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APPROXIMATIVE QUANTITATIVE ASPECTS OF A HOT SPOT

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Summary

To understand the phenomena of initiation and low velocity detonation in liquids an approximate generalized description of bubble motion is suggested. Within this framework it is essential for any detonation to have a two-phase system of high and low compressibility of the components. The dynamic activated high compressibility component (bubble or void, cluster of chemical reaction) always has a phase-locked conservative radiation loss, and in addition, dissipative losses. These force a chemical decomposition in reactive liquids, so that a pressure-coupled chemical reaction is possible. In media of poor reactivity a decoupling may also occur, and, if the radiation loss dominates, even a nonchemical "detonation", in the sense of a shock wave amplification, becomes possible. The dissipative loss at the boundary of a bubble or void is governed by the medium's viscosity, and is, under some circumstances, the controlling factor. Questions concerning Bowden's hot spots are discussed, and another suggestion, that initiation should occur via dynamic bubble surface instabilities, is explored.

Introduction

In spite of the fact that it is mostly accepted that a low velocity detonation (LVD) involves a two-phase system (matrix with low compressibility and second phase — bubble, void or crack etc. — with high compressibility), several questions are not well understood, mainly initiation problems, and the coupling or decoupling of the chemical reaction with the pressure wave. Accepting Bowden's adiabatic hot spots [1,2], it is not easy to understand that different bubble contents do not lead to accordingly different sensitivities. Thus Hay and Watson [3] have found a LVD threshold of >2 kbar for the system of nitroglycerine/EGDN = 50/50 in the presence of voids, about 1.5 kbar for air and CO_2 bubbles, and for Ar bubbles somewhat less, <1.5 kbar. Since Mader's [4] hydrodynamic hot spot approach does not work for such low pressures, one may ponder the question of what really initiates the reaction? Some authors [5–7] have discussed the concept that initiation may take place via dynamic bubble surface instabilities, but considering the experimental results of Coley and Field [8,9] no such mechanisms are to be detected.

A further point of concern with respect to questions of safe handling is the nitromethane (NM) problem. For a long time it had been assumed that neat NM would not undergo a LVD; a theoretical model [10] had also confirmed this. Groothuizen [11] has demonstrated that a LVD of neat NM is possible, but its existence seemed to depend on the presence of a probe for measuring the detonation velocity. Kozak et al. [12] have shown that a LVD in thick-walled cylinders really is a reproducible event, where detonation velocity depends on the thickness of the walls, and Schilperoord [13] has confirmed this. Nevertheless, in 1958 there were two accidental NM tank car explosions with no apparent stimulation [14]. These accidents are very similar to those of tank car explosions of pressurized liquid gases, which sometimes occur spontaneously [15]. From the evidence given by the distance of the debris, we have to conclude that only an explosion within the tank can explain this occurrence. From the classical point of view explosions of chemical inert liquid gases are impossible, but the cited accidents and experimental evidence [16] of shock wave amplifications in chemically inert two-phase liquids suggest that one has to consider this somewhat unusual option. Mainly with respect to safety considerations, it is desirable to find a key to understand in a better way the underlying principles of this behaviour.

In the following sections, therefore, the dynamics of a single bubble or void are considered. Usually we do not know in practical cases the exact status of such a bubble or void, so we are not interested in exact solutions. More helpful is a simple analytical model, which allows an approximate generalized description of the possible behaviour. Such a description has long been available for small-amplitude motions of bubbles [17]. This solution is applied to large-amplitude motions. This step is justified by the fact that the time of collapse of a bubble in a loss-free medium corresponds to that of the classical Rayleigh collapse [18] and more refined versions of the Rayleigh equation. Medium nonlinearities are not considered. In the following, the algorithms of this estimate are presented, which will be applied in another paper to practical problems of safety.

Devin's bubble dynamics

From the Lagrangian equation Devin [17] has found for small-amplitude motions of spherical bubbles of initial volume $V_0 = \frac{4}{3}\pi R_0^3$ actuated by an external stimulation with a pressure $-p(t)$ the apparently "simple" harmonic equation

$$m\ddot{V} + b\dot{V} + KV = \begin{cases} 0 \\ -p(t) \end{cases} \tag{1}$$

if the coefficients are constant (which is not actually the case).

Devin determines the coefficient of mass as follows

$$m = \rho_\infty / 4\pi R_0 \ . \tag{2}$$

As shown later, for larger bubbles of size kR one obtains

$$m = \rho_\infty / 4\pi R(1 + k^2 R^2) . \tag{3}$$

For a constant polytropic index, γ', one gets for the stiffness, K

$$K = \gamma' p_0 / V_0 \tag{4}$$

and the damping coefficient

$$b = \omega_0 m \delta_{tot} . \tag{5}$$

As usual, one gets by

$$\sqrt{\frac{K}{m}} = \omega_0 = 2\pi f_0 = \frac{1}{R_0}\sqrt{3\gamma' \frac{p_0}{\rho_\infty}} = \frac{c'}{R_0}\sqrt{3\frac{\rho'}{\rho_\infty}} \tag{6}$$

or

$k'R = \sqrt{3\rho'/\rho_\infty}$ (based on bubbles content)

or

$kR = \dfrac{c'}{c_\infty} \sqrt{3\rho'/\rho_\infty}$ (based on the surrounding medium)

a resonance frequency of the bubble, or a resonance size, which corresponds to that of Minnaert [19]. Later this expression will be expanded for larger sources of size $kR = 2\pi R/\lambda$.

As a rule of thumb one may take for not too unusual liquids at the ambient pressure p, in bar, where f_0 is given in Hz, and R_0 in cm

$$f_0 R_0 \simeq 300\sqrt{p} , \tag{7}$$

$$kR \simeq 0.02\sqrt{p} . \tag{8}$$

In these expressions ρ_∞ is the density of the surrounding medium, γ' is the appropriate radius dependent polytropic index of the bubble content and p_0 its pressure, c' and ρ' are the corresponding sound velocity and density, and $k' = \omega / c'$; δ_{tot} is the total loss of bubble vibration, which consists of a conservative radiation loss, δ_{rad}, and dissipative losses.

