Flow and mixing dynamics of phase-transforming multicomponent fluids

Saiikat Mukherjee and Hector Gomez
School of Mechanical Engineering, Purdue University, 585 Purdue Mall, West Lafayette, IN 47907, USA

(Dated: 21 August 2019)

Despite the importance of phase-transforming, multicomponent fluids in medical diagnostics, atmospheric flows, or supercavitating vehicles our understanding of their flow and mixing dynamics is very limited. Here, we investigate two-component flows, where one of the components is an incondensable gas and the other one is a fluid that undergoes liquid-vapor phase transformations accompanied by changes in its miscibility with the gas. We derived a continuum model from a Gibbs free energy that includes gradients of the fluid density and gas concentration, leading to a generalization of the classical equations of multiphase flow hydrodynamics. High-fidelity numerical simulations of the model show a very complex interplay between flow, mixing and phase transformations. The model predicts quantitatively the saturation vapor pressure of water for a given mixture of air and water vapor at different temperatures. When applied to the problem of collapse of cavitation bubbles, the model allows to study the role of gas dissolved in the liquid phase on the dynamics of the collapsing bubble. Our findings on the collapse of multicomponent bubbles have a strong bearing on the multiple applications of cavitation bubbles. The proposed model opens entirely different ways to study phase-transforming multicomponent fluids.

Many problems of interest in fluid dynamics involve several phases (i.e., states of matter) of the same fluid, several components (i.e., materials with different chemical compositions) in the same phase, or multiple phases and components simultaneously. Prime examples occur in atmospheric chemistry, industrial liquid sprays, and microfluidics. Compared to single-phase, single-component flows, multiphase and multicomponent flows introduce two major elements of complexity — phase transformations and miscibility. These two elements are not necessarily independent because when a fluid changes phase it can also change its miscibility properties. Although a lot of progress has been made understanding changes phase it can also change its miscibility properties.

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We developed our model postulating a Gibbs free energy, using standard balance laws for mass of each component and linear momentum of the mixture, and applying the Coleman-Noll approach. For isothermal conditions, our free-energy can be written as

\[ \psi_{\text{free}}(\rho, c) = \psi_f(\rho) + \frac{\lambda}{2} |\nabla \rho|^2 + \frac{1}{M_b} B(\rho, c) + \frac{\rho c^2}{2} |\nabla c|^2, \] (1)

where \( \rho \) and \( c \) denote, respectively, the density of the fluid and the concentration (mass fraction) of incondensable gas (air in what follows). The function \( \psi_f(\rho) \) represents the free energy density per unit volume of a van der Waals fluid and can be expressed as

\[ \psi_f(\rho) = k_\text{B} (\rho c - |\rho - \rho_c|) - \alpha \rho^2, \] where \( \alpha \) is...
The parameters \( \lambda \) and \( \epsilon \) can be obtained, respectively, from the surface tension at the liquid-vapor interface \( (\sigma_a) \) and at the liquid-gas interface \( (\sigma_g) \) as
\[
\sigma_a = \int_l -\lambda (\nabla \rho_0 \cdot \mathbf{n})^2 \mathrm{d}m_b^2
\]
and
\[
\sigma_g = \int_l c^2 \rho (\nabla \cdot \mathbf{n})^2 \mathrm{d}m_b^2,
\]
where \( n \) represents a spatial coordinate perpendicular to the relevant interface. The proof for the expression of liquid-gas surface tension has been included in the Supplement. The function \( B(\rho, c) \) is a measure of the energy of miscibility of gas in the fluid that will be defined later. \( M \) represents a time scale for the mixing of the incondensable gas in the phase-transforming fluid. We now resort to standard balance laws for mass of the mixture, linear momentum, and mass of incondensable gas,

\[
\rho + \rho \mathbf{v} \cdot \mathbf{v} = 0, \quad \rho \mathbf{v} = \nabla \cdot \mathbf{T}, \quad \rho c + \mathbf{v} \cdot \mathbf{j} = 0. \tag{2}
\]

