

Periodic explosions by positive feedback in a rising foam column

(surfactants/micelles/thermal conductivity)

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ABSTRACT An aqueous foam rising adiabatically in a column suffers a drop in temperature. Under appropriate conditions, such a column periodically explodes. We here trace this explosion to the tight thermal coupling between the foam and its enclosing glass column. When the surface surfactant concentration is unbuffered by micelles, a positive feedback exists between the flow of heat from the walls into the foam and the thermal conductivity of the foam itself. In our highly expanded foam, heat is conducted through the foam cells' interior primarily by the heat-pipe effect. Such an effect is retarded by a dense layer of surfactant molecules. Heat absorption causes cell expansion, which, in a foam unbuffered by micelles, causes a reduction in surface concentration of surfactant molecules and, hence, in an increase in thermal conductivity. This interpretation of our observed periodic explosions is in agreement with all of our observations.

Zener and Fetkovich (1) have suggested a potential low-capital-cost method of generating power from the tropical oceans, where the surface water is relatively warm ($>25^{\circ}\text{C}$) with respect to the deep water ($<5^{\circ}\text{C}$). We foam the surface water and expose this foam to the vapor in equilibrium with the cold water from the ocean depths. The low foam density ensures that the foam will rise to a great height. Thus, under isentropic conditions, this height is given by

$$gh \leq \int_{p(25^{\circ}\text{C})}^{p(25^{\circ}\text{C})} \frac{dp}{\rho},$$

where $p(T)$ is the vapor pressure of water at T . When all of the work potential thereby released goes into potential energy, the equality sign is appropriate and

$$h = 293 \text{ m for } \Delta T = 20^{\circ}\text{C}.$$

The essential correctness of these concepts were demonstrated by Zener and Greenstein (2, 3). Using a 10-cm-diameter 9.1-m-high foam column and mass flux rates in the range of 0.2–0.7 $\text{g}/\text{cm}^2\text{-sec}$, they demonstrated that the steady-state rise of foam obeyed simple principles. Thus, the flow work function generated by a gram of foam in flowing from T to $T - \Delta T$,

$$\int_{P(T-\Delta T)}^{P(T)} \frac{dP}{\rho},$$

was consumed in increasing its potential energy, its kinetic energy, and supplying the losses attributable to the wall drag. They were puzzled, however, by the periodic foam-column breakdown that occurred when the surfactant concentration was lowered below a critical value. Just prior to breakdown, the foam velocity in the upper half of the column would rise to more than twice its normal value. The foam column appeared to lit-

erally explode. These explosions would repeat at constant intervals of about 4 min. Kay[‡] has repeated their experiment with similar results, with equipment on the coast of Puerto Rico using fresh sea water. We planned the experiments herein reported in the hope of clarifying the origin of these repeated explosions.

NEW EXPERIMENTS

To have our foam column under better control, we decreased the column height from 9.1 to 1.8 m. This enabled us to make all of the observations from a single floor. By using the same mass flux rate of $\approx 0.4 \text{ g}/\text{cm}^2\text{-sec}$, the required temperature decrease between condenser and incoming warm water was from $\approx 7^{\circ}\text{C}$ to $\approx 4^{\circ}\text{C}$. The critical surfactant concentration range separating steady flow from periodic explosions decreased from ≈ 300 to ≈ 100 ppm.

The intent of the foam generator had been to generate a uniform close-packed array of spherical bubbles, which would then expand into polygonal cells of continually increasing size as the foam rose. Toward this end, our foam generator contained a forest of vertical capillary tubes of 0.02-cm bore. In principle, the air rising within the tubes would mix with the input warm water rising between the tubes to form the desired close-packed array of uniform-size bubbles. In our original experiments (2, 3), the warm-water input came directly from the warm-water tap and was saturated with air. As this water flowed through the pressure reduction valves into the foam generator, many bubbles of uncontrolled size would spontaneously arise. Recognizing that bubbles of especially large size might be responsible for the observed foam breakdown at low surfactant concentrations, we introduced a continuous flash deaeration system. The water flowed directly from the low-pressure flash chamber into the foam generator with no further reduction of pressure. This input water was completely free of bubbles. The foam generated was radically improved. The generated close-packed bubbles were of the desired uniform size. The rising foam was completely free of turbulence. Periodic foam explosion still took place as the surfactant concentration was decreased to <100 ppm.

In the original experiments, the upper 0.6 m of the column was horizontal to facilitate foam destruction by a surfactant drip just prior to the foam entering the spray condensing chamber. Suspecting that the bend between the initial vertical section and the final horizontal section was the catalyst for the observed foam failure, we removed this bend. A vertical cone was placed just above the last vertical section of the column. This cone spread the existing foam radially so that it could still be destroyed by a surfactant drip before entering the spray condenser. This bend removal did remove the discontinuity in the

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[‡] Kay, M. (1979) *Proceedings of the Sixth Ocean Thermal Energy Conversion Conference*, Washington, D.C., pp. 9.3.1–9.3.5.

slope of the plot of ΔT vs. Z , which had occurred frequently at the bend. However, it did not effect the periodic foam explosions at low surfactant concentrations.