As will be seen in the case of a conservative loss, $b\dot{V}$ corresponds to a pressure source, where $\dot{V}$ is given by

$$\dot{V} = 4\pi R^2 \dot{R} \tag{9}$$

In the case that no mass transfer between the content of the bubbles and the surrounding medium takes place, the identity due to Plesset and Prosperetti [20] holds

$$\dot{R} = \frac{\rho_\infty}{\rho_\infty - \rho'} u_{r_\infty} + \frac{\rho'}{\rho_\infty - \rho'} u_r \simeq u_{r_\infty} \tag{10}$$

which is connected with the "plane wave" particle velocity, u_p. Obviously the condition in eqn. (10) only holds approximately in the case of the onset of chemical reaction at the bubble surface or in the case of evaporation—condensation processes.

Radiation loss

Assuming again harmonic V variations, one gets for the wave impedance, $\tilde{Z}$, at the surface of the monopole source ($r = R$), see Ref. [21]

$$\begin{aligned} \tilde{Z} = \frac{\tilde{p}}{\tilde{u}_p} = \frac{\tilde{p}}{\tilde{u}_r} &= \rho_\infty c_\infty \frac{k^2 R^2}{1 + k^2 R^2} + \mathrm{i}\omega \frac{\rho_\infty R}{1 + k^2 R^2} \\ &= R_r + \mathrm{i}\omega m_r \end{aligned} \tag{11}$$

The real part of eqn. (11) is the radiation resistance, R_r, and the imaginary part, m_r, corresponds to the frequency-dependent acoustic mass. This latter part is sensitive to the shape of the source, whereas the radiative part is not.

Combining now the radiative part of eqn. (1) with eqns. (9) to (11), one gets, by using the identity for harmonic motions,

$$\ddot{V} = \mathrm{i}\omega \dot{V} \tag{12}$$

$$b\dot{V} = \frac{R_r}{4\pi R^2} \dot{V} + \frac{m_r}{4\pi R^2} \ddot{V} \tag{13}$$

So in eqn. (1) $\dot{V}$ is related to a pressure wave emission, and $\ddot{V}$ with a pressureless (near field) flow, and one gets for monopole sources of arbitrary size kR for the mass in eqn. (1) the formerly given eqn. (3), which now also changes Minnaert's resonance frequency, ω_0, to

$$\hat{\omega}^2 = \omega_0^2 (1 + \hat{k}^2 R^2) = \frac{c'^2}{R_0^2} \frac{3(\rho'/\rho_\infty)}{1 - 3(\rho'/\rho_\infty)(c'/c_\infty)^2} \tag{14}$$

For the radiation loss one gets

$$\begin{aligned} \delta_{\mathrm{rad}} &= \frac{R_r}{4\pi R^2 m \hat{\omega}} = \hat{k}R = \sqrt{\frac{3\gamma' p_0}{\rho_\infty c_\infty^2 - 3\gamma' p_0}} \\ &= \sqrt{\frac{3\rho' c'^2}{\rho_\infty c_\infty^2 - 3\rho' c'^2}} = \frac{c'}{c_\infty} \sqrt{\frac{3(\rho'/\rho_\infty)}{1 - 3(\rho'/\rho_\infty)(c'/c_\infty)^2}} \end{aligned} \tag{15}$$

The term

$$b\,\dot{V} = \frac{\pi \rho_\infty c_\infty \dot{V}}{\lambda^2 (1 + k^2 R^2)} \tag{16}$$

corresponds to the real part of the pressure, and we can attribute the imaginary part of the pressure to the near-field term governed by $\ddot{V}$, which is out of phase with the radiation governed by $\dot{V}$.

For low pressures the radiation loss may also be calculated according to the methods of Devin [17] or Nishi [24].

Dissipative losses

Up to now the most pronounced dissipative losses have been formulated by several authors as the thermal loss, δ_{th}, and the viscous loss, δ_η. In detonics this thermal loss corresponds to Bowden's adiabatic hot spot [1,2], and it will appear that this, of course, is not strictly valid. The physical reason is quite clear: If the sources are small, so that the mean free pathlength of the molecules is comparable to the dimensions of the bubble, an adiabatic heating is unrealistic. On the other hand, if the sources are large, and their pulsation becomes long in time, heat conduction again causes adiabatic heating to fail. So there exist optimum bubble sizes for adiabatic hot spots.

Less well known is the effect of viscous loss, in spite of the fact that viscosity had been considered by several authors in a somewhat different context, see for example the Summary [2]. The dynamic activated bubble experiences a powerful shear generator at the boundary layer to the viscous medium. Under some circumstances this viscous loss exceeds the thermal loss.

Thermal loss

Using the thermal diffusivity of the bubble content

$$D' = \kappa'/\rho' c'_p \tag{17}$$

where κ' is the heat conductivity, ρ' the density, and c'_p the heat capacity at constant pressure of the bubble content, Pfriem [22], Devin [17] and Kapustina [23] obtain for the case of resonance

$$\delta_{th} = \frac{\dfrac{\sinh z + \sin z}{\cosh z - \cos z} - \dfrac{2}{z}}{\dfrac{\sinh z - \sin z}{\cosh z - \cos z} + \dfrac{z}{3(\gamma' - 1)}} \tag{18}$$

where

$$z = 2\phi_1 R = 2R\sqrt{\frac{\pi f}{D'}} \tag{19}$$

Whereas Pfriem takes for R Minnaert's radius, R_0, and further assumes a constant polytropic index, γ', Devin [17] and Kapustina [23] additionally take into account the surface tension, σ_∞, of the liquid as well as a variable polytropic index, (γ'/α). For the correction of R they use

$$R = R_0\sqrt{\frac{g}{\alpha}} \tag{20}$$

where

$$\alpha = 1 + \frac{3(\gamma' - 1)}{z}\left[1 + \frac{3(\gamma' - 1)}{z}\right] \tag{21}$$

$$g = 1 + \frac{2\sigma_\infty}{p_0 R} - \frac{2\sigma_\infty}{3p_0 R(\gamma'/\alpha)} \tag{22}$$

The last part of eqn. (22) contains the dependence of the polytropic index as (γ'/α), and one sometimes obtains by calculation lower values than 1. This has to be avoided, of course. Within this set of equations δ_{th} may be calculated by iteration.