Here, a dot denotes material derivative, and \( \mathbf{v} \) is the fluid velocity. The Coleman-Noll procedure\(^{26}\) allows us to determine the Cauchy stress tensor \( \mathbf{T} \) and the mass flux \( \mathbf{j} \) from the condition that the Gibbs free energy must decrease in time along solutions to the balance equations. This leads to

\[
\mathbf{T} = -p \mathbf{I} + \tau + \xi + \zeta, \tag{3}
\]

\[
\mathbf{j} = -x \nabla \left( \frac{1}{\rho M} \frac{\partial}{\partial c} \frac{\rho^2}{\rho} \nabla \left( \rho \mathbf{v} \cdot \xi \right) \right), \tag{4}
\]

where \( p = \rho \mathbf{v}^2 - \mathbf{v} \cdot \mathbf{v} \) is the van der Waals equation of state and \( \tau = \mu (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) + \eta \nabla^2 \mathbf{v} \) is the classical viscous stress tensor. Here, \( \mu \) and \( \eta \) are the viscosity coefficients that will be assumed to satisfy the Stokes hypothesis, i.e., \( \eta = -2\mu/3 \).

The tensor \( \xi = -\lambda \nabla p \otimes \nabla p + \chi (\frac{1}{2} \nabla p^2 + \rho \nabla^2 p) \) is the Korteweg stress which accounts for the stresses developed at the liquid-vapor interface. \( \zeta = -\rho c^2 \nabla c \otimes \nabla c + \frac{1}{2} (B - \rho \frac{\partial G}{\partial \rho}) \mathbf{I} \) is the contribution to stress emanating from the multi-component nature of the mixture, and \( \kappa \) is a positive constant which represents a time scale for diffusion of the incondensable gas. The details of the derivation may be found in Supplement.

The mixing energy is defined as \( B(\rho, c) = g(\rho) |f(c)| + (1 - g(\rho)) |f(c)| \). It can be decomposed into two parts: gas miscibility in the liquid phase and in the vapor phase. Miscibility in the liquid phase is governed by Henry's law which states that for a given temperature, solubility of a gas into a liquid is proportional to its partial pressure. Solubility of gas into the liquid is modeled with the term \( g(\rho)|f(c)| \) in \( B(\rho, c) \). Here,

\[
f(c) = c \ln(c) + (1 - c) \ln(1 - c) = c \ln(c) + \alpha_l (1 - c) - (1 - c) \ln(1 - c) - \beta_l c \]

is a mixing energy proposed by Wilson\(^{18}\), where the parameters \( \beta_l \) and \( \alpha_l \) determine the equilibrium concentration of gas in the liquid at vapor pressure \( (c_l) \). The term \( g(\rho) \frac{\partial p}{\partial \rho} \) accounts for the increase in gas solubility in the liquid phase when pressure is increased; see data showing the compliance of the model with Henry's law in the

FIG. 1. Time evolution of the gas concentration (A), density (B) and streamlines (C) for two bubbles side by side in a pool of liquid at temperature \( \theta \, / \, \theta_b = 0.85 \). The Maxwell states \( (\rho_0, b = 0.106 \) and \( \rho_1, b = 0.602) \), which define equilibrium conditions are not altered by the distribution of incondensable gas. For clarity, we only show the central part of the computational domain. The plot shows a very complex interplay between phase transformations and miscibility.

Supplement. Here, \( \rho_0 \) and \( \rho_1 \) represent the Maxwell states of the liquid-vapor phase, respectively, and are determined using common tangent constructions on the van der Waals energy density \( \psi(\rho) \). The Maxwell states correspond to conditions of equal pressure and chemical potential \( (\psi(\rho)) \) in the liquid and vapor phases. The miscibility of gas in the vapor phase is governed by the laws of gas mixing and is modeled in our approach by the function \( f_3(c) = c \ln(c) + (1 - c) \ln(1 - c) - c \ln(c) + \alpha_g (1 - c) - (1 - c) \ln(1 - c) + \beta_g c \). The parameters \( \beta_g \) and \( \alpha_g \) establish the equilibrium concentration of gas in the vapor phase \( (c_g) \). The concentration dependence of the equilibrium densities \( (\rho_0 \) and \( \rho_1 \)) is taken into account by the function \( g(\rho) \) in \( B(\rho, c) \). Depending on the nature of gas miscibility in the phase-transforming fluid, this relationship may change. For a linear relationship between \( g(\rho) \) and \( \rho \), the Maxwell states are independent of gas concentration; proof included in Supplement. A comparison between our model and the van der Waals theory for binary mixtures\(^{27}\) under the assumption of low gas density has been presented in the Supplement.

