

Theoretical evidence for inconsistencies in experimental bubble nucleation rates of propane/CO₂ and R22/CO₂ mixtures

Tomáš Němec

Institute of Thermomechanics of the CAS, v.v.i., Dolejškova 5, 18200 Praha 8, Czech Republic
E-mail: nemec@it.cas.cz

Abstract. A binary formulation of the classical nucleation theory (CNT) is developed for homogeneous bubble nucleation in systems composed of a liquid solvent and a dissolved gas. The CNT predictions coincide with experimental nucleation data from the literature for diethylether/N₂ and isobutane/CO₂ mixtures, while several inconsistencies are identified for propane/CO₂ and R22/CO₂ experimental datasets.

1. Introduction

The homogeneous nucleation of bubbles in liquids [1] can be influenced considerably by the presence of a dissolved gas. 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. during geyser eruptions, cavitation in fluid machinery, or production of carbonated beverages.

In 1970, Ward *et al* [2] formulated the nucleation theory for the case of a liquid solvent and a dissolved gas, which was based on the assumption of a weak solution. In more detail, the differences of chemical potentials between the gas phase and the liquid phase required for the evaluation of the nucleation work were written in an approximate form appropriate for weak solutions. And the surface tension of the pure solvent was used instead of the unknown surface tension of the liquid mixture. These assumptions enabled to simplify the resulting expressions for the binary nucleation work and the nucleation rate, resembling the simpler unary theoretical formulation. The theory was validated by the authors for the experimental bubble nucleation rates of the diethylether/N₂ mixture. Since the mole fraction of N₂ in diethylether was rather low, reaching roughly 5 %, the weak-solution assumption of the Ward theory was satisfied. The Ward theory, due to its simplicity, was used by many authors to describe the effect of a dissolved gas on bubble nucleation [3, 4, 5].

The Ward theory was later applied to the experimental nucleation rates measured in the propane/CO₂ system by Mori *et al* [6]. Their calculations show a very good agreement between the theoretical predictions and the measured nucleation rates, roughly within the experimental uncertainty of the bubble column experiment of ± 1.5 K. However, due to mole fractions of CO₂ reaching up to 30 %, it is surprising that the weak-solution assumption within the Ward theory lead to such precise predictions of the nucleation rate. It is the value of the surface tension that is crucial for the calculation of the theoretical nucleation rate since it is located in the exponent and raised to the power of 3 in the theoretical expression for the nucleation rate. As the surface



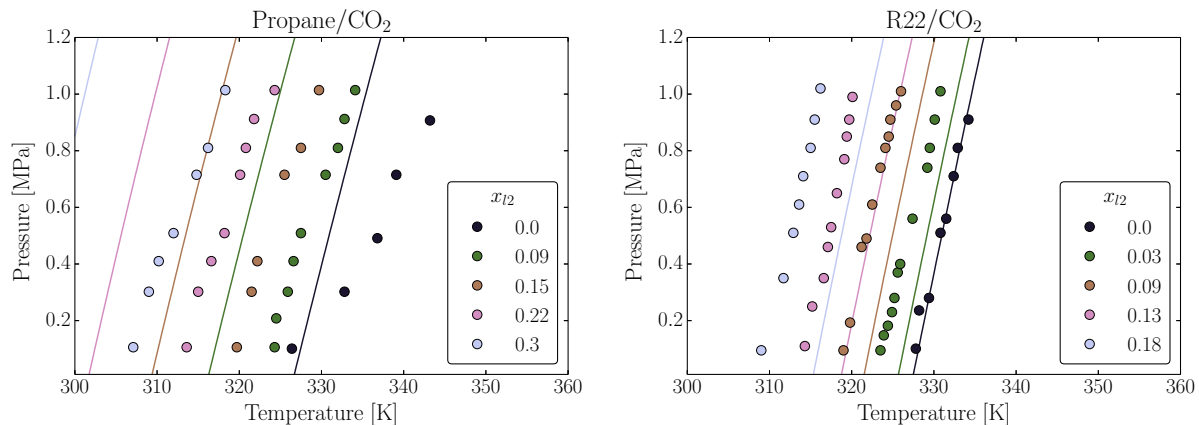


Figure 1. Experimental nucleation rates of $10^{10} \text{ m}^{-3} \text{ s}^{-1}$ [6] in propane/CO₂ (left) and R22/CO₂ (right) mixtures (dots) compared to the predictions of the binary CNT (full lines).

tension of propane/CO₂ at the high concentrations of CO₂ studied in Mori's experiment can drop to almost one half of the surface tension of pure propane [7], the nucleation rates predicted with the Ward theory using the real surface tension of the mixture no longer coincide with the experimental data.