Contrary to the above authors Nishi [24] calculates D' by using the specific heat capacity at constant volume c'_{V}. Using

$$z = d = \sqrt{2\gamma'}R\sqrt{\frac{\omega}{D'}} \tag{23}$$

he calculates with eqn. (18) an intermediate value at resonance δ_{t}. He corrects Minnaert's resonance frequency by

$$\overline{\omega}_0 = \omega_0\sqrt{\frac{g}{\epsilon}} \tag{24}$$

where the stiffness correction is

$$\epsilon = (1 + \delta_{\text{t}})^2\left[\frac{3(\gamma' - 1)}{d}\,\frac{\sinh d - \sin d}{\cosh d - \cos d} + 1\right] \tag{25}$$

and

$$g = 1 + \frac{2\sigma_\infty}{Rp_0}\left(1 - \frac{\epsilon}{3\gamma'}\right) \tag{26}$$

Finally he gets for the thermal loss for arbitrary driving frequencies, ω,

$$\delta_{\text{th}} = (\overline{\omega}_0/\omega)^2\,\frac{\delta_{\text{t}}}{g}\left(1 + \frac{2\sigma_\infty}{Rp_0}\right) \tag{27}$$

He further obtains a polytropic index not below 1.

Viscous loss

As the source changes its volume the elements of the surface boundary are distorted, so that in this boundary layer rate-dependent viscous losses are activated.

In the case of resonance Devin uses

$$\delta_\eta = \frac{8\pi f \eta_\infty \alpha}{3\gamma' p_0 g} = \frac{4\eta_\infty}{\omega \rho_\infty R^2} \tag{28}$$

and for arbitrary frequencies ω one gets according to Nishi

$$\delta_\eta = \frac{4\bar{\omega}_0^2 \eta_\infty \epsilon}{3\omega\gamma p_0 g} = \frac{4\eta_\infty}{\omega \rho_\infty R^2} \tag{29}$$

where η_∞ is the viscosity of the medium.

All the above formulae have been obtained by small argument approximations, and so will hold for small sources only. Also, the validity of the expressions has been checked by ultrasonic experiments, and the errors are small (see Refs. [17,23, and 25].

Examples for calculated losses

As shown, the losses are to be calculated using physical quantities. The data from various references of some possible bubble contents are summarized in Table 1, and of some reactive liquids in Table 2.

In Fig. 1 the losses are calculated for a very sensitive and powerful explosive like nitroglycerine (NG) with bubbles of various sizes and gas content. As can be seen, the quality of gas content shows no very important in-

TABLE 1

Properties of some gases as bubble content (normal condition)

	γ'	κ' (μW/cm K)	ρ' (10^{-3} g/cm^3)	c'_p (J/g K)	c'_V (J/g K)	D'[a] (cm^2/s)	D'_V (cm^2/s)
Helium	1.66	1430	0.1787	5.172	3.116	1.547	2.568
Argon	1.67	164	1.783	0.520	0.312	0.177	0.295
Hydrogen	1.41	1810	0.08987	14.312	10.196	1.407	1.975
Nitrogen	1.40	240	1.251	1.040	0.743	0.185	0.259
Air	1.40	260	1.2505	1.0398	0.7427	0.200	0.280
Methane	1.30	303	0.7168	2.228	1.712	0.190	0.247
Propane	1.13	151	2.019	1.668	1.480	0.045	0.051
NM vapor, 1 bar	1.20	135	2.72	0.823		0.0603	0.0724
27.3 Torr			0.098			1.65	

[a] D varies with pressure approximately as $1/p$.

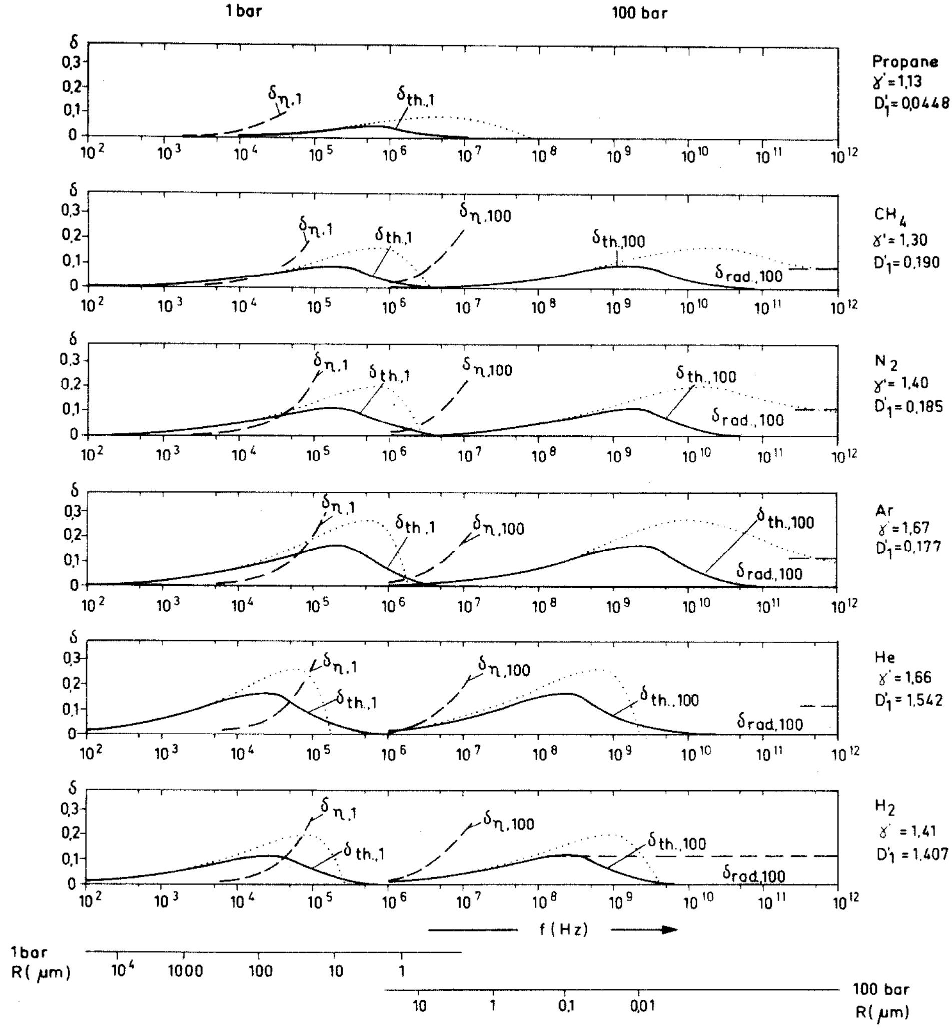

Fig. 1. Losses of resonant bubbles in NG at 1 bar and 100 bar ambient pressure. The losses are shown for very different gas content of the bubbles. The radiation loss for 1 bar is not drawn, it amounts to 0.01. The pointed lines indicate a low-frequency approximation given by Devin for the thermal loss.

fluence, in spite of the fact that large variations of γ' and the thermal conductivity have been considered. Also, the losses for an ambient hydrostatic pressure of 100 bar are calculated, where these are shifted into a high frequency region (or tiny bubbles). So it is possible that they may not be activated by a usual stimulation of lower frequency. The overall sensitivity of NG is caused possibly by the superimposition of the thermal and viscous losses.

