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# Quasistatic model for foam fractionation

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### HIGHLIGHTS

## G R A P H I C A L A B S T R A C T

- Simple quasistatic model for foam fractionation is considered.
- Over time, foam columns become taller/drier, but enriched in surface active material .
- Enriched systems however recover surface active material at comparatively low rates.
- High air velocity detrimental to enrichment, but larger bubbles are beneficial.
- Lower specific surface area of large bubbles outweighed by foam becoming much drier.

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### 1. Introduction

Foam fractionation is a chemical engineering separation technique that relies on surface active materials reporting to bubble surfaces (Lemlich, 1968; Lemlich, 1972; Stevenson, 2014). It is a low energy separation technique involving just the energy needed for a supply of bubbles, with (by contrast with a technique such as distillation) no requirement either to supply or to remove significant amounts of heat during the process. It is also a gentle technique which (again, by contrast with distillation) does not

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## ABSTRACT

A simple model is presented for foam fractionation. The basis of the model is that the liquid fraction profile across the foam column is known quasistatically at any instant in time, and only varies gradually as the foam column height itself varies. Using suitable boundary conditions, the model provides a relation between liquid flux through the foam column and instantaneous foam column height. The flux of surface active material through the column can then also be determined. The model makes it possible to explore how design and operational parameters of a fractionation system influence performance. Indeed the model clarifies that tall columns enrich surfactant, but high velocities of air through the column are detrimental to enrichment. Having larger bubbles in the column helps enrichment though, despite reducing specific surface area and thereby despite reducing the total amount of surface active material adsorbed. © 2023 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY licenses (http://creativecommons.org/licenses/by/4.0/).

> require elevated temperatures to operate. This feature then makes foam fractionation particularly suitable for separating delicate biomolecules including proteins (Lockwood et al., 1997; Schügerl, 2000; Crofcheck et al., 2003; Gerken et al., 2006; Linke et al., 2007; Shea et al., 2009; Mukhopadhyay et al., 2010).

> Foam fractionation generally proceeds as follows (Stevenson, 2014; Martin et al., 2010). Bubbles (typically air bubbles) are introduced into a column containing a liquid feed solution of surface active material. Surface active material from the feed adsorbs onto bubbles surfaces, forming a so called excess of surface active material at those surfaces (Chattoraj and Birdi, 1984). The bubbles then rise up through the column, and form a foam above the liquid feed.



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### Nomenclature

		L <sub>initial</sub>	dimensionless initial foam column height
Dimensional quantities:		$L_{\text{final}}$	dimensionless final foam column height
С	concentration of surface active	$M_s$	dimensionless protein amount recovered
Co	selected feed concentration of surface active	$M_{*}$	dimensionless protein amount recovered since $L = 0$
g	gravity acceleration	Q	dimensionless liquid flux
$\tilde{l}_{ch}$	characteristic length scale	$Q_{\rm thru}$	dimensionless liquid flux through the foam
$t_{\rm ch}$	characteristic time scale	$Q_{peak}$	peak flux on inverted parabola
$v_{\rm ch}$	characteristic velocity scale	$Q_s$	dimensionless protein flux
Γ	surface excess	R	dimensionless bubble radius
$\overline{\Gamma}_0$	typical surface excess	$V_{\rm air}$	dimensionless air velocity
μ	liquid viscosity	Т	dimensionless time
ρ	liquid density	Y	dimensionless vertical coordinate
$\sigma$	surface tension	$\Gamma_{0*}$	dimensionless protein adsorption parameter
		$\phi$	liquid fraction
Dimensionless quantities:		$\phi_{bot}$	liquid fraction at the bottom of the foam
Coff	dimensionless effective protein concentration	$\phi_{top}$	liquid fraction at the top of the foam
Coff ave	dimensionless average effective protein concentration	$\phi_{peak}$	liquid fraction at peak on inverted parabola
L	dimensionless foam column height		
-			

Subsequently the foam flows out of the column and is collected. Due to having the aforementioned excess of surface active material adsorbed on bubble surfaces (Chattoraj and Birdi, 1984), any liquid accompanying these foam bubbles (the so called foamate) will be richer on average than the underlying feed liquid was. Once the bubbles that have been collected are broken, the surface active material in the accompanying liquid (the foamate) is found to be enriched relative to the feed.

However there is competition occurring between enrichment and recovery here (Gerken et al., 2006; de Lucena et al., 1996; Stevenson, 2012). If little liquid accompanies the bubbles (as in a dry foam), a highly enriched solution will be obtained, but with a small volume of foamate ultimately recovered. On the other hand, if large amounts of liquid flow with the bubbles (as in a wet foam), larger volumes of foamate are recovered but with low enrichment: any surfactant that was adsorbed on bubble surfaces then has little impact compared to the amounts already carried within the liquid. Hence design and operation of foam fractionation relies on selecting a suitable balance between enrichment and recovery (Rajabi and Grassia, 2023).

To help develop more robust design and operation of fractionation processes, it is useful to have models (Du et al., 2000; Stevenson and Jameson, 2007). Modelling fractionation typically involves however two distinct physical ingredients which are all too often studied only separately: namely, on the one hand, the gas and liquid flow behaviours occurring in the foam itself (Leonard and Lemlich, 1965; Verbist et al., 1996), and, on the other hand, the adsorption of surface active materials such as proteins on film surfaces (Fainerman et al., 2003; Fainerman et al., 2006; Gochev et al., 2013). Combining these distinct physical ingredients together into a usable model for fractionation is therefore the task at hand here.

In the next section (Section 2) we review a recent study (namely the work of Keshavarzi et al. (2022)) which succeeded in doing just that, and we describe some of the interesting predictions which that study made, considering also the context of other relevant literature to be discussed. We then go on (in Section 3) to explain some of the opportunities for novel research arising from the aforementioned study of Keshavarzi et al. (2022): in particular we explain the opportunities for making significant simplifications within the modelling framework, whilst still capturing key interesting predictions. A suitably reformulated and simplified mathematical model is then presented in Section 4, considering again the context of other relevant literature. Various analyses upon that simplified model are considered in Section 5 and Section 6. Subsequently, Section 7 then presents results (i.e. model predictions) and Section 8 offers conclusions. Overall, the importance of the present work is that it offers a simple modelling framework for analysing design and operation of fractionation processes.

### 2. Framework for modelling foam fractionation

A recent combined experimental and modelling study tackled foam fractionation (Keshavarzi et al., 2022) by coupling a model for foam drainage with a model for adsorption of a surface active protein. The resulting model predictions for operation of a fractionation column compared favourably with experiment.

Using the model, the effect of changing various operational parameters (e.g. amount of foam within the column, air velocity through the column, bubble size, etc.) could then be interrogated. One result that was particularly remarkable was the following (Keshavarzi et al., 2022): it was found that as a fractionation batch proceeded, the amount of enrichment could actually *increase* over time.

The reason that this is remarkable is that, as surface active material is removed via fractionation, the liquid that is retained in the fractionation column itself (the so called retentate) actually depletes in surface active material over time. Despite processing a retentate that is leaner and leaner in surfactant over time, the foamate surprisingly becomes richer and richer.

The explanation for this turned out to be as follows (Keshavarzi et al., 2022). As foamate is removed from the fractionation column over time, the liquid level within the column itself necessarily falls. The height of the foam column sitting above that liquid therefore needs to increase to compensate: note the distinction being made here between the fractionation column (i.e. the container) and the foam column within and filling just part of that container: see Fig. 1 for a sketch to help to visualise this.

It is known however that as foam columns become taller they also tend to become much drier (Weaire and Hutzler, 1999). Studies by Hutzler et al. (2013) and Tobin et al. (2014), specifically in the context of foam fractionation, also concur with this. Drier



Fig. 1. Schematic of a foam fractionation column. Air is introduced to the bottom of a column containing liquid with surface actives, and a foam column is formed above the liquid. Foam then flows up and out of the fractionation column. Over time, as the system evolves, the liquid level falls, and the foam column height increases to compensate. The foam column then becomes drier, but also richer in surface active material.

foams meanwhile, as already alluded to, enrich surfactant to a much greater extent than wet foams do: again the sketch in Fig. 1 indicates this. Having a taller and drier foam column can thereby outweigh the effect of gradual depletion of surfactant in the retentate, which was exactly what was found (Keshavarzi et al., 2022).

These predictions relied amongst other things on solving a partial differential equation for the foam drainage behaviour (Keshavarzi et al., 2022). This partial differential requires an initial condition (i.e. a specified initial liquid content in the foam column) and also boundary conditions. The boundary condition at the bottom boundary of the foam is straightforward, since there is a well defined liquid fraction at which a bubbly liquid becomes a foam (Verbist et al., 1996; Weaire and Hutzler, 1999; Cantat et al., 2013).

One of the insights which the model of Keshavarzi et al. (2022) offered however was a specification of the boundary condition at the top boundary. It was assumed that the liquid and air moved upward with the same speed at the top boundary, so there was effectively "no slip" between the phases at this point. The same boundary condition has in fact been proposed previously in the fractionation literature (Tobin et al., 2014), specifically for a device called a skimmer which has a geometry such that foam is collected directly from the top of a straight vertical fractionation column.

Moreover this sort of boundary condition is actually familiar from the closely related field of gravity thickening of solid–liquid suspensions: solid and liquid are then assumed to leave the bottom of the thickener at the same speed (Fitch, 1966; Concha and Bustos, 1992; Martin, 2004; Usher and Scales, 2005; Grassia et al., 2014). In fractionation of course we have a gas–liquid system rather a solid– liquid system, and material is collected from the top rather than from the bottom, but nonetheless the analogy still applies.

The "no slip" top boundary condition differs however from one that is commonly applied in minerals froth flotation, a process that is otherwise closely allied to foam fractionation. In that particular process (discussed further in the supplementary material), there can be significant bubble bursting at the top boundary. Hence air, as it escapes from bursting bubbles, might well be moving upward faster than the liquid is (Neethling et al., 2003; Neethling, 2008; Neethling and Brito-Parada, 2018).

However a fractionation system with foam collected near the top of the system and without significant bursting in situ right at the top of the foam would behave differently from how minerals froth flotation conventionally behaves (Neethling and Brito-Parada, 2018). During fractionation in fact, just as Tobin et al. (2014) proposed for a skimmer, the bubbles plus accompanying liquid could be collected from the top, with foam then only being

broken upon exit from the fractionation column so as to recover foamate. The "no slip" condition at the top boundary of the fractionation column is then the appropriate condition to use (Keshavarzi et al., 2022). We will discuss more implications of using this particular boundary condition later on, to help to understand various contributions to liquid transport through a foam column.

For now however we focus instead on whether there might be some way to retain that boundary condition, but avoid dealing with the complexity of a partial differential equation altogether. This is addressed in the next section, and it leads to a far simpler framework for modelling fractionation. Parts of the framework have already been developed previously by Hutzler et al. (2013) and Tobin et al. (2014), so we review that work, but there are also novel aspects, which we will highlight. Exploring this simpler framework and the results that it predicts are thus the novel contributions of the present work. With the aim of keeping the approach in the present work as simple as possible, we do not attempt a direct comparison between the results of the simple model used here and the results of the rather more complex one used by Keshavarzi et al. (2022). We will however present later on mathematical arguments to support the notion that the two models should indeed agree. Before engaging with that mathematics however, first in what follows we describe the framework physically.