In the attempt to approach the “accuracy paradox” described in the previous paragraph from an independent theoretical viewpoint, a binary CNT formulation was developed focusing on the case of a liquid solvent with a dissolved gas [8]. The binary CNT approach presents an evolution of the Ward theory since the chemical potentials of both components are evaluated properly for the concentrated solution, and the real surface tension of the concentrated liquid mixture is used. The predictions of the binary CNT are shown in Fig. 1 and compared to the experimental data. For propane/CO₂, the CNT nucleation rates overestimate the reported experimental data considerably. The overestimation is manifested in the fact that the isolines of the constant theoretical nucleation rate of $10^{10} \text{ m}^{-3} \text{ s}^{-1}$ are shifted to lower temperatures compared to the measured data. This discrepancy between theory and experiment increases as the mole fraction x_{l2} of CO₂ in propane grows, reaching almost 20 K difference for $x_{l2} = 0.3$. Moreover, the unary nucleation rates in the pure propane are not predicted correctly as well; the slope of the experimental datapoints in Fig. 1 for $x_{l2} = 0.0$ is significantly lower than the slope predicted by the theory. For R22/CO₂, opposite to the propane/CO₂ case, the predictions of the binary CNT shown in Fig. 1 underestimate the experimental data. An agreement between theory and experiment is observed for pure R22 data.

There are only two more bubble nucleation rate datasets in the literature that are large enough to allow for a comprehensive analysis in terms of pressure, temperature, and concentration dependence of the nucleation rate, namely the diethylether/N₂ [2] and isobutane/CO₂ [9]. Both of these datasets are predicted correctly by the binary CNT [8].

2. Scaled analysis of unary nucleation data

To investigate the difference in the slope of the theoretical $10^{10} \text{ m}^{-3} \text{ s}^{-1}$ isoline and the slope of experimental nucleation rates for pure propane ($x_{l2} = 0.0$) as observed in Fig. 1, a comparison with nucleation data of similar substances in terms of the scaled theory [10, 11] can be performed. In the scaled approach, all substances behave similarly in the way that the nucleation data of a constant nucleation rate align on a single line in the scaled plot. The scaling behavior was verified for a set of 14 substances including normal alkanes, halogenated hydrocarbons, and

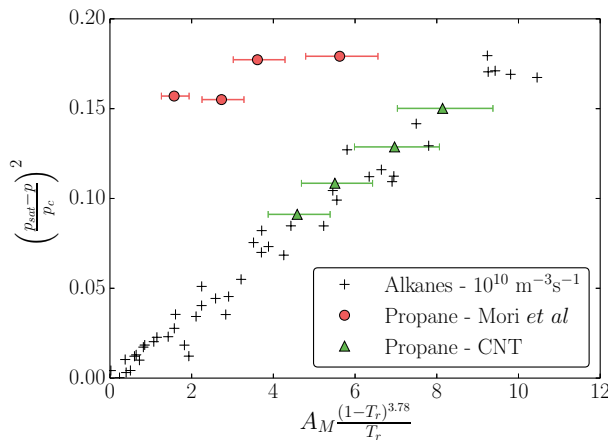


Figure 2. Scaled plot of experimental nucleation rates for alkanes shows the relation between the scaled temperature (horizontal axis) and the scaled pressure (vertical axis) for a fixed value of the measured nucleation rate; see [11] for details of the scaled variables. The $10^{10} \text{ m}^{-3}\text{s}^{-1}$ dataset includes nucleation rate data of n -alkanes for $n = (1, \dots, 8)$. The errorbars show the uncertainty in the temperature of $\pm 1.5 \text{ K}$.

aromatic hydrocarbons [11]. The propane data of Mori *et al* [6] behave anomalously in the scaled plot as shown in Fig. 2 (red dots); the data clearly deviate from the scaling behavior of other alkane experimental data for the nucleation rate of $10^{10} \text{ m}^{-3}\text{s}^{-1}$. However, the predictions of CNT for pure propane follow properly the scaling law in Fig. 2 (green triangles).

3. Inconsistency of binary experimental data

As shown in Fig. 1, the experimental nucleation rates of propane/ CO_2 are overpredicted considerably by CNT, while the nucleation rates of R22/ CO_2 are underpredicted by CNT. To explain such contradictory behavior, the thermophysical properties of both mixtures related to the nucleation rate can be analyzed. Actually, propane and R22 have almost identical thermophysical properties, their mixtures with CO_2 have also similar densities and surface tensions, and the only considerable discrepancy lies in the Henry constant of CO_2 , which is roughly twice as large in propane than in R22. A higher Henry constant means that the dissolved gas for a given concentration of the liquid mixture creates a higher gas pressure above the liquid, and, therefore, results in a higher tendency of the liquid mixture to nucleate, see [8] for a detailed discussion. In other words, the nucleation rates in propane/ CO_2 should be higher than in R22/ CO_2 for a given CO_2 concentration. However, a closer look at the experimental nucleation rates in Fig. 1 reveals that the nucleation rates measured for the CO_2 mole fraction of $x_{l2} = 0.09$ are lower for propane/ CO_2 than for R22/ CO_2 , i.e. the experimental datapoints for $x_{l2} = 0.09$ are located at higher temperatures for propane/ CO_2 . This relation between the measured nucleation data is in a direct opposition to the expectation based on the relation between the Henry constants.