New and significant information was obtained by equipping the foam generator with a continuously recording pressure gauge. We found that the pressure remained constant as we decreased the surfactant concentration until we passed the critical concentration. Passing this critical concentration was accompanied by a rapid increase in pressure of several torr, followed at once by an explosive foam rupture and a decrease in pressure. This rapid increase in pressure was coincident with the previously mentioned rapid increase in velocity preceding foam rupture.

The present writers improved the original apparatus in order to understand the origin of these explosions. A full description of the new apparatus and of the experimental data has been presented elsewhere.[§] Here we present our final analysis of the origin of these repeated explosions in a rising foam column.

INTERPRETATION

We attribute the periodic explosion of our rising foam column at low surfactant concentration to the thermal coupling of the foam to the enclosing glass tube. Lord Rayleigh (4) demonstrated in the 1870s that quarter-wave-length oscillations in a tube closed at one end and open at the other will grow in amplitude if the closed end is sufficiently warmer than the open end. During that half of the cycle when an element of foam is closest to the warm closed end, it has adiabatically heated itself above its average temperature. In spite of its above normal temperature, it finds itself in contact with still warmer tube walls. Therefore, heat flows into the element of mass from the walls. Correspondingly, when the element of foam is in the half cycle closest to the open end, it has been cooled by an adiabatic expansion but gives out heat to the still colder tube walls. The work performed by the gas during each cycle of vibration goes into increasing the energy of vibration. Lord Rayleigh's singing tubes are providing cryogenic laboratories with a simple tool for measuring the level of cryogenic fluids in their thermos bottles (5, 6).

Whereas our rising foam column is not identical to a Rayleigh singing tube, it has one essential feature in common. The heat that flows into the foam from the glass wall at T is lowered to $T - \Delta T$ by the adiabatic expansion of the foam. The fraction $\Delta T/T$ of this heat is converted, thereby, into free energy. When the foam enters the constant-pressure condenser, the work potential generated by the lowering of the heat input has gone into increasing the kinetic energy of the foam. An absorption from the wall of only 1 cal/g of foam, together with an adiabatic decrease of 1°C prior to entering the condenser, would provide enough work potential to impart a final velocity of 12 m/sec to the foam. Such an exit velocity is consistent with our observations during foam explosion.

Is it possible for our rising foam to acquire such heat inputs from the enclosing glass tube? A cursory analysis might conclude that such a heat input is quite impossible. After only a 1°C decrease in temperature, a close-packed array of bubbles becomes a foam whose volume is 99% water vapor. The thermal conductivity of this vapor is low,

$$k_{\text{vapor}} = 0.00005 \text{ cal/cm}\cdot\text{sec}\cdot\text{C},$$

giving a thermal diffusivity coefficient of

$$D = \frac{k_{\text{vapor}}}{\rho C} \approx 0.005 \text{ cm}^2/\text{sec}.$$

The relaxation time for establishment of temperature equilibrium throughout a cross section of the 10-cm-diameter foam column is given by

$$\tau = \frac{(d/4.8)^2}{D} \approx 800 \text{ sec}.$$

This time is so long that heat diffusion inward from the glass tube can have no significant influence on a foam that remains in the tube only several seconds.

Heat conduction within a foam cell's interior also occurs by the heat-pipe effect, namely the mass transport of vapor accompanied by the evaporation/condensation at the adjacent wall surfaces. This thermal conductivity is given by

$$k_{\text{heat pipe}} \approx d \cdot \frac{d}{dT} (SnhV_{\text{eff}})$$

in terms of the mean cell diameter d and of the following properties of the water vapor molecules: S , sticking coefficient; n , number of molecules per cm^3 ; h , heat of vaporization; V_{eff} , effusive velocity. Using the observed value of ≈ 1 cm for d , we obtain

$$k_{\text{heat pipe}} \approx 0.33 S \text{ cal/cm}\cdot\text{sec}\cdot\text{C}.$$

Recent experiments (7) indicate that S approaches 1.0 for clean water surfaces. When the surfactant does not appreciably retard evaporation, we expect the thermal conductivity of our foam to be nearly 10,000 times greater than that given by thermal diffusivity. With this high thermal conductivity, heat can now rapidly diffuse into the foam column from the enclosing glass tube.

The above discussion suggests that the periodic explosions of our foam column arises from the sudden 4-order-of-magnitude jump in foam thermal conductivity as the foam expansion begins to relax the tight packing of the surfactant molecules on the foam wall surfaces. This relaxation of tight packing has the positive feedback necessary for an explosion. The beginning of this relaxation increases the foam's thermal conductivity, which allows an influx of heat from the column walls into the foam interior, which in turn expands the foam, further relaxing the surfactant packing, and so on to an explosion. This interpretation of our observed explosions predicts that the observed critical surfactant concentration below which explosions occur is that concentration at which tight packing is being relaxed. In the following paragraph, we show that our experimental data support this interpretation.