### 3. Simpler framework for modelling foam fractionation

It is known (Verbist et al., 1996; Weaire and Hutzler, 1999) that liquid typically drains out of an initially wet foam until such point as an equilibrium profile (balancing gravity and capillary suction) is achieved. The equilibrium state has a very specific dependence of liquid fraction upon vertical coordinate, wet at the bottom and increasingly dry moving upwards (Verbist et al., 1996; Weaire and Hutzler, 1999). The profile then ensures that there is no longer any liquid flux leaving the foam, nor is there any liquid flux at any point within it.

In a system (such as occurs in fractionation as studied here), in addition to liquid draining, bubbles are driven to flow upwards relative to a container (Neethling et al., 2000; Neethling et al., 2003; Neethling et al., 2003; Stevenson, 2006; Stevenson, 2007). In that case, in lieu of an equilibrium state there might be instead a more general steady state (Grassia et al., 2001). Indeed the work of Hutzler et al. (2013) and Tobin et al. (2014) (to be discussed shortly) highlighted the relevance of a state like this to analysing fractionation systems. The steady state again has a profile of liquid fraction that is wet at the bottom and drier moving upwards. However (as will be verified later on) it is not quite as dry as in the equilibrium profile, since the flow of the bubbles driven upwards helps to promote liquid hold up. Moreover, unlike the equilibrium state which has no liquid flux at all, in the steady state there is a spatially uniform flux of liquid upwards through the foam. The profile of liquid fraction is not uniform, and the speed of the liquid is not uniform either, but the flux certainly is (Grassia et al., 2001; Hutzler et al., 2013; Tobin et al., 2014).

For a foam column of specified height, foam drainage theory (i.e. the governing partial differential equation representing drainage) describes the process of evolving over time from an initially wet foam to either an equilibrium or steady liquid fraction profile. By solving that partial differential equation, the time scale for such evolution is obtained (Cox et al., 2000).

However in the context of foam fractionation (Keshavarzi et al., 2022), this ignores the fact that another time scale is relevant here. This is the time scale for the height of the foam column itself to evolve. As already mentioned (see Fig. 1), any liquid flowing up through the foam column will lower the liquid level remaining underneath the foam, and hence cause the foam column height to increase to compensate.

If however the foam column is tall enough so as to be rather dry at the top as has indeed been found (Keshavarzi et al., 2022), then the net flux of liquid flowing up through the foam column is likely to be rather low: a dry foam typically can only deliver a small liquid flux up from below. As a result, the foam column height should change only slowly over time. It is then expected that foam drainage should bring the liquid fraction profile close to a steady state, long before the foam column height changes significantly. As is discussed later on, we will in fact verify a posteriori that this expectation is borne out. Furthermore, subsequent changes in the foam column height should also be so gradual that the liquid fraction profile remains close to steady state thereafter, i.e. the system evolution is quasistatic. This approach then represents a significant simplification compared to prior work (Keshavarzi et al., 2022), and as has been mentioned, exploiting this is a novel contribution of the present study.

To set the contribution of the current work in context, we reiterate that a steady state drainage formula has been already used previously to analyse the operation of a fractionation system (Hutzler et al., 2013; Tobin et al., 2014). The work of Hutzler et al. (2013) for instance treated a specific geometry for a fractionation column, namely an inverted U-shape tube, in which foam flowed up one leg of the inverted U-shape and down the other. That configuration turned out to affect the boundary condition imposed at the top of the leg containing upward moving foam: a "no slip" boundary condition did not actually apply. It was recognised though by Hutzler et al. (2013) that changing the boundary condition could change the solutions.

Follow up work by Tobin et al. (2014) still using a steady state model quantified the amount by which reducing foam column height, increased liquid flux through it. It also explored the role of different boundary conditions, considering not just the inverted U-shape, but also a skimmer configuration: as already mentioned, the skimmer has the same "no slip" boundary condition as the one that Keshavarzi et al. (2022) also proposed. In finite height columns (Tobin et al., 2014) found that the boundary condition certainly influenced the liquid flux. However for very tall columns, that influence was lost, as we will verify later on.

Despite containing many useful results, both Hutzler et al. (2013) and Tobin et al. (2014) considered just an "instantaneous" steady state solution for any specified fractionation system. It was not considered what the implications of those instantaneous steady solutions were for how the system would gradually evolve quasistatically, with the foamate then potentially becoming richer

and richer as time proceeds. These issues are however addressed as novel contributions in the present work.

To summarise, we still retain here the top boundary condition that was used in prior work (Keshavarzi et al., 2022), but knowing just the instantaneous foam height, we will now be able to deduce directly the instantaneous liquid flux through the foam, and hence the consequent rate of change of height of the foam column. As we will see, this leads to a very simple model explaining how increasing foam height increases the amount of enrichment realised in a fractionation process. This then allows us to interrogate very easily how the fractionation process responds to various design and operational parameters, not just foam column height (which can be set at different initial levels and which of course varies with time), but also air velocity through the column and bubble size as well. Modelling how a fractionation process responds to varying operational parameters like those is a key objective here. As has been alluded to already, to avoid complicating the discussion, what we will present here does not extend as far as comparing results of the current simple model with the more complex one of Keshavarzi et al. (2022). Later on though we will provide arguments as to why we expect the two models to agree. The mathematics of the simple model itself are described in the next section.

### 4. Mathematical model

This mathematical modelling section is divided into a treatment of foam drainage aspects of fractionation (Section 4.1 and Section 4.2) followed by a treatment of adsorption and mass transport aspects (Section 4.3 and Section 4.4). Although the model can be considered generic to adsorption and transport of any surface active material, we will often employ instead the term "protein" since protein separation is the main target application of interest in the present study. What we are ultimately working towards here is a set of Eqs. (1)–(6) describing drainage and adsorption behaviour together. Some readers may wish to consult those equations immediately and then skip directly to Section 5 in which we begin to analyse them.

### 4.1. Making foam drainage system dimensionless

Here in the interests of generality, we will work in terms of dimensionless variables and dimensionless parameters, with dimensional analogues for the most part relegated to supplementary material. Given the various different physical ingredients in the model (i.e. part of the model deals with foam drainage and part of it deals with adsorption) we need to make certain variables dimensionless on scales related to drainage (dealt with in the present section) and certain other variables dimensionless on scales related to adsorption (dealt with in a later section).

Note that the work of Hutzler et al. (2013) and Tobin et al. (2014) also considered how to make at least drainage-related variables dimensionless. However in what follows we deliberately choose different scales from the ones chosen there. The scales of Hutzler et al. (2013) and Tobin et al. (2014) are sensitive to the size of the bubbles making up the foam. This makes it less straightforward to compare and contrast systems with different bubble sizes. Of course the work of Hutzler et al. (2013) and Tobin et al. (2014) did not set out to consider different bubble sizes, so the chosen scaling was never problematic. Here however bubble size is a variable we wish to interrogate, so scalings need to be chosen slightly differently. Indeed, looking at different bubble sizes is important because, as we will see later on (Eq. (17)), changing bubble size can lead to trends contrary to initial expectation.

Despite working for generality primarily in terms of dimensionless variables, in order to maintain a sense of scale, we will also relate a number of our dimensionless variables back to dimensional ones. To achieve that we will assume a set of base case parameter values comparable with parameters considered in the experiments of Keshavarzi et al. (2022): further details of parameter values can be found in the supplementary material Section S1. In what follows we consider length, velocity and time scales in turn.

### 4.1.1. Length scales

To start with we define a characteristic length scale that we denote  $l_{ch}$ . Lengths will be made dimensionless with respect to  $l_{ch}$ .

The value of  $l_{\rm ch}$  is obtained by balancing gravity and capillary effects. Essentially  $l_{\rm ch} \sim (\sigma/(\rho g))^{1/2}$ , where  $\sigma$  is surface tension,  $\rho$  is density of liquid and g is gravity acceleration, although there are also some numerical prefactors in the definition which arise from foam geometry (see the supplementary material Section S1). For base case parameter values (as given in the supplementary material Section S1) it turns out that we obtain  $l_{\rm ch} \sim 1.3 \times 10^{-3}$  m.

Note that the definition of  $l_{\rm ch}$  itself involves just continuum properties of the liquid in the fractionation column. It does not involve any design and operational parameters of the fractionation process itself such as foam column height, air flow velocity or (as alluded to earlier) bubble size. By choosing  $l_{\rm ch}$  as our unit of length, we can therefore compare different design and operational conditions, confident of the basis for that comparison, since the unit of length itself is not changing. Indeed  $l_{\rm ch}$  should only ever vary modestly from one fractionation system to another: liquid density  $\rho$  and surface tension  $\sigma$  might be sensitive to protein concentration, but will not vary by orders of magnitude, so  $l_{\rm ch}$  will always turn out to be on the order of magnitude of  $10^{-3}$  m.

Having defined  $l_{ch}$ , we can now measure any other relevant length scales relative to it. For example we define a dimensionless bubble radius R. Predicting sizes of bubbles that form within a given fractionation column (or within a multiphase flow more generally) is a non-trivial task (Sarhan et al., 2016; Sarhan et al., 2017a; Sarhan et al., 2017; Sarhan et al., 2017b; Sarhan et al., 2018) with models generally needing to consider processes both in the foam and in a bubbly liquid region underneath it (Sarhan et al., 2017; Sarhan et al., 2018). In the present work however, we simply set the bubble radius in the foam. The base case system we consider will set dimensionless R equal to 0.25 (see Table 1), corresponding to a physical bubble radius of very roughly  $3\times 10^{-4}$  m, which is comparable with bubble radii considered by Keshavarzi et al. (2022). We can vary *R* about the base case value of 0.25, but it is clear that dimensionless *R* should typically be a parameter somewhat smaller than unity.

Note that although we allow dimensionless bubble size R to vary from system to system, in the interests of simplicity, we do not allow R to vary spatially within a given system. In fact Keshavarzi et al. (2022) considered some cases which R varied very little spatially, and other cases in which R varied spatially more substantially. Increasing protein concentrations correlated with

### Table 1

Dimensionless parameters. In the present work  $V_{\rm air}$ , R,  $L_{\rm initial}$  and  $L_{\rm final}$  are varied about base case values, but  $\phi_{\rm bot}$  and  $\Gamma_{0*}$  are taken to be fixed.

Parameter	Symbol	Base case value	
Dimensionless air velocity	Vair	0.00195	
Dimensionless bubble radius	R	0.25	
Dimensionless initial foam column height	Linitial	40	
Dimensionless final column height	L <sub>final</sub>	100	
Liquid fraction at bottom of foam	$\phi_{\rm bot}$	0.36	
Dimensionless protein adsorption parameter	$\Gamma_{0*}$	0.025	

less spatial variation in R. In the present work though, R is taken to be spatially uniform.

Yet another dimensionless parameter we define is the dimensionless initial foam column height  $L_{initial}$ . This must be at least as large as the dimensionless bubble diameter 2*R*: physically the foam must be at least several bubbles deep. As we will see later on though and as Tobin et al. (2014) also found, it can actually be advantageous to choose  $L_{initial}$  substantially larger than 2*R*, and that then is what we will do.

Here a base case value for  $L_{\text{initial}}$  is taken as 40 (again see Table 1), corresponding to a foam column of height 0.052 m. A foam column of that height would be readily achievable in the experimental set up of Keshavarzi et al. (2022) since the height of the entire fractionation column (containing feed liquid plus foam) was 0.16 m. Again however we can vary this parameter  $L_{\text{initial}}$  about the base case. Sometimes we will consider  $L_{\text{initial}} \sim 20$  in fact, whereas sometimes we will consider  $L_{\text{initial}} \approx 20$  in fact, whereas sometimes we will consider  $L_{\text{initial}}$  and larger  $L_{\text{initial}}$  implies a drier one. It is clear that throughout  $L_{\text{initial}}$  is typically a value rather larger than unity.

