

## VAPOR EXPLOSIONS: A CRITICAL REVIEW

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Four stages of the vapor explosion phenomenon are distinguished: premixing, triggering, escalation and propagation. Fauske proposed that spontaneous nucleation upon contact of the hot and cold liquids was a necessary condition for the first three stages, while Board, Hall and Hall have proposed a thermal detonation theory based upon purely hydrodynamic fragmentation behind the shock front for the fourth stage. The evidence concerning both concepts is discussed, and some tentative conclusions drawn. Some data relevant to the triggering and escalation steps, together with some brief comments concerning cyclic propagation models, are presented.

NOMENCLATURE

Bo = Bond number  
 $C_D$  = drag coefficient  
 $E$  = fraction of mass of drop stripped away  
 $a$  = acceleration  
 $M_J$  = Mach number at C-J plane  
 $P$  = pressure  
 $r_d$  = drop radius  
 $t_b$  = break up time  
 $T_b$  = dimensionless break up time  
 $T$  = temperature  
 $u_r$  = relative velocity between drops and surrounding fluid  
 $\bar{v}$  = mixture specific volume  
 $We$  = Weber number  
 $x_1$  = volumetric fraction vapor in coolant ahead of shock  
 $x_d$  = volumetric fraction of drops ahead of shock  
 $\rho$  = density  
 $\sigma$  = surface tension

SUBSCRIPTS

c = critical  
d = drop  
r = surrounding  
H = hot liquid

hn = homogeneous nucleation

i = interface

io = initial interface

mfb = minimum film boiling

sn = spontaneous nucleation

1. INTRODUCTION

We shall define a vapor explosion as the result of rapid self-mixing of a hot liquid and a cold vaporizable liquid such that a significant fraction of the theoretical energy release appears in the form of a pressure shock wave. The time scale for the mixing process is  $< 10^{-4}$  s, based upon a 0.01 m initial dispersal scale and a shock velocity through the liquid-vapor mixture  $> 10^2$  m/s. Slower fragmentation and energy transfer result only in violent boiling, which is relatively harmless. The key problem from the safety viewpoint, therefore, is to identify the conditions under which vapor explosions cannot occur, rather than those under which they can. This is indeed a difficult exercise, since vapor explosions are notoriously non-reproducible. The stochastic nature appears to stem from the random occurrence of a local pressure wave strong enough to collapse the vapor blankets around the fuel (hot liquid) particles before substantial solidification has taken place. There are actually two related, but quite different, questions:

1. Assuming that the liquids are poured (or injected) one into the other, what are the necessary conditions for a vapor explosion to be triggered and to escalate in intensity and size to a full-scale detonation wave?

2. Without considering the escalation process, under what conditions will a steady-state detonation wave propagate through the coarsely-dispersed mixture?

There have been two major contributions to these problems. One is the set of necessary conditions formulated by Fauske<sup>1</sup> for the free-contacting mode, which has been loosely termed\* the spontaneous

\*The term is frequently extended to include the capture theory of Henry and Fauske<sup>2</sup>, which is a cyclic propagation theory for the escalation phase.

nucleation theory.\*\* The other is the thermal detonation wave theory due to Board, Hall and Hall<sup>2</sup>, which draws on the analogy to chemical explosions. Some features of both theories have been criticized, and we will focus below on a consideration of the questions surrounding them. In addition to these two major concepts, a number of theories have been proposed for the mixing or fragmentation step, or more elaborately, for the elementary cyclic process of mixing and energy transfer by which the chain reaction escalates<sup>3</sup>. These are much difficult to verify (and hence speculative) in view of the extremely small length and time scales in the fine mixing process. We shall discuss some of the common features of these theories, without going into too much detail.

## 2. SPONTANEOUS NUCLEATION (SN) THEORY

Fauske<sup>1,3</sup> proposed the following necessary conditions for a vapor explosion when the hot liquid (fuel) is poured or injected into the cold liquid (coolant), or vice versa:

1. Initially stable film boiling, so that a vapor film separates the two liquids and permits course premixing without excessive energy transfer.
2. Liquid-liquid contact due to breakdown of film boiling (either due to cooling of the hot liquid or arrival of a pressure wave).
3. Spontaneous nucleation upon contact\*\*.
4. Adequate physical and inertial constraints to sustain a shock wave.