An analysis of what happens to the surfactant molecules during foam expansion reveals that the described positive feedback is suddenly turned on during the foam expansion. The total number n_{tot} of surfactant molecules per g of foam is distributed in three modes. Some, n_{sol} , are molecularly dispersed as a solute in the bulk of the liquid. This number is prevented from exceeding a critical concentration n_{cr} by the "precipitation" of small surfactant aggregates known as micelles. Thus, the number of surfactant molecules, n_{mic} , so distributed is restricted by

$$n_{\text{mic}} = 0 \text{ if } n_{\text{sol}} < n_{\text{cr}}.$$

Finally, some of these surfactant molecules, n_{surf} , are on the liquid/vapor interface. Their surface density one denotes by Γ . Thus, the number of surfactant molecules so distributed is given by

$$n_{\text{surf}} = \Gamma A,$$

where A is the surface area per g of foam. During the initial foam

[§]Zener, C. & Noriega, J. (1981) *Proceedings of the Eighth Ocean Thermal Energy Conversion Conference*, Washington, D.C., in press.

expansion, the increase in area A causes n_{surf} to grow at the expense of n_{mic} , while n_{sol} and Γ remain essentially constant at their initial values

$$n_{\text{sol}} = n_{\text{cr}}$$

and

$$\Gamma = \Gamma(n_{\text{cr}}).$$

Only after the micelle population is completely depleted does Γ decrease with further foam expansion. Only then is the foam susceptible to catastrophic explosion.

We can readily estimate the surface density Γ of our surfactant molecules when the thermal positive feedback first becomes operative. At this critical moment, the number of surface molecules per g of foam is just equal to the number of molecules in micelles in the original solutions. Thus,

$$A\Gamma = n_{\text{mic}}$$

We obtain n_{mic} from the relation

$$n_{\text{mic}} = \frac{N}{M_r} (C_{\text{tot}} - C_{\text{sol}}),$$

where N is Avogadro's number, C_{tot} is the total surfactant mass concentration, and C_{sol} is the surfactant mass concentration that is molecularly dissolved. The M_r of our surfactant, Neodol 25-3A, is given as 432 g/mol by its supplier.[†] The mass concentration C_{tot} at which instability first occurs in our column is 135 ppm. The maximum concentration in solution we estimate as 14 ppm from Greenstein's (3) Γ vs. C plot. We thereby obtain

$$n_{\text{mic}} = 17 \times 10^{16} \text{ molecules/per g.}$$

To estimate A we assume all of the mass is in the walls, thereby obtaining[‡]

$$A = 6/(\rho_f d).$$

At the column exit, our ΔT is 3°C, giving from ref. 1

$$\rho_f = 0.0038 \text{ g/cm}^2.$$

In our present experiments, we find $d \approx 1.0$ cm at the foam exit, thereby giving

$$A = 1,600 \text{ cm}^2/\text{g}$$

$$\Gamma = (17 \times 10^{16}/1,600) \text{ molecules per cm}^2$$

[†] Shell Chemical Company, Catalog No. SC: 7-79.

[‡] This equation follows from area per g = area per cell \times (volume per g/volume per cell).

or, for the mean area per surface surfactant molecule,

$$\Gamma^{-1} = 93 \text{ \AA}^2.$$

This value of Γ^{-1} is the minimum area per surfactant molecule obtainable from a solution. An increase in overall concentration will simply provide more micelles but will not provide a closer packing of surface surfactant molecules. In comparing this value from our foam column experiments with literature values obtained from direct measurement, we note that our surfactant is a mixture of the molecules



where r ranges from 12 to 15. Rosen (8) gives comparable values for Γ^{-1} in a surfactant in which NH_3 is replaced by Na. Our value of 93 \AA^2 lies between his values of 74 \AA^2 when $r = 10$ and 126 \AA^2 when $r = 16$.

PREDICTIONS

The above interpretation of the periodic explosions in our foam column leads to an interesting prediction. The essence of this interpretation is the positive feedback of an inward flow of heat from the containing wall into the rising foam. An inescapable corollary of this interpretation is that these explosions would not take place if we arranged for a small outward heat flow from the foam to the containing wall. We also predict that such explosions would be prevented by sufficient insulation between the foam and the surrounding wall. Such insulation could be provided by a thin film of high surfactant concentration falling down the inner surface of the containing wall. The high surfactant concentration would retard rapid evaporation from the outermost water/vapor interface, and would thereby block the above positive feedback.

Finally, we predict that this explosion will not take place when the surfactant heads are very large. The tails will then be so far apart that they will not significantly impede evaporation.

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