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MODELINIG OF GAS RELEASE AND ABSORPTION IN LIQUIDS WITHIN A CONSISTENT THERMODYNAMIC FRAMEWORK

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Abstract. *This work presents a mechanical model, with strong thermodynamic basis, to describe gas release and absorption in flows of liquids when the gas-liquid mixture is submitted to changes of pressure and volume. The mixture is supposed to be comprised by a liquid with an inert gas dissolved in it, along with free gas dispersed throughout. The simplifying assumptions are isothermal transformation, homogeneous mixture with no slip condition, and no surface stress between phases. The capability of the model in coherently describe irreversible processes of gas release and absorption as well as reversible ones as limiting cases is illustrated by a means of a simple numerical example involving air and a typical lubrication oil.*

Keywords: *gaseous cavitation; gas-liquid flows, thermodynamics; irreversible processes*

1. INTRODUCTION

Liquids are able to absorb certain amount of gas in contact with their free surfaces through a diffusive process. The amount of dissolved gas in the liquid depends on the gas and liquid as well as on thermodynamic properties of the mixture such as temperature and pressure. For instance, in the case of a liquid in a recipient open to the atmosphere, the liquid will retain certain amount of dissolved air according to the atmospheric conditions of pressure and temperature. If the pressure above the liquid rises or its temperature decreases, an extra amount of air will be absorbed by the liquid. On the other hand, if the pressure decreases or the temperature increases, air will be released from the liquid as small bubbles. This process is known in the literature as gaseous cavitation. In such a case, the dissolved gas that comes out of solution either is carried by the fluid flow stream as free gas or migrate towards the free surface or the upper parts of the systems where the liquid is confined, forming small and discrete cavities. Internal as well as external flows may be subjected to gaseous cavitation under steady and unsteady regimes. Some typical examples of sources responsible for triggering the gas release phenomenon are boundary curvature of solid surfaces in contact with the liquids, vortices, turbulence and transient expansion waves.

The most relevant problems in which gaseous cavitation plays an important role on practical engineering applications are those associated with transient fluid flows in piping systems. Typical examples include water distribution systems, sewage networks, nuclear reactor piping systems and aviation fuel pipelines (Bergant, *et al.*, 2006; Swaffiled, 1972; Wylie and Streeter, 1993). When wave propagation phenomena are involved in, the presence of free gas in the liquid, even in tiny quantities, is responsible for reducing the wave front speed in the medium and for attenuating the pressure peaks due to the added compressibility of the gas.

Since, in general, gaseous cavitation precedes and influences vaporous cavitation (the phenomenon in which the liquid turns into vapor at almost constant temperature whenever the pressure falls below the liquid vapor pressure) many of the studies address both issues simultaneously (Baasiri and Tullis, 1983; Kranenburg, 1974; Wiggert and Sundquist, 1979; Wylie, 1984), despite having quite distinct time scales. Whereas the gas release takes place in a scale of the order of seconds, the vaporous cavitation is a faster process, occurring on a few microseconds.

In general, the models available in the literature used to describe the transient fluid flow with entrained gas do not consider the gas absorption and release phenomena. The ones which do take it into account either employs an extension of the Henry's law to states of non-equilibrium or makes use of empirical correlations without thermodynamic grounds. As a result, those approaches do not describe the physical phenomenon properly, especially with regard to the energy dissipation mechanism, generating erroneously predictions of the fluid behavior, as shown by for Kim and Murrenhoff, (2012), Zhou (2013) and Gholizadeh, *et al.* (2014).

To get round this problem, a new model to describe the gas release and absorption phenomena is presented in this paper. The model is developed within a consistent framework of the thermodynamics of irreversible processes, being

able to adequately quantify the energy dissipation in these processes. For the sake of simplicity, the hypothesis of isothermal and homogeneous flow is assumed and the fluid is treated as a continuum pseudo mixture of a liquid and an inert gas, which coexist at the same material point and time instant. The gas constituent exists as free gas in the gaseous phase as well as dissolved gas in the liquid phase. Under this context, the governing equations are formed by three mass balance equations (one for the liquid, one for the dissolved gas and one for the free gas) and one momentum balance equation for the mixture as whole. The constitutive equation that describes the gas mass transfer between the liquid and gaseous phases is derived based on two thermodynamic potentials, the Helmholtz free energy and a pseudo potential of dissipation, in such a way that the second law of the thermodynamics is unconditionally satisfied.

2. THEORETICAL BASIS

Before presenting the balance and constitutive equations that form the proposed model, it becomes convenient to remember some basic concepts associated with the solubility of a gas in a liquid at constant temperature. The most important law governing the solubility of gas solute in a liquid solvent is due to Henry, a chemist English who studied this subject in the early nineteenth century. As it will be seen next, the Henry's law is a departure point for not only understanding the gaseous cavitation mechanism but also properly modeling it.

2.1 Henry's Law

The Henry's law states that under thermodynamic equilibrium the partial pressure of the gas phase is proportional to the concentration of dissolved gas in the liquid. Among the many ways in the literature of expressing this law, we have chosen the following one for the sake of convenience:

$$p_g = K_H c, \tag{1}$$

in which, c stands for the dissolved gas concentration in the liquid, i.e., the mass of dissolved gas per unit volume of liquid, $p_g$is the partial pressure of the gas in the gaseous phase and K_H is Henry's law solubility constant, which depends on the gas-liquid pair and on the temperature. Under constant temperature, this law states that the higher the partial pressure is, the greater the amount of dissolved gas in the liquid becomes.

To give a simple example of application associated with the Henry's law, we appeal to a common experience with bottled carbonated drinks. For giving a cool sensation drinking, dissolved carbon dioxide is added to these beverages. Whatever the drink is, before opening the bottle, the gas above the drink is almost pure carbon dioxide, at a pressure higher than the atmospheric pressure. The opening of the bottle makes the partial pressure of carbon dioxide above the liquid to decrease. The liquid is then degassed, as the dissolved carbon dioxide comes out of solution as small bubbles. Since soft drinks are bottled with a lower pressure than carbonated sparkling wines, the amount and size of the bubbles coming out from soft drinks is less than those observed in those wines.

