the growth constant β can be evaluated from Eq. (12) together with Eqs. (13) and (14), in such a way that Eq. (15) is also satisfied. Finally the change of the radius of the bubble as a function of time is obtained from Eq. (7).

When the diffusion coefficient is constant ($A=0$), the solution of the problem is [5]

$$\mathrm{Fm}=2\beta^3\exp(3\beta^2)\int_\beta^\infty\frac{1}{x^2}\exp\left(-x^2-2\frac{\beta^3}{x}\right)dx \tag{17}$$

Some numerical values of Eq. (17) are given in Table 1. Scriven also presented asymptotic values for $\beta\to 0$ (slow growth rates)

$$\beta=\sqrt{\frac{\mathrm{Fm}}{2}} \tag{18}$$

and for $\beta\to\infty$ (fast growth rates)

$$\beta=\sqrt{\frac{3}{\pi}}\mathrm{Fm} \tag{19}$$

For the case of a variable diffusion coefficient liquid ($A\neq 0$), a complete analytical solution of the problem cannot be obtained. Some numerical results for the growth constant as a function of Fm and A, are listed in Table 2.

Table 1
Numerical values of the function β(Fm,0)

Fm	β(Fm,0)
0.001	0.0228
0.01	0.0753
0.1	0.273
1	1.32
10	10.2
100	98.2
1000	978

Table 2
Numerical values of the function $\beta(\mathrm{Fm},A)/\beta(\mathrm{Fm},0)$

Fm	$A=2$	$A=4$	$A=6$	$A=8$	$A=10$
0.001	1.78	3.63	8.10	19.1	46.3
0.01	1.76	3.56	7.91	18.6	45.0
0.1	1.71	3.38	7.40	17.2	41.4
1	1.61	3.00	6.25	14.0	32.9
10	1.54	2.67	5.18	10.9	24.4
100	1.52	2.60	4.94	10.2	22.3
1000	1.52	2.59	4.91	10.1	22.0

It is convenient to define an effective diffusion coefficient as follows

$$D^*_{\mathrm{eff}}=\left[\frac{\beta(\mathrm{Fm},A)}{\beta(\mathrm{Fm},0)}\right]^2 \tag{20}$$

With this definition, one can calculate the radius of the bubble as a function of time from Eq. (7), if D_s is substituted by D_{eff} and if β is substituted by Scriven's β given by Eq. (17).

2.1. Slow growth rates

At steady state and in the absence of a velocity field, Eq. (1) expresses only radial diffusion

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(Dr^2\frac{\mathrm{d}c}{\mathrm{d}r}\right)=0 \tag{21}$$

The solution of Eq. (21) together with Eqs. (3) and (4), and assuming the correlation given in Eq. (11) for the variable diffusion coefficient, results in

$$c^*=\frac{1}{A}\ln\left\{\exp(A)-[\exp(A)-1]\frac{R}{r}\right\} \tag{22}$$

The molar flux (N) of the volatile solvent from the liquid to the bubble is defined and derived from Eq. (22) to give

$$N=k(c_\infty-c_s)=D_s\left(\frac{\mathrm{d}c}{\mathrm{d}r}\right)_R$$
$$=D_s\left[\frac{\exp(A)-1}{A}\right]\left(\frac{c_\infty-c_s}{R}\right) \tag{23}$$

where k is mass transfer coefficient. The molar flux may be written dimensionlessly in terms of the Sherwood number (Sh) as

$$\mathrm{Sh}=\frac{kR}{D_s}=\frac{\exp(A)-1}{A} \tag{24}$$

Note that when the diffusion coefficient is constant ($A=0$) then $\mathrm{Sh}=1$. Rearranging Eq. (6), leads to an expression for the growth rate of the bubble

$$\frac{\mathrm{d}R}{\mathrm{d}t}=\mathrm{Fm\ Sh}\frac{D_s}{R} \tag{25}$$

Using a quasi-steady-state approach by substituting the steady-state solution (for the Sherwood number) into the equation for the unsteady-state (Eq. (25)), and integrating from $R=0$ at $t=0$ to $R=R$ at $t=t$, gives an asymptotic solution for slow growth rates

$$R(t)=\sqrt{2\left[\frac{\exp(A)-1}{A}\right]\mathrm{Fm}D_st} \tag{26}$$

or

$$\beta(\mathrm{Fm},A)=\sqrt{\frac{1}{2}\left[\frac{\exp(A)-1}{A}\right]\mathrm{Fm}} \tag{27}$$

or

$$\frac{\beta(\mathrm{Fm},A)}{\beta(\mathrm{Fm},0)}=\sqrt{\frac{\exp(A)-1}{A}} \tag{28}$$

