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Introduction of an equation of state for nitrogen based described by the free Helmholtz energy in the model of a spherical cavitation bubble (type Rayleigh-Plesset)

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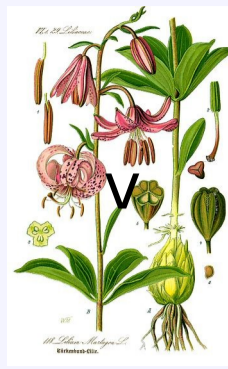
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Introduction

In the last instants of the contraction of an inertial cavitation bubble, the gases pressure value of hundred of MPa and up to several GPa. Van der Waals equation of state which have replace the ideal gas law long time ago starts to diverge from experimental value of the gas behaviour typically as pressure overdrives 1 GPa [1,2]; for example, for fixed temperature and gas concentration, the real pressure is not so important than the calculated pressure with the Van der Waals pressure. Others equations of state or correlations exist to describe gases at such high pressure among which: the 'cubic' said equation of state, extension of Van der Waals formulation, as the Peng-Richardson (PR) state or correlation founded on the free energy of Helmholtz [3,4].

According to Storey and Szeri [5] who modelised the chemical activity of a bubble, using equation of state for very high pressure do not change the nature of the physics and chemical phenomena in the bubble, but modify their quantification.

The target that drives this work is to precise temperature and pressure close to the bubble in an undercooled water to forecast the number of crystal ice a bubble can produce (a continuation of [6]); it can be approximated that undercooled water is free of vapor and chosen to work with only nitrogen in the bubble, as it is experimentally rather easily practicable.

The dynamic equation

Whatever the bubble dynamics (Rayleigh-Plesset, Gilmore, Keller-Miksis), it is expressed with the second derivative of the radius R which contains both the gas pressure P_g and its derivative \dot{P}_g (below, Keller-Miksis' one from [7])

$$\ddot{R} = \frac{1}{R} \left(1 - \frac{\dot{R}}{c_l}\right) \left[-\frac{3}{2} \dot{R}^2 \left(1 - \frac{\dot{R}}{c_l}\right) + \frac{1}{\rho} \left(1 + \frac{\dot{R}}{3c_l}\right) (P_g - P_a - P_o) + \frac{R}{\rho_1 c_1} \dot{P}_g - 4\mu \frac{\dot{R}}{R} - \frac{2\sigma}{\rho R} \right]$$

With R, \dot{R} and \ddot{R} the bubble radius and its two first derivatives according to time; c_l the wave celerity, ρ the liquid volumic mass and μ the dynamic viscosity.

'Cubic' equations of state

This expression contains both the gas pressure P_g and its derivatives against time, which depends of the chosen equation of state and the gas-liquid thermal transfert:

Van der Waals gas and a polytropic gas transformation (coef. κ):

$$P_g = \left(P_o + \frac{2\sigma}{R_o} \right) \left(\frac{R^3 - 8,54^3}{R^3 - 8,54^3} \right)^\kappa \quad \begin{array}{l} T: \text{the gas temperature, 8,54 coefficient for } N_2 \\ T \text{ is directly deducted from VdW law} \end{array}$$

Van der Waals gas and explicit model of gas-liquid heat transfert:

$$P_g(t) = \frac{N_{tot} k T}{\frac{4\pi}{3} [R(t)^3 - R_o/8,54]} \quad \begin{array}{l} N_{tot}: \text{total number of gas molecules} \\ R_o: \text{the initial bubble radius} \end{array}$$

For explicit gas-liquid transfert, a 'cubic equation of state' as Peng-Robinson (PR) is possible:

$$P_g = \frac{R T}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)} \quad \begin{array}{l} V_m: \text{molar volume;} \\ 'a' \text{ and 'b', coefficients.} \end{array}$$

When using an explicit heat transfert, T is determined through internal energy U and results from statistic thermodynamics.