To study the model, we scale length by \( L_0 \) mass by \( mL_0^2 \), time by \( t_0 = L_0 / \sqrt{ab} \) and temperature by the critical temperature of a van der Waals fluid \( \theta = \theta_b / (27R) \). From this scaling, it follows that the solution depends only on the Wilson mixing energy parameters \( (\alpha_l, \beta_l, \alpha_g, \beta_g) \) and the following dimensionless groups: Reynolds number \( Re = b \sqrt{\pi} \rho_0 / \mu \), Weber number of the liquid-vapor interface \( W_{lv} = a b \rho_0 / \sqrt{\pi} \), Peclet number \( Pe = L_0 \sqrt{ab} / (\kappa \lambda) \), and \( S_e = Ma = b^2 \). The dimensionless number \( S_e \) represents a balance of the mixing velocity to the liquid-vapor interface velocity, whereas \( Pe \) is the ratio of the strength of advection relative to the strength of diffusion. Because surface tension and the length scale \( L_0 \) are not independent in the model, we took \( L_0 = 75 \) nm, such that \( \sigma_0 = \sigma_{tg} = 0.075 \) N/m, which are accurate val-
FIG. 2. Saturation vapor pressure for air-water mixtures. The model results (solid line) accurately match the experiments [27] (dashed line). The model results were obtained by running dynamic simulations (each one marked with a symbol) with different temperatures and water mole fractions. The magnified snapshots showcase steady state density distributions for $\theta = 498.42$ K ($\rho_w/b = 0.0668$, $p_b = 0.66669$), $p = 100$ bar, corresponding to $x_w$ values of 0.3420 and 0.3490 which are representative of density distribution for unsaturated and saturated conditions respectively.

and $S$ eters rated and saturated conditions respectively.

$\theta$ (ing with time and at equilibrium one large bubble is formed

$\rho$ = $\rho_w$ and a smaller bubble saturated with gas ($\rho = \rho_w$, $c = c_1$) side by side in a pool of liquid ($\rho = \rho_1$, $c = c_1$) at temperature $\theta/\theta_0 = 0.85$. Right after the simulation starts, gas is drawn from the liquid into the large vapor bubble (not shown).

After this initial phase, we observe the gradual movement of gas from the smaller bubble into the larger bubble and corresponding movement of liquid from the vicinity of the smaller bubble to occupy that space, as the equilibrium value for the density remains equal to $\rho_1$; see the streamlines in Fig. 1C ($t/t_0 = 1$ and $t/t_0 = 2$). The smaller bubble keeps shrinking with time and at equilibrium one large bubble is formed ($\rho = \rho_w$, $c = c_1$).

The ability of the model to predict water phase transformations in the presence of air was quantitatively evaluated by determining the saturation vapor pressure of water ($p_{sat}$) for a given mixture of air and water vapor at different temperatures. We identified our pressure and temperature scales equating the critical pressure and temperature of a van der Waals fluid ($p_c = ab^2/27$ and $\theta_c = SabR^{-1}/27$) to the critical pressure and temperature of water-steam mixtures ($p_c = 220.64$ bar and $\theta_c = 647.2$ K); see [27]. We considered air-water mixtures with uniform density such that the total pressure of the fluid according to van der Waals equation was $p = 100$ bar. However, the concentration field was not uniform, and we consider a small water vapor bubble in a pool of uniform water vapor-air mixture. We ran multiple simulations, where the mole fraction of water $x_w$ was gradually increased, by increasing the radius of the spherical vapor bubble, in order to simulate the addition of water vapor into a partially saturated air-steam mixture. This mixture was used as an initial condition for our simulations, which evolved toward a stationary state. For very small values of $x_w$, we observed complete miscibility with uniform concentration and density throughout (representative simulations are marked with triangles in Fig. 2). With the addition of more water, we obtained a general increase in density. Further addition of water leads to the formation of liquid water droplets (squares in Fig. 2). We defined the saturation pressure $p_{sat}$ as the partial pressure of water corresponding to the smallest value of $x_w$ for which liquid droplets are observed, that is, $p_{sat} = p_{w, min}$.