The dimensionless height of the foam column, which we will denote L, varies over time from  $L_{\text{initial}}$  to a final foam column height  $L_{\text{final}}$  at the end of the fractionation process. A dimensionless  $L_{\text{final}} \sim 120$  would correspond to a foam column of height roughly the same as the height of the entire fractionation column used by Keshavarzi et al. (2022). Of course in the work of Keshavarzi et al. (2022) there would be no advantage in emptying the column entirely so as to transfer all of the feed to foamate: there would then be no enrichment. To leave at least some retentate behind, we will assume here instead a base case  $L_{\text{final}} \sim 100$  (see Table 1) although variations about this base case value will be considered too.

It could be possible though to redesign the process of Keshavarzi et al. (2022) using a rather taller fractionation column. In that case a foam column height with  $L_{\text{final}}$  well above 120 could be attainable, whilst still not removing all the liquid feed. An industrial scale system could also be designed to be taller than the bench scale system of Keshavarzi et al. (2022), in which case values of *L* and hence  $L_{\text{final}}$  up to a few hundred might be conceivable.

There are however some caveats here. There are limitations not just on how tall a foam column can reasonably become (clearly the foam must not collapse entirely before reaching the top of the column (Tobin et al., 2014)), but also on what might be a reasonable batch time scale to attain the chosen final foam column height. Time scales will be discussed later on, but first velocities are considered.

### 4.1.2. Velocity scales

Having defined a characteristic length scale, we can now define a characteristic velocity scale  $v_{ch}$ . This is essentially  $v_{ch} \sim \rho g_{ch}^2/\mu$ , where  $\mu$  is liquid viscosity, specifically viscosity for the liquid feed. Thus we are balancing gravity and viscous effects. However again there are some numerical prefactors involved in the definition associated with foam geometry (Keshavarzi et al., 2022; Pitois et al., 2009; Weaire, 2008; Kraynik, 1983; Verbist et al., 1996) (see the supplementary material Section S1). For base case parameter values (again see the supplementary material Section S1) we estimate  $v_{ch} \sim 0.056$  m s<sup>-1</sup>.

Physically what  $v_{ch}$  is measuring is the drainage velocity due to gravity from a (hypothetical) channel with a cross sectional area on the order of  $l_{ch}^2$ . The actual gravity drainage velocity from a foam will be rather smaller than that because channels in the foam (specifically so called Plateau border channels (Weaire and Hutzler, 1999)) have a correspondingly smaller cross section.

Note that  $v_{ch}$  also has the feature that it depends on continuum properties of the liquid, but not on operational parameters of the fractionation process (e.g. air flow velocity). Hence if we make velocity variables dimensionless on the scale  $v_{ch}$ , it is easy to compare different operational conditions, confident that the unit of velocity does not itself depend on those conditions. Of course  $v_{ch}$ does depend on viscosity  $\mu$  which in a fractionation system is sensitive to protein concentration. The viscosity of a dilute feed containing protein has a well known behaviour with protein concentration (Huggins, 1942), and so could be readily accounted for if need be. Remember though that the purpose of the fractionation process is to take a rather dilute feed liquid and then enrich it by producing foamate. This then limits how much feed viscosity  $\mu$ and hence  $v_{ch}$  varies from system to system: in fact the work of Keshavarzi et al. (2022) considered a viscosity comparable with that of water. The same will be done here, and the  $v_{\rm ch}$  value quoted earlier was based on that.

Having defined  $v_{ch}$ , it is possible to define a dimensionless air velocity  $V_{air}$  for the air coming out of the fractionation column. A base case value for dimensionless  $V_{air}$  will be taken to be 0.00195 (see Table 1) corresponding to an air velocity roughly on the order of  $10^{-4}$  m s<sup>-1</sup> which is comparable with the air velocity values considered by Keshavarzi et al. (2022) (see also the supplementary material Section S1).

We can of course vary  $V_{air}$  about the base case. What is evident though is that  $V_{air}$  is a small parameter. Indeed it is clear that the base case  $V_{air}$  is even smaller than  $R^2$  where R is the dimensionless bubble radius, which is itself a parameter rather smaller than unity. This observation about the relative size of  $V_{air}$  and  $R^2$  will turn out to be important to the discussion later on.

### 4.1.3. Time scales

A characteristic time scale  $t_{ch}$  is now defined as  $t_{ch} = l_{ch}/v_{ch}$ . The evolution time for the fractionation process can now be made dimensionless on this scale  $t_{ch}$ .

Using our earlier values of  $l_{\rm ch}$  and  $v_{\rm ch}$ , we estimate that  $t_{\rm ch} \sim 0.023$  s. Recall here that  $l_{\rm ch}$  is typically rather smaller than the physical height of the foam column, whereas  $v_{\rm ch}$  is typically rather larger than the actual drainage velocity in the foam. As a result, the dimensionless time scale over which the fractionation process evolves will typically be many dimensionless units.

Note that the work of Keshavarzi et al. (2022) considers batch times up to 6000 s long. This corresponds to around  $2.6 \times 10^5$ dimensionless time units. There is no physical barrier to considering even longer batch times, e.g. on the order of several million dimensionless time units, but these would correspond to batch times on the order of a day or more, which may be impractical. Indeed one of the issues we will face is that attaining large values of  $L_{\text{final}}$  might be beneficial for enriching protein but would involve batch times too long to be practical.

# 4.2. Equations for liquid flux through the foam & evolution of foam height

Having specified length, velocity and time scales, we can now use foam drainage theory (Verbist et al., 1996; Weaire and Hutzler, 1999) to write an equation for liquid flux through the foam. We make liquid flux dimensionless on the scale  $v_{ch}$  and we use the symbol  $Q_{thru}$  to denote dimensionless liquid flux through the foam.

The resulting dimensionless equation is

$$Q_{\rm thru} = V_{\rm air}\phi - R^2\phi^2 - R\phi^{1/2}d\phi/dY \tag{1}$$

where  $\phi$  denotes liquid fraction (specifically liquid volume fraction at any point in the foam), *Y* denotes a dimensionless vertical coor-

dinate, and other parameters are as above. Details of how this equation is obtained (starting from its dimensional analogue) are given in the supplementary material Section S1. It is also the same equation as obtained and analysed by Hutzler et al. (2013) and Tobin et al. (2014), apart from a different choice of scaling, as has already been mentioned. Physically the terms on the right hand side here represent respectively liquid carried by rising air bubbles, gravity drainage downward and capillary suction from wet to dry. Recall also that *R* is treated here as spatially uniform: there is a slight change if *R* varies spatially, albeit not discussed here.

To convert driving forces (i.e. gravity, capillary suction) to liquid fluxes, it is necessary to know the viscous resistance associated with that flux. Here, in order to obtain Eq. (1), we employ the so called channel-dominated drainage equation (Verbist et al., 1996; Weaire and Hutzler, 1999) in which resistance to motion is associated with Plateau border channels, and not alternative formulations in which resistance is tied to vertices at which those channels meet (Koehler et al., 1999; Koehler et al., 2000).

We also consider in Eq. (1) the resistance to motion just in the dry limit in which Plateau border channels have a well defined tricuspid triangular geometry (Leonard and Lemlich, 1965). The work of Keshavarzi et al. (2022) generalised this beyond the dry limit by using an expression developed by Pitois et al. (2009) for foam permeability (a quantity which itself scales inversely with resistance). For simplicity however, we employ the dry limit formula here, even when we extrapolate to the bottom of the foam (where it meets underlying liquid and where foam is therefore often quite wet). Mostly however our focus will be on drier regions of the foam higher up where the dry limit formula applies anyway.

Another consequence following from assuming a dry limit (Grassia et al., 2001; Hutzler et al., 2013; Tobin et al., 2014) is that we do not need to distinguish between the air flux and the air velocity, the velocity being strictly speaking a factor  $(1 - \phi)^{-1}$  larger than the flux, but with  $\phi$  assumed small. For simplicity we refer then to  $V_{\text{air}}$  just as air velocity (rather than air flux) and treat it as if it were spatially uniform. All this limit means is that when the foam is comparatively dry, in relative terms, there are no large variations in the volume fraction of air from one location in the foam to another.

What is more important here however is, as has already been mentioned, that the liquid flux through the foam  $Q_{thru}$  is spatially uniform. Formally we can think of the terms on the right hand side of Eq. (1) as combining to define a (local) liquid flux Q, and the physical content of Eq. (1) then becomes that Q at all locations must equal the spatially uniform value  $Q_{thru}$ . This is a consequence of the key assumption which underlies the present model, namely that the system evolves guasistatically.

The quasistatic assumption (which we will verify a posteriori later on) turns out to provide a relationship between  $Q_{thru}$  and the instantaneous foam column height *L*, and as per Tobin et al. (2014), this relationship is what we seek to establish. Mathematically this relationship comes about as follows.

At the lower boundary of the foam Y = 0, we impose  $\phi = \phi_{bot}$ , where  $\phi_{bot}$  is some known value at which the foam would break up into a bubbly liquid. Often it is assumed (Cantat et al., 2013; Hutzler et al., 2013; Tobin et al., 2014) that  $\phi_{bot} \sim 0.36$  (see also Table 1) corresponding to the volume fraction of the voids in a random close packing. As already noted, formally this extrapolates Eq. (1) beyond the dry limit, but typically most of the height of the foam remains unaffected by that.

At the top boundary of the foam Y = L, we impose  $\phi = \phi_{top} \equiv Q_{thru}/V_{air}$  which then ensures, as Keshavarzi et al. (2022) supposed, that the liquid velocity at the top (formally  $Q_{thru}/\phi_{top}$ ) has "no slip" relative to the velocity of the air  $V_{air}$ . Clearly two boundary conditions have been imposed on Eq. (1),

even though it is only a first order differential equation. Both boundary conditions can however be satisfied provided, as mentioned, there is a relationship between  $Q_{thru}$  and *L*.

Details of exactly how this relationship behaves will be described later on. Once it is obtained however, we then have an equation for how *L* evolves. Liquid flowing through the foam column implies less liquid remaining underneath the foam, so to keep the total height (liquid plus foam) constant, the value of *L* must increase. Specifically

$$dL/dT = Q_{thru} \tag{2}$$

where T here denotes a dimensionless time variable.

Eqs. (1) and (2) coupled with the relationship between  $Q_{thru}$  and L to be given later on, constitute the model that we require for liquid transport in foam fractionation. In the next section we switch from considering liquid transport through the foam to considering the associated protein mass transport.

### 4.3. Making foam adsorption systems dimensionless

Having already explained how to make foam drainage variables and parameters dimensionless, we now aim to do the same for foam adsorption variables and parameters. Firstly however we switch briefly back to dimensional variables. Predicting the overall amount of material that attaches or adsorbs to bubble surfaces in a fractionation column (or within a multiphase flow more generally) is a non-trivial task (Sarhan et al., 2018). Ordinarily though, when adsorption of surface actives in particular is considered, it is possible to find a relationship between surfactant concentration in the bulk (denoted in dimensional form c) and surface excess (denoted in dimensional form  $\overline{\Gamma}$ ). For simple surfactants, this typically takes the form of a nonlinear relationship between *c* and  $\overline{\Gamma}$  (e.g. a so called Langmuir isotherm is often used (Chang and Franses, 1995)). Compared to surfactants though, proteins are rather more complicated (Latour, 2015). They can adopt many different conformational states on a surface (Fainerman et al., 2003). Moreover proteins are potentially quite slow to adsorb, so that kinetics (Fainerman et al., 2006; Hibbert et al., 2002) and hence contact time of the foam film with bulk solution might impact the amount of surface excess.