Eq. (27) reduces to Eq. (18) when $A=0$. Eq. (28) is plotted in Fig. 1 and some numerical values of this equation are given in Table 3. By comparing Tables 2 and 3, one concludes that the approximation for slow growth rates is valid, in practice, when $\mathrm{Fm}<0.1$. Note also that the expression for the Sherwood number given in Eq. (24) is also the effective diffusion coefficient in this case.

2.2. Fast growth rates

When the growth rate of the bubble is very fast, one can imagine a thin shell concentration boundary layer which its thickness is much smaller than the radius of the bubble. In practice, this implies that the second term on the right hand

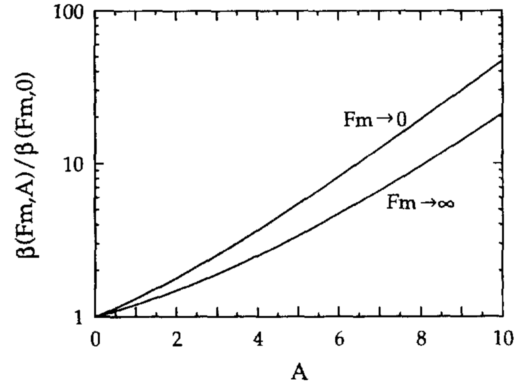

Fig. 1. The ratio $\beta(\mathrm{Fm},A)/\beta(\mathrm{Fm},0)$ as a function of A for the asymptotic cases of slow and fast growth rates according to Eqs. (28) and (43) respectively.

Table 3
Numerical values of the function $\beta(\mathrm{Fm},A)/\beta(\mathrm{Fm},0)$ for slow growth rates

A	$\beta(\mathrm{Fm},A)/\beta(\mathrm{Fm},0)$
2	1.79
4	3.66
6	8.19
8	19.3
10	46.9

side of Eq. (1) is neglected compared to the other two terms on that side.

It is also common to solve Eqs. (1) and (2) by using a Lagrangian transformation, defined (for example) by Plesset and Zwick [8] as follows

$$y=\frac{1}{3}[r^3-R^3(t)] \tag{29}$$

$$h=t \tag{30}$$

The new variables eliminate the convective term, and transform Eq. (1) into

$$\frac{\partial c^*}{\partial h}=D_sR^4(h)\left(D^*\frac{\partial^2 c^*}{\partial y^2}+\frac{\partial D^*}{\partial y}\frac{\partial c^*}{\partial y}\right) \tag{31}$$

Note that the expression on the left hand side is exact, while that on the right hand side is only an approximation close to the surface of the bubble. A similar approach has been applied by Plesset and Zwick [8] and by Barlow and Langlois [9] for the case of constant diffusion coefficient.

If the following function is introduced

$$g(h)=\int_0^h D_sR^4(x)\mathrm{d}x=\frac{16}{3}\beta^4D_s^3h^3 \tag{32}$$

then Eq. (31) is simplified to

$$\frac{\partial c^*}{\partial g}=\frac{\partial}{\partial y}\left(D^*\frac{\partial c^*}{\partial y}\right) \tag{33}$$

Eq. (33) has to be solved with Eqs. (3)–(5) which in the new coordinates transform to

$$c^*=0 \text{ at } y=0 \tag{34}$$

$$c^*=1 \text{ at } y=\infty \tag{35}$$

$$c^*=1 \text{ at } g=0 \tag{36}$$

Note that Eq. (33) together with Eqs. (34)–(36) expresses now an unsteady one dimension mass transfer problem, with variable diffusion coefficient, in a semi-infinite wall. We are searching for a solution of the form of $c^*=c^*(\mu)$, where μ is a new dimensionless similarity variable

$$\mu=\frac{y}{2\sqrt{g}} \tag{37}$$

The new similarity variable transform Eq. (33) into

$$\frac{\mathrm{d}^2c^*}{\mathrm{d}\mu^2}+\frac{1}{D^*}\frac{\mathrm{d}D^*}{\mathrm{d}c^*}\left(\frac{\mathrm{d}c^*}{\mathrm{d}\mu}\right)^2+\frac{2\mu}{D^*}\frac{\mathrm{d}c^*}{\mathrm{d}\mu}=0 \tag{38}$$

