

CAVITATION PROCESSES IN BINARY SYSTEMS – THE EFFECT OF A DISSOLVED GAS ON THE NUCLEATION RATE DESCRIBED BY THE CLASSICAL NUCLEATION THEORY

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ABSTRACT

The Classical Nucleation Theory (CNT) is applied to nucleation in cavitation processes in binary mixtures of a liquid component and a dissolved gas component. The multi-component form of the CNT allows to study the influence of the dissolved gas concentration on the resulting nucleation rate. Four binary mixtures are studied, diethylether – nitrogen, propane – carbon dioxide, isobutane – carbon dioxide, and chlorodifluoromethane – carbon dioxide, whose experimental nucleation rates are available in the literature. The nucleation rates and their dependence on concentration of the dissolved gas calculated according to the CNT show good agreement with the experimental data.

INTRODUCTION

The nucleation of bubbles is an important phenomenon in a range of physical and technological processes[4, 14] – cavitation erosion in hydraulic machinery[20], ultrasound-induced cavitation used to destroy kidney, bladder, or gall stones in medical lithotripsy, ultrasound-induced cavitation enhancing chemical reactions in sonochemistry, and other industrial applications like homogenization, composites processing, fermentation, plastic foam processing. The theoretical description of nucleation evolved since the pioneering work of Gibbs[7] into a generally accepted theory – the Classical Nucleation Theory (CNT). The initial works on nucleation treated one-component systems in condensation[2] and cavitation[26]. Later, the influence of other components on the nucleation process was studied[17, 21, 16, 3, 19]. Nowadays, a commonly accepted theoretical apparatus describing the nucleation process in a general multi-component system is available[12]. In the case of multicomponent cavitating systems, the influence of the dissolved gases on the nucleation of liquids was studied[23, 15, 11] both experimentally and theoretically.

In this paper, a general CNT approach to the description of multicomponent nucleation processes in cavitation is presented. The theory is applied to several cavitating binary mixtures and the results are compared to the available experimental data. The CNT nucleation rates are compared with the previous theoretical treatment and they show increased accuracy.

NOMENCLATURE

A	[m ²]	surface area
c	[m ⁻³]	number concentration
f	[Pa]	fugacity
J	[m ⁻³ s ⁻¹]	nucleation rate
k	[J/K]	Boltzmann constant (1.38×10^{-23})
k_H	[Pa]	Henry constant
n		number of molecules
N		number of components
N_A	[mol ⁻¹]	Avogadro's number (6.023×10^{23})
p	[Pa]	pressure
p_{sat}	[Pa]	saturation pressure
r	[m]	cluster radius
S	[J/K]	entropy
T	[K]	temperature
v	[m ³]	molecular volume
V	[m ³]	volume
W	[J]	nucleation work
x		mole fraction

Subscripts

g	gas-phase
i	mixture component
l	liquid-phase

Superscripts

*	critical property
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Greek symbols

μ	[J]	chemical potential
σ	[N/m]	surface tension
Ω	[J]	grand thermodynamic potential

NUCLEATION THEORY

The goal of the CNT analysis is the evaluation of the nucleation rate J , i.e. the estimation of the number of newly created clusters per unit time and unit volume inside a metastable thermodynamic system. CNT shows that the nucleation rate is exponentially proportional to the critical nucleation work W^* ,

$J = J_0 \exp(-W^*/kT)$. It is the nucleation work W that needs to be properly evaluated for the respective cavitating system under investigation in order to get accurate results. In general, the nucleation work for a cluster of a given size and composition under certain thermodynamic state of the surrounding phase is evaluated as an increase of a suitable thermodynamic potential. In the case of cavitation, the grand thermodynamic potential Ω is used; its total differential reads

$$d\Omega = -SdT - pdV - \sum_i n_i d\mu_i + \sigma dA \quad (1)$$

where the independent variables are the temperature T , volume V , chemical potential μ_i , and surface area A . The remaining dependent variables are entropy S , pressure p , numbers of molecules n_i , and surface tension σ , and these are known functions of the independent ones. The total differential (1) is integrated from the initial thermodynamic state of the cavitating mixture to the final thermodynamic state of a given cluster inside the mixture yielding the nucleation work