This complex situation for proteins was managed by Keshavarzi et al. (2022) through allowing a given amount of protein to adsorb on a bubble surface during a specified time, and then contracting the surface to alter surface excess. This established a relation between surface tension and surface excess. Subsequently bubbles in the fractionation column with different residence times were considered by Keshavarzi et al. (2022), and by measuring surface tension, the surface excess of protein corresponding to each residence time was thereby deduced.

Provided the bulk protein concentration in the liquid was also known, a relation between protein on the surface and protein in the bulk then followed. A significant complication however was that a different relation between surface excess and residence time of bubbles was found for each different bulk protein concentration. Thus results for this presented by Keshavarzi et al. (2022) become sensitive to how concentrated or how dilute the feed liquid is to start with. Moreover, as has been alluded to (see Section 2), the retentate liquid in a fractionation column typically also depletes in concentration over time, so its concentration as time proceeds deviates more and more from the original feed concentration. Equivalently it is found that the relation between bulk protein concentration and the resulting protein surface excess is dependent on bubble residence time.

Here we simplify by assuming just one feed concentration out of several that were considered by Keshavarzi et al. (2022). Specifically we choose a concentration (that we denote  $c_0$ ) of 0.1 kg m<sup>-3</sup>. Also we make a simplification that the retentate does not deplete despite the foamate being enriched: thus *c* and  $c_0$  are assumed the same, and effectively we are treating the retentate as a reservoir. From the point of view of calculation, one advantage of doing this is that we obtain an upper bound for the amount that the foamate can be enriched: indeed, as we will see, enrichment of the foamate with time then follows due to the foam column becoming taller and hence drier, and this is now never offset by retentate depletion.

In effect then, since we are just looking at one typical bulk concentration, and we can simplify further by looking in turn at just one typical surface excess. The data of Keshavarzi et al. (2022) suggest that a typical surface excess (that we now denote  $\bar{\Gamma}_0$ ) encountered is on the order of  $10^{-6}$  kg m<sup>-2</sup> at least for the particular protein (bovine serum albumin) considered there.

We can also define a dimensionless analogue of this (i.e. a dimensionless protein adsorption parameter) that we denote  $\Gamma_{0*}$ . This is essentially given by  $\Gamma_{0*} \sim \overline{\Gamma}_0/(c_0 l_{ch})$ , but with some prefactors associated with foam geometry (Keshavarzi et al., 2022; Pitois et al., 2009; Kraynik et al., 2003; Weaire, 2008) (see the supplementary material Section S2). We find  $\Gamma_{0*} \sim 0.025$  (see Table 1). For simplicity we will assume this parameter is fixed throughout the present work.

It is now straightforward to estimate the flux of surface active material (i.e. protein) out of the system. Some of this is carried by the flux of bulk liquid at the specified bulk concentration. Some of it is carried as surface excess. This latter contribution is determined via a known surface excess per film area, via the specific surface area of the bubbles and via the air flux (with the product of specific surface area and air flux then giving the specific surface area flux (Sarhan et al., 2018)). The amount of protein collected (per unit cross sectional area of the fractionation column) is the integral over time of the protein flux. Also an effective protein concentration, accounting for surface and bulk together, can be defined as the instantaneous ratio between protein flux and liquid flux. These quantities can all be made dimensionless in a straightforward fashion, i.e. effective concentrations are made dimensionless on the scale  $c_0$ , protein fluxes are made dimensionless on the scale  $c_0 v_{ch}$ , protein amounts per cross section of the column are made dimensionless on the scale  $c_0 v_{ch} t_{ch}$  (equivalent to  $c_0 l_{ch}$ ). Dimensionless governing equations are given in the next section.

### 4.4. Equations for protein concentration and protein mass transport

We denote dimensionless protein flux (i.e. the dimensionless flux of surface active material) by  $Q_s$ , dimensionless effective protein concentration by  $C_{eff}$ , and dimensionless protein amount recovered by  $M_s$ . Just as was the case with liquid flux  $Q_{thru}$ , we also assume a spatially uniform protein flux  $Q_s$ , corresponding again to a quasistatic theory. The following dimensionless equations then arise (with dimensional analogues given in supplementary material Section S2, which also describes some slight differences from analogous equations developed by Hutzler et al. (2013))

$$Q_s = Q_{\rm thru} + V_{\rm air} \Gamma_{0*} / R \tag{3}$$

$$C_{\rm eff} = Q_s / Q_{\rm thru} = 1 + V_{\rm air} \Gamma_{0*} / (RQ_{\rm thru})$$
<sup>(4)</sup>

$$dM_s/dT = Q_s = C_{\rm eff}Q_{\rm thru} = C_{\rm eff}\,dL/dT.$$
(5)

In the above equations, notice how increasing  $V_{\text{air}}$  (i.e. increasing air flux) and decreasing *R* (i.e. decreasing bubble radius, which gives a larger specific surface area) tend, at first sight, to lead to larger  $Q_s$  and larger  $C_{\text{eff}}$  and hence larger  $M_s$ . However we need to establish

how varying  $V_{air}$  and varying *R* might also influence the value of  $Q_{thru}$ .

In fact remembering the top boundary condition  $Q_{\rm thru} = V_{\rm air} \phi_{\rm top}$ , it follows that

$$C_{\rm eff} = Q_s/Q_{\rm thru} = 1 + \Gamma_{0*}/(R\phi_{\rm top}). \tag{6}$$

This no longer involves  $V_{air}$  explicitly: any dependence of  $C_{eff}$  upon  $V_{air}$  is implicit upon how  $\phi_{top}$  responds to  $V_{air}$ . There is still explicit R dependence of course (i.e. the explicit effect of specific surface area), but the impact of R upon  $\phi_{top}$  also needs to be taken into account. Eq. (6) is actually a very useful one, since it clarifies how changes in the foam column height can influence the foamate enrichment: provided a taller foam column height makes the foam drier and thereby reduces  $\phi_{top}$ , the effective concentration  $C_{eff}$  in the foamate increases. This then is the very effect that Keshavarzi et al. (2022) identified in their work (see the discussion already given in Section 2).

A final comment we make here is that  $M_s$  can also be thought of as an equivalent liquid height. The actual (dimensionless) height of liquid we remove from the fractionation column is L, but  $M_s$  (which is always greater than L) tells us the height of bulk liquid that we would need to remove to obtain the same amount of protein as has actually been removed. This can also be seen from Eq. (5), which can be written in the form  $dM_s/dL = C_{eff}$  and hence  $M_s = \int C_{eff} dL$ , with Eq. (6) implying  $C_{eff} > 1$  always.

### 5. Relationship between liquid flux and foam column height

As is clear from the previous section, the model proposed here can be closed provided we have a relationship between liquid flux Q<sub>thru</sub> and foam column height *L*. In mathematical terms, in order to close the model we need, as has been explained, to use Eq. (1) along with suitable boundary conditions. This ultimately results in Eq. (10) to be given shortly. Some readers may wish to consult Eq. (10) and then skip to the next section. In the present section however, we aim to explain what closing the model means not in mathematical terms, but rather in physical terms, by looking at the various contributions that make up the flux (see Section 5.1). This will then in turn allow us to appreciate physically how Q<sub>thru</sub> must depend on L. Equivalently what we will do (since it turns out to be slightly simpler to formulate) is explain physically how *L* depends on *Q*<sub>thru</sub> (see Section 5.2). Following that (see Section 5.3) we will explore the relevance of the values chosen for dimensionless air velocity  $V_{air}$  and dimensionless bubble size R, and how those choices support the assumptions underpinning the model.

### 5.1. Role of contributions to the liquid flux

To facilitate the discussion we refer to Fig. 2. This shows various contributions to the liquid flux Q or more specifically to the uniform  $Q_{thru}$  (see Eq. (1)) as a function of liquid fraction  $\phi$ . The sloping straight line in Fig. 2 is the contribution to  $Q_{thru}$  from air flow alone, namely  $V_{air}\phi$ . Meanwhile the curve, which is an inverted parabola, is the contribution from air flow and gravity drainage taken together, namely  $V_{air}\phi - R^2\phi^2$ , albeit neglecting the effect of capillary suction.

Suppose now we specify a value of  $Q_{\text{thru}}$ , including contributions from air flow, gravity drainage and capillary suction all together. Even though  $\phi$  varies at different coordinate locations moving through the foam, and thus the individual contributions to  $Q_{\text{thru}}$  likewise vary, the value of  $Q_{\text{thru}}$  itself does not vary, since (as has been mentioned) liquid flux is spatially uniform in a quasistatic system.

On Fig. 2 therefore we show  $Q_{thru}$  as a horizontal line. The "no slip" top boundary condition of Keshavarzi et al. (2022) requires

that the intersection between this horizontal line and the aforementioned sloping line  $V_{\rm air}\phi$  specifies the top boundary value of  $\phi$ , namely  $\phi_{\rm top} = Q_{\rm thru}/V_{\rm air}$ . However since the bottom boundary value of  $\phi$  is also given (having a specified value  $\phi_{\rm bot}$ , see Section 5.3), we know exactly the domain of  $\phi$  covered by the horizontal line.

In Fig. 2 the difference between the horizontal line and the inverted parabola is nothing more than the capillary suction term. However the capillary suction term (given within Eq. (1)) depends on  $d\phi/dY$ . Hence the value of  $d\phi/dY$  is known for any  $\phi$  value. Rearranging Eq. (1) we then deduce

$$\mathrm{d}\phi/\mathrm{d}Y = -R^{-1}\phi^{-1/2}\Big(Q_{\mathrm{thru}} - V_{\mathrm{air}}\phi + R^2\phi\Big). \tag{7}$$

It is through knowing the value  $d\phi/dY$  and also knowing  $\phi_{top}$  and  $\phi_{bot}$  that the foam column height can be computed.

In Fig. 2(a) we have set the value of  $Q_{thru}$  comparatively high, so the horizontal line is much higher up than the inverted parabola. This means  $|d\phi/dY|$  (which is effectively  $R^{-1}\phi^{-1/2}Q_{thru}$  in this limit) can be comparatively large. Also it is clear from Fig. 2(a) that by setting  $Q_{thru}$  comparatively high,  $\phi_{top}$  (at the intersection between the sloping and horizontal lines) is not too far away from  $\phi_{bot}$ . A large  $|d\phi/dY|$  coupled with a small difference between  $\phi_{bot}$  and  $\phi_{top}$  implies a comparatively short foam column, i.e. a small *L*.

On the other hand on Fig. 2(b) we have set  $Q_{thru}$  at a rather smaller level. It is clear moreover that the inverted parabola has a peak value  $Q_{peak}$  at some liquid fraction  $\phi_{peak}$ . It is easy to demonstrate that

$$Q_{\text{peak}} = V_{\text{air}}^2 / (4R^2) \tag{8}$$

and

$$\phi_{\text{peak}} = V_{\text{air}} / (2R^2) = 2Q_{\text{peak}} / V_{\text{air}}.$$
(9)

In Fig. 2(b),  $Q_{thru}$  (the horizontal line) is set just very slightly above  $Q_{peak}$ . As a result  $\phi_{top} \equiv Q_{thru}/V_{air}$  is just very slightly above  $Q_{peak}/V_{air}$ , which according to Eqs. (8) and (9) is the same as  $\phi_{peak}/2$ , a point already noted by Tobin et al. (2014). Indeed  $\phi_{top}$  can now be quite a considerable amount below  $\phi_{bot}$ , so the domain of  $\phi$  values covered by the horizontal line in Fig. 2(b) can likewise be considerable.