Formulation for the Helmholtz free energy correlation

Free Helmholtz energy based correlation have been introduced in bubble model by way of tabulated value []; for nitrogen, the correlation used was limited to 2 GPa and 1000 K [] but other correlation is given up to 25 GPa and 5000K [2]. The correlation is build from the ideal α^o and the residual α^r free energy, given by the following kind of expressions; coefficients are given in references.

$$\alpha^o(\delta, \tau) = \ln(\delta) + \alpha_1 \ln(\tau) + \alpha_2 + \alpha_3 \ln(\tau) + \alpha_4 \ln(\tau^{-1}) + \alpha_5 \ln(\tau^{-2}) + \alpha_6 \ln(\tau^{-3}) + \alpha_7 \ln(1 - e^{-\alpha_8 \tau})$$

$$\alpha^r(\delta, \tau) = \sum_1^6 N_k \delta^{i_k} \tau^{j_k} + \sum_7^{32} N_k \delta^{i_k} \tau^{j_k} e^{-\delta^k} + \sum_{33}^{36} N_k \delta^{i_k} \tau^{j_k} e^{(-\gamma_k (\delta-1)^2 - \beta_k (\tau-\gamma_k)^2)}$$

With: $\delta = \frac{\rho}{\rho_c}$, $\tau = \frac{T_c}{T}$ and 'c' the index for critical values.

Thermodynamics magnitudes are defined from α^o, α^r and derivatives, for example P, U, Z (and also Cv, Cp, S and sound velocity not displayed here).

$$P_g = \rho R_g T \left[1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right) \right] \quad Z = \frac{P_g}{\rho R_g T} = 1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right) \quad U = R_g T \tau \left[\left(\frac{\partial \alpha^o}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^r}{\partial \tau} \right)_{\delta} \right]$$

Introduction in a cavitation bubble

The formulation of free Helmholtz energy equation of state does not permit to express directly P_g nor \dot{P}_g .

The system of differential equations of the bubble model (dynamic, heat transfert, molecule transfert) enable to get each time of their integration R, U and the total number N_{tot} of gas molecules because their derivatives can be analytically expressed: from R and N_{tot} them, it is possible to calculate the volumic mass (ρ) or molecule concentration: with given U and ρ, it is possible thanks to the equation of state, to research the corresponding temperature by resolving a first order equation in T then to calculate the pressure.

It still misses \dot{P}_g to calculate \ddot{R} first it is calculated R(t+dt), N(t+dt) and U(t+dt) with dt small compared to the dt use to integrate the system of differential equation of the bubble model: then the same procedure used at t gives: T(t+dt) and P_g(t+dt); the same calculation backward to t-dt gives T(t-dt) and P_g(t-dt); so are estimated:

$$\dot{T} = \frac{T(t-dtt) - T(t+dt)}{2dt} \quad \dot{P}_g = \frac{P_g(t-dtt) - P_g(t+dt)}{2dt}$$

