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# Ostwald ripening in a yield-stress fluid under uniform gas production

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ABSTRACT

The evolution kinetics of a bubble population driven by a uniform production of gas in a yield-stress fluid matrix is investigated in the context of the long time swelling of bitumen drums in which radioactive salts have been dispersed (salts suspensions in a bitumen matrix). Radioactivity generates uniform volume production of hydrogen by radiolysis of bitumen chains. Since the production rate of gas occurs on very long time scales (more than a hundred years), one needs to set up theoretical models to predict the material swelling. It has been shown in previous studies that bitumen is a yield stress fluid. Therefore, the present work proposes to study the influence of a yield stress and of the production rate of gas on the evolution kinetics of a bubbles population. Usually, in a non-yield stress fluid and without gas creation, a supersaturation of gas leads to a scenario of germination, bubble growth and Ostwald ripening (growth of large bubbles at the expense of smaller ones). Over long times, a self-similar distribution of large bubbles is selected, independent of the initial distribution of nuclei. In this work, it is shown that there exist conditions for which the yield stress competes with the kinetics of ripening and induces hysteresis phenomena on the kinetics of bubbles distribution. The coupled effect of gas production rate and yield stress on the final population is discussed.



## 1. Introduction

Since 1966 in France (and in other countries such as Belgium, Japan...), radioactive wastes of low activity have been stored in metallic drums, after encapsulation into bitumen by an extrusion process (typically, 60 wt% of bitumen mixed with 40 wt% of radioactive salts). During storage, nuclides produce alpha, beta and gamma rays which induce the radiolysis of the bitumen chains [1]. It results a uniform volume production of hydrogen. This gas generation develops on very large time scales (over hundred years) and could lead to a macroscopic swelling of the drums. It is thus of primary importance to be able to predict this swelling, i.e. to develop a theoretical model of bubble creation, growing and migration into the bitumen matrix. It has been shown in a previous study that salt suspension in the bitumen behaves as a yield stress fluid [2]. Therefore, the present study proposes to characterize the influence of the yield stress on the kinetic evolution of a bubble population, and in particular with respect to the Ostwald ripening.

Ostwald ripening is a well-known phenomenon that occurs whenever several bubbles of various sizes are present in a fluid. It has been explained independently by Lifshitz and Slyozov, and Wagner through the so-called LSW theory [3,4]. Its principle is that the larger bubbles grow at the expense of the smaller ones, which collapse. The resulting effect is a spreading of the size distribution of the population and its impact is stronger for small, polydisperse bubbles.

Long time asymptotic behavior of Ostwald ripening leads to a self-similar size distribution under the scaling of average particle size $\bar{R}_t$ (mean radius at time $t$): the shape of the distribution is unchanged while its scale varies with the evolution of the mean radius. When this regime is reached, the cube of the mean radius of the population (i.e. the mean volume of the bubbles) changes almost linearly with time $t$ and the number of bubbles per unit volume decreases linearly in time [3–6]:

$$\bar{R}^3 - \bar{R}_0^3 = K_{LSW} t \tag{1}$$

where $\bar{R}_0$is the mean initial radius and $K_{LSW}$ is a constant coarsening rate given by Lifshitz and Slyozov [3].

However, during transient state, ripening can be accelerated, in particular in the case of a bimodal population: the peak of small bubbles is then quickly reduced [5]. This is explained by the fact that, for a bimodal population, the size difference between small and large bubbles is larger, resulting in a faster ripening.

It should be noticed that the coarsening rate $K_{LSW}$ is proportional to the diffusion coefficient and the surface tension [7–9],

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which indicates that a high diffusion coefficient accelerates the growth of large bubbles. The viscosity and the interfacial tension have no effect on the ripening speed [10]. However, the volume fraction of the bubbles has an impact on the Ostwald ripening. The theoretical system corresponding to LSW distribution is indeed strictly valid in the dilute case [3,4]. Experimentally, the observed distributions are broader than the ideal shape described by the LSW regime and the population does not follow strictly the previously described kinetics (Eq. (1)) [11]. To overcome this problem, many theories have been developed to take into account the influence of the volume fraction on ripening [12–15]. The higher the volume fraction, the more broadened the population. Eq. (1) remains valid regardless the volume fraction, but the latter influences the value of the coarsening rate $K_{LSW}$.

Ratke and Beckermann [16], in the case of grain growth in a molten metal by heat extraction, have studied the influence on ripening of a heat extraction rate. This system is similar to that of this study, the heat extraction rate being equivalent to the gas production rate. Ripening and gas production rate will actually oppose each other. The larger the gas production rate, the larger the number of non-collapsing bubbles. Nevertheless, the presence of a gas production rate does not change the law of evolution of the mean radius as a function of time (Eq. (1)), except that the coarsening rate $K_{LSW}$ increases with the gas production rate. Furthermore, increasing the gas production rate leads to a relative narrower population, approaching a monodisperse one.

Despite these extensions to the LSW theory, no studies have been carried out in the specific case of Ostwald ripening of bubbles within a yield-stress fluid matrix. In a recent paper [17], Venerus has proposed a properly formulated model for a single bubble growth and collapse in a yield-stress fluid that take into account elastic deformations before yielding, allowing bubble growth/collapse in an arbitrary large surrounding domain. Consequently, we propose to investigate the effect of the yield-stress and a gas production rate using a simplified version of the Venerus model. The model formulation (Section 2) is first proposed for a single bubble growth (Section 2.1). Then the specific application to salts suspensions in bitumen is proposed (Section 2.2), leading to a model formulation for bubble populations (section 2.3). Finally, Section 3 is devoted to applications and sensitivity analysis.

