



Bubble coarsening dynamics in fluorinated and non-fluorinated firefighting foams



Matthew J. Kennedy^{a,*}, Michael W. Conroy^b, John A. Dougherty^c, Nicholas Otto^c, Bradley A. Williams^b, Ramagopal Ananth^b, James W. Fleming^{d,1}

^a Former National Research Council Associate at the Naval Research Laboratory

^b Naval Research Laboratory, Chemistry Division, 4555 Overlook Ave., SW, Washington, DC 20375, USA

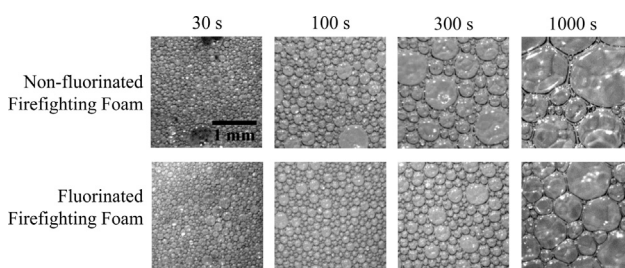
^c Former Naval Research Enterprise Internship Program Intern at the Naval Research Laboratory

^d Senior Staff Scientist, Nova Research Inc., 1900 Elkin Street, Suite 230, Alexandria, VA 22308, USA

HIGHLIGHTS

- Firefighting foams followed the self-similar bubble growth law known for SDS foam.
- Fluorinated foams coarsened slower than non-fluorinated foams.
- The evolutions of the bubble-size distributions depended on foam chemistry.
- Diffusion rate differences were not explained by surface tension differences alone.

GRAPHICAL ABSTRACT



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ABSTRACT

We have quantified the dynamics of bubble coarsening in some commercial firefighting foams. These multi-component foams contain unique chemical formulations leading to different coarsening and drainage behaviors. We show that these firefighting foams, some of which contain fluorocarbon surfactants and one of which contains only fluorine-free ingredients, as well as single-component, relatively well understood, sodium dodecyl sulfate (SDS) foam follow the self-similar bubble growth law that predicts increasing average bubble size with time. Further, the experimentally measured effective diffusion coefficients for coarsening are smallest for fluorinated foams, followed by a non-fluorinated firefighting foam, followed by SDS foam, as expected based on differences in surface tension. However, the effective diffusion coefficients derived from experiments on multi-component foams are smaller than predicted by the classical theory, which considers several physical properties including surface tension and lamella thickness. In contrast, the measured effective diffusion coefficient for SDS foam agrees with the theory. Therefore, the commercial firefighting foams coarsened slower than theoretically predicted relative to SDS foam, even after accounting for differences in surface tension and initial liquid content

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1. Introduction

Bubble size impacts foam drainage [1] and foam rheology [2]. In the case of firefighting foam, bubble size can affect fire suppression by controlling the dynamics of liquid drainage from the foam and by affecting the ability of the foam to spread over a fire and blanket flammable vapors [3]. Thus, knowledge of bubble size is important

* Corresponding author.

E-mail addresses: matthewjohnkennedy@gmail.com (M.J. Kennedy),

jim.fleming_ctr@nrl.navy.mil (J.W. Fleming).

¹ Formerly at the Naval Research Laboratory, Chemistry Division, 4555 Overlook Ave., SW, Washington, DC 20375, USA.

for the design and effectiveness of foam-based fire-suppression systems.

Bubble size in foam evolves with time. Large bubbles grow dynamically at the expense of small bubbles. This phenomenon, known as coarsening, leads to growth of average bubble size according to a self-similar growth law [4–6]. In dry foam, the average bubble size grows proportionally to $(2D_{\text{eff}}t)^{1/2}$ [4,7], where D_{eff} is a diffusion coefficient associated with the rate of coarsening. In wet foam, average bubble size grows slower than in dry foam, possibly due to reduced fractional surface area of lamellar films and increased plateau border thickness [5]. Coarsening in foam is believed to occur as a result of the diffusion of gas between bubbles [5].

Coarsening has been examined previously in aqueous foams produced from single-component hydrocarbon surfactant compositions such as sodium dodecyl sulfate (SDS) [5,8] and alpha-olefinsulfonate [6]. However, bubble coarsening in multi-component, low surface energy, slow draining, aqueous foams is not well understood. In particular, very few studies [9] have examined coarsening in fluorinated foams. Fluorocarbon surfactants are important ingredients in firefighting foams. These unique chemicals are highly surface-active, thus they reduce the surface tension of aqueous solution to lower levels than achievable by hydrocarbon surfactants. Aqueous film forming foams (AFFFs), which contain both fluorocarbon surfactant and hydrocarbon surfactant, find widespread use in military and civilian applications because of their ability to spread out and suspend themselves on top of burning liquids [10]. Currently, the dynamics of bubble size coarsening in fluorinated foams are not well understood relative to foams produced from exclusively hydrocarbon surfactant systems such as SDS.