$$W = V(p - p_{sat}) + A\sigma + \sum_{i=1}^N n_i \Delta\mu_i \quad (2)$$

where N is the number of components of the cluster and p_{sat} is the equilibrium (saturation) pressure of the multicomponent system. In the case of a binary system of a liquid and a dissolved gas the nucleation work (2) of a spherical bubble can be evaluated as

$$W = 4\pi\sigma r^2 + \frac{4}{3}\pi r^3(p - p_{sat}) + kTn_1 \ln \frac{x_{g1}p_g}{p_{sat1}x_{l1}} + kTn_2 \ln \frac{x_{g2}p_g}{k_{H2}x_{l2}} \quad (3)$$

where the solvent component is denoted by the subscript 1, and the dissolved-gas component is labeled 2. The pressures in Eq. (3) are as follows – p is the total pressure of the binary system, p_{sat} the equilibrium pressure of the binary system, p_{sat1} the equilibrium pressure of the pure liquid component, and p_g the pressure inside the bubble. Further, x_{li} and x_{gi} are the mole fractions of both components in the liquid mixture, and inside the bubble gas respectively, r is the cluster radius, and k_{H2} is the Henry law constant of the dissolved gas component.

Being able to evaluate the nucleation work of every possible cluster $W(n_1, n_2)$ at a given thermodynamic state of the mixture (T, p, x_{li}) with Eq. (3), we can search for the critical nucleation work W^* . As shown in Fig. 1, the nucleation work forms an energetic barrier that the cluster needs to overcome to become a stably growing bubble. The height of this barrier (maximum of W in one-component nucleation, or the saddle point in a general multicomponent case) denotes the critical nucleation work. We search for the location of the saddle point (in the cluster radius and cluster concentration variables) using a custom numerical least-increase algorithm. Once the saddle point W^* is found the nucleation rate J can be readily evaluated. The general CNT nucleation rate formula[22] is

$$J = \frac{c_0(1)|\lambda|}{\sqrt{2\pi kT \det \mathbf{D}}} \exp\left(-\frac{W^*}{kT}\right) \quad (4)$$

where the pre-exponential factor is a slightly altered concentration of monomers in the mother liquid mixture $c_0(1)$.

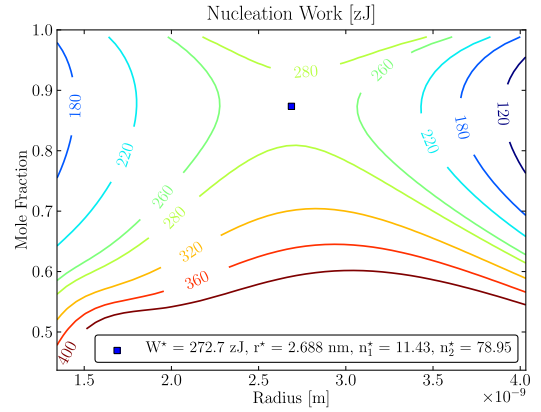


Figure 1: The saddle-shaped nucleation work (1 zJ = 10^{-21} J) surface of a binary system of isobutane and carbon dioxide shown as a function of cluster size and mole fraction of CO_2 . The thermodynamic state of the nucleating system is $T = 318$ K, $p = 718$ kPa, $x_{\text{CO}_2} = 0.33$ resulting in the nucleation rate $J = 10^6 \text{ m}^{-3}\text{s}^{-1}$. The composition of the critical bubble is 11.43 molecules of isobutane and 78.95 molecules of carbon dioxide. The saddle point (critical nucleation work W^*) is denoted by the blue square.

RESULTS

The theoretical description of multicomponent nucleation process presented in the preceding section was applied to four binary mixtures of the liquid solvent – dissolved gas type. The diethylether – nitrogen system was the first that was extensively investigated both experimentally and theoretically[25, 23, 6, 5] to evaluate the influence of the dissolved gas concentration on the nucleation process. Later three mixtures of the refrigerant – carbon dioxide type were experimentally measured in the work of Mori *et al.*[15]. We therefore utilized the measured nucleation rates of these four mixtures and compared them with our CNT predictions.