Several such families of simulations were run for different values of $\theta$ in order to determine the saturation vapor pressure curve. Fig. 2 shows that the values calculated with the model are very close to those obtained experimentally [27]. Another important application of our model is the dynamics of cavitation nanobubbles [28-32]. The field has been traditionally divided into pure vapor bubbles [3] and pure gas bubbles [33]. However, the study of the general problem in which vapor and an incondensable gas interact chemically and mechanically has remained qualitative [32] due to the absence of a firm theoretical framework. To study this problem, we initially ran simulations with a uniform gas concentration of $c = c_1$ throughout. A vapor bubble with a radius $R_0$ initially in equilibrium was subjected to a far field overpressure $\Delta p = p_0 - p_b$. The pressures $p_{sat}$ and $p_0$ were set using their corresponding densities $\rho_{sat}$ and $\rho_0$ according to the van der Waals equation of state. We took $\theta/\theta_0 = 0.85$, $R_0/L_0 = 0.05$, $\rho_b/b = 0.7028$, $p_0/b = 0.0800$. We show snapshots of the time evolution of the density (Fig. 3A) and concentration of incondensable gas (Fig. 3B). Figs. 3C-D show the time evolution of pressure and gas concentration (insets) along the radial direction ($r$) in the pre-collapse (C) and post-collapse (D) stages.
bubble with large density and pressure gradients at the liquid-vapor interface, and a large amount of incondensable gas in its interior, which was quickly drawn from the liquid phase due to the higher miscibility of gas in the vapor phase (compare the snapshots of gas concentration at times $t/\tau_D = 0$ and $t/\tau_D = 0.14$). During the pre-collapse phase, the model predicts a strong compression wave and an increase in the pressure at the bubble interface that reaches its maximum at the collapse time; see Fig. 3C. The post-collapse phase is marked by the propagation of a rarefaction wave away from the bubble (Fig. 3D). The speed of this rarefaction wave is much higher than that of the incoming compression wave which was responsible for the bubble collapse. The pressure peaks in the post-collapse phase follow a power law relationship similar to that proposed by Hickling-Plesset.$^{31}$

To compare the results reported in Fig. 3 to those of an identical situation but without incondensable gas, we repeated our simulation taking $\epsilon = 0$ throughout. We focused on two quantities of interest: the time evolution of the bubble radius $R_b$ and the interface Mach number $M_i$. To define the radius we identified the bubble boundary as the curve along which the pressure gradient was maximum. The Mach number was defined as $M_i = |v|/\sqrt{\gamma R b^2 (\rho - \rho b)/2 \rho b}$, where $\gamma = 1.4$ is the adiabatic constant. The data in Fig. 4 shows three major differences produced by the presence of incondensable gas: i) Bubble collapse is slower ($t/\tau_D = 0.180$ vs $t/\tau_D \approx 0.162$), ii) The Mach number at the interface is lower ($M_i \approx 0.593$ vs $M_i \approx 0.633$), iii) The minimum bubble radius is greater than zero. The results show that the presence of incondensable gas inhibits bubble collapse, which is consistent with$^{21}$.

This is expected because vapor converts to liquid on the application of sufficient pressure but gas miscibility in the liquid at a particular temperature and pressure is limited by Henry’s law. From Fig. 4 it is also clear that the final phase of bubble collapse is characterized by rapid compression. This can be explained by the sharp increase in the pressure at the interface right before bubble collapse; see Fig. 3C. The high pressure promotes conversion from vapor phase to liquid phase. Although the rate of decrease of bubble radius is slower when incondensable gas is present, it still accelerates in the later stages owing to enhanced gas miscibility in the liquid with an increase in pressure.