In order to predict the rate of foam coarsening, Hilgenfeldt et al. developed a theoretical model for bubble coarsening in foam based on von Neumann's growth model [5]. They experimentally verified this model for foams produced from SDS in water [5]. The theory assumes thin films with a constant thickness (35 nm) and neglects film thinning due to liquid flow from films into Plateau borders [11]. Also, their theory considers an average characteristic length scale of idealized monodisperse bubbles rather than the polydisperse bubble size distribution found in real foams. Despite these simplifying assumptions, their experimental data for foam drainage in SDS foams showed excellent agreement with their theoretical model, which considers both drainage and coarsening. In the present paper, we ask whether this theoretical model can quantitatively describe the bubble coarsening in commercial firefighting foams, which contain complex chemical formulations.

In a previous effort to describe bubble coarsening in AFFF, Magrabi et al [9], developed a theoretical model for foam coarsening which considers a unimodal distribution of spherical bubbles. They showed good agreement between their model predictions and experiments for the evolution of bubble-size distributions when drainage effects were considered. However, they did not quantify the rate of coarsening in AFFF relative to an exclusively hydrocarbon foam such as SDS foam. Therefore, at this time, the contribution of fluorocarbon surfactant to the dynamics of coarsening in AFFF is not well understood.

New firefighting foam formulations are continuously being developed partly due to environmental issues associated with traditional AFFFs. Some newer AFFFs may include fluorocarbon surfactants with a different carbon chain length that is more environmentally friendly. In addition, fluorine-free alternative formulations to AFFF are emerging which contain exclusively hydrocarbon surfactants, for example: Re-Healing Foam 6% (RF6, Solberg Inc.). It is unclear what effect the ratio of fluorocarbon surfactant to hydrocarbon surfactant has on coarsening dynamics. Furthermore, these commercial formulations are multicomponent

and contain additives to control their mechanical stability, liquid drainage dynamics, and rheology. In addition, the fluorine-free formulations contain new chemical additives to compensate for their higher surface tension. Few works [12] have studied the effect of chemical additives on coarsening.

In this work, we have quantified the dynamics of coarsening in four foams containing different chemical formulations, specifically (1) a commercial AFFF (Buckeye Inc.) containing both hydrocarbon surfactant and fluorocarbon surfactant in water, (2) a lab-mixed foam containing fluorocarbon surfactants at a greater ratio of fluorocarbon to hydrocarbon surfactant than AFFF, henceforth called a high fluorinated fraction foam (HFFF), (3) a commercial fluorine-free firefighting foam, RF6 (Solberg Inc.), containing hydrocarbon surfactant and various hydrocarbon-based additives in water including viscosifiers, and (4) a foam produced from a mono-surfactant solution of sodium dodecyl sulfate (SDS) in water. We produced all of these foams using a single foam generator operated under a fixed set of flow parameters. We measured bubble-size distributions and liquid drainage over a duration of more than 45 min. These are the first measurements comparing the progressions of bubble size distribution between fluorinated and non-fluorinated foams. We compared average measured bubble size versus time with the self-similar growth law, thereby obtaining the effective diffusion coefficients of the various foams. Further, we compared these measured effective diffusivities with a theoretical model developed previously by Hilgenfeldt et al. [5], which predicts the rate of coarsening based on the mechanical properties of the liquid foam solution and based on the physicochemical properties of the gas in the liquid. We have quantified the extent to which the commercial firefighting foams, which contain multiple surfactants and additives, follow this idealized model.

1.1. Theory of foam coarsening

The average bubble radius, R , in foam has been predicted to grow according to the following coarsening equation [4–6]:

$$\frac{dR}{dt} = D_{\text{eff}} \frac{F(\alpha)}{R}, \quad (1)$$

where D_{eff} is the effective diffusivity of gas between bubbles and $F(\alpha)$ is a function of the local liquid volume fraction, α . This equation is sometimes referred to as the self-similar bubble growth law for foam. The term $F(\alpha)$ accounts for the effect of foam wetness on coarsening. In our analysis, we took $F(\alpha) = \left(1 - \sqrt{\alpha/0.44}\right)^2$, following Hilgenfeldt et al. [5].

The quantity D_{eff} from Eq. (1) provides a useful metric for the rate of coarsening of a foam. Hilgenfeldt et al. developed a simple analytical model for predicting D_{eff} based on the mechanical properties of the liquid and the physicochemical properties of the gas in the liquid [5]. For our analyses, we adapted their expression to the following:

$$D_{\text{eff}} \approx 1.94 \frac{4\delta_A}{3\delta_V\beta} \frac{D_f He \gamma V_m}{\lambda}, \quad (2)$$

where D_f is the nitrogen gas diffusivity in the liquid $D_f = 2.6 \times 10^{-5} \text{ cm}^2/\text{s}$ [13,14], He is the Henry's Law constant for nitrogen gas in the liquid solution, γ is the surface tension of foam solution, V_m is the ideal gas molar volume ($0.0245 \text{ m}^3 \text{ mol}^{-1}$ at 25°C), λ is the thickness of lamellar films, and the geometrical constants $\delta_A = 27$, $\delta_V = 11.3$, and $\beta \approx 11$ are taken to be the same as those used by Hilgenfeldt et al. [5]. The factor of 1.94 appears in Eq. (2) because we express Eq. (1) in terms of R rather than the characteristic Plateau border length, L , as used by Hilgenfeldt et al. [5]. This allows us to compare the theory with measurements

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