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Homogeneous bubble nucleation in binary systems of liquid solvent and dissolved gas

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ABSTRACT

A formulation of the classical nucleation theory (CNT) is developed for bubble nucleation in a binary system composed of a liquid solvent and a dissolved gas. The theoretical predictions are compared to the experimental nucleation data of four binary mixtures, i.e. diethylether – nitrogen, propane – carbon dioxide, isobutane – carbon dioxide, and R22 (chlorodifluoromethane) – carbon dioxide. The presented CNT formulation is found to improve the precision of the simpler theoretical method of Ward et al. [J. Basic Eng. 92 (10), 71–80, 1970] based on the weak-solution approximation. By analyzing the available experimental nucleation data, an inconsistency in the data reported by Mori et al. [Int. J. Heat Mass Transfer, 19 (10), 1153–1159, 1976] for propane – carbon dioxide and R22 – carbon dioxide is identified.

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1. Introduction

The homogeneous nucleation of bubbles in liquids can be influenced considerably by the presence of a dissolved gas. The rate of nucleation is increased in binary systems compared to pure liquids, and also the composition of bubbles can be significantly different from the composition of the parent liquid mixture. The effects of the dissolved gas come into play in many natural and technological processes where the liquid mixture is put in a metastable state, e.g. by a fast depressurization of the liquid system, by a rapid increase of temperature, or by supersaturating the liquid with the gas evolved by a chemical reaction.

Compared to nucleation processes in one-component systems, i.e. the unary nucleation, the binary systems feature increased complexity due to non-ideal mixing of the two components and due to surface adsorption effects causing the surface composition to differ from the composition of bulk phases. As a result, nucleation processes in binary systems represent a challenge for both the theoretical description and experimental investigation. For the case of unary nucleation processes, however, the classical nucleation theory [1,2] (CNT) provides a simple and reliable way for qualitative and also quantitative prediction of bubble nucleation rates [26].

Experimental data of homogeneous bubble nucleation in binary systems of a liquid solvent and a dissolved gas were first measured for the diethylether – nitrogen system [3,4], and for three refrigerant – carbon dioxide systems [5]. The experimental bubble nucle-ation data obtained by investigators until 1985 were reviewed by Avedisian [6]. Later, several nitrogen-based mixtures were measured [7–9] as reviewed in 2003 by Lubetkin [10]. In the recent review from 2013, Baidakov [11] reported nucleation data for cryogenic mixtures. For water, the influence of various dissolved gases on bubble nucleation was measured [12,10,13,14]. Molecular dynamics simulations present a complementary technique to experimental measurements of bubble nucleation [15]. Nowadays, molecular systems of half a billion Lennard-Jones atoms are simulated to observe bubble formation events [16].

The first theoretical description of the homogeneous bubble nucleation in a binary mixture with a dissolved gas was presented by Ward et al. [3]. The Ward theory is a weak-solution approximation to the binary case and was successfully applied to the diethylether – nitrogen system, with up to 5% nitrogen mole fraction. Later, the Ward theory was applied to aqueous systems [17,10] and also to the propane – carbon dioxide system [5], where the mole fraction of the dissolved gas reached up to 30%. Several theories exist that are not restricted to weak solutions. The modified Gibbs approach by Schmelzer et al. [18] presents a general theoretical framework for bubble nucleation in multi-component systems. Other theoretical approaches to the nucleation theory include the kinetic theory of homogeneous bubble nucleation [19] and the multivariable kinetic theory [20]. An alternative method to CNT is the density functional theory (DFT), which was developed to circumvent the often criticized capillary approximation of CNT. DFT was first applied to the binary bubble nucleation problem by Talanquer and Oxtoby [21,22].

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In this work, CNT is formulated for the case of a binary system of a liquid and a dissolved gas to provide a more accurate alternative to the weak-solution approximation of the Ward theory for higher concentrations of the dissolved gas. The theory is formulated in the spirit of the modified Gibbs approach [18], but it further specifies the form of the nucleation work to account for the special case of the liquid – dissolved gas system. The composition-dependent surface tension, which is treated in the modified Gibbs approach as dependent on the composition of both phases (i.e. the parent liquid system and the gaseous bubble), is taken as a function of the composition of the more dense phase only (i.e. the parent liquid mixture). Four experimental datasets available from the literature are analyzed, namely diethylether – nitrogen, propane – carbon dioxide, isobutane – carbon dioxide, and R22 (chlorodifluoromethane) – carbon dioxide systems. These four experimental datasets are the only datasets with sufficient amount of datapoints enabling to observe the pressure, temperature, and concentration dependence of the nucleation rate. The experiments in the other binary systems mentioned earlier in this section provide mostly just one experimental datapoint, they do not enable a comprehensive comparison to the theory, and are therefore not analyzed here.