In order to evaluate the CNT nucleation rate several thermophysical properties of the mixture under investigation should be collected. We found all of them except the surface tension in the literature. The known thermophysical properties are summarized in Table 1. The equation of state (EOS) is used to calculate the partial molecular volume in the gaseous phase. We used the B-truncated virial EOS in the case of diethylether – nitrogen and the Peng–Robinson EOS with refrigerants. The saturation pressures of the pure liquid solvents p_{sat1} was fitted to the data from the NIST Webbook[13]. The Henry constants k_{H2} of carbon dioxide in refrigerants were calculated from the PC-SAFT equation of state[8].

Table 1: Thermophysical properties of the binary mixtures.

	EOS	p_{sat1}	k_{H2}
Diethylether – N_2	Virial[5]	[13]	[5]
Propane – CO_2	PR[24]	[13]	SAFT[10]
Isobutane – CO_2	PR[24]	[13]	SAFT[10]
R22 – CO_2	PR[18]	[13]	SAFT

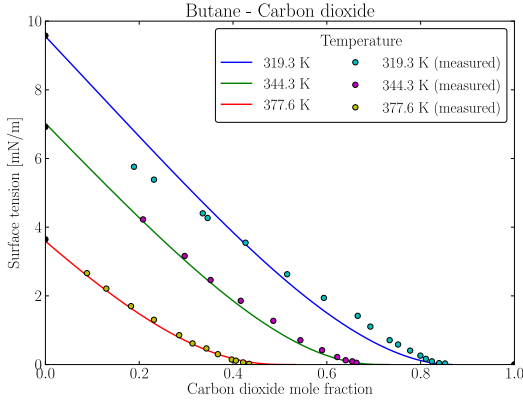


Figure 2: The surface tension of the butane – carbon dioxide liquid mixture predicted by the Parachor method and compared with experimental data[9].

The only unknown thermophysical property of our binary mixtures is the surface tension. We chose to predict its temperature and concentration dependence with the Parachor method[1, 27]. There is experimental data on the surface tension of a similar binary mixture, butane – carbon dioxide, available in the literature[9]. We therefore used this data to test the accuracy of our Parachor algorithm. A quite good agreement with experimental data was achieved as shown in Fig. 2, although the deviation reaches 10% at the lowest temperature.

Our predictions of the surface tension of the binary mixtures are shown in Fig. 3. The concentration dependence of the surface tension shows a similar, decreasing, concave tendency as we see in the case of butane – carbon dioxide experimental data. The fits also reproduce the pure solvent surface tension data (available in the NIST Webbook[13]) denoted by the black dots • in Fig. 3.

The results of our CNT nucleation rate predictions are shown in Fig. 4. The measured nucleation rates were of the order of $10^7 \text{ m}^{-3}\text{s}^{-1}$ in the case of ether[23] and $10^6 \text{ m}^{-3}\text{s}^{-1}$ in the case of refrigerants[15]. The experimental nucleation rate data were extracted from the graphs in the respective papers using the DataThief tool; the error produced by this procedure is however negligible.

The predicted nucleation rates show good agreement with the experimental data in all binary mixtures but the propane – carbon dioxide. The deviations in this case will be discussed in the next section.

DISCUSSION

Two aspects of our study will be discussed in this section, first, the comparison of our results to the original theoretical description of binary nucleation by Ward et al.[6], and second, the reason for the deviations of the calculated nucleation rates from the experimental data of propane – carbon dioxide.

The results of Forest and Ward[25, 23, 6, 5] were the first that described the effect of the dissolved gas on the nucleation process in cavitation. They experimentally measured the binary mixture of diethylether and nitrogen, and they also developed

a thorough theory to describe the dissolved-gas effect. The theory, on the contrary to our multicomponent treatment, results into a unary nucleation-rate formula[5] with an additional term involving the gas concentration

$$J = Z \exp \left(\frac{16\pi\sigma^3}{3kT \left(\frac{\eta p_{sat1}}{\nu_1} + \frac{c_2 p}{c_{sat2}\nu_2} - p \right)^2} \right) \quad (5)$$

In this equation, Z is a factor of the order of 10^{36} , c_2 is the dissolved-gas concentration in the binary solution (more precisely the mole fraction of the gas component vs. the mole fraction of the solvent), c_{sat2} is the saturated gas concentration at a given temperature, and ν_i are activity coefficients, usually taken as unity. The important thing to point out is that the surface tension σ in the nucleation rate formula (5) was that of the pure liquid solvent in the calculations of Forest and Ward and also in the work of Mori *et al.*, even though the surface tension of the solution is specified in the theoretical derivation of Forest and Ward.