It is also clear in Fig. 2(b), that for  $\phi$  values in the neighbourhood of  $\phi_{\rm peak}$  ,the difference between the horizontal line and the inverted parabola is now small. Thus  $|d\phi/dY|$  becomes small, and the foam column height can become large. Furthermore, over much of that height, the foam necessarily has a liquid fraction close to  $\phi_{\text{peak}}$ . This same  $Q_{\text{peak}}$  value was also found for an arbitrarily tall foam column by Hutzler et al. (2013), despite that work considering a different geometry (namely an inverted U-shape) with different boundary conditions (in particular a different  $\phi_{top}$  admitting slip between liquid and air). In fact any system which is arbitrarily tall and which has  $\phi_{top}$  less than  $\phi_{peak}$  must have this same  $Q_{thru}$ value. The follows because, as we have mentioned, irrespective of the boundary condition used (Tobin et al., 2014), the way in which the system becomes arbitrarily tall is to have an extensive region in which liquid fraction  $\phi$  is barely changing vertically and is very nearly  $\phi_{\text{peak}}$ . Below this extensive region however,  $\phi$  is somewhat greater than  $\phi_{\text{peak}}$ , whereas above it,  $\phi$  is somewhat less than  $\phi_{\text{peak}}$ : in both cases  $\phi$  is now changing vertically, and so capillary suction is active, albeit over a somewhat restricted height.

### 5.2. Formula for foam column height

Formally, via Eq. (7), the height *L* can be related to the liquid flux  $Q_{\text{thru}}$  by the relationship



Fig. 2. (a) Relationship between contributions to the dimensionless liquid flux Q and liquid fraction  $\phi$ . For a (dimensionless) air velocity  $V_{air}$ , the sloping line shows the liquid flux  $V_{air}\phi$  that is convected by the air. Assuming a dimensionless bubble radius R, the curve (an inverted parabola) meanwhile shows the combined contribution  $V_{air}\phi - R^2\phi^2$ from air convection plus gravity drainage. The difference between the sloping line and the curve is  $-R^2\phi^2$ , the effect of gravity drainage. A break in the curve is shown, because in reality near  $\phi_{\text{bot}}$ , the contribution from gravity drainage tends to be much larger than the contribution from air convection. If a spatially uniform dimensionless liquid flux Q<sub>thm</sub> is now made to flow through the foam (horizontal line), the difference between the horizontal line and the curve represents the effect of capillary suction. The liquid fraction at the bottom of the foam  $\phi_{bot}$  has a well defined value (vertical dashed line), and the liquid fraction at the top of the foam  $\phi_{top}$  (again a vertical dashed line) is obtained by the intersection between the sloping line and the horizontal line. Since the capillary suction term depends on  $d\phi/dY$  (where Y is dimensionless vertical coordinate), specifying values for  $\phi_{bot}$  and  $\phi_{top}$  also specifies the dimensionless foam column height L. (b) Relationship between contributions to the dimensionless liquid flux Q and liquid fraction  $\phi$ , but assuming now a much smaller uniform liquid flux through the foam  $Q_{thru}$  (horizontal line). Again liquid fraction at the bottom of the foam  $\phi_{bot}$  is well defined, and again liquid fraction at the top  $\phi_{top}$  is determined by the intersection between the sloping line (representing liquid flux convected by air) and the horizontal line. Given the smaller  $Q_{thru}$ , the value of  $\phi_{top}$  is much smaller than before. The value of  $Q_{thru}$  is now so small that the horizontal line passes just slightly above the top of the curve. This curve (an inverted parabola), which represents the net effect of convection by air plus gravity drainage, has a peak value  $Q_{peak}$  occurring at a liquid fraction  $\phi_{peak}$ . The difference between the horizontal line and the curve represents the effect of capillary suction. This difference is small in the neighbourhood of  $\phi_{\text{peak}}$ , and since capillary suction depends on  $d\phi/dY$ , it turns out that liquid fraction  $\phi$  changes only very slowly with dimensionless vertical coordinate Y in this neighbourhood. Large foam column heights L then result.

$$L = \int_{\phi_{\text{top}}}^{\phi_{\text{bot}}} \left| \frac{\mathrm{d}\phi}{\mathrm{d}Y} \right|^{-1} \mathrm{d}\phi = \int_{Q_{\text{thru}}/V_{\text{air}}}^{\phi_{\text{bot}}} \frac{R\phi^{1/2} \,\mathrm{d}\phi}{Q_{\text{thru}} - V_{\text{air}}\phi + R^2\phi^2}.$$
 (10)

In this relationship, it is the value of  $Q_{thru}$  which determines L by governing both how big the domain of integration can be and also how small the denominator of the integrand is allowed to become.

In reality at any instant during the fractionation process we know the value of L, and must instead solve Eq. (10) for  $Q_{thru}$ . This is however easily done by generating a look up table i.e. generating *L* versus  $Q_{thru}$  for a large set of  $Q_{thru}$  values (see Section 7.1 for more detail). Subsequently for any specified L value we just find elements of the look up table bracketing that particular value, and interpolate to obtain the corresponding Q<sub>thru</sub>.

Note that the "no slip" condition applicable at the top of the foam constrains the domain of permitted Q<sub>thru</sub> values which can be accessed in the look up table. In fact  $Q_{thru}$  values must always lie between  $Q_{\text{peak}}$  and  $V_{\text{air}}\phi_{\text{bot}}$ . The fact there is an upper limit to liquid flux that can be delivered through the foam column is unsurprising. The fact that there is also a lower limit however is less intuitive. In fact it turns out that fluxes even below the lower limit are permissible under certain physical circumstances as studied by Grassia et al. (2001). However such cases can no longer satisfy a no slip boundary condition at the top. Studying them can nevertheless be physically insightful (particularly in the context of minerals froth flotation (Neethling and Brito-Parada, 2018) as opposed to foam fractionation), so we discuss them further in the supplementary material Section S3. The focus in the present work however will be upon  $Q_{thru}$  values at least as large as  $Q_{peak}$ .

### 5.3. Significance of having $V_{air}$ smaller than $R^2$

We have already commented (see Section 4.1) that both  $V_{air}$ (the dimensionless air velocity) and R (the dimensionless bubble radius) are small parameters, but the parameter  $V_{air}$  is rather smaller than  $R^2$ . The significance of this is now discussed in the context of what was just presented in Sections 5.1-5.2.

5.3.1. Implications for liquid fractions  $\phi_{\text{peak}}$  and  $\phi_{\text{top}}$ Firstly we consult the formula for  $\phi_{\text{peak}}$  in Eq. (9). It is clear that when  $V_{\rm air} \ll R^2$ , the value of  $\phi_{\rm peak}$  satisfies  $\phi_{\rm peak} \ll 1$ , corresponding to dry foam. Suppose we have a foam tall enough that  $Q_{thru}$  is close to  $Q_{\text{peak}}$  as given by Eq. (8). Then  $\phi_{\text{top}} = Q_{\text{thru}}/V_{\text{air}}$  is around  $\phi_{\text{peak}}/2$ , and so the top of the foam is indeed dry, although the bottom of the foam at liquid fraction  $\phi_{\rm bot}$  is certainly wet (see Section 4.2 and Table 1 for the value of  $\phi_{\text{bot}}$ ). Having a foam that is dry at the top is of course important for fractionation applications: the foamate is more enriched when the foam is drier as Eq. (6) shows.

Implications also follow however for behaviour near the bottom of the foam as we discuss next.

### 5.3.2. Implications near the bottom of the foam

Note that the right hand side of Eq. (7) involves three terms. Near the bottom of the foam, the term  $V_{air}\phi$  on the right hand side of Eq. (7) is never larger than  $V_{\rm air}\phi_{\rm bot}$ , which is itself smaller than  $V_{\rm air}$  (see also Section 4.2 and Table 1 for the value of  $\phi_{\rm bot}$ ). Meanwhile, owing to the top boundary condition, the term  $\boldsymbol{Q}_{thru}$  on the right hand side of Eq. (7) is equal to  $V_{\rm air}\phi_{\rm top}$ . This is always smaller than  $V_{\rm air}\phi$  (for  $\phi$  at any location below the top boundary), and so will in turn be smaller than  $V_{\rm air}\phi_{\rm bot}$  and hence smaller than  $V_{\rm air}$  also. Indeed  $V_{\rm air}\phi_{\rm top}$  may be much smaller than  $V_{\rm air}$  if the foam is tall enough. Note also that the difference between these terms  $V_{\rm air}\phi$  and  $Q_{\rm thru} = V_{\rm air}\phi_{\rm top}$  is  $V_{\rm air}(\phi - \phi_{\rm top})$ , which is always positive.

The remaining term on the right hand side of Eq. (7) is  $R^2 \phi^2$ , which physically represents gravity drainage. Near the bottom of the foam, where  $\phi$  is not too far from  $\phi_{\rm bot}$  this term is on the order of  $R^2$ . If  $V_{air} \ll R^2$  as we have here, then that term is clearly the dominant one.

The content of Eq. (7) is now that the capillary term on the left balances at leading order the gravity drainage term on the right. This is why Fig. 2 shows a break on the approach to  $\phi_{bot}$ : the break indicates that for  $\phi$  close to  $\phi_{bot}$  the gravity contribution to liquid drainage is far bigger than any contribution of air convection. In other words, the fact that the inverted parabola in Fig. 2 first rises to a local maximum and only then starts decreasing is not really evident once  $\phi$  values have become as large as  $\phi_{bot}$ : instead the value of  $V_{air}\phi - R^2\phi^2$  (on the inverted parabola) is nearly the same as  $-R^2\phi^2$ .

The dominant balance in Eq. (7) is actually the exact same balance as would occur for an equilibrium foam profile, with no air flow and no net liquid flux. Hence sufficiently near the bottom of the foam, the profile of  $\phi$  versus *Y* is the same as in the equilibrium profile (Weaire and Hutzler, 1999). Thus to a reasonable approximation

$$\phi \approx \phi_{\rm bot} \left( 1 + (R\phi_{\rm bot}^{1/2}/2)Y \right)^{-2}.$$
 (11)

This profile will apply near the bottom of the foam, but the issue with it more generally is that it allows  $\phi$  to decay too quickly with Y. This follows because the profile given in Eq. (11) ignores a positive term involving  $V_{air}\phi - Q_{thru} \equiv V_{air}(\phi - \phi_{top})$  that appears on the right hand side of Eq. (7), once we account properly for the overall minus sign also appearing there. This then is the reason why Eq. (11) appears to predict  $\phi$  decaying to zero for a very tall foam, whereas we know that in fact  $\phi$  can never fall below  $\phi_{peak}/2$  (which is the value of  $\phi_{top}$  realised in the limit as  $Q_{thru}$  approaches  $Q_{peak}$ ).

We will analyse the behaviours admitted by Eq. (7) (and Eq. (10) that derives from it) in more detail in a later section. Before that however we want to explore one further implication of having  $V_{\text{air}}$  much smaller than  $R^2$ .

### 5.3.3. Implications for rate of growth of foam column height

Recall that our approach here is a quasistatic one in which the typical time for a foam to reach a steady state profile at a given foam column height is assumed to be much shorter than the typical time for the foam column height itself to evolve. We are now in a position to verify a posteriori that this assumption is reasonable.