2.2 Balance Equations

If the homogeneous assumption and isothermal transformation are assumed to hold, it is possible to consider the balance equations of mass and momentum along with one version of the second law for the mixture as a whole, instead of doing it for each phase separately. Besides assuming that the two phases coexist in the same material point and time instant, this approach implies that the phases have the same velocity and share the same temperature during the phenomenon of gas release or absorption, considering the fluid as a pseudo-mixture of liquid and gaseous phases with average properties. Therefore, the problem can be described by the following system of equations:

$$\dot{\rho} + \rho\nabla \cdot \mathbf{v} = 0, \tag{2}$$
$$\rho\dot{\mathbf{v}} = -\nabla p + \nabla \cdot \mathbf{S} + \rho\mathbf{g}, \tag{3}$$
$$d := -(p + \Psi)\nabla \cdot \mathbf{v} - \dot{\Psi} + \mathbf{S} \cdot \mathbf{D} \geq 0. \tag{4}$$

The above equations represent the mixture mass balance equation, linear momentum balance equation and the Clausius-Duhen inequality, respectively. The superimposed dot stands for the material derivative, ρ is the mass density of the pseudo-mixture, $\mathbf{v}$ is the velocity field, $\mathbf{S} = \mathbf{S}^{\mathrm{T}}$ is the extra stress tensor due to motion, $\mathbf{g}$ is the gravitational acceleration and $\mathbf{D} = \frac{1}{2}[\nabla\mathbf{v} + (\nabla\mathbf{v})^{\mathrm{T}}]$ is the strain rate tensor. Since all the constituents are compressible, p stands for the thermodynamic pressure and Ψ represents the Helmholtz free energy of the mixture per unit of volume. Eq. (4) is a local version of the Second Law of the Thermodynamics (SLT) and implies that the rate of energy dissipation, d, be nonnegative, establishing possible $(d \geq 0)$ and impossible $(d < 0)$ prosses. Moreover, processes where $(d = 0)$ are classified as reversible or noun dissipative and prosses where $(d > 0)$ are classified as irreversible or dissipative.

To account for the dissolved and the free gas existence, the dissolved gas concentration c and the free gas volumetric fraction α are considered. Here, α is defined by the ratio of the free gas volume per mixture volume unity,

while c is defined as the mass of dissolved gas per liquid phase volume unity. Disregarding the presence of vapor in the gaseous phase, the mixture is considered a pseudo fluid, sharing the averages of the thermodynamic properties of liquid and gas with α as a weight factor. Based on this approach, the mixture mass density can be written as:

$$\rho \coloneqq (1-\alpha)(\rho_l + c) + \alpha\rho_g, \tag{5}$$

in which ρ_l e ρ_g are respectively the mass densities of the liquid and free gas, both assumed as compressible. According to Eq. (5), it becomes implicit that the liquid and the dissolved gas coexist in the liquid phase and that the free gas is the unique constituent in the gaseous phase. By considering that there are three different constituents in the mixture as defined in Eq. (5), Eq. (2) is split into three mass balances for accounting the gas release and absorption phenomena as:

$$(1-\alpha)\dot{\rho}_l - \dot{\alpha}\rho_l + (1-\alpha)\rho_l\nabla\cdot\mathbf{v} = 0, \tag{6}$$
$$(1-\alpha)\dot{c} - \dot{\alpha}c + (1-\alpha)c\nabla\cdot\mathbf{v} = -\Gamma, \tag{7}$$
$$\alpha\dot{\rho_g} + \dot{\alpha}\rho_g + \alpha\rho_g\nabla\cdot\mathbf{v} = \Gamma, \tag{8}$$

where Γ represents the mass transfer rate of gas per mixture volume unity. In the above formulation, when $\Gamma > 0$ gas is released from the liquid. On the other hand, when $\Gamma < 0$ the gas is absorbed by the liquid. Finally, when $\Gamma = 0$ there is no mass transfer between the liquid and gaseous phases, and so the mass balance equations for the dissolved gas e free gas become independent.

3. CONSTITUIVE THEORY

Based on the approach used by Freitas Rachid (2003and 2013), the constitutive relationships used to describe the mixture behavior are derived in the framework of the Thermodynamics of Irreversible Processes. The state variables used in this approach are the liquid mass density ρ_l, the gas mass density ρ_g, the dissolved gas concentration c, the free gas volumetric fraction α and the mixture temperature θ. Here the free gas volumetric fraction α is restricted to the constraint $0 < \alpha < 1$. Besides the state variables, two thermodynamics potentials are used, the Helmholtz free energy and a pseudo potential of dissipation.

3.1 Helmholtz Free Energy

The Helmholtz free energy per volume unity Ψ is taken as a function of the state variables ρ_l, ρ_g, c, α and θ. As the fluid is taken as a mixture of three constituents, its properties are assumed as being the average of its constituents' properties. Therefore, the mixture free energy is chosen as:

$$\begin{aligned}
&\Psi \coloneqq \Psi(\rho_l,\rho_g,c,\alpha,\theta) = \Psi'(\rho_l,\rho_g,c,\alpha,\theta) + I(\alpha),\\
&\Psi'(\rho_l,\rho_g,c,\alpha,\theta) \coloneqq (1-\alpha)\big(\rho_l\Psi_l(\rho_l,\theta) + c\Psi_c(c,\theta)\big) + \alpha\rho_g\Psi_g(\rho_g,\theta),\\
&\Psi_l(\rho_l,\theta) = -c_{v_l}\theta\ln(\theta) + a_l^2\left(\ln\rho_l + \frac{\rho_l^0}{\rho_l}\right),\\
&\Psi_g(\rho_g,\theta) = -c_{v_g}\theta\ln(\theta) + a_g^2\ln(\rho_g),\\
&\Psi_c(c,\theta) = -c_{v_g}\theta\ln(\theta) + a_g^2\ln\left(\frac{K_H}{a_g^2}c\right),\\
&I(\alpha) \coloneqq \begin{cases} 0, & \text{if } \alpha \in (0,1),\\ +\infty, & \text{otherwise,}\end{cases}
\end{aligned} \tag{9}$$

where Ψ_l and Ψ_g represents the liquid's and free gas' free energies per unit mass, respectively. Ψ_c is the dissolved gas free energy per unit mass, which is taken in account to represent the gas release and absorption, according to the Henry's law in states of equilibrium.