Actually, the principal concepts of initial film boiling, followed by collapse of the vapor blankets around the hot liquid and very rapid vapor formation due to homogeneous nucleation, were enunciated earlier in connection with LNG explosions in water<sup>4-6</sup>. Fauske sharpened the concepts by recognizing that the interfacial contact temperature, rather than the hot liquid bulk temperature, was the important quantity, and that spontaneous nucleation (due to statistical density fluctuations, rather than pre-existing nucleation sites) can occur, particularly with water, in poorly-wetting systems. Another important contribution was the distinction between large and small scale explosions.

The three stages of an explosion proposed by Board and Hall<sup>7</sup>, namely coarse pre-dispersal, triggering and propagation, (which are implicit in the necessary conditions due to Fauske) should properly be supplemented by a fourth stage: escalation. This recognizes that the early propagation, or escalation, phase may have an entirely different mixing mechanism than the steady, fully-developed shock propagation phase.

One must take into account explosions in which the contact temperature is supercritical, a preferable formulation is the following. 1. Immediate local pressurization upon contact. This is automatically satisfied above the critical temperature. Below this temperature a sufficient condition for immediate ( $\sim 10^{-4}$ s) local pressurization is spontaneous nucleation, although this condition might be met at a dirty surface (large numbers of pre-existing sites) at temperature below, but close to, the spontaneous nucleation threshold.

## 2.1 Experimental Evidence

The strongest evidence in favor of the SN hypothesis is the extensive work<sup>4,5,9</sup>, ranging in scale from laboratory flasks to tank-car spills on the surface of a bay, on explosions of cryogenic hydrocarbons poured onto or injected into water. As LNG "ages", its boiling point increases, due to differential distillation of methane away from the heavier components. In a large number of experiments it was found that the homogeneous nucleation temperature,  $T_{hn}$ , of the hydrocarbon mixture had to lie in a narrow band around the ambient water temperature in order to obtain a vapor explosion. For any particular mixture there was thus an explosive composition envelope, outside of which film boiling and ice formation occurred without an explosion. For example, only after 93% boil-off did spillage of commercial LNG in tank load quantities result in explosions. It was also possible to obtain delayed explosions with less-enriched mixtures in sufficient quantity by boil off from the hydrocarbon layer as it spread over the water surface, which could be predicted from a simple model of the spill spreading and vaporization rate<sup>8</sup>. The spontaneous nucleation requirement was thus found consistently to be operative over a wide range of hydrocarbon mixtures and spill sizes.

There is probably no real disagreement that extensive liquid-liquid contact with interfacial temperatures at or above the spontaneous nucleation temperature is a sufficient condition to produce at least a local explosion. This is shown by experiments<sup>10,11</sup>, in which a small volatile drop rose slowly through a column of a second liquid with a vertical temperature gradient. Drops of various organic liquids exploded at temperatures within 1 K of the theoretical  $T_{hn}$ , but water droplets rising in silicone oil behaved quite differently. Despite the fact that significant miscibility of the two liquids was observed above 473 K, the explosion range was generally 523-548 K, as compared to the theoretical value of 586 K. Some drops (0.1-0.5 mm) appeared to nucleate bubbles at 473-513 K, while some larger (1 mm) drops evolved a continuous train of bubbles from their surface until they reached a high temperature where they exploded<sup>11</sup>. This indicates that heterogeneous nucleation can proceed with water from a pre-existing site, while the liquid superheats and nucleates explosively in a nearby region. The special nucleation properties of water are well-known, as shown by measurements of liquid tensile strengths by spinning freshly-drawn glass capillary tubes<sup>12</sup>, and of the heating time,  $\tau_h$ , to  $T_{hn}$  of a pulsed platinum wire in various liquids necessary to suppress pre-existing sites<sup>13</sup>. For a variety of organic liquids  $\tau_h \sim 10^{-4}$ s, but for water  $\tau_h \sim 40$ s.