The nucleation rate predictions of Ward *et al.* show a very good agreement with experimental data. As we see a serious deficiency in using the pure solvent surface tension in the nucleation rate calculations, we tried to find out the reason Eq. 5 predicts the measured nucleation rates so accurately. We recalculated the nucleation rates of our four binary mixtures with the Forest–Ward nucleation-rate. The results are shown in Fig. 5. As expected, the results of the ether – nitrogen mixture coincide with the experimental data, the refrigerant mixtures show underprediction of the nucleation rates. The reason lies in the surface tension – as the ether mixtures have low concentration of nitrogen, their surface tension is close to the surface tension of pure ether used in Forest–Ward nucleation rate calculation. The refrigerant mixtures, however, reach the concentration of carbon dioxide up to 33% and their surface tension is significantly different from the pure refrigerant surface tension, see Fig. 3. The resulting nucleation rates show therefore larger deviation; the nucleation rates are significantly lower due to the higher surface tension used in the calculation.

We also treat the chemical-potential term in the nucleation work in a slightly different way than the Forest–Ward theory (5). To assess the influence of such a difference in theoretical description we ran our calculations with a simplified form of the nucleation work, ignoring the chemical-potential terms completely and retaining the surface and volumetric terms only

$$W = 4\pi\sigma r^2 + \frac{4}{3}\pi r^3(p - p_{sat}) \quad (6)$$

The results are shown in Fig. 6 and we see that there are no significant differences from the nucleation rate calculated with the complete nucleation work formula (3). This tells us that the chemical terms in the nucleation work formula are not significant in the case of cavitation processes that we consider, and so does their theoretical description regardless of its accuracy. This important conclusion is elucidated in Fig. 7 where the decomposition of the nucleation work into the surface/volume part and the chemical part is shown. The sum of both parts of the nucleation work in Fig. 7 then gives the nucleation work surface shown in Fig. 1.