Suppose we were to solve the full unsteady state problem (rather than the quasistatic one) starting from an initial foam column height  $L_{\text{initial}}$  and starting also from an initially uniformly wet foam with  $\phi = \phi_{\text{bot}}$  at all locations in the foam. It is clear from the discussion just given in Section 5.3.2 that when  $V_{\text{air}} \ll R^2$  and also  $\phi \approx \phi_{\text{bot}}$ , gravity drainage dominates convection by air. However in a uniformly wet foam capillary suction also is negligible. The drainage rate of liquid from the foam is therefore on the order of  $R^2 \phi_{\text{bot}}^2$ . Given there is an amount  $L_{\text{initial}} \phi_{\text{bot}}$  of liquid initially in the foam, the time to drain towards a steady state profile can be estimated as  $L_{\text{initial}}/(R^2 \phi_{\text{bot}})$ .

On the other hand, the time scale for foam column height *L* to evolve significantly away from *L*<sub>initial</sub>, according at least to the prediction of the quasistatic state approach, is  $L_{initial}/(dL/dT) \sim L_{initial}/Q_{thru}$ . The largest permitted value of  $Q_{thru}$ , again according to the quasistatic approach, is  $V_{\rm air}\phi_{\rm bot}$ . Hence  $L_{\text{initial}}/Q_{\text{thru}}$  is at least  $L_{\text{initial}}/(V_{\text{air}}\phi_{\text{bot}})$ . Provided that  $V_{\text{air}} \ll R^2$ , it is clear that the time scale for L to evolve away from  $L_{initial}$  is much longer than the time scale needed to drain from a uniform profile of liquid fraction towards a steady state one. Hence the quasistatic state approach is expected to be valid. Moreover if we choose an even smaller  $Q_{\text{thru}}$  on the order of  $Q_{\text{peak}} \sim V_{\text{air}}^2/(2R^2)$ , the aforementioned time scale  $L_{initial}/Q_{thru}$  for L to evolve becomes longer still. Indeed as *L* becomes larger over time, Q<sub>thru</sub> tends to fall eventually

towards  $Q_{\text{peak}}$ , so the justification for assuming a quasistatic state becomes even stronger.

To summarise, the time scales that the quasistatic theory predicts for foam column heights to evolve are entirely consistent with the notion that liquid fraction profiles can approach toward steady state. The assumptions underlying the quasistatic theory are thereby borne out. Formally though it is still necessary to verify that a quasistatic theory applies not just for liquid transport, but also for protein mass transport. This is easy to do and is discussed in the supplementary material Section S4.

### 6. Asymptotic behaviours for foam fractionation

Although Eq. (10), is, as we have said, a nonlinear equation for  $Q_{thru}$  given L, which generally needs to be tackled numerically, there are some asymptotic limits in which we can gain analytical insights. These limits are discussed below. Specifically we will consider relations for  $Q_{thru}$  versus L for the case of a short, wet foam column (Eq. (13) in Section 6.1 and a tall, dry one (Eq. (16) in Section 6.2). Some readers may wish to consult those equations and then skip directly to the results in Section 7.

### 6.1. Foam column with a near equilibrium profile

We have already argued (see Section 5.3.2) that in those parts of the foam column with a comparatively high liquid fraction, to a good approximation, the liquid fraction profile can be represented by an equilibrium profile (see Eq. (11)). Moreover, if the foam column is not too tall, then the entire column will remain comparatively wet. Then we have a formula for the liquid fraction at the top (i.e. at coordinate location Y = L) which follows directly from Eq. (11)

$$\phi_{\rm top} \approx \phi_{\rm bot} \left( 1 + (R\phi_{\rm bot}^{1/2}/2)L \right)^{-2}.$$
 (12)

Since  $Q_{thru} = V_{air}\phi_{top}$ , we also have an explicit  $Q_{thru}$  versus *L* relation

$$Q_{\rm thru} \approx V_{\rm air} \phi_{\rm bot} \left( 1 + (R\phi_{\rm bot}^{1/2}/2)L \right)^{-2}.$$
 (13)

It is clear from the above formulae that  $\phi_{top}$  only falls significantly below  $\phi_{bot}$  (equivalently  $Q_{thru}$  only falls significantly below  $V_{air}\phi_{bot}$ ) when the foam column height *L* reaches order  $R^{-1}$ . Remembering that *R* is rather smaller than unity, it is evident that  $R^{-1}$  is larger than unity, and *L* must be larger still for  $\phi_{top}$  to fall very significantly below  $\phi_{bot}$ .

Now consider a case in which *L* is on the order of  $V_{\rm air}^{-1/2}$  or greater, remembering here also (see Section 4.1 and Section 5.3) that  $V_{\rm air}^{-1/2} \gg R^{-1}$  since  $V_{\rm air} \ll R^2$ . Eq. (12) then appears to predict a  $\phi_{\rm top}$  value on the order of  $\phi_{\rm peak}$  or less (see Eq. (9)). Thus we now have a foam column height that is sufficiently tall not merely for  $\phi_{\rm top}$  to fall significantly below  $\phi_{\rm bot}$  (or equivalently not merely for  $Q_{\rm thru}$  to fall significantly below  $V_{\rm air}\phi_{\rm bot}$ ), but also for  $\phi_{\rm top}$  to become small in absolute terms (i.e.  $\phi_{\rm top}$  on the order of  $\phi_{\rm peak}$ , which based on Eq. (9) is itself necessarily much smaller than unity when  $V_{\rm air} \ll R^2$ ).

Although this prediction of column height needed to achieve a dry foam is useful, note that we have pushed the equilibrium profile in Eq. (11) and hence also Eq. (12) that is derived from it, outside their regime of validity. The equilibrium profile in Eq. (11) was derived assuming that the air convection term  $V_{\text{air}}\phi$  and the net liquid flux term  $Q_{\text{thru}}$  on the right hand side of Eq. (7) could both individually be discarded by comparison with the gravity drainage term  $R^2\phi^2$ . Such an assumption is invalid for parts of a profile in which  $\phi$  values have fallen to the order of  $\phi_{\text{peak}}$ . Discarding those

terms as Eq. (11) has done causes  $\phi$  to decay more rapidly than Eq. (7) permits (as Section 5.3.2 also mentions).

On the other hand, very close to the top, even though  $V_{\rm air}\phi$  and  $Q_{\rm thru}$  are not negligible within Eq. (7) when taken as individual terms, their difference does actually vanish right at the top, as a consequence of the top boundary condition chosen, namely  $Q_{\rm thru} \equiv V_{\rm air}\phi_{\rm top}$ . Thus a balance between gravity (on the right hand side of Eq. (7)) and capillarity (on the left hand side) is actually recovered right at the top of the foam column. This suggests that, despite Eqs. (11) and (12) breaking down, supposing that *L* needs to be at least order  $V_{\rm air}^{-1/2}$  to ensure that the top of the foam can become dry might actually be a reasonable estimate. We can verify this using an analysis specific to a very tall foam column which we discuss next.

### 6.2. Case of a very tall foam column

We have already discussed (see Section 5.1) that an arbitrarily tall foam column necessarily has  $Q_{thru}$  approaching  $Q_{peak}$ . This then begs the question for a very tall but nonetheless finite height foam column, how close to  $Q_{peak}$  the value of  $Q_{thru}$  should be.

This can be determined by writing Eq. (10) in the equivalent form

$$L = \int_{\phi_{\text{top}}}^{\phi_{\text{bot}}} \frac{R\phi^{1/2} \,\mathrm{d}\phi}{Q_{\text{thru}} - Q_{\text{peak}} + R^2 (\phi - \phi_{\text{peak}})^2}.$$
 (14)

Note that the denominator of the integrand here has a minimum value  $Q_{\text{thru}} - Q_{\text{peak}}$  when  $\phi = \phi_{\text{peak}}$ , but the denominator is significantly larger than that when  $|\phi - \phi_{\text{peak}}|$  exceeds order  $(Q_{\text{thru}} - Q_{\text{peak}})^{1/2}/R$ . If the value of  $Q_{\text{thru}} - Q_{\text{peak}}$  is small, as we assume here, then most of the height of the foam column therefore is associated with a narrow domain of  $\phi$  values very close to  $\phi_{\text{peak}}$  for which the denominator is close to its minimum.

The limits of the integral from  $\phi_{top}$  to  $\phi_{bot}$  are moreover well outside that narrow domain, with in particular  $\phi_{top} = Q_{thru}/V_{air} \sim Q_{peak}/V_{air}$  being close to  $\phi_{peak}/2$  rather than close to  $\phi_{peak}$  (see Eqs. (8) and (9)). The integral then becomes to a reasonable approximation

$$L \sim \int_{-\infty}^{\infty} \frac{R\phi_{\text{peak}}^{1/2} \,\mathrm{d}\phi}{Q_{\text{thru}} - Q_{\text{peak}} + R^2 (\phi - \phi_{\text{peak}})^2} = (\phi_{\text{peak}}/(Q_{\text{thru}} - Q_{\text{peak}}))^{1/2} \pi.$$
(15)

This rearranges to

$$(\mathbf{Q}_{thru} - \mathbf{Q}_{peak})/\mathbf{Q}_{peak} \sim \phi_{peak} \pi^2 / (L^2 \mathbf{Q}_{peak}) = 2\pi^2 / (V_{air}L^2). \tag{16}$$

For any given *L*, but supposing as suggested earlier that *L* is rather larger than  $V_{\rm air}^{-1/2}$ , we now have an explicit formula for liquid flux  $Q_{\rm thru}$  delivered through the foam. Observe also that for  $Q_{\rm thru}$  to be close  $Q_{\rm peak}$ , i.e. for a finite height foam column to behave similar to an arbitrarily tall one, *L* does indeed need to be rather larger than  $V_{\rm air}^{-1/2}$  according to Eq. (16). The fact that smaller air velocities require greater heights for the system to behave as if it were arbitrarily tall was already recognised by the work of Hutzler et al. (2013), albeit the specific  $V_{\rm air}^{-1/2}$  scaling was only identified later on by Tobin et al. (2014).

Another result that follows from Eqs. (15) and (16) is that, as alluded to earlier,  $Q_{thru}$  is insensitive to the top boundary condition we impose, provided the foam column is tall. This follows, as noted by Tobin et al. (2014), because the integration limits of Eq. (15) have been shifted. Any  $\phi_{top}$  strictly less than  $\phi_{peak}$  leads in fact to Eq. (16). It is not necessary to have  $\phi_{top} \sim \phi_{peak}/2$ . By the same arguments, Eq. (4) for foamate enrichment is insensitive to the

boundary condition, provided the foam column is tall. On the other hand, a particular boundary condition is assumed in going from Eq. (4) to Eq. (6). If we substitute  $\phi_{top} \sim \phi_{peak}/2$  into this latter equation (with  $\phi_{peak}$  given by Eq. (9)), we obtain an estimate in the case of a tall foam column for the effective protein concentration  $C_{eff}$  of the foamate including the contribution of surface excess

$$C_{\rm eff} \sim 1 + 4R\Gamma_{0*}/V_{\rm air}. \tag{17}$$

Note the interesting prediction here:  $C_{\text{eff}}$  increases as *R* increases, i.e. having larger bubbles helps to enrich the foamate. At first sight this appears contrary to the prediction of Eq. (6) which suggests that having smaller bubbles, i.e. larger specific surface area, is better for enrichment. Of course there is no contradiction: larger bubbles dry out the foam so much that protein is predominantly transported as surface excess, which still enriches the foamate, despite having a reduced specific surface area.