Substituting Eq. (11) into Eq. (38) results in

$$\frac{\mathrm{d}^2c^*}{\mathrm{d}\mu^2}+A\left(\frac{\mathrm{d}c^*}{\mathrm{d}\mu}\right)^2+\frac{2\mu}{\exp(Ac^*)}\frac{\mathrm{d}c^*}{\mathrm{d}\mu}=0 \tag{39}$$

which has to be solved with the following conditions

$$c^*=0 \text{ at } \mu=0 \tag{40}$$

$$c^*=1 \text{ at } \mu=\infty \tag{41}$$

When the diffusion coefficient is constant ($A=0$), $c^*=\mathrm{erf}(\mu)$ and after some algebraic manipulation we obtain

$$\left(\frac{\mathrm{d}c^*}{\mathrm{d}\eta}\right)_{\eta=\beta}=\sqrt{3}\left(\frac{\mathrm{d}c^*}{\mathrm{d}\mu}\right)_{\mu=0}=2\sqrt{\frac{3}{\pi}} \tag{42}$$

which after substituting in Eq. (15) results (as expected) in Scriven's approximation for fast growth rates given by Eq. (19). Note that the first equality of Eq. (42) is valid also for $A\neq 0$.

An analytical solution for the case of a variable diffusion coefficient liquid ($A\neq 0$) cannot be obtained. Table 4 gives some numerical results for fast growth rates. Note that the (exact) values listed in Table 4 are the same to those of Table 2 for the case of Fm = 1000.

Table 4
Exact and approximated numerical values of the function $\beta(\mathrm{Fm},A)/\beta(\mathrm{Fm},0)$ for fast growth rates

A	$\beta(\mathrm{Fm},A)/\beta(\mathrm{Fm},0)$ (exact)	$\beta(\mathrm{Fm},A)/\beta(\mathrm{Fm},0)$ (approximated)
2	1.52	1.48
4	2.59	2.49
6	4.91	4.69
8	10.1	9.64
10	22.0	21.0

Polyanin and Dil'man [10] suggested an approximated method for solving Eqs. (33)–(36). By applying the Laplace–Carson transformation they derived an approximated formula, which in terms of the dimensionless parameters of this work it reduces to

$$\frac{\beta(\mathrm{Fm},A)}{\beta(\mathrm{Fm},0)}\approx\left[2\int_0^1(1-c^*)D^*\mathrm{d}c^*\right]^{1/2}=\frac{\sqrt{2}}{A}[\exp(A)-A-1]^{1/2} \tag{43}$$

The values suggested by Eq. (43) have an error of less then 5% compared to the exact values (see Table 4). Eq. (43) is plotted in Fig. 1. Note that according to our representation, all the numerical results lie in a relatively narrow stripe.

3. Conclusions

The results presented here for the mass-transfer-controlled spherical bubble growth in a quiescent liquid, in which the variable diffusion coefficient depends exponentially on the concentration, indicate that the effective diffusion coefficient is much closer to $D_s^*=1$ than to $D_\infty^*=\exp(A)$. The correlation for the variable diffusion coefficient which was used in this work, was selected specially for the industrial process of polymer melt devolatilization. However, other types of correlations can be used and appropriated solutions can be obtained by the procedure described in this work.

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Appendix A. Nomenclature

A	Dimensionless constant
c	Molar concentration
D	Diffusion coefficient
Fm	Foaming number
g	Dimensionless function
h	Lagrangian coordinate
k	Mass transfer coefficient
N	Molar flux
P_b	Pressure in the bubble
R	Radius of the bubble
R_g	Universal gas constant
Sh	Sherwood number
t	Time
T	Absolute temperature
v	Velocity
y	Lagrangian coordinate

Greek letters

β	Dimensionless growth constant
η	Dimensionless similarity variable
μ	Dimensionless similarity variable

Subscripts

eff	Effective
s	At the bubble's surface
∞	Far away from the bubble

Superscripts

*	Dimensionless

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