The paper is structured as follows. The Ward theory is reviewed in Section 2. The predictions of the nucleation rate by the Ward theory are compared to available bubble nucleation data showing quite large discrepancies. In Section 3, the CNT is formulated for the binary case of bubble nucleation in a liquid with a dissolved gas. The improvements over the Ward theory are aiming at the correct use of the surface tension of binary mixtures in CNT calculations and the proper evaluation of the chemical potentials for concentrated solutions. In Section 4, predictions of the developed binary CNT approach are shown and compared to experimental data. The theoretical analysis presented in this work helps to identify an inconsistency in two nucleation datasets, propane – carbon dioxide, and R22 – carbon dioxide measured by Mori et al. [5]. In Section 2.1, the predictions of the Ward theory for the nucleation rate of the propane – carbon dioxide mixture are found accurate when using the surface tension of pure propane. However, the deviation of the theoretical predictions from the experimental data is increased when the surface tension for pure liquid is replaced by the surface tension of the binary mixture. Then in Section 4.4 it is shown that the measured nucleation data [5] for the propane – carbon dioxide system and the R22 – carbon dioxide system are inconsistent with the values of the Henry constant of carbon dioxide in the respective solvent.

2. Ward theory overview

The theoretical treatment of bubble nucleation by Ward et al. [3] was developed for the description of liquid solutions with small concentrations of a dissolved gas. The assumptions used in the theory limit its applicability to weak solutions, on the other hand, they enable the binary nucleation rate to be expressed in a simple analytical form, similar to the case of unary nucleation. For a thermodynamic state of the parent liquid mixture given by temperature T [K], pressure p_l [Pa], and concentration of the dissolved gas c_{l2} (in moles of solute per mole of solvent) the nucleation rate is calculated as [3,23]

$$J_W = \sqrt{\frac{2\sigma}{\pi M_1}} \rho_l \exp\left(-\frac{4\pi\sigma(r^\star)^2}{3kT}\right) \tag{1}$$

where M_1 [kg/mol] is the molar weight of the solvent and $k = 1.38 \times 10^{23}$ J/K is the Boltzmann constant. In Eq. (1), the surface tension σ [N/m] and the liquid number density ρ_l [m^{-3}] are approximated by the respective properties of the pure solvent and the

influence of the dissolved gas is included only in the formula for the critical bubble radius $r^\star$ as follows

$$r^\star = \frac{2\sigma}{p_{g1} + p_{g2} - p_l} \tag{2}$$

In Eq. 2, the pressure inside the bubble is evaluated as a sum of the vapor pressure of the solvent p_{g1} and the partial pressure p_{g2} of the dissolved gas. The solvent vapor pressure in the critical bubble is calculated as [3]

$$p_{g1} = p_{e1} \exp\left(\frac{v_{l1}(p_l - p_{e1})}{kT} - c_{l2}\right) \tag{3}$$

where p_{e1} is the vapor–liquid equilibrium (saturation) pressure of the pure solvent, v_{l1} [m^3] is the molecular volume of the pure liquid solvent, and c_{l2} is the concentration of the dissolved gas in the liquid mixture, $c_{l2} = x_{l2}/x_{l1}$, where x_{li} is the mole fraction of component i. The partial pressure of the dissolved gas in the critical bubble was derived as [3]

$$p_{g2} = p_l \frac{c_{l2}}{c_{e2}} \tag{4}$$

where c_{e2} is the equilibrium concentration of the dissolved gas, i.e. its concentration in the liquid saturated with the gas under the pressure p_l [23].

The validity and accuracy of the Ward theory was confirmed by the measurements of bubble nucleation in the diethylether – nitrogen binary system [3]. Later, the measurements were extended to pressures above the vapor–liquid equilibrium pressure of pure diethylether [4]. The weak-solution assumption of the Ward theory is adequate for the binary diethylether – nitrogen system since the mole fraction of nitrogen was lower than 5%.

2.1. Applicability of Ward theory to concentrated solutions

Due to the weak-solution assumption of the Ward theory, the discrepancies between experimental nucleation data and the predictions of the Ward theory are expected to gradually increase with increasing the concentration of the dissolved gas in the binary solution. Such behavior is not observed in the results of Mori et al. [5] for the propane – carbon dioxide system, however. Even though the mole fraction of the dissolved carbon dioxide reaches up to 30%, the difference between the Ward theory and the measured nucleation rates is quite small and constant. The top graph in Fig. 1 shows the agreement between the binary experimental data and the predictions of the Ward theory, which are based on Eqs. (1)–(4) and the thermophysical properties of the propane – carbon dioxide system summarized in Appendix A. An even better agreement is observed in the original paper of Mori et al. [5] (in their Fig. 7), who used a slightly different parametrization of the surface tension of pure propane and an alternative expression for the pre-exponential term of the nucleation rate in their calculations.

Note that a considerable discrepancy in the slope of the 10^{10} m^{-3} s^{-1} isoline is observed for the unary nucleation data of pure propane (blue line) in the top graph in Fig. 1. This discrepancy was already discussed elsewhere [26] concluding that the unary experimental data of propane violate a general scaling law rendering these data unreliable. However, the pure propane data will be kept in the respective graphs of this work for the sake of completeness.

Nevertheless, the binary nucleation data are reproduced accurately by the Ward theory, even though the surface tension of pure propane is used for a concentrated mixture of 30% mole fraction of carbon dioxide. Carbon dioxide decreases the surface tension of refrigerants considerably as was measured for the butane – carbon dioxide mixture [27] and predicted theoretically for several other