The term $I(\alpha)$ is the indicator function of convex set $(0,1) \in \mathbb{R}$. It is included in the free energy potential to take the internal constraint of the mixture into account as a constitutive assumption. It prevents α to get out the admissible interval since it would require infinity amount of energy.

The state laws for the fluid, relating the reversible components of the thermodynamic forces to the state variables, are obtained from the free energy potential and defined as bellow:

$$B^{\rho_l} \coloneqq \frac{\partial\Psi'}{\partial\rho_l} = (1-\alpha)\left(\Psi_l + \rho_l\frac{\partial\Psi_l}{\partial\rho_l}\right) = (1-\alpha)\left(\Psi_l + \frac{p_l}{\rho_l}\right) = (1-\alpha)g_l, \tag{10}$$
$$B^{c} \coloneqq \frac{\partial\Psi'}{\partial c} = (1-\alpha)\left(\Psi_l + c\frac{\partial\Psi_c}{\partial c}\right) = (1-\alpha)\left(\Psi_c + \frac{p_c}{c}\right) = (1-\alpha)g_c, \tag{11}$$

$$B^{\rho_g} \coloneqq \frac{\partial \Psi'}{\partial \rho_g} = \alpha\left(\Psi_g + \rho_g \frac{\partial \Psi_g}{\partial \rho_g}\right) = \alpha\left(\Psi_g + \frac{p_g}{\rho_g}\right) = \alpha g_g, \tag{12}$$

$$B^{\alpha} \coloneqq \frac{\partial \Psi'}{\partial \alpha} + h = \rho_g \Psi_g - \rho_l \Psi_l - c\Psi_c + h, \qquad \text{with } h \in \partial_\alpha I(\alpha), \tag{13}$$

where, g_l, g_c and g_g are the Gibbs free energies of the liquid, dissolved gas and free gas respectively, and p_l, p_c and p_g are the liquid, dissolved gas and free gas partial pressures, respectively. The term $\partial_\alpha I(\alpha)$ is a subdifferential of the indicator function $I(\alpha)$ at α, which is given by (Ekeland and Teman, 1976) and (Moreau and Panagiotopoulos, 1988):

$$\partial_\alpha I(\alpha) = \{h \in \mathbb{R} | I(\alpha^*) - I(\alpha) \geq h(\alpha^* - \alpha);\ \forall a^* \in [0,1]\}. \tag{14}$$

From the above definition, we can see that $\partial_\alpha I(\alpha = 0) = \{h \in \mathbb{R} | h \leq 0\}$, $\partial_\alpha I(0 < \alpha < 1) = \{h \in \mathbb{R} | h = 0\}$ and $\partial_\alpha I(\alpha) = \emptyset$ if $\alpha \ni [0,1)$.

The material time derivative $\dot{\Psi}$ can be written as:

$$\dot{\Psi} = \frac{\partial \Psi'}{\partial \rho_l}\dot{\rho}_l + \frac{\partial \Psi'}{\partial c}\dot{c} + \frac{\partial \Psi'}{\partial \rho_g}\dot{\rho_g} + \frac{\partial \Psi'}{\partial \alpha}\dot{\alpha} + \lim_{\Delta t \to 0} \frac{I\big(\alpha(t)\big) - I\big(\alpha(t - \Delta t)\big)}{\Delta t}. \tag{15}$$

Care should be taken in computing $\dot{\Psi}$, since Ψ is not a smooth function. By using the definition of the subdifferential Eq. (16) it can be shown that:

$$\lim_{\Delta t \to 0} \frac{I\big(\alpha(t)\big) - I\big(\alpha(t - \Delta t)\big)}{\Delta t} \leq h\dot{\alpha}, \qquad \forall h \in \partial I\big(\alpha(t)\big). \tag{16}$$

Applying the above result to the state laws presented by Eqs. (10) to (13), the following inequality can be written:

$$\dot{\Psi} \leq B^{\rho_l}\dot{\rho}_l + B^{c}\dot{c} + B^{\rho_g}\dot{\rho_g} + B^{\alpha}\dot{\alpha}. \tag{17}$$

The inequality above can be used to determine a lower bound $\hat{d}$ for the dissipation d defined in Eq. (4) as:

$$d \geq \hat{d} = -(p + \Psi)\nabla \cdot \mathbf{v} + \mathbf{S} \cdot \mathbf{D} - B^{\rho_l}\dot{\rho}_l - B^{c}\dot{c} - B^{\rho_g}\dot{\rho_g} - B^{\alpha}\dot{\alpha} \geq 0. \tag{18}$$

To obtain a complete set of constitutive equations, it suffices to specify a pseudo-potential of dissipation from which complementary laws are derived in such way that the second law is always verified.

3.2 Pseudo-Potential of Dissipation

To introduce the irreversible behavior of the mixture and ensure that the SLT is always satisfied, it is assumed the existence of a pseudo potential of dissipation Φ, which is an objective, convex and differentiable function of $\mathbf{D}$ and Γ. Moreover, it is assumed that the pseudo potential has the follow properties for any $\mathbf{D}$, Γ, α, c e θ:

$$\Phi(\mathbf{D}, \Gamma; \alpha, c, \theta) \geq 0, \qquad \forall(\mathbf{D}, \Gamma) \quad \text{and} \quad \Phi(\mathbf{0}, 0; \alpha, c, \theta) = 0. \tag{19}$$

The additional information associated with the dissipative behavior can be obtained from Φ through the following complementary laws:

$$\mathbf{S} = \frac{\partial \Phi}{\partial \mathbf{D}}, \qquad B^{\Gamma} = \frac{\partial \Phi}{\partial \Gamma}, \tag{20}$$

in which B^{Γ} is the thermodynamic force associated with the phase change transformation and $\mathbf{S}$ is the force associated with the viscous dissipation.