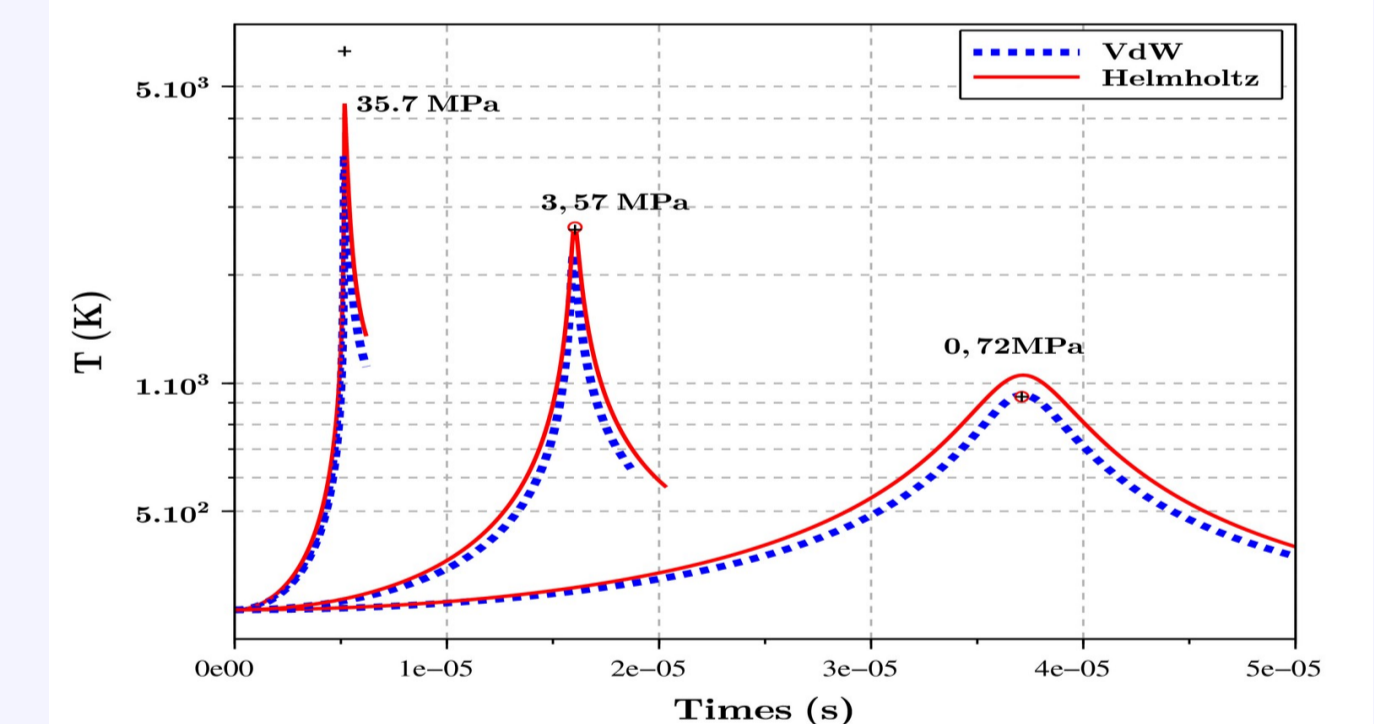
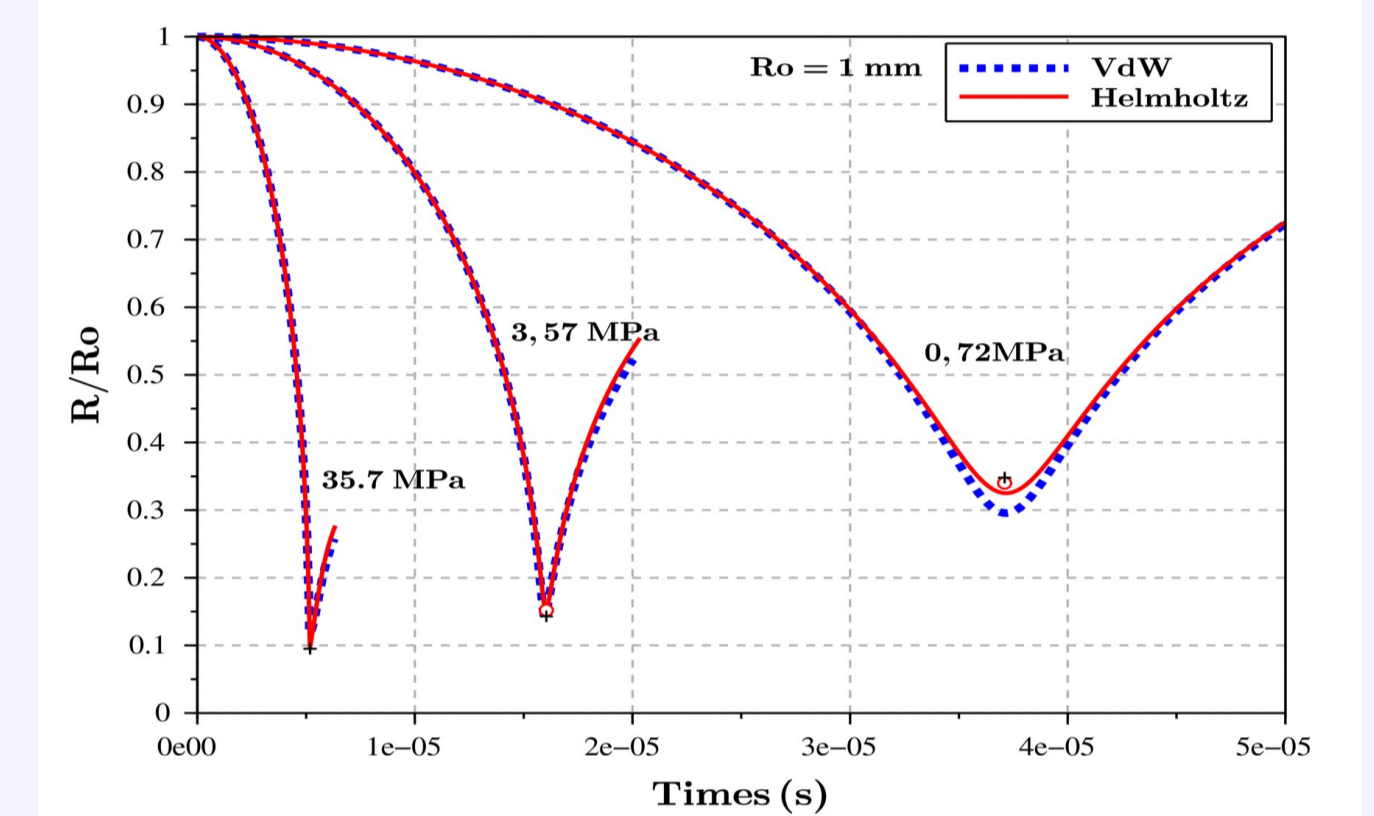
\dot{T} is obtained with no element external to the equation of state