TABLE 2

Properties of some liquid reactive substances

	t (°C)	ρ_∞ (g/cm³)	η_∞ (poise)	σ_∞ (dyn/cm)	c_∞ (10^5 cm/s)	Vapor pressure (Torr)
Nitroglycerine, NG	20	1.594	0.36	50.73	1.485	$2.5\ 10^{-4}$
Glycoldinitrate, GDN	20	1.488	0.0421		1.414	0.038
Diethyleneglycoldinitrate, DEGN	20	1.38	0.081			0.0036
Nitromethane, NM	20	1.130	0.00613	37.0	1.313	30
Tetranitromethane, TNM	20	1.64	0.0176	30.34	1.039	8.04
i-Propylnitrate, i-PN	20	1.049	0.0066			38
n-Propylnitrate, n-PN	20	1.0573	0.0069	27.24	ca. 1.1	18.65
Liquid TNT	81	1.462	0.1198	47.0	1.61 (?)	0.0139
	85	1.455	0.109	46.6		0.0185
	100	1.443	0.0762	45.1		0.0514
Liquid ammonium nitrate	150				1.050	

In Fig. 2, the case of nitromethane (NM) (which usually is a flammable liquid but sometimes behaves like an explosive) is considered. This occurrence may be caused by the separation of the thermal and viscous losses, which leads to a dissipative loss-gap for activating frequencies of 10^5—10^6 Hz, which is more pronounced for voids than for air bubbles. At the top of Fig. 2, the losses of tetranitromethane (TNM) are shown. In these cases the radiation loss is not presented.

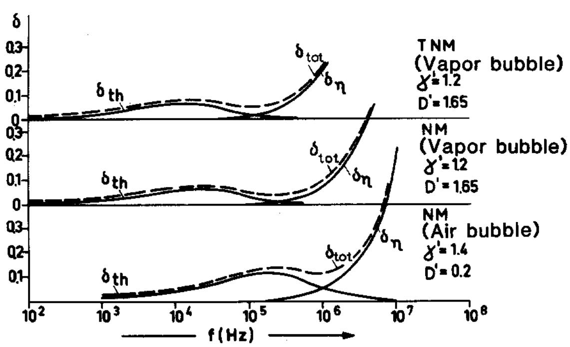

Fig. 2. Thermal and viscous losses of a vapor-cavity in TNM and NM, and of an air bubble in NM as a function of the frequency, with respect to the corresponding source size. Note the dissipative loss gaps for 10^5—10^6 Hz for the cavitation bubbles in TNM and NM.

Figure 3 compares the results for air bubbles in NM using Devin's and Nishi's algorithms.

Finally, Fig. 4 shows the loss factors of a chemically inert liquid, cold pressurized liquid carbon dioxide, which nevertheless sometimes produces explosions due to the radiation loss in the two-phase state.

In summary, the radiation loss and the dissipative losses are phase locked. If these dissipative losses force a chemical reaction, a pressure-coupled chemical reaction is possible. Contrary to the classical view, in systems of marginal

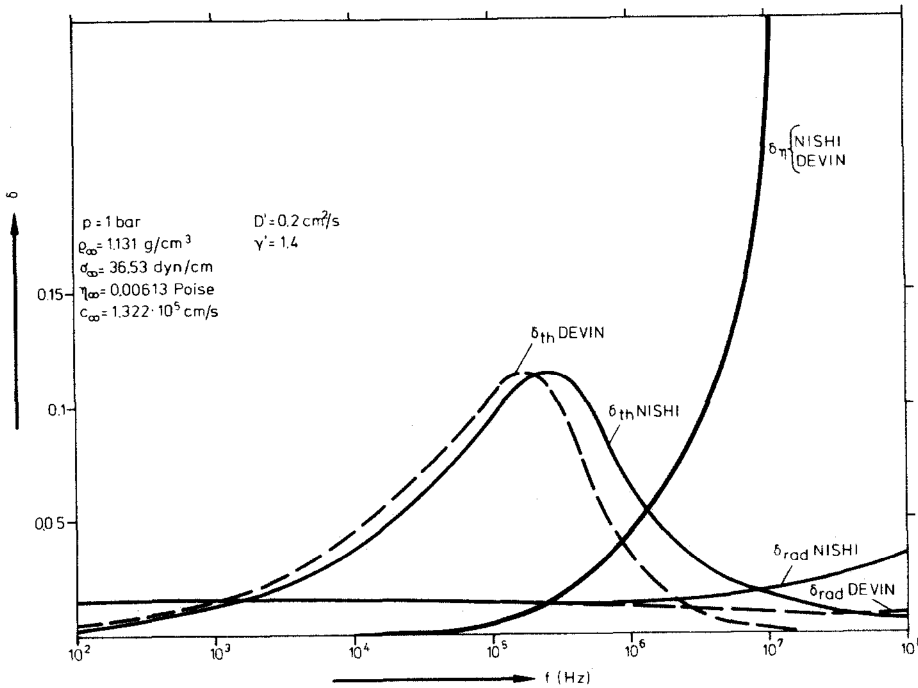

Fig. 3. Comparison of the algorithms of Devin—Kapustina and Nishi for air bubbles in NM. *D'* is a constant value for both calculations. The radiation loss is calculated for the low-pressure approximation of the mentioned authors.

chemical reactivity a decoupling of pressure and reaction waves becomes possible — and in the limiting case of an inert liquid a pressure wave without any reaction — provided that a non-chemical energy content allows this.

Surface oscillations

In addition to pulsations, a bubble may also produce surface oscillations, which have been related by various authors [5—7] to initiation phenomena. The idea is that such surface motions destroy the shape of a bubble, and consequently droplets of the surrounding medium are injected into the adiabatically heated gas content of this (former) bubble. An initiation should occur via a droplet/(air) combustion or explosion. However, this concept ignores the fact that even an onset of combustion depends on certain critical geometrical dimensions. Therefore such a mechanism may be excluded, at least for tiny bubbles.