Without losing generality, if we assume the mixture behaves as a Newtonian fluid one possible choice for Φ is:

$$\Phi(\mathbf{D}, \Gamma; \alpha, c, \theta) = \frac{\lambda}{2}(\mathrm{tr}(\mathbf{D}))^2 + \mu\mathbf{D} \cdot \mathbf{D} + \frac{\beta}{2}\Gamma^2, \tag{21}$$

where β is a material positive constant. The material parameters $\lambda = \hat{\lambda}(\alpha)$ and $\mu = \hat{\mu}(\alpha)$ are respectively the bulk viscosity and the dynamic viscosity of the mixture, given for the liquid and free gas average properties, with α as the weight factor, where $\mu \geq 0$ and $\lambda + (2/3)\mu \geq 0$.

Taking in account that the whole dissipation experienced by the pseudo fluid may be accounted for as the sum of the individual contributions of different irreversible mechanisms, the lower bound $\hat{d}$ given by Eq. (18) can be written as:

$$\hat{d} \coloneqq \mathbf{S} \cdot \mathbf{D} + B^{\Gamma}\Gamma - I(\alpha)\nabla \cdot \mathbf{v} \geq 0. \tag{22}$$

From the mechanical viewpoint, Eq. (22) establishes that the dissipated energy rate in the fluid is due to the viscous effects and to gas mass transfer between the liquid and gaseous phases. The rate of energy dissipated associated with these two mechanisms are quantified by the two first parcels in Eq. (22). The last term does not express any dissipation at all for actual evolutions since *I(α)*=0 for α ∈(0,1). It is incorporated into Eq. (22) to give coherence to the model. It means that to force α to get out of the interval (0,1) either an infinite rate of energy would be required or the SLT would be violated.

3.3 Constitutive Laws

Since the mass balance equations given by Eq. (6) to (8) define subspaces of the linear space spanned by $\mathbf{v}$, $\dot{\rho_l}$, $\dot{\rho_g}$, $\dot{c}$ and $\dot{\alpha}$, then in order that Eq. (22) be equal to Eq. (18) for any actual evolution we must have:

$$\begin{aligned} -(p + \Psi')\nabla \cdot \mathbf{v} - B^{\rho_l}\dot{\rho_l} - B^{c}\dot{c} - B^{\rho_g}\dot{\rho_g} - B^{\alpha}\dot{\alpha} \\ = B^{\Gamma}\Gamma + \eta\big((1-\alpha)\dot{\rho_l} - \dot{\alpha}\rho_l + (1-\alpha)\rho_l\nabla \cdot \mathbf{v}\big) \\ + \xi\left((1-\alpha)\dot{c} + \alpha\dot{\rho_g} + \big(\rho_g - c\big)\dot{\alpha} + \Big((1-\alpha)c + \alpha\rho_g\Big)\nabla \cdot \mathbf{v}\right), \end{aligned} \tag{23}$$

in which η and ξ are the Lagrange multipliers. Since Eq. (23) holds for any independent evolution of $\mathbf{v}$, $\dot{\rho_l}$, $\dot{\rho_g}$, $\dot{c}$ and $\dot{\alpha}$, it comes out that:

$$-B^{\rho_l} = (1-\alpha)\eta, \tag{24}$$
$$-B^{\rho_g} = \alpha B^{\Gamma} + \alpha\xi, \tag{25}$$
$$-B^{c} = (1-\alpha)\xi, \tag{26}$$
$$-B^{\alpha} = \rho_g B^{\Gamma} - \rho_l\eta + \big(\rho_g - c\big)\xi, \tag{27}$$
$$-(p + \psi') = \alpha\rho_g B^{\Gamma} + (1-\alpha)\rho_l\eta + \Big((1-\alpha)c + \alpha\rho_g\Big)\xi. \tag{28}$$

By applying the state laws given by Eqs. (10) to (13) on the system of equations above, taking into consideration the definitions of Ψ_l, Ψ_c and Ψ_g presented on Eq. (9), the partial pressures p_l, p_c and p_g defined on Eqs. (10) to (12), the definition of Φ presented on Eq. (21) and the definition of B^{Γ} presented on Eq. (20), the Lagrange multipliers can be eliminated form Eqs. (24) to (28), rendering the following constitutive equations:

$$\mathbf{S} = \lambda\mathrm{tr}(\mathbf{D})\mathbf{I} + 2\mu\mathbf{D}, \tag{29}$$
$$p = (1-\alpha)(p_l + p_c) + \alpha p_g, \tag{30}$$
$$p_l = a_l^2\rho_l - p_l^0, \tag{31}$$
$$p_c = a_g^2 c, \tag{32}$$
$$p_g = a_g^2\rho_g, \tag{33}$$
$$\alpha(1-\alpha)B^{\Gamma} = \alpha(1-\alpha)\big(g_c - g_g\big), \tag{34}$$
$$\Gamma = \frac{B^{\Gamma}}{\beta}, \tag{35}$$
$$p_l + p_c = p_g - h + \Big((1-\alpha)\rho_g + \alpha c\Big)\big(g_c - g_g\big) - \big(\alpha c + (1-\alpha)\rho_g\big)B^{\Gamma}. \tag{36}$$

in which $p_l^0 = a_l^2\rho_l^0$.

The mass balance equations given by Eq. (6), Eq. (7) and (8), the momentum balance equation given by Eq. (3) with the mixture mass densities given by Eq. (5) and the above constitutive laws, completed by suitable boundary and initial conditions are sufficient to describe the isothermal momentum-driven gaseous cavitation of a mixture formed by compressible Newtonian liquid and inert gas. We will now focus attention on the gas absorption and release and on the gaseous volume fraction evolution.

4. THE PHYSICAL INTERPRETATION OF THE MODEL

To better understand the transformations described by the proposed model, it is convenient to analyze the model for the non-dissipative and dissipative behaviors for $\alpha \in (0,1)$.