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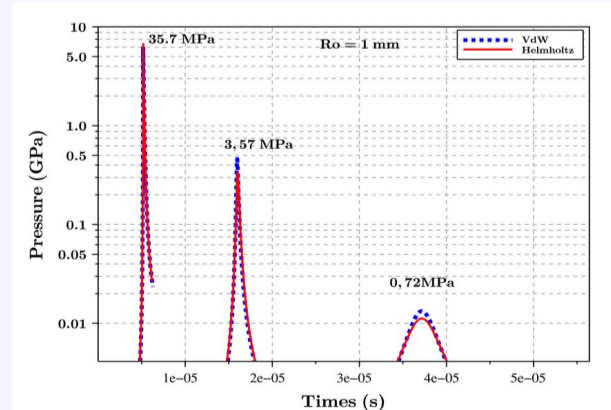
Results and comparison with [1]

Calculation for a 1 mm initial radius bubble submitted to a constant pressure, as does Bidi *et al.* [1] The model of these authors is more more sophisticated than ours; we compare the radius and temperature evolution for our model with Helmholtz free energy and a VdW law; the minimum radii and maximum averaged temperature given by Bidi *et al.*, with o for the Helmholtz model and + for Peng-Robinson model.



The scheme of calculation we use gives similar result than the one employed by Bidi *et al.* [1], for the radius, rather similar for temperature for PR and Helmholtz.

Considering pressure (no result displayed in [1]), Helmholtz and VdWs are close in this case, but for smaller bubble [2], first result have shown larger differences.



Conclusion

This calculation scheme have to be introduced in the ice nucleation model to evaluate its quantitative influence.

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