It is therefore necessary to consider this idea in more detail. The bubble surface motion may be described by a Mathieu-type differential equation. Therefore, it is possible that such motions are powerfully amplified in a parametric way, but the sources show a multipole character, and therefore their effectiveness fails [20] for low Mach numbers.

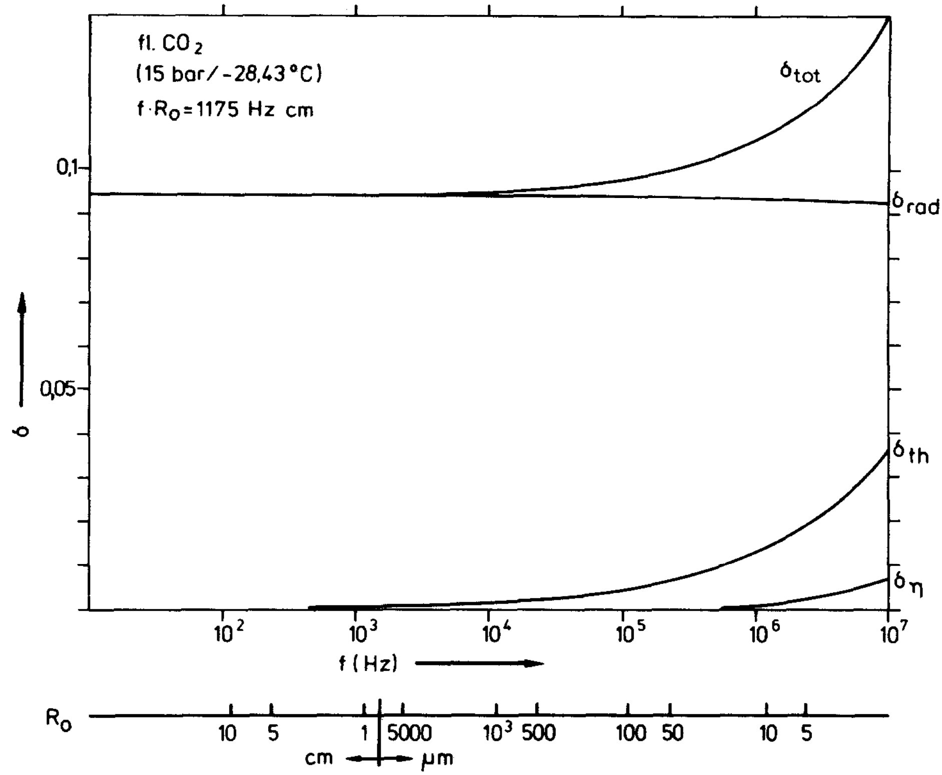

Fig. 4. Losses of a resonance bubble in liquid pressurized carbon dioxide. The radiation loss dominates due to the ambient pressure of 15 bar and the low sound velocity of the liquid.

A summarizing description of sources is possible by calculating relative scattering cross-sections equal to $Q_s/\pi R^2$. These cross-sections describe the factor by which the obstacle changes the corresponding properties of the surrounding medium of the same dimensions. For acoustically soft obstacles ($\rho' c' \ll \rho_\infty c_\infty$), like a bubble, Nishi gives the expression

$$Q_s = \frac{\lambda^2}{\pi} \sum_{l=0}^{\infty} (2l+1) \frac{j_l^2(kR)}{j_l^2(kR) + n_l^2(kR)} \tag{30}$$

where $j_l(\ )$, and $n_l(\ )$ are the spherical Bessel and Neumann functions (spherical Bessel functions of first and second kind) of order l corresponding to the type of source. In Fig. 5 this expression is given as a function of kR. As is well known, for small soft obstacles one gets the limiting value 4 and for large ones the value 2. More informative, however, is the calculation of the components of this expression for the orders $l = 0$ (monopole type), $l = 1$ (dipole type) and $l = 2$ (quadrupole type). These components are shown in Fig. 6. As may be seen, for $kR < 1$ the monopole type is deciding, whereas for larger sources the multipole character becomes more and more dominant.

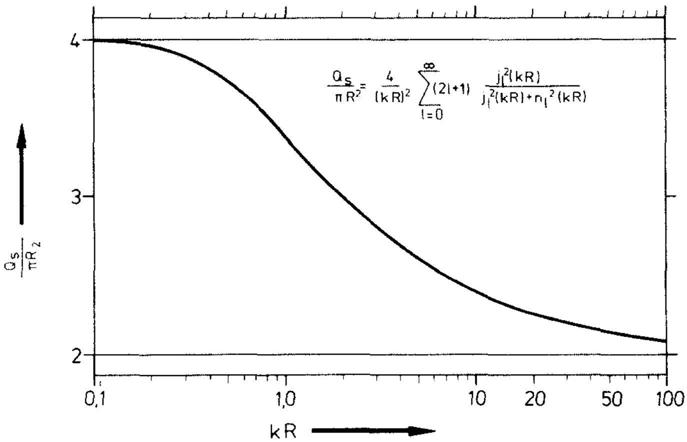

Fig. 5. Relative cross-section of scattering of acoustically soft obstacles as a function of *kR*. For small obstacles this value is 4 and for large, 2. This does not hold for hard spheres. A resonance is not included here.

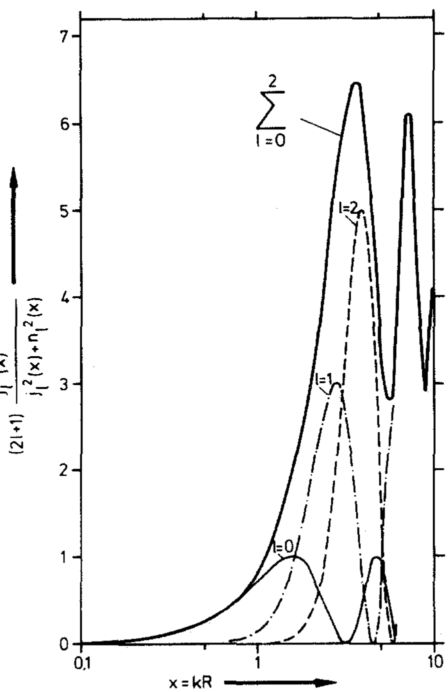

Fig. 6. Components of eqn. (30). As may be seen, for $kR < 1$ the monopole character ($l = 0$) is deciding. For larger sources the multipole character becomes more and more dominant.