4.1 Non-dissipative behavior

In such a case Φ does not depend on Γ and $B^{\Gamma} = 0$. Therefore, for a case where $\alpha \in (0,1)$ the system of equations given by Eq. (30) to (36) can be rewritten as:

$$p = (1-\alpha)(p_l + p_c) + \alpha p_g, \tag{37}$$
$$g_c = g_g, \tag{38}$$
$$p_l + p_c = p_g. \tag{39}$$

Equations (37) to (39) grant the thermodynamic requirements associated with reversible processes or equilibrium conditions. Equations (37) and (39) require that mixture pressure be equal to the free gas pressure, which in turn is the sum of the partial pressures of the liquid and dissolved gas; $p = p_g = p_l + p_c$. On the other hand, the chemical equilibrium requires that Gibbs free energies of the gas in the liquid and gaseous phases be the same, as stated by Eq. (38). Taking Eqs. (11) and (12) into account, it is equivalent to require that $p_g = K_H c$. In other words, it means that the Henry's law given by Eq. (1) holds, as it should be expected.

4.2 Dissipative behavior

In such a case Φ depends on Γ and $B^{\Gamma} \neq 0$ giving rise to non-equilibrium states and time-rate-dependent constitutive equations. As it has been done in the previous section, for a case where $\alpha \in (0,1)$ the system of equations given by Eq. (30) to are reduced to:

$$p = (1-\alpha)(p_l + p_c) + \alpha p_g, \tag{40}$$
$$\Gamma = \frac{g_c - g_g}{\beta}, \tag{41}$$
$$p_l + p_c = p_g. \tag{42}$$

The above equations, along with the balance equations, govern the gas release and absorption phenomena under a more realistic situation in which these processes are treated as irreversible ones. They characterize the evolution of p_l, p_c, p_g, Γ and α along the motion. According to Eq. (41), the gas mass transfer rate between phases is proportional to the difference between the dissolved gas and free gas Gibbs free energies. It should noticed that combining Eqs. (40) and (42), $p = p_g = p_l + p_c$, as it has been observed for the non-dissipative behavior. However, the unique condition which renders the Henry's law to hold is the one in which there is no mass transfer, i.e., $\Gamma = 0$. When either $\Gamma < 0$ or $\Gamma > 0$ the Henry's law is no longer valid and the mass transfer phenomena (release and absorption) are treated as irreversible processes, having a rate of energy dissipation ΓB^{Γ} associated to them.

5. NUMERICAL SIMULATION AND MECHANICAL RESPONSE

To better understand the dynamic behavior of the model, the dynamic of gas release and absorption is investigated from a theoretical point of view. The model capability to describe typical situations is illustrated by simple quantitative example. To do it, a simple lubricant oil-air mixture at a constant temperature of 20°C is considered. The lubricant oil is the Shell Tellus S ISO 32, for which density and compressibility properties are presented by Zhou, *et al.* (2013) and the Henry's law proportional constant for the air–oil pair is given by Will *et al.* (2007). Zhou *et al.* (2013) presents the oil properties in terms of the oil's bulk modulus and its mass density at atmospheric pressure. Will *et al.* (2007) presents a general value for the Bunsen coefficient for mineral oil and air mixture, which varies between 0.08 and 0.09. In the present paper we have assumed the mean value of 0.085. The Bunsen coefficient is one of the many forms that the Henry's law constant can be presented, as demonstrated by Young *et al.* (1982). As the proposed equation of state for the liquid written in Eq. (31) is in terms of a_l and p_l^0, and the Henry's law presented in Eq. (1) is not in terms of the Bunsen coefficient, we have adequately converted the values presented by those authors to the ones used on our equations. These values are presented with a_g in Table 1.

Table 1. Constitutive parameters of the constituents.

$a_l(m/s)$	$p_l^0(MPa)$	$a_g(m/s)$	$K_H\left(m^2/s^2\right)$
1254.01	1,321.	290.11	922,558.13

To investigate the gas release and absorption phenomena with the presented model, it is considered that the mixture is confined into a device and can have its original volume expanded or contracted along the time by the action of external forces. It is also assumed that, at any time instant, the mixture is almost everywhere homogenous throughout its volume, so that the convective terms of the balance equations can be neglected. With those assumptions, the time rate of volume change per unit volume of the whole mixture is described by $\nabla \cdot \mathbf{v}$ and is assumed a prescribed function of time. The function used in the simulation shown ahead is presented in Fig. 1 and consists in an expansion of the original volume which arrives to a maximum volume and decreases to its original volume. If we choose the initial gas volume fraction small and greater than zero, the input function given by Fig. 1 leads to $\alpha \in (0,1)$. Therefore, the equations formed by Eqs. (6), (7) and (8), with ρ_l, c, ρ_g and Γ defined by Eqs. (31), (32), (33) and (41), respectively, along with Eqs. (40) to (42), give rise to an initial-value non-linear problem of ordinary differential equations for the unknowns p, p_c and α. This problem is solved using the NDSolve toll provided by the Mathematica software, using default options.

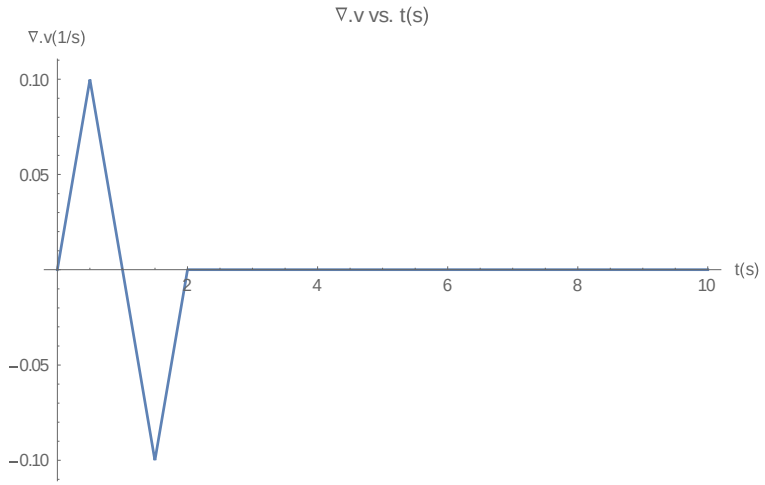

Figure 1. Input function for $\nabla \cdot \mathbf{v}$ as a function of the time t.