It is not necessary to have long heating times and intimate liquid-liquid contact throughout the experiment in order for small drops to explode<sup>14,15</sup>. Small ( $\sim 3$  mm) drops of several organic liquids, including methanol, ethanol, and pentane, were allowed to fall 0-15 cm. onto the surface of a pool of hot silicone oil or glycerol. A stable liquid-liquid contact was obtained if the Weber number upon impact exceeded a critical value, which depended weakly on the surface temperature. In this case the droplet evaporated smoothly to



curvature effects may be neglected, and the shock treated as a plane, steady one-dimensional detonation proceeding through initially coarsely-mixed fuel, coolant liquid and coolant vapor. The shock collapses the vapor blankets, inducing a large relative velocity between the fuel drops and surrounding coolant liquid. ~~These calculations are sensitive to both  $C_D$  and  $T_b$ , it is clear that additional data in fragmenting liquid-liquid systems, both with and without surface solidification, and both with single drops and with dense dispersions, are required.~~

The latter mode is predicted to be dominant for Bond numbers,  $Bo > 10^3$ , based on local relative velocities<sup>28</sup>. The proportionality constant in the theoretical expression for the dimensionless breakup time was estimated from air-water data:

$$T_b = (2d/\sigma)^{1/2} (u_F t_b / r_d) = 44 Bo^{-1/2} \quad (1)$$

$$Bo = \rho_F r_d^2 / \sigma = 3u_F^2 r_d C_D / 8 = \frac{3}{8} We \quad (2)$$

for  $C_D = 2$

with  $C_D = 2$ , which is the drag coefficient for a single smooth spherical drop. The time for velocity equilibrium was estimated from the time for acceleration of an isolated drop up to the free-stream velocity. Taking the Chapman-Jouguet condition<sup>29</sup> for the end of the fragmentation region, and solving the jump shock balance, supercritical pressures were predicted behind the shock ( $\sim 10^2$  MPa for tin-water and  $\sim 10^3$  MPa for  $UO_2/Na$ ). These calculations did not take into account the slowing-down of the coolant in a dense droplet dispersion, and more detailed analyses have therefore been performed.

~~Reanalysis of the breakup of the separated multi-phase flow conditions...~~

~~...the fragmented fuel particles were assumed to equilibrate immediately in velocity and temperature with the coolant, and the rate of mass stripping was estimated from a formula due to Reinicke and Waldman<sup>31</sup>. The following parameter values were used:  $T_b = 3$ , based on air-water<sup>31,32</sup>, and mercury-water ( $T_b = 3-5$ ) data<sup>33</sup> (although some new mercury-water data give considerably faster breakup<sup>34</sup> ( $T_b = .4$ );  $C_D = 2$ , which agrees with observations of single mercury drops fragmenting in water. However, Fauske<sup>35</sup> has estimated that  $C_D \sim 65$  for dense dispersions, based on the mercury-water flooding data of Kutateladze<sup>36</sup>. Fig. 1 shows the tin-water calculations for example initial conditions<sup>2</sup> (equal volumes tin at 1273 K, water and steam at 173 K). The fraction of drop mass stripped at the end of the reaction zone,  $E$ , is a free parameter, giving a family of partial Hugoniot for  $0 \leq E \leq 1$ . All curves exhibit a sharply-defined knee, corresponding to the disappearance of vapor at subcritical pressures. Hence the tangency point dictated by the Chapman-Jouguet (C-J) condition is always below 13 MPa, which implies that vapor is present throughout the reaction zone. Similar results are obtained with  $UO_2/Na$ . Nevertheless, as shown in Fig. 1, it is theoretically possible to obtain sonic end conditions ( $M = 1$ ) with high pressure at smaller initial void fractions. However, the reaction zone length  $\sim 0.5-1$  m for  $T_b = 3$ , which would be difficult to sustain. For  $T_b \sim 0.5$ , however, the~~