In summary, for small sources a multipole character may be excluded; this means that the mechanism of surface vibration cannot work for small sources. This has also been found by Batchelor [26], that small voids behave as though they were rigid. For larger sources, however, this mechanism of surface instabilities may well be at work. Hullin [27] shows by experiments that the limit of bubble size stability seems to be defined by such a surface motion contrary to Levich's assumptions [28]. Therefore we may state that the ideas presented apply to small sources. If this condition does not hold, all the presented algorithms must be changed accordingly.

For small-kR-resonance-monopole sources the appropriate scattering cross-section is [24]:

$$Q_s = \frac{4\pi R^2}{(1 - \overline{\omega_0^2}/\omega^2)^2 + \delta_{tot}^2} \tag{31}$$

In Fig. 7 for air bubbles in NG, such cross-sections are presented, indicating a pronounced influence of bubbles on sensitivity.

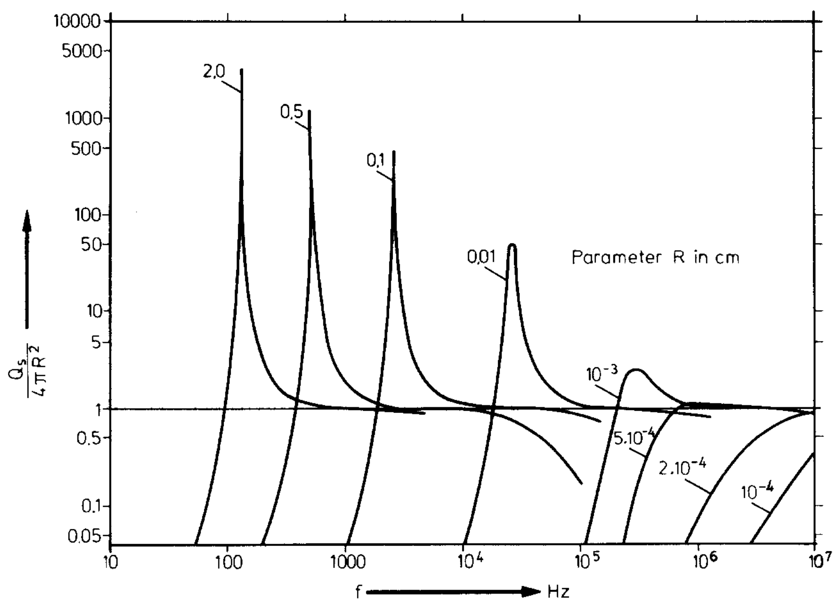

Fig. 7. Relative cross-section of scattering for air bubbles, diameter 2*R*, in NG. As can be seen, tiny voids do not influence this value, whereas larger bubbles do by orders of magnitude. It is to be noted that this also agrees with experimental [29] evidence as will be discussed in more detail in a future paper.

On the validity of this approach for small sources

As shown, eqn. (1) for small amplitude vibrations actually has no constant coefficients. To assess the applicability of this equation in the case $kR < 1$ to problems of initiation and detonation, we compare the results of this equation with the well-known Rayleigh equation on bubble motion:

$$R\ddot{R} + \tfrac{3}{2}\dot{R}^2 + \frac{p_0}{\rho_\infty} = 0 \qquad (32)$$

which gives a good approximation even for large amplitude motions. Starting with eqn. (1) with constant coefficients, and assuming $(R/R_0) \to 1$, $b = 0$, and $\gamma' = 1$, one gets a very similar expression

$$R\ddot{R} + 2\dot{R}^2 + \frac{p_0}{\rho_\infty} = 0 \qquad (33)$$

The reason for the difference 3/2 versus 2 is not resolved.

In Rayleigh's equation only the time of total collapse may be obtained in an analytic way

$$t = 0.9147\, R_0 \sqrt{\frac{\rho_\infty}{p_0}} \qquad (34)$$

whereas we get for zero loss from eqn. (1)

$$t = \frac{0.9060}{\sqrt{\gamma'}}\, R_0 \sqrt{\frac{\rho_\infty}{p_0}} \qquad (35)$$

So we get the result that for approximation purposes eqn. (1) is far more suitable than Rayleigh's equation. Equation (1) contains more information, and it may be treated in an analytic way; it may also be useful for generalizations.

Generalization of equation (1) [30]

Due to our interest in the general behaviour of bubbles, we make the following generalization in the case of constant coefficients. Using a dimensionless time

$$\tau = \omega_0 t\,, \qquad (36)$$

and using the quantities

$$V'' = \ddot{V}/\omega_0^2 \qquad (37)$$

$$V' = \dot{V}/\omega_0 \qquad (38)$$

$$V_\infty = -p(t)/K \qquad (39)$$

one gets for eqn. (1)

$$V'' + \delta V' + V = \begin{cases} 0 \\ V_\infty \end{cases} \tag{40}$$

and the initial conditions are found accordingly.

A particle velocity jump is expressed in an appropriate initial value of V_0' in the homogeneous eqn. (40); a jump of a constant pressure $p(t) = -p \mathrel{\hat{=}} -V_\infty$ is treated by the inhomogeneous eqn. (40). Both cases are tractable in an analytic way.

With the abbreviation

$$A = V_0 - V_\infty \tag{41}$$

one gets for the initial conditions for $\tau = 0$: V_0' and V_0:

Case $\delta < 2$:

$$\sqrt{1 - \delta^2/4} = \nu \tag{42}$$

$$V = V_\infty + e^{-\delta\tau/2} \left(A \cos \nu\tau + \frac{V_0' + A\delta/2}{\nu} \sin \nu\tau \right) \tag{43}$$

$$V' = e^{-\delta\tau/2} \left(V_0' \cos \nu\tau - \frac{A + V_0'\delta/2}{\nu} \sin \nu\tau \right) \tag{44}$$

$$V'' = e^{-\delta\tau/2} \left[\frac{A\delta/2 + (\delta^2/2 - 1) V_0'}{\nu} \sin \nu\tau - (\delta V_0' + A) \cos \nu\tau \right] \tag{45}$$

Case $\delta > 2$:

$$\sqrt{\delta^2/4 - 1} = \nu' \tag{46}$$

In the above eqns. (43)—(45), ν is replaced by ν', sin by sinh, and cos by cosh.