The above contradiction between the experimental nucleation rates and the respective Henry constants supports a hypothesis of an accidental interchange of the experimental datasets reported in the original work of Mori *et al* [6]. Indeed, a very good agreement can be observed when the original R22/ CO_2 experimental data are utilized as propane/ CO_2 data in the comparison with CNT and vice-versa as shown in Fig. 3.

4. Conclusion

A thorough CNT analysis of bubble nucleation data reported by Mori *et al* [6] for two binary mixtures, propane/ CO_2 and R22/ CO_2 , revealed essential inconsistencies in these experimental datasets. First, the precise predictions of the nucleation rate with the Ward theory for propane/ CO_2 contrasts with the fact that the inaccurate surface tension of pure propane is used in the calculations. Second, the pressure and temperature dependence of the measured

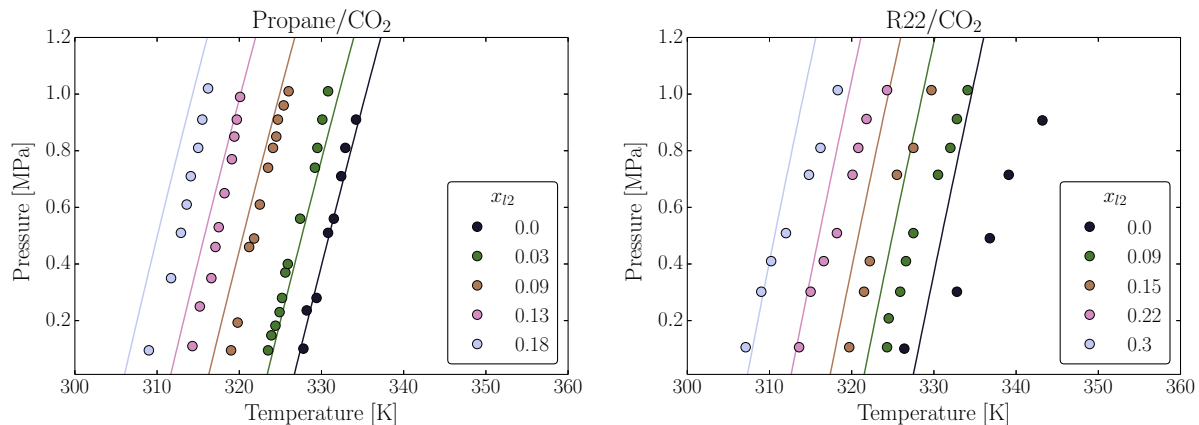


Figure 3. Nucleation rates of $10^{10} \text{ m}^{-3}\text{s}^{-1}$ predicted by the binary CNT (lines) for propane/ CO_2 (left) and R22/ CO_2 (right) compared to experimental data interchanged between the two respective mixtures (dots).

nucleation rate for pure propane violates a general scaling law, while the CNT nucleation rates obey the scaling relation correctly. Third, the experimental nucleation rates in propane/ CO_2 are lower than in R22/ CO_2 , while a higher nucleation rate should be observed due to the higher Henry constant of CO_2 in propane. The higher nucleation rate in propane/ CO_2 is indeed predicted by the CNT.

It is the goal of this work to point out that more bubble nucleation data should be acquired experimentally for the binary systems of a liquid solvent and a dissolved gas. Obtaining experimental data complementary to the existing measurements of the nucleation rate in the propane/ CO_2 and R22/ CO_2 systems would help to clarify the inconsistencies presented in this work, and measuring new nucleation data for other binary mixtures would stimulate further development of the binary nucleation theory.

Acknowledgments

The author would like to acknowledge the institutional support RVO:61388998 of the Institute of Thermomechanics of the CAS, v. v. i., and the support by the Czech Science Foundation (projects GAP101/10/1819 and GA13-23550S), and by the Technology Agency of the Czech Republic (project TA03030978).

References

- [1] Baidakov V G 2013 *Low Temperature Physics* **39** 643–664
- [2] Ward C A, Balakrishnan A and Hooper F C 1970 *J. Basic Eng.* **92** 71–80
- [3] Hemmingsen E A 1975 *J. Appl. Phys.* **46** 213–218
- [4] Wilt P M 1986 *J. Colloid Interface Sci.* **112** 530–538
- [5] Lubetkin S D 2003 *Langmuir* **19** 2575–2587
- [6] Mori Y, Hijikata K and Nagatani T 1976 *Int. J. Heat Mass Transfer* **19** 1153–1159
- [7] Němec T 2014 *Experimental Fluid Mechanics 2014* ed Dančová P and Vít T (Český Krumlov (CZ), 18. 11. 2014 – 21. 11. 2014) pp 383–388
- [8] Němec T 2015 *to be submitted*
- [9] Avedisian C T 1985 *J. Phys. Chem. Ref. Data* **14** 695–729
- [10] Hale B N 1986 *Physical Review A* **33** 4156–4163
- [11] Němec T 2014 *Eur. Phys. J. E* **37** 111