reaction length is  $\sim 10$  cm, and a broad range of initial conditions might result in sustained shocks (Fig. 3). Moreover, reasonable agreement is obtained with  $Al/H_2O$  shock propagation data<sup>27,37</sup> (10 MPa; 0.1 m reaction zone length), but only if  $T_b \sim 0.5$ . However, such fast breakup at subcritical pressures may result from violent boiling, rather than Taylor instability. As shown in Fig. 4,

since these calculations are sensitive to both  $C_D$  and  $T_b$ , it is clear that additional data in fragmenting liquid-liquid systems, both with and without surface solidification, and both with single drops and with dense dispersions, are required.

#### 4.0 Triggering Phase

It is generally accepted that the triggering step consists of vapor blanket collapse, either spontaneously due to reduction of the fuel and/or coolant temperature, or increase in system pressure, or due to an external trigger, consisting of a pressure wave arriving at the fuel-coolant interface<sup>1,19</sup>. Inoue, et al.<sup>38</sup> have recently investigated the destabilization of film boiling on a heated horizontal nickel tube in Freon-113 and ethanol due to a pressure shock of 0.1-0.5 MPa with a rise time of 0.08-3 ms. Surprisingly, the collapse visually appeared to be complete in  $\sim 1$  frame (5000 f/s), even at these low shock overpressures and at reduced surface temperatures ( $T_s/T_b$ ) as high as 1.5. Furthermore, the heat flux, averaged over 1 ms after collapse, showed a maximum at surface temperatures well above  $T_b$ . ~~These calculations show that triggering of three-scale phenomena, such as ...~~

#### 5.0 Escalation Phase

This phase depends upon elementary reaction steps involving mixing, formation of new contact area and vapor production, and is least understood of all the phases of the explosion. A number of cyclic models have been proposed<sup>39-43</sup>, none of which can at present be considered to be on a firm theoretical and experimental footing. We confine ourselves to a few remarks on the general nature of several of these theories. One group of theories is based on the notion of fragmentation due to bubble collapse, while another focusses on mixing during the expansion stage. The bubble collapse theories generally make use of a calculation<sup>44</sup> of the asymmetric collapse of a cavitation bubble initially tangent to a solid wall, from which the length, velocity and diameter of the entering jet can be estimated. The difficulty in applying this model to vapor-blanketed fuel particles is that the tangency condition is not even approximately satisfied, except for the special case of  $UO_2$  drops in subcooled sodium<sup>45</sup>, where subcooled nucleate boiling can be expected. On the other hand, films of tin drops fragmenting in water show repeated bubble growth and collapse due to penetration of water into the drop, followed by rapid vaporization. In some respects the observations correspond more closely to the cratering theory sketched by Colgate<sup>39</sup>, in which coolant penetrates the fuel due to surface instabilities and turbulent mixing occasioned by large relative velocities. It then vaporizes rapidly, blowing a crater of material whose mass is  $\sim 10^4$  times the mass of "equivalent

$$L_2 = 4(E/\sigma)$$

why is  $E$  free from  $T_b$ ?



explosive" (TNT), in turn depending on coolant and fuel temperatures and physical properties. The Ochiai-Bankoff theory<sup>43</sup> is somewhat more specific concerning the nature of the surface instability, modeling it by an annular splash jet following contact of a liquid coolant tongue with the fuel surface and rapid local pressurization.

### CONCLUSIONS

1. Despite the criticisms which have been voiced, the spontaneous nucleation condition for a large-scale vapor explosion, which implies instantaneous local pressurization upon vapor film collapse, has not been violated in practice, and appears to be reasonably intact. Extrapolated to the LMFBR, this implies that a  $\text{UO}_2/\text{Na}$  vapor explosion is unlikely in the reactor environment.