Because the gas is practically immiscible with the liquid phase and highly miscible in vapor, even small amounts of gas dissolved in the liquid can produce changes in the dynamics of bubble collapse. To study this, we carried out additional simulations varying the initial degree of saturation of the fluid ($\phi$) and the dimensionless parameter $S_b$ which controls the time scale of the mixing process, because different gases have different characteristic time scales of mixing in a vapor bubble$^{34}$. As we do not have (at the scales studied here) experimental data to estimate the value of $S_b$, we show simulations for a wide range of values. A vapor bubble with some gas ($\rho/b = 0.0800$, $c = c_b$) was placed in a bath of liquid with varying concentrations of dissolved gas ($\rho/b = 0.7028$, $c = \phi c_b$). We applied an excess far field pressure identical to that used in the previous simulation and studied the time evolution of the average concentration of gas inside the bubble ($c_b$). For the parameters used in the simulation corresponding to the thickest (black) curve in Fig. 5, we can partition the process into four stages marked in the figure with different colors. In the first stage, $c_b$ increases quickly because gas is being drawn from the liquid into the bubble. Also, the low miscibility of gas into the liquid keeps the gas practically confined into the shrinking bubble, leading to an increase in $c_b$. In the second stage, $c_b$ increases more slowly. Because the bubble is still shrinking at a fast rate, this can only be explained by the dissolution of gas into the liquid. This is a consequence of the large pressure in the liquid phase (cf. with Fig. 3C) that according to Henry’s law increases the solubility of gas into the liquid. The data show that this behavior is naturally captured by the model. The plateau in $c_b$ is reached faster for larger $\phi$ and smaller $S_b$ because in this parameter range the gas can move more easily into the bubble. In the third stage, $c_b$ grows again because the size of the bubble is decreasing very quickly right before the collapse and the pressure is not high enough to allow for dissolution of all of the excess gas into the liquid. In the fourth stage, due to the dramatic increase of the pressure right before bubble collapse, the liquid phase becomes much more soluble and $c_b$ decreases quickly.

In all, the simulations show a very complex interplay between mass conservation, linear momentum balance and solubility that cannot be quantitatively understood without a computational model.

In conclusion, we have presented a model of two-component flows, where one of the components is an incon- densable gas and the other one is a fluid that undergoes liquid-vapor transformations. The model is derived from a higher-order Gibbs free energy that includes gradients of the density and gas concentration, constituting a generalization of classical equations of multiphase hydrodynamics that is consistent
with recent efforts in porous media flows. The model predicts quantitatively the saturation vapor pressure of water for a given mixture of air and water vapor at different temperatures. The model highlights the importance of dissolved gas in the collapse of cavitation bubbles. In this context, the extension of the proposed model to non-isothermal conditions is particularly promising for the study of the post-collapse phase. This extension can be done by factoring the temperature dependence of the equilibrium concentrations into the model, by suitably varying the parameters $\alpha$, $\beta$, $\alpha'$ and $\beta'$ with the temperature and adding an equation for conservation of energy. After the collapse, the concentration and density at the sharp bubble boundary. This suggests that classical models based on ordinary differential equations for the bubble radius may be inadequate in the multicomponent, multiphase problem even if the solution remains axisymmetric. We believe our model can also have significant impact in other problems that involve simultaneous several phase and several components, for example, diesel engines, methane venting and focused ultrasound therapy.

I. SUPPLEMENTARY MATERIAL

The supplementary material contains details of the derivations of our model starting from the free energy formulation proposed in (1), applying the Coleman-Ncole procedure. It has a derivation for $\sigma_g$ and details of the comparison of the presented model with the van der Waals theory for binary mixtures under the assumption of low gas density. It also contains the details regarding non-dimensionalization, numerical procedure followed for solving the family of equations (2) and a derivation for speed of sound in van der Waals fluids.

II. REFERENCES

Temperature (K)  

Saturation vapor pressure (bar)  

Droplet nucleation  
Vapor-gas mixture  
Experiment  
Model
With gas

Without gas

t/t

D

Interface

Rz/R_{eq}

100

A

B

Rz

0.20

0.15

0.10

0.05

0.00

0.20

0.15

0.10

0.05

0.00

Interface Mz

Without gas

With gas

PLEASE CITE THIS ARTICLE AS DOI: 10.1063/1.5109889