If the coefficients are time dependent, one gets from eqn. (1) with the new variable

$$y = V e^{1/2 \int (b/m) dt} \tag{47}$$

$$\ddot{y} + \left[\frac{K}{m} - \frac{1}{4} \left(\frac{b}{m} \right)^2 - \frac{1}{2} \frac{d}{dt} \left(\frac{b}{m} \right) \right] y = 0 \tag{48}$$

leading to a Mathieu-type differential equation. Such an equation describes spontaneous explosions, as will be outlined in the appendix.

Relations of energy and power

By multiplication of eqn. (1) with $\dot{V}$ or $\dot{V}/K\omega_0$ one gets

$$\frac{d}{dt} \left(\frac{m}{2} \dot{V}^2 + \frac{K}{2} V^2 \right) = [p(t) - b \dot{V}] \dot{V} \tag{49}$$

or

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\left(\frac{V'^2}{2} + \frac{V^2}{2}\right) = [V_\infty(\tau) - \delta V']\,V' \tag{50}$$

The terms in brackets on the left hand side represent the kinetic and potential energy of the vibratory system, whereas the first part on the right hand side is the term added by the power of excitation, and the second part is the consumed power of the vibratory system. Integration leads to a form

$$E_{\text{kinetic}} + E_{\text{potential}} = E_{\text{excitation}} - E_{\text{dissipated}} + E_0$$

describing the energy distributions.

The dissipative power of a source may be related to the actual original volume V_0 or to the instantaneous volume $V(t)$. If this dissipative power is high, onset of chemical reaction becomes possible. Within this view, we do not know whether this chemical reaction is thermal decomposition, or possibly also bond scission reaction within the viscous shear layer. This link between dissipative power and chemical behavior is still not clear.

Conclusion

An attempt is made to describe and quantify approximately a single hot spot in a matrix. A dynamically activated hot spot emits pressure waves and the dissipative losses force the onset of a chemical reaction. A pressure coupled chemical reaction is caused by these phase locked losses. The introduction of viscous losses on the bubble surface, which acts as a dynamic shear generator, is new, and had first been suggested by this author [31]. In accordance with experiments all steps distinctively require dynamic components to work.

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Appendix 1 — Spontaneous explosions

From the study of accidents [15] we know that explosions have occurred with no apparent initiation source or only a weak source, which is not linked with the onset of reaction in deliberate experiments. Such reactions we call spontaneous explosions. From case histories of these accidents we conclude that such explosions are only possible for mobile liquids such as nitromethane or liquefied gases under pressure. In addition to these liquid systems, similar reaction in solid primary explosives such as lead azide is possible.

It is appropriate to outline the principal mechanism of spontaneous explosions in liquids, since up to now no classical explanation has been given.

Mechanism of spontaneous explosions

From the generalized eqn. (40) of source vibration the solution

$$V(\tau) = V e^{i\Omega\tau} \qquad \text{(A.1)}$$

is possible. Inserting this into eqn. (40) one gets

$$V'' + (1 + i\delta\Omega)V = 0 \qquad \text{(A.2)}$$

Using the identities

$$1 = \lambda \qquad \text{(A.3)}$$

and

$$i\delta\Omega = \gamma \cos \tau' \qquad \text{(A.4)}$$

one gets the well known Mathieu-type differential equation

$$V'' + (\lambda + \gamma \cos \tau')V = 0 \qquad \text{(A.5)}$$

This equation is characterized by both stable and unstable solutions depending on the values of λ and $\gamma \cos \tau'$. From stability charts of the Mathieu differential equation one gets the proper domains of the different kinds of solution. Only for $\lambda = 1$ and $i\delta\Omega = 0$ do we have stable solutions in each case. If $i\delta\Omega$ increases, the domain of possible unstable solutions also increases. This region of instability is characterized by the chance of an exponential pressure amplification, if δ is time dependent. This type of amplification is called parametric amplification, and was described for the first time by Lord Rayleigh [32]. Among all possible mechanisms of amplification this type is the most powerful instrument for attaining high output very quickly, whereas the starting point is nearly (but not absolutely) zero. In the case of low viscous losses δ is practically represented by the acoustic radiation loss, eqn. (15), which is time and pressure dependent. $\Omega = \omega/\omega_0 \simeq 1$ (approximately) is necessary for maximum output. This means that resonance conditions are required. For an ergodic source system, resonance is obtained if there are present a great number of very similar sized sources of the same phase within a vessel having the eigenfrequencies ω of the natural frequencies of the sources ω_0.

Physically the pressure sources (bubbles) in the liquid are collapsing in a coherent way. This process shows some similarities to the mechanism of a laser or maser. Lee et al. [33] call a similar process a swacer = *s*hock *w*ave *a*mplification by *c*oherent *e*nergy *r*elease.

Vessel resonances

According to the outlined idea, the probability of explosion of a two-phase system depends on the probability of occurrence in the vessel of volume V, a number of Δm eigenfrequencies in the range of $\Delta f/f$ of source frequency. An estimation of possible eigenfrequencies of a vessel is required. This task is simplified greatly for large vessels due to the fact that Weyl [34] derived an asymptotic expression for

$$\Delta m = 4\pi V \frac{f^3}{c_\infty^3} \frac{\Delta f}{f} = 4\pi \frac{V}{\lambda^3} \frac{\Delta f}{f} \qquad \text{(A.6)}$$

This means that the probability of spontaneous explosions increases with the volume of the vessel and decreasing sound velocity c_∞ of the vessel content. In addition, explosion probability depends on the radiation loss, δ_{rad}, increasing with pressure.

In this way we have obtained for the first time a way to estimate the risk of an explosion from a specified physical model.

Explosion risk prediction — comparison with reality

From the Railroad Tank Car Safety Research and Test Project [35] we obtained figures to test out the presented ideas.

As is known, pressurized liquid gases and other liquids are transported in tank cars of mostly two sizes. The most frequently used type (in the U.S.A.), 105A, has a volume of the order 41.6 m^3, and the modern types 112A (114A), known as jumbo tank cars, range in volume from 110 up to 135 m^3. The above-mentioned study compared the frequency of physical explosions (to be more exact, BLEVEs caused by an external fire) for LPG, NH_3, vinyl chloride monomer, butadiene, and other flammable gases and liquids as a function of the tank car volume and the frequency of transportation over the years 1965 up to 1972/1973. The results are given as casualities per 10^9 ton miles in Fig. 8.