2. Theoretical studies indicate that a supercritical thermal detonation propagating steadily through a coarse fuel-coolant ( $\text{Sn}/\text{H}_2\text{O}$  or  $\text{UO}_2/\text{Na}$ ) mixture would be difficult to attain if  $T_b \approx 3$  (boundary layer stripping). However, reasonable agreement can be obtained with  $\text{Al}/\text{H}_2\text{O}$  shock data at subcritical pressures by assuming very fast breakup, possibly to local boiling. However, these predictions are sensitive to the drag coefficient and dimensionless breakup time, which to date have been estimated from data under conditions far removed from those in a vapor explosion.

3. Relatively low-pressure shocks can collapse the vapor film, even when the hot surface temperature is supercritical, indicating that triggering and escalation in most large-scale explosions proceeds independently of nucleation.

4. The escalation and possibly also the propagation step probably proceeds by a cyclic process in which coolant is entrapped in the fuel, vaporizes explosively with fragmentation, followed by overexpansion, collapse and further penetration of the fuel by coolant. Although various models have been proposed, the details are not well understood at this time.

### ACKNOWLEDGMENT

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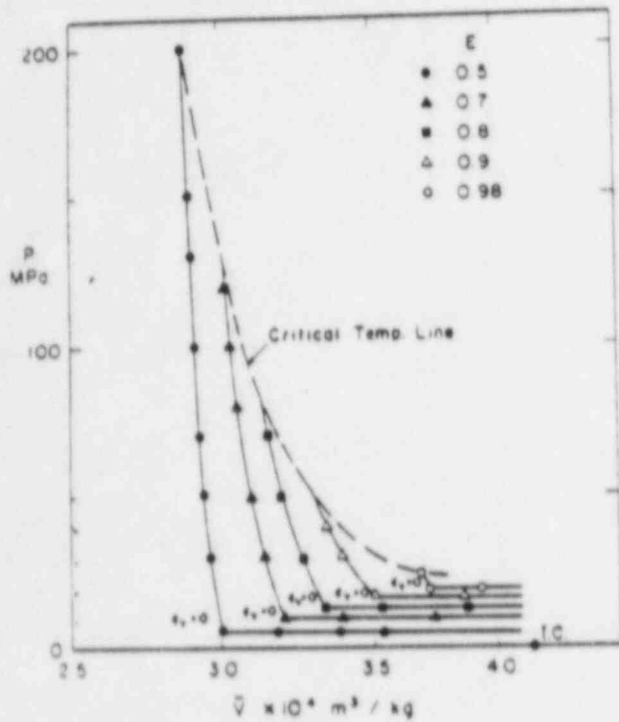


Figure 1 Partial detonation Hugoniot for  $\text{Sn}/\text{H}_2\text{O}$ .  $\mu_{d1} = 1/3$ ;  $\epsilon_{v1} = 0.5$ ;  $m_{\text{fuel}}/m_{\text{coolant}} = 0.5$

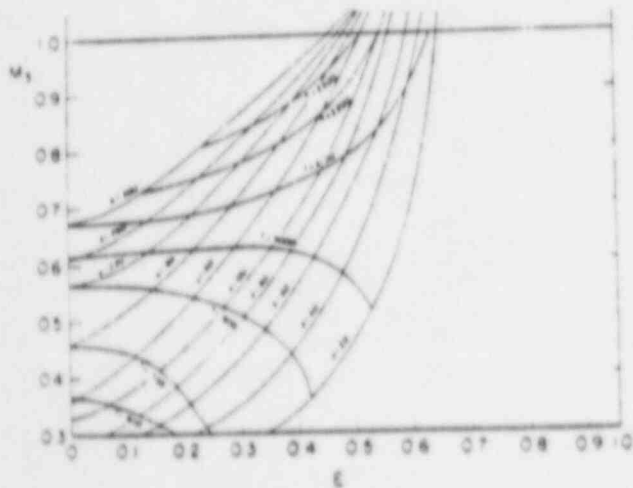


Figure 2 Equilibrium Mach number vs. mass fraction scripped for  $\text{UO}_2/\text{Na}$ .  $\epsilon_{v3} = 0$ ;  $\mu_{d1} = 0.25$ ;  $\epsilon_{v1} = 0.38$ ;  $m_{\text{fuel}}/m_{\text{coolant}} = 2.1$