On the other hand, it is clear from Eq. (17) that increasing  $V_{\rm air}$  is detrimental to enrichment. It makes the foam somewhat wetter at the top, so reduces the enrichment, even though foamate is recovered more quickly. Fortunately however, in the system of interest here, there is a limitation upon how much the enrichment can reduce according to Eq. (17). We have imposed a constraint that  $V_{\rm air} \ll R^2$  (as already discussed in Section 4.1 and also Section 5.3) which prevents  $C_{\rm eff}$  within Eq. (17) from falling too far. Remember also though that Eq. (17) specifically applies to a tall foam column. Foamate from a shorter foam column would be rather less enriched.

This completes our discussion of various asymptotic cases which can be tackled analytically. In what follows we present numerical results obtained from the model, albeit comparing with asymptotic expressions when relevant.

### 7. Results

This results section is laid out as follows. In Section 7.1 the relation between liquid flux  $Q_{thru}$  and foam column height *L* is analysed. Then in Section 7.2 it is shown how foam column height *L* varies with time *T*. Section 7.3 and Section 7.4 respectively show results for effective concentration  $C_{eff}$  of surface active material and amount  $M_s$  of surface active material (i.e. protein) recovered. Results up until this point focus on base case parameter values. Section 7.5 and Section 7.6 however consider the effect of varying parameters about the base case, firstly varying air velocity  $V_{air}$  and then varying bubble radius *R*.

### 7.1. Liquid flux Q<sub>thru</sub> as a function of foam height L

Here we present results from Eq. (10) obtained numerically via quadrature. Specifically we used Simpson's rule with  $\phi$  interval size of 0.0005 for each Q<sub>thru</sub>, and also stepped Q<sub>thru</sub> in units of  $0.0005 V_{air}$ . Note that carrying out a simple Simpson's rule quadrature on Eq. (10) relies on the parameter R (dimensionless bubble radius) not varying spatially, and there are other complications from a spatially varying bubble size as supplementary material Section S1 explains. Here however R is spatially uniform and quadrature applies. This then generates the look up table already referred to in Section 5.1. The data thereby obtained are in fact entirely analogous to data already presented by Tobin et al. (2014) in the case of a skimmer, just with a different dimensionless scaling. However, since these data are required to generate results that we consider in later sections (Section 7.2 onward), for completeness they are still presented here. Note that mathematically we can solve Eq. (10) for any L from 0 to infinity, i.e. any  $Q_{thru}$  from  $V_{\rm air}\phi_{\rm bot}$  (the largest value of liquid flux permitted by Eq. (13)) down

to  $Q_{\text{peak}}$  (as given by Eq. (8)). Of course there are also physical limitations on the values that *L* can take.

Indeed we are only interested in dimensionless foam column heights L rather larger than the bubble diameter 2R: it is meaningless to consider foams that are less than one bubble high. In our base case however, R is selected as 0.25 (see Table 1) so is already rather smaller than unity. Hence values of L less than unity can at least be considered, even though it is unlikely that L values this small would be selected in practice. As regards an upper limit for L, the foam column cannot be so tall that the foam would collapse entirely before reaching the top of the fractionation column (Tobin et al., 2014). For that matter, the foam column height L cannot exceed the height of the fractionation column itself. As discussed in Section 4.1.1 though, the fractionation column is likely to be rather more than 100 dimensionless units high.

To cover the above mentioned domain of values, as well as possible variations in parameters relative to a base case, in Fig. 3 we plot a domain of *L* from 0.1 up to several hundred. The main observation is that increasing *L* causes  $Q_{thru}$  to fall quite significantly. Since our top boundary condition requires that  $\phi_{top} = Q_{thru}/V_{air}$ , it is clear from Fig. 3 that increasing *L* causes  $\phi_{top}$  to fall, i.e. the foam becomes much drier at the top. As we know from Sections 6.1–6.2, asymptotic formulae are available in the limits of comparatively small *L* (up to order  $R^{-1}$ ) and comparatively large *L* (in excess of order  $V_{air}^{-1/2}$ , with  $V_{air} = 0.00195$  in Table 1). These are given by Eqs. (13) and (16) respectively, and are plotted in Fig. 3 also. They fit well with the predictions from Eq. (10). The large *L* data are of particular interest because, as Tobin et al. (2014) already identified, having a tall and hence dry foam column is typically good for fractionation performance.

### 7.2. Foam height L as a function of time T

Now that the relationship between  $Q_{thru}$  and L has been elucidated, we are in a position to solve Eq. (2) for column height L versus time T. Numerically this is achieved by rewriting Eq. (2) in the form  $\int dT = \int dL/Q_{thru}$ , and then applying quadrature (specifically the trapezoidal rule) to evaluate  $\int dL/Q_{thru}$ . We need however to specify an initial L value.

We could use the base case  $L_{initial}$  quoted in Table 1. However in the interests of generality it is easier to set the initial *L* equal to zero, and use that to generate a master curve for *L* versus *T*. At first sight this choice seems counterintuitive, since as already mentioned to have a foam at all, the foam column height *L* needs to be rather larger than bubble diameter 2*R*. In reality though, having generated a master curve, all we then need to do is select intervals of *L* and corresponding intervals of *T* from that curve. We then simply avoid selecting any data with very small *L*.

On the log–log plot in Fig. 4 we see a straight line up to *L* roughly on the order of 10, then a transition, and then another straight line for *L* greater than about 100. This reflects how  $Q_{thru} \equiv dL/dT$  and  $\phi_{top} \equiv Q_{thru}/V_{air}$  evolve: there is a high dL/dT for a shorter and wetter foam column, but a low dL/dT for a taller and drier one. Note however that the batch time required to reach a *L* value of around 100 (starting at least from small *L* values as is the case here) is already on the order of a million dimensionless time units. As Section 4.1.3 explains, this may be inconveniently long when converted back to dimensional time.

One way to shorten batch times is to restrict the interval of *L* values considered. In Table 2 for instance, we consider various different  $L_{\text{initial}}$  and  $L_{\text{final}}$  values, but with  $L_{\text{final}}$  being always 20 units higher than  $L_{\text{initial}}$ . Going from  $L_{\text{initial}} = 20$  to  $L_{\text{final}} = 40$  corresponds to a batch time comparable with the one considered by Keshavarzi et al. (2022) (see Section 4.1.3). However going from  $L_{\text{initial}} = 80$  to  $L_{\text{final}} = 100$  takes around three times longer.

Table 3 shows similar data but now for cases with various different  $L_{\text{initial}}$  but all with the same  $L_{\text{final}} = 100$ . The base case here (see also Table 1) is considered to have  $L_{\text{initial}} = 40$  and  $L_{\text{final}} = 100$ . It recovers three times as much foamate liquid as the case  $L_{\text{initial}} = 80$  and  $L_{\text{final}} = 100$ , but recovering that liquid takes less than three times as long.

### 7.3. Effective protein concentration C<sub>eff</sub>

Once we know  $Q_{\text{thru}}$  for any given *L*, we can also work out the effective protein concentration  $C_{\text{eff}}$  that is entering the foamate: see Eq. (4). Data are plotted in Fig. 5. What is clear is that  $C_{\text{eff}}$  increases by an order of magnitude going from a short, wet foam column (small *L* and comparatively high  $\phi_{\text{top}}$ ) to a tall, dry one (large *L* and much smaller  $\phi_{\text{top}}$ ).

Asymptotic formulae for  $C_{\rm eff}$  follow in these respective cases by substituting either Eq. (13) or Eq. (16) into Eq. (4). These match up with the data plotted in Fig. 5. Clearly it is the tall column limit that gives better enrichment performance, as per findings of Tobin et al. (2014).

In Fig. 5, small kinks appear in the curve at very high *L* values, but these are artifacts of how data are sampled within Eq. (10). We choose to sample at a limited number of  $Q_{\text{thru}}$  values (see Section 7.1), and when  $Q_{\text{thru}}$  is close to  $Q_{\text{peak}}$ , even very small changes in  $Q_{\text{thru}}$  and hence in  $\phi_{\text{top}} \equiv Q_{\text{thru}}/V_{\text{air}}$ , can produce large changes in



**Fig. 3.** Relationship between dimensionless liquid flux through the foam  $Q_{thru}$  and dimensionless foam column height *L*. Base case parameter values for dimensionless air velocity  $V_{air} = 0.00195$  and dimensionless bubble radius R = 0.25 are assumed. In addition the liquid fraction at the bottom of the foam is  $\phi_{bot} = 0.36$ . Asymptotic formulae for  $Q_{thru}$  valid in the respective limits of small *L* and large *L* are also shown.



**Fig. 4.** Evolution of dimensionless foam column height *L* vs dimensionless time *T*, assuming base case parameter values for  $V_{\text{air}}$  and *R* (see Table 1 for actual values of these, as well as the value of  $\phi_{\text{bot}}$ ). It is assumed here also that *L* is zero at initial time T = 0, although ultimately all that matters in practice are intervals of *L* and intervals of *T*.

Table 2

Effect of incrementing foam column height by 20 dimensionless units, between selected initial heights  $L_{\text{initial}}$  and final heights  $L_{\text{final}}$ . Effects upon dimensionless time elapsed  $T_{\text{elapsed}}$ , dimensionless protein amount recovered  $M_s$  and dimensionless average effective protein concentration  $C_{\text{eff},\text{ave}}$  are all reported. Meanwhile values of dimensionless air velocity  $V_{\text{air}}$ , dimensionless bubble radius R, liquid fraction at the bottom of the foam  $\phi_{\text{bot}}$ , and dimensionless protein adsorption parameter  $\Gamma_{0_s}$  which affect the results, are selected as per Table 1.

L <sub>initial</sub>	L <sub>final</sub>	T <sub>elapsed</sub>	$M_s$	C <sub>eff,ave</sub>
20	40	$2.45 imes10^5$	68	3.40
40	60	$4.26\times 10^5$	103	5.16
60	80	$5.90\times 10^5$	135	6.76
80	100	$7.26\times 10^5$	161	8.09
100	120	$8.33\times10^5$	182	9.14

### Table 3

Effect of incrementing foam column height by various amounts dimensionless units, to reach a final height  $L_{\text{final}} = 100$ , starting from selected initial heights  $L_{\text{initial}}$ . Data reported namely  $T_{\text{elapsed}}$ ,  $M_s$  and  $C_{\text{eff.ave}}$  are analogous to data in Table 2, and values of  $V_{\text{air}}$ , R,  $\phi_{\text{bot}}$  and  $\Gamma_{0*}$  which affect the results, are selected as per Table 1.

L <sub>initial</sub>	$L_{\mathrm{final}}$	T <sub>elapsed</sub>	$M_s$	C <sub>eff,ave</sub>
20	100	$1.989\times 10^6$	468	5.85
40	100	$1.743\times 10^{6}$	400	6.67
60	100	$1.317\times 10^{6}$	297	7.43
80	100	$0.726\times 10^6$	161	8.09



**Fig. 5.** Dimensionless effective concentration  $C_{\text{eff}}$  vs dimensionless foam column height *L*. Base case parameter values are assumed, namely dimensionless air velocity  $V_{\text{air}} = 0.00195$ , dimensionless bubble radius R = 0.25, liquid fraction at the bottom of the foam  $\phi_{\text{bot}} = 0.36$ , and dimensionless protein adsorption parameter  $\Gamma_{0*} = 0.025$ . Asymptotic formulae for  $C_{\text{eff}}$  valid in the limits of small *L* and large *L* are also shown.