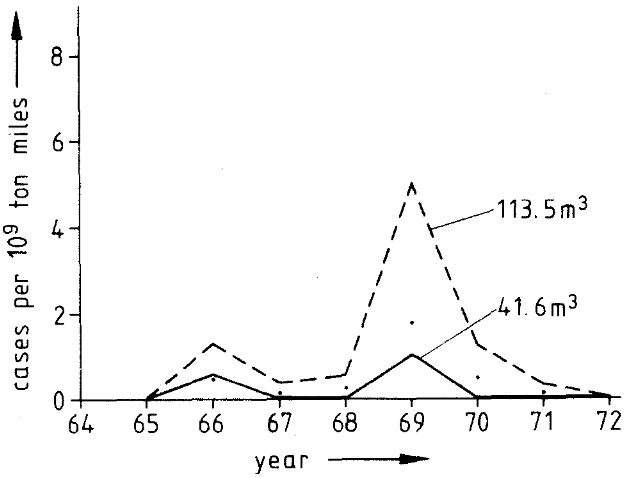

Fig. 8. Frequency of BLEVEs over the years as a function of the volume of the tank cars according to the Railroad Tank Car Safety Research and Test Project [35]. Comparison is made by comparing the accident rate per *car* mile. The dotted points are frequencies reduced by a factor of 2.73 according to the volume ratio of the tank cars. Apparently jumbo tank cars are at least two times more vulnerable than the smaller cars.

To compare the casualities per tank car, we reduce the frequency of the jumbo tank car explosions by the volume ratio, 113.5/41.6 = 2.73. These figures are dotted in the above-mentioned Fig. 8. One can see that the actual explosion frequencies of jumbo tank cars are at least double those of the normal small tank cars. From the model we expect a ratio of 2.73, and this compares favorably with reality.

In Ref. [15], the author summarized catastrophic tank car explosions of all kinds in the U.S.A. over more than a decade. The result was that pressurized liquid gas tank cars exploded more frequently than cars containing liquid cargo at ambient pressure. The transportation volume is not known, but it may be assumed that it was comparable. As a result one liquid tank car exploded versus 4.5 pressurized liquid gas tank cars, where the volume had not been determined.

We now theoretically compare the explosion risk probabilities of a jumbo tank car filled with pressurized liquid gases of sound velocity of the order 1000 m/s or less with the normal tank cars filled with liquids of sound velocities 1300 m/s or more. We get a ratio of explosion risks: jumbo tank cars filled with liquid pressurized gases to normal tank cars filled with liquids > 6. This figure compares well with the actual ratio of 4.5 for *all* tank car sizes.

From the concept of volume-dependent explosion probability, one can extrapolate toward more suitable measures: Replacement of the gross liquid volume by multiple cells of small volume, see Fig. 9, drastically reduces the

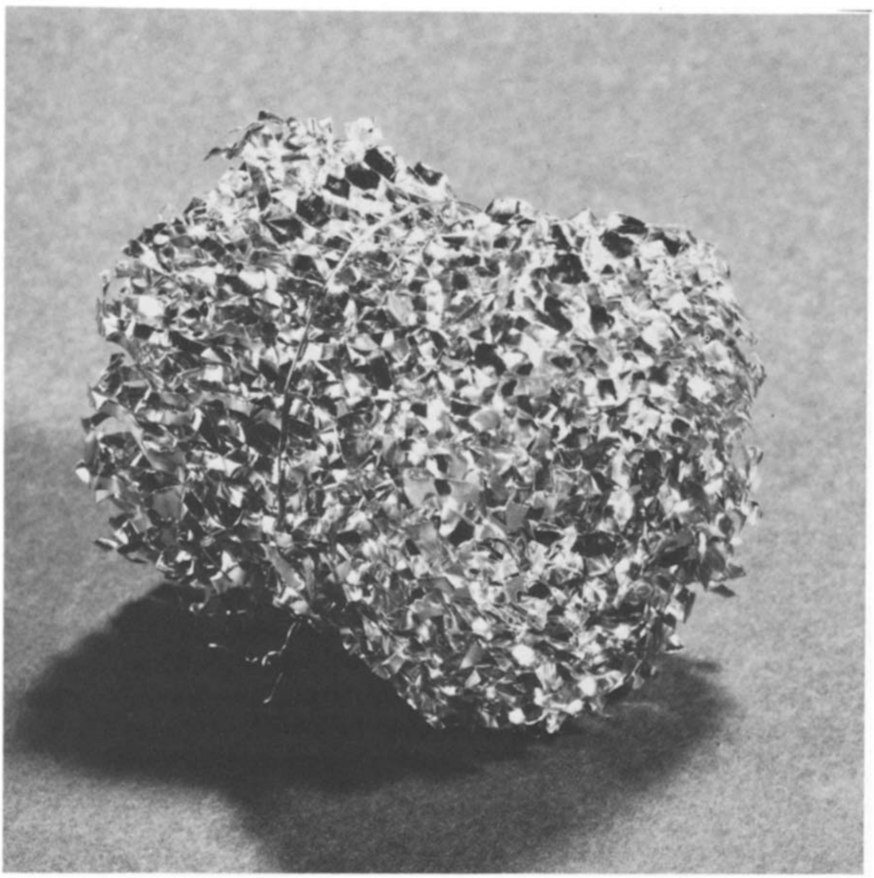

Fig. 9. Coil of expanded metal to be inserted into a vessel of somewhat smaller volume. This coil shows a porosity in excess of 95 vol.%. In the case of BLEVEs this coil additionally acts as a heat-conductive element for preventing retardation of ebullition [15,36].

explosion probability. Expanded metals would seem eminently suitable for this purpose. It is noteworthy that the porosity of this body, shown in Fig. 9, is about 95%. Whereas in the case of BLEVEs this tool worked [36], it failed in the case of shooting tests on nitromethane [37].

According to the outlined model, explosion probability additionally depends on the radiation loss, which increases with ambient static pressure. Indeed tank cars with higher gauge safety valves exploded more frequently than those with a lower value, see [15]. This, however, does not provide verification of the presented idea, since the gauge of the safety valves is in practice not adjusted to the actual cargo.