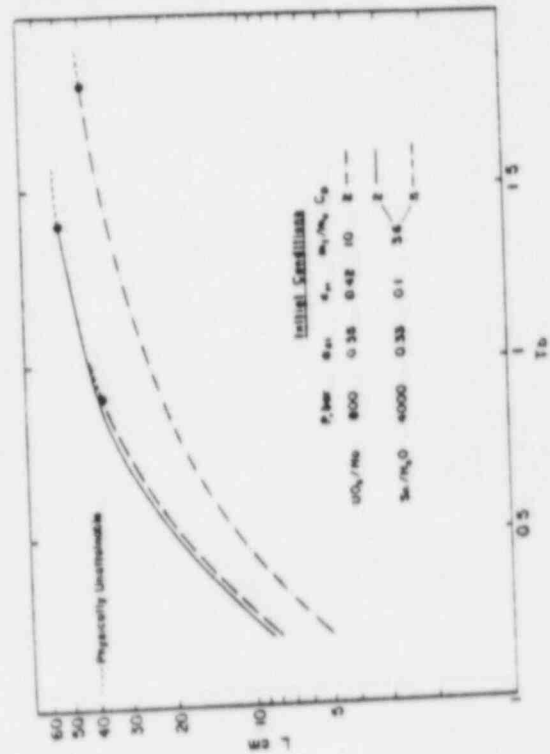


Figure 3 Reaction zone length vs. dimensionless breakup time for  $\text{Sn}/\text{H}_2\text{O}$  and  $\text{UO}_2/\text{Na}$ .

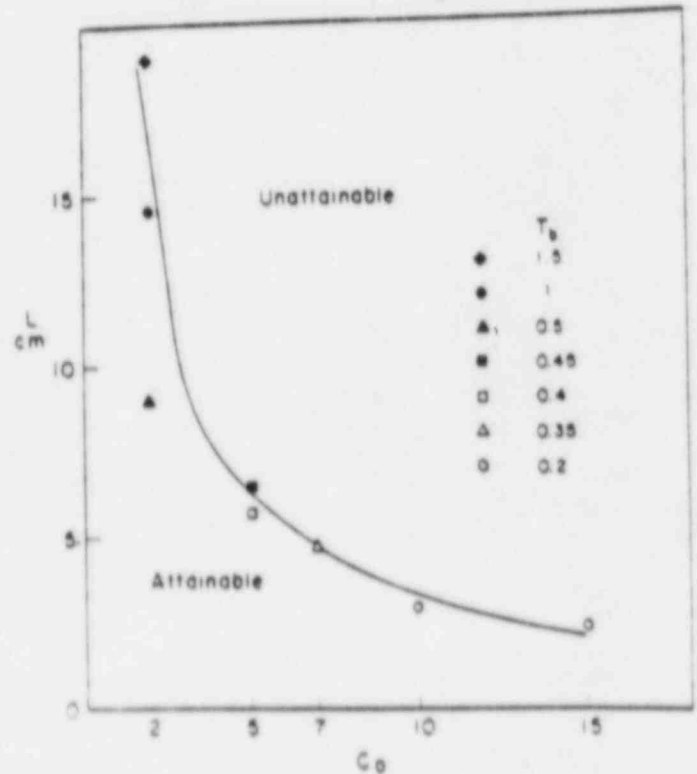


Figure 4 Reaction zone length vs. drag coefficient and dimensionless breakup time for  $\text{Al}/\text{H}_2\text{O}$ .  $\mu_{d1} = 0.4$ ;  $\epsilon_{v1} = 0.3$ ;  $m_f/m_c = 2.2$ ;  $\epsilon_{v3} = 0.38$ ;  $\mu_{d1} = 0.25$ ;  $\epsilon_{v1} = 0.38$ ;  $m_{\text{fuel}}/m_{\text{coolant}} = 2.1$ ;  $E = 0.8$ ;  $P_3 = 10 \text{ MPa}$