The simulations was carried out with the initial conditions $\alpha_0 = 0.5\%$, $p_0 = 100kPa$ and $p_{c,0} = 9.122kPa$ (which is the condition of equilibrium for p_0) along with the constitutive parameters of Table. 1, for three different values of β ($\beta = 1;\ 10^7$ and $10^{14}\ Jm^3s/kg^2$). The results are compared with the behavior predicted by the non-dissipative cases, which are very well described by the extremes values of β for which there is no energy dissipation, as it will be seen later on. The results for the time evolution of p, p_c and α are displayed in Figs. 2, 3 and 4, respectively.

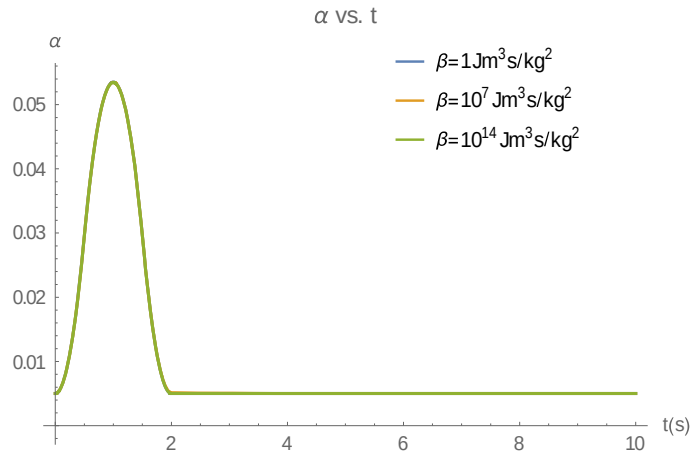

Figure 2. Gas volume fraction as a function of time for different values of $\beta(\beta = 1, 10^7$ and $10^{14}\ Jm^3s/kg^2)$.

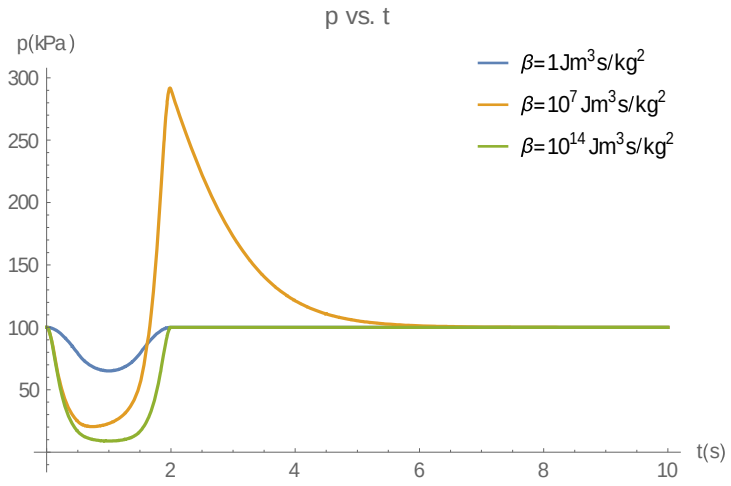

Figure 3. Mixture pressure as a function of time for different values of $\beta(\beta = 1, 10^7$ and $10^{14}\, Jm^3s/kg^2)$.

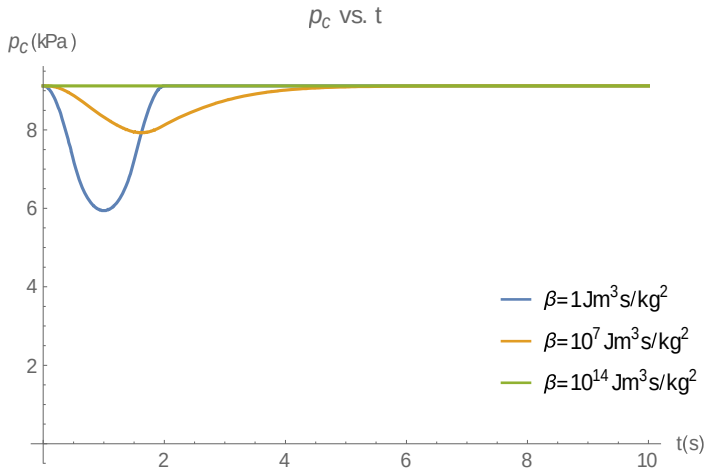

Figure 4. Dissolved gas pressure as a function of time for different values of $\beta(\beta = 1, 10^7$ and $10^{14}\, Jm^3s/kg^2)$.

Figure 2 shows that the free gas volume fraction evolution is almost the same for each value of β. It happens because the liquid is almost incompressible and as we impose the volumetric evolution, the main volumetric changes happens on the gaseous phase with the liquid phase almost keeping its original volume, increasing α with the mixture volume.

Figure 3 shows that in the case where $\beta = 1\, Jm^3s/kg^2$, as the gas is "free" to be released or absorbed, the overall mixture pressure does not change so much. In the case where $\beta = 10^{14}\, Jm^3s/kg^2$, the gas is "locked" and no release or absorption is possible, a bigger pressure reduction is noted when the system is expanded. Moreover, it is observed that when the mixture returns to its original volume, the pressure instantaneously comes back to its initial state. Finally in the case where $\beta = 10^7\, Jm^3s/kg^2$, the gas can be released and absorbed, but those transferences do not happens instantaneously due to dissipative effects, therefore the pressure reduces more than in the first case and lass than in the second one during the expansion and raises above its initial value during the compression due to the delay in the absorption, it leads to states where there is more free gas than the predicted for the equilibrium state. Moreover, as the pressure holds higher than its initial value after the mixture returns to its original volume at $t = 2\, s$ it can be concluded that gas is still being absorbed after $t = 2s$, it happens due to the delay in gas absorption.