*L*. However since the aforementioned kinks only appear for *L* values that are larger than those typically encountered in experiment (see Section 4.1.1), there is little incentive to sample in even finer increments of  $Q_{thru}$  merely to eliminate these small kinks.

### 7.4. Protein amount recovered M<sub>s</sub>

Now we examine the quantity  $M_s$  which measures the amount of protein recovered. In the first instance we compute this via quadrature (using again a trapezoidal rule) for the integral  $M_s = \int C_{\text{eff}} dL$  (see Section 4.4). We need however to specify the lower limit of integration.

Ordinarily we would take this lower limit to be the initial foam column height  $L_{initial}$ . For now though, consistently with what we already did in Section 7.2, we take the lower limit all the way to L = 0. As in Section 7.2, this allows us to generate a master curve. All we are ultimately interested in are intervals of  $M_s$  and intervals of L on that curve. We will however use the symbol  $M_*$  (as opposed to  $M_s$ ) to remind us that we are dealing with a master curve. Formally  $M_s(L) = M_*(L) - M_*(L_{initial})$ , with  $M_*$  vanishing only in the limit when L vanishes. The curve  $M_*(L)$  itself is plotted in Fig. 6. As was the case in Fig. 4 we see a straight line up to *L* roughly 10 then a transition, and eventually another straight line for *L* greater than roughly 100. However now, owing to  $C_{\text{eff}}$  increasing with *L*, the transition involves the curve shifting upward not downward.

It is also possible to generate a plot of  $M_*$  versus T (as opposed to  $M_*$  versus L). There are two opposing trends in that case. As time T proceeds, the liquid flux  $Q_{thru}$  through the foam decreases. However the effective protein concentration  $C_{eff}$  increases. The product of these two quantities determines  $dM_*/dT$  or equivalently  $dM_s/dT$  (see Eq. (5)).

It turns out that the decrease of  $Q_{thru}$  is rather more significant than the increase of  $C_{eff}$ , as can be seen in Fig. 3 and Fig. 5 for instance. Hence the net effect is a decrease in  $dM_*/dT$ . This would result in a plot which qualitatively at least looks like the plot of *L* versus *T* already shown in Fig. 4, so we choose not to present a plot of  $M_*$  versus *T* here.

Now we switch back to considering not  $M_*$  but instead the protein amount  $M_s$  recovered since a finite  $L_{initial}$ . We also define an average effective protein concentration  $C_{eff,ave}$  between some initial and final foam column heights as  $M_s/(L_{final} - L_{initial})$ : whereas  $C_{eff}$ applies for a specific foam column height, this new quantity  $C_{eff,ave}$  applies instead over an interval of foam column heights. Relevant data are presented in Table 2 in a case with  $L_{final} - L_{initial}$  fixed



**Fig. 6.** Dimensionless protein amount recovered  $M_*$  vs dimensionless foam column height *L*. Here  $M_*$  is defined to be zero when *L* is zero. Base case parameter values apply: see values for  $V_{\text{air}}$ , R,  $\phi_{\text{bot}}$  and  $\Gamma_{0*}$  in Table 1.

at 20. Here taller foam columns give an almost threefold increase in  $C_{\text{eff,ave}}$  but at the cost of a more than threefold increase in batch time elapsed  $T_{\text{elapsed}}$ .

In Table 3 meanwhile we show cases with  $L_{\text{final}}$  fixed at 100 but various different  $L_{\text{initial}}$ . Changes in  $C_{\text{eff,ave}}$  within Table 3 are comparatively modest compared to those in Table 2. This is because even cases with comparatively low  $L_{\text{initial}}$  benefit from collecting more enriched foamate towards the end of the process. Another observation from Table 3 is that the average rate of removing protein  $M_s/T_{\text{elapsed}}$  is not strongly sensitive to the  $L_{\text{initial}}$  values chosen. Cases with larger  $L_{\text{initial}}$  remove liquid more slowly, but to compensate, the liquid that they remove is richer in protein.

### 7.5. Varying air velocity V<sub>air</sub>

Recall (see Section 3) that one of our objectives here is to describe how fractionation systems might respond to different operational conditions. Thus far we have considered a number of different initial and final foam column heights,  $L_{\text{initial}}$  and  $L_{\text{final}}$ . However other parameters, namely air flow velocity  $V_{\text{air}}$  and bubble radius *R*, have been fixed at base case values specified in Table 1. In this section and the following one we consider varying those parameters, but now keeping  $L_{\text{initial}}$  and  $L_{\text{final}}$  fixed (again see Table 1) at  $L_{\text{initial}} = 40$  and  $L_{\text{final}} = 100$  respectively.

We begin by varying  $V_{air}$  at a fixed base case value of *R*. It is clear from Fig. 7 that increasing  $V_{air}$  allows us to recover foamate liquid more quickly: *L* grows faster. However the trade off here is that less protein is recovered from a given amount of foamate liquid as Fig. 8 shows: the final  $M_s$  is lower. Certainly in enrichment terms it is better to have  $V_{air}$  as low as possible as Tobin et al. (2014) also identified.

Which of the situations (i.e. which choice of  $V_{air}$ ) in Fig. 7 and Fig. 8 is deemed best overall largely depends on how long a batch time it is possible to contemplate. For instance, even the fastest evolving case here (i.e. the high  $V_{air}$  case) already involves a batch time around twice as long as the one contemplated by Keshavarzi et al. (2022) (see Section 4.1.3).

### 7.6. Varying bubble radius R

Now we vary dimensionless bubble radius *R*, but keeping  $V_{\text{air}}$  fixed at its base case value. Again we set  $L_{\text{initial}} = 40$  and  $L_{\text{final}} = 100$ . Fig. 9 shows that smaller *R* allows us to recover foamate more quickly. This is due to the foam being wetter (larger





**Fig. 8.** Dimensionless protein amount recovered  $M_s$  vs dimensionless time *T*. Here  $M_s = 0$  when T = 0, and  $L_{\text{initial}}$  is as per Fig. 7. Data are presented for the base case dimensionless air velocity  $V_{\text{air}} = 0.00195$ , as well as a larger  $V_{\text{air}}$  (twice the base case value) and a smaller  $V_{\text{air}}$  (half the base case value). Base case values are selected for dimensionless bubble radius R = 0.25, liquid fraction at the bottom of the foam  $\phi_{\text{bot}} = 0.36$ , and dimensionless protein adsorption parameter  $\Gamma_{0*} = 0.025$ .



**Fig. 9.** Dimensionless foam column height *L* vs dimensionless time *T*. Data are presented for the base case dimensionless bubble radius R = 0.25, as well as a larger *R* (1.4 times the base case value) and a smaller *R* (0.7 times the base case value). In all cases, initially the foam column height is set to  $L_{\text{initial}} = 40$ . Likewise in all cases, dimensionless air velocity  $V_{\text{air}}$  is set to the base case value  $V_{\text{air}} = 0.00195$ . In addition  $\phi_{\text{bot}} = 0.36$ .



**Fig. 10.** Dimensionless protein amount recovered  $M_s$  vs dimensionless time *T*. Here  $M_s = 0$  when T = 0, and  $L_{\text{initial}}$  is as per Fig. 9. Data are presented for the base case dimensionless bubble radius R = 0.25, as well as a larger R (1.4 times the base case value) and a smaller R (0.7 times the base case value). Base case values are selected for dimensionless air velocity  $V_{\text{air}} = 0.00195$  and dimensionless protein adsorption parameter  $\Gamma_{0*} = 0.025$ . In addition  $\phi_{\text{bot}} = 0.36$ .

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 $\phi_{top}$ ) hence permitting more liquid flux (larger  $Q_{thru}$  with  $Q_{thru} \equiv V_{air}\phi_{top}$  here).

However Fig. 10 shows the trade off: less protein is recovered (smaller final  $M_s$ ) because the foamate is less enriched. Smaller bubbles have higher specific surface area, but, in enrichment terms, this effect is overwhelmed by smaller bubbles also giving wetter foams. As was the case in Section 7.3, whether one would tolerate the less enriched foamate would depend on how long a batch time it is practical to consider.

### 8. Conclusions

We have presented a simple model for foam fractionation of a surface active material such as a protein. A feature of the model is a top boundary condition as proposed by Keshavarzi et al. (2022) that liquid and air at the top of the foam column have the same velocity. Compared to the work of Keshavarzi et al. (2022) though, the model presented here is far simpler, and builds upon some earlier analyses of Hutzler et al. (2013) and Tobin et al. (2014). The simplifying feature is that the liquid fraction within and the height of the foam column are assumed to evolve only quasistatically due to having comparatively modest liquid fluxes through the foam. This allows us to specify a direct relation between liquid flux and foam column height.

According to the relation thereby obtained, as liquid is removed from the system over time, and the foam column becomes taller to compensate, the foam also becomes drier, and the liquid flux through it falls. However, in a taller column, the foamate that is recovered is enriched in protein. In effect, in a sufficiently dry foam, the surface active material that is carried within the liquid itself no longer dilutes the surface active material adsorbed on foam films. What this means in practical terms for a fractionation process is that the longer the process operates, the richer in surface active material the foamate can become.

In addition, the response of the fractionation column to air velocity and to bubble size has been considered. Increasing air velocity makes the foam wetter (specifically it increases liquid fraction at the top) and recovers liquid more quickly (liquid flux through the foam is greater). However, the foamate liquid that is recovered is less enriched in surface active material. On the other hand, increasing bubble size helps to enrich the foamate. This is counterintuitive because larger bubbles actually lead to less specific surface area and hence less adsorbed surfactant. However increased bubble size also leads to much drier foam, and in enrichment terms this more than compensates for a decrease in specific surface area.

Overall the model provides a straightforward framework describing how fractionation performance depends on design and operational parameters. One caveat however is that more enriched systems also recover liquid at a slower rate. This might then result in low recovery of surface active material within any convenient fractionation batch time, or else a requirement for abnormally long batch times to recover adequate material.

The model used here benefits from simplicity but makes many assumptions. For instance, it uses formulae for liquid drainage specific to dry foam, and then extrapolates them even into parts of the foam that are wetter. It also assumes, at least in the present work, just one specific bulk concentration of surface active and one specific surface excess, whereas in reality adsorption of e.g. a protein is a complex process. It also treats retentate liquid as a reservoir of surface active material, ignoring the fact that enrichment of foamate should actually be accompanied by depletion of retentate. These are all assumptions that should be revisited in the future. Likewise, although we have presented mathematical arguments to explain why the simple model developed here should agree with the more complex model of Keshavarzi et al. (2022), a direct comparison between results of the two models has not yet been carried out. Yet another assumption here is that bubble size is taken as spatially uniform, whereas Keshavarzi et al. (2022) suggested that it could actually vary spatially, particularly when protein concentration is lowered. We have already described the benefits in enrichment terms of selecting taller foam columns and separately the benefits in enrichment terms of selecting large bubble sizes. If however bubble size changes spatially, i.e. if bubble size grows moving up through a tall foam column, then those benefits might well combine synergistically: the model as considered here does not manage to capture such effects. Despite these various limitations, having a model that can predict liquid flux very simply in terms of foam column height and from that evolution of a fractionation process is certainly useful.

### Data statement

Data presented here can be obtained from simple quadrature of governing equations using parameter values that are provided in the text. Data files are provided with the supplementary material.

### **CRediT statement**

This is a single author work. The author was responsible for: Funding acquisition; Conceptualization; Methodology; Investigation; Formal analysis; Visualization; Writing: Original Draft; Writing: Review and Editing.

### **Declaration of Competing Interest**

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ces.2023.118721.

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