## 2. Model formulation

Let us consider a domain (drum of height $h \approx 1$ m) occupied by the material. The salts mixed with the bitumen have a maximum size of the order of $R_{salt} = 10^{-5}$ m and are assumed uniformly distributed. Consequently, the gas production rate is considered equal at each point of the material. The gas is dissolved at a mass concentration $c$ and, in a first analysis, the following scenario is considered:

- The pressure $p_\infty$ far from the domain is supposed constant,
- Self-radiation generates in the fluid a hydrogen mass production rate $Q_{sm}$ which is constant over time,
- The solubility (limit mass concentration) $c_s$ is $4.5\times10^{-3}$ kg m$^{-3}$,
- When the concentration sufficiently exceeds the solubility limit $c_s$, a number of bubble nuclei can grow,
- All bubbles are spherical, their radius is denoted $R$,
- The pressure $p_i$ in a bubble induces a hydrodynamic growth,
- The diffusion is isotropic and constant, the diffusion coefficient is denoted $D$,
- The velocity field in the fluid around a growing bubble is purely radial,
- The fluid is incompressible and obeys an Oldroyd [19] elasto-viscoplastic model:

$$\tau = \begin{cases} G\left[F.F^T - \delta\right] & \text{for} \quad \|\tau\| = \sqrt{\mathrm{tr}(\tau.\tau)} < 2\sigma_y \\ \left[\eta \pm \sigma_y/\sqrt{\mathrm{tr}(\dot\gamma.\dot\gamma)/2}\right]\dot\gamma & \text{for} \quad \|\tau\| = \sqrt{\mathrm{tr}(\tau.\tau)} \geq 2\sigma_y \end{cases}, \tag{2}$$

where the notations of Venerus [17] were used ($\tau$, $G$, $F$, $\eta$, $\sigma_y$ and $\dot\gamma$ are respectively the extra-stress tensor, the shear elastic modulus, the deformation gradient tensor, the viscosity, the yield-stress and the strain rate tensor).

### 2.1. Single bubble growth

#### 2.1.1. Hydrodynamic growth

We first study the growth of a single spherical bubble of initial radius $R_0$. We consider in this part that the gas concentration far from the bubble is imposed (boundary value) and we observe the bubble growth. This will be different in the next Section (2.2) dedicated to a bubble population kinetics, where the concentration will be an evolving quantity. It has been shown by Yang and Yeh [18] that a necessary condition for bubble growth in an incompressible Bingham fluid was (i) to consider a finite domain around the bubble and (ii) to yield this whole domain.

This constraint can be avoided by considering an elastic behavior below the yield-stress, as proposed by Venerus [17], who investigated a single bubble growth in an Oldroyd yield stress fluid [19]. Using again the same notations as Venerus [17], let us define:

- $R$as the bubble radius,
- $r$ as the radial coordinate,
- $N_\sigma = \sigma_y/G$,
- $S$ so that for $R \leq r < S$ (resp. $S \leq r < \infty$), the stress is determined by the second (resp. first) line in (2),
- $R_{\text{yield}}$ so that, for bubble growth (resp. collapse), the medium remains unyielded for $R < R_{\text{yield}}$ (resp. $R > R_{\text{yield}}$).

For small values of $\sigma_y$ and large values of $G$ ($N_\sigma \ll 1$), equation (19) in [17] implies that $R_{yield}$ is very close to $R_0$, which means that the radius barely varies when the medium is unyielded. When the medium is yielded, one gets $R/S \ll 1$, as shown by Venerus, and equation (20) implies that $|R^3 - R_0^3|/S^3 \cong \sqrt{3}\sigma_y/2G = \sqrt{3}N_\sigma/2$. Substituting this last term in equation (22) in [17], on obtains the kinetics of growth/collapse of a single bubble:

$$4\eta\frac{\dot R}{R} = (p_i - p_\infty) - \frac{2\gamma}{R} - K_y(N_\sigma)\sigma_y \quad \text{if} \quad \|\tau\| = \sqrt{\mathrm{tr}(\tau.\tau)} \geq 2\sigma_y \text{ and } \dot R \geq 0 \tag{3}$$

$$4\eta\frac{\dot R}{R} = (p_i - p_\infty) - \frac{2\gamma}{R} + K_y(N_\sigma)\sigma_y \quad \text{if} \quad \|\tau\| = \sqrt{\mathrm{tr}(\tau.\tau)} \geq 2\sigma_y \text{ and } \dot R < 0, \tag{4}$$

$$\dot R = 0 \quad \text{if} \quad \|\tau\| = \sqrt{\mathrm{tr}(\tau.\tau)} < 2\sigma_y \tag{5}$$

where $p_i$ is the internal pressure in the bubble, $\gamma$ is the interfacial tension between dihydrogen and bitumen and $K_y(N_\sigma) = -2[Ln(\sqrt{3}N_\sigma/2) - 1]/\sqrt{3}$. Consequently, for sufficiently small values of $N_\sigma$, the grow/collapse kinetics is governed by the viscoplastic behavior, while the elastic behavior allows yielding the surrounding medium up to finite values of $S$. Let us notice that $N_\sigma$ can be seen as a linear elastic limit before yielding.

#### 2.1.2. Diffusive growth

The existence of a concentration gradient in the fluid around a bubble generates diffusion mechanisms coupled to the convection