Looking at Fig. 4 it can be noticed that for $\beta = 10^{14}\, Jm^3s/kg^2$ p_c is constant, which means none gas is being transferred. For $\beta = 1\, Jm^3s/kg^2$, p_c is close to the one predicted for equilibrium states, which means gas is free to be transferred and, finally, for $\beta = 10^7\, Jm^3s/kg^2$, p_c has intermediate values and keep reducing after the mixture original volume been restored due to the same reasons explained in the above paragraph.

By knowing the α, p and p_c evolution in time, it is possible to measure the gas mass transference rate Γ and the energy dissipation rate $B^\Gamma\Gamma$ evolution in time. They are presented for the three cases in Fig. 5 and Fig. 6, respectively. As the energy dissipation for the case where $\beta = 10^7\, Jm^3s/kg^2$ is much higher than the one in the other cases, Fig. 7 shows the energy dissipation rate only for the cases of $\beta = 1$ and $10^{14}\, Jm^3s/kg^2$ for a better understanding of the different sales of energy dissipations in those cases.

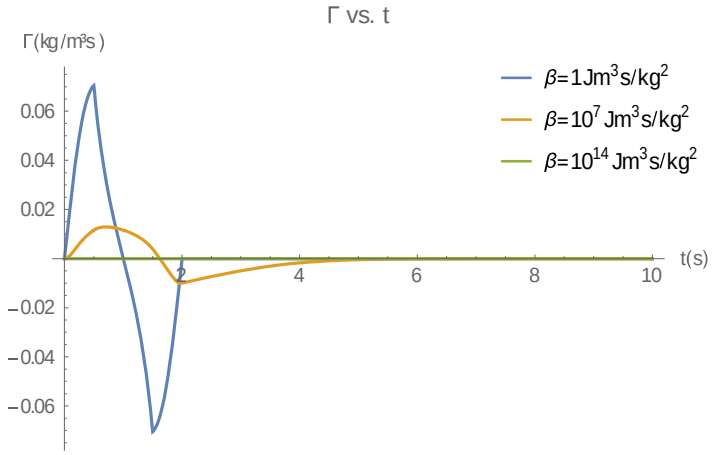

Figure 5. Mass transference rate of gas as a function of time for different values of $\beta(\beta = 1, 10^7 \text{ and } 10^{14}\, Jm^3s/kg^2)$.

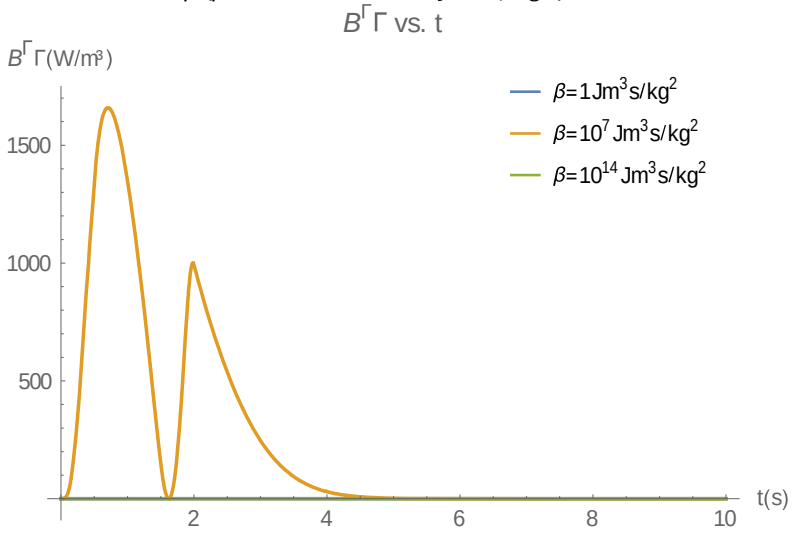

Figure 6. Rate of energy dissipation as a function of time for different values of $\beta(\beta = 1, 10^7 \text{ and } 10^{14}\, Jm^3s/kg^2)$.

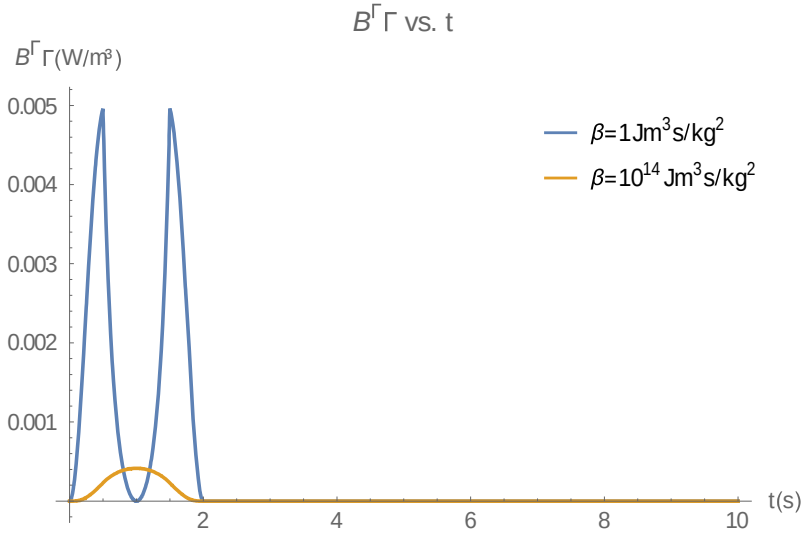

Figure 7. Rate of energy dissipation as a function of time for different values of $\beta(\beta = 1 \text{ and } 10^{14}\, Jm^3s/kg^2)$.

Quite distinct behavior is also observed for the different values of β when the mass transference rate is plotted in Fig. 5. The response associated with $\beta = 1\ Jm^3s/kg^2$ represents states close to the non-dissipative case and the mas

transference rate is the one needed to keep the system in the equilibrium state. The response associated with $\beta = 10^{14}\ Jm^3s/kg^2$ represents no mass transference at all. Finally, the response associated with $\beta = 10^7\ Jm^3s/kg^2$ represents states of non-equilibrium when dissipation occurs, resulting in mass transference rates smaller than the ones of the non-dissipative cases.

Figures 6 and 7 presents the plots of the rate of energy dissipation for each case as a function of the time. As it can be seen, almost no energy is dissipated for both $\beta = 1\ Jm^3s/kg^2$ and $\beta = 10^{14}\ Jm^3s/kg^2$ and a significant amount of energy is dissipated when $\beta = 10^7\ Jm^3s/kg^2$. Figure 7 is plotted to ensure the huge difference observed in the rate of energy dissipated in each case. By comparing Fig. 6 and Fig. 7, the maximum rate of energy dissipation of the dissipative case is 3.4×10^5 times greater than the maximum one for the other cases.

By plotting the free gas volumetric fraction and the mixture mass density against the mixture pressure in Figs. 8 and 9, different physical situations are also observed, and the hysteresis loop is clearly noticed for the dissipative case. The hysteresis loops demonstrates, as seen in the previous analyzes, that the greatest dissipation occurs for $\beta = 10^7\ Jm^3s/kg^2$ and almost no dissipation takes place for $\beta = 1\ Jm^3s/kg^2$ and $\beta = 10^{14}\ Jm^3s/kg^2$.

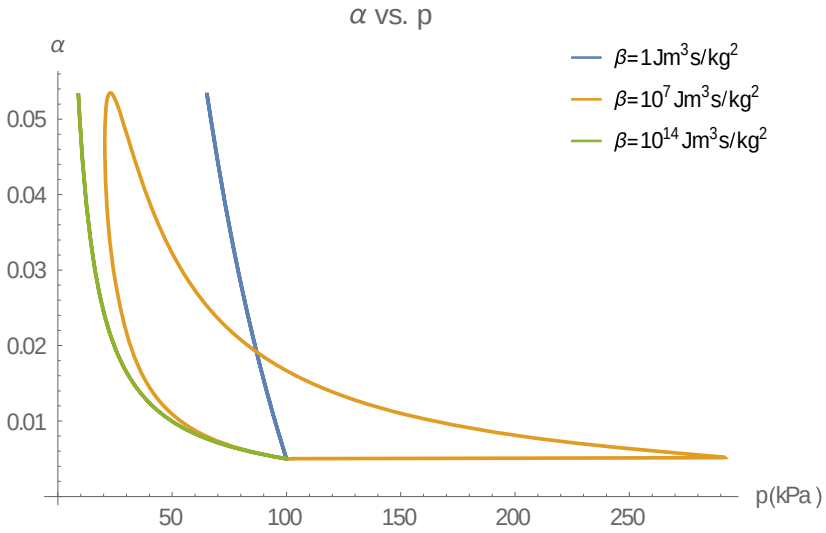

Figure 8. Gas volume fraction against pressure for different values of $\beta (\beta = 1, 10^7 \text{ and } 10^{14}\ Jm^3s/kg^2)$.

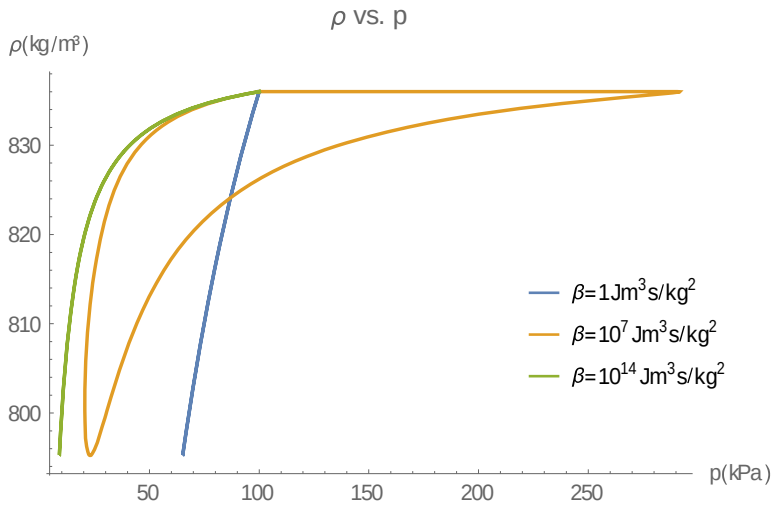

Figure 9. Mixture mass density against pressure for different values of $\beta (\beta = 1, 10^7 \text{ and } 10^{14}\ Jm^3s/kg^2)$.

6. CONCLUSIONS

A simple coherent thermodynamic model for describing gaseous cavitation in homogeneous isothermal fluids flows has been proposed and analyzed in this paper. The fluid is considered a compressible mixture of liquid and gas which coexist in the same material point and time instant. Being that the gas can exist as dissolved gas and free gas. The void

fraction and dissolved gas concentration are considered as internal variables and its constraint is treated as material properties. The rate of gas evolution is defined based on the Thermodynamic of the Irreversible Process, using two thermodynamic potentials: the Helmholtz free energy and a pseudopotential of dissipation. By using this approach, it was found that the gas evolution rate must be a function of the differences of the Gibbs free energy of the dissolved gas and the Gibbs free energy of the free gas. The derivation based in this approach enables the computation of the dissipated energy due to gas phase change using Eq. (22).

The capability of the model in describing different behaviors observed in practice is illustrated by means of a limit analysis. By modifying only one material parameter, it is possible to simulate transformations ranging from the simple and classical non-dissipative cases to complex rate-dependent situations in which relaxation phenomena are present. It is shown that the dissipation renders a rule for cavitation threshold that can lead to cavity formation under greatly diferent fluid flow conditions than that observed for the non-dissipative (reversible) process. The simulations results show that the dissipation affects the pressure pike on the compression tests, what makes the prevision of the gas transference very important to correct design equipment. More over the tests has shown hysteresis due to the irreversibility of the processes of gas release and absorption. The model simplicity and capability to properly describe real physical situations enable its usage as a promising tool in the study of gaseous cavitation.

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