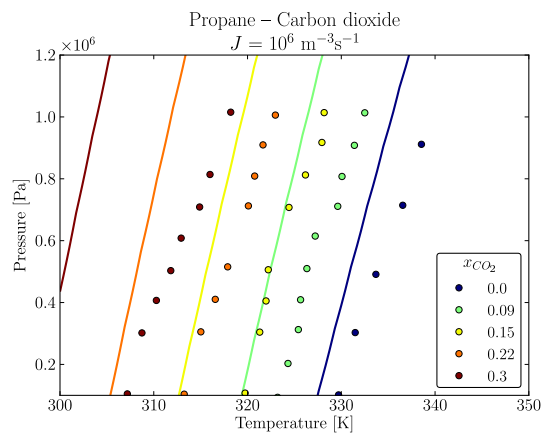
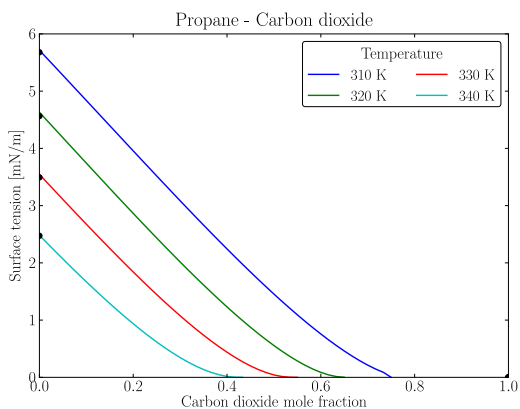
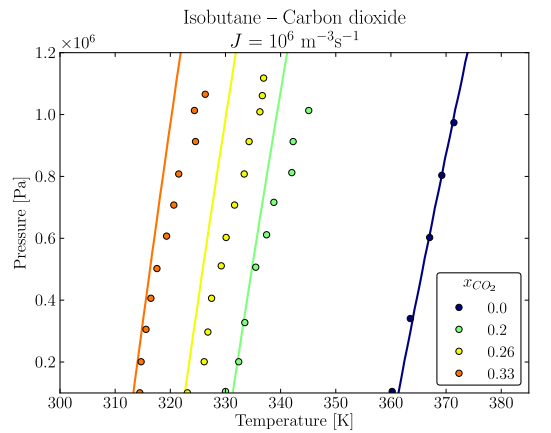
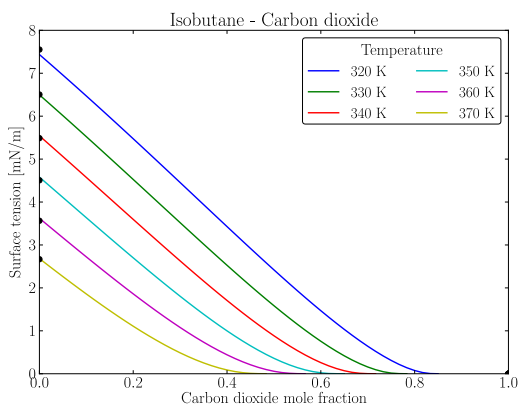
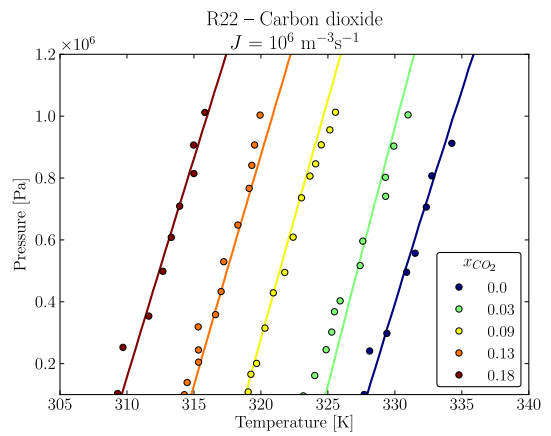
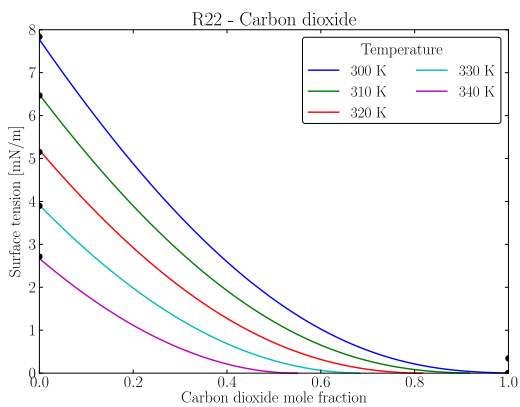
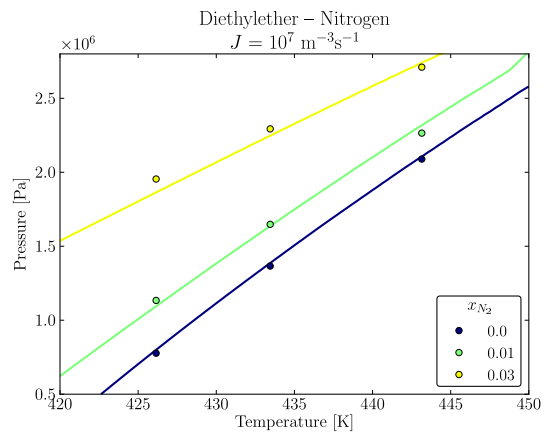
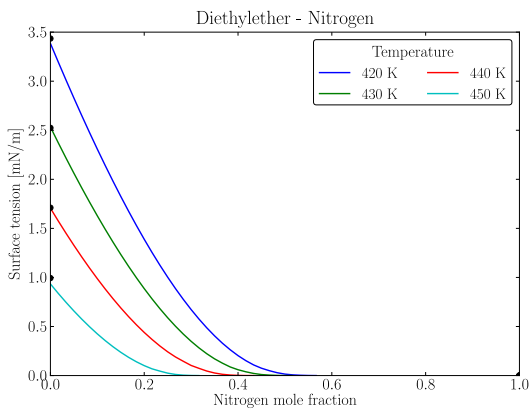


Figure 3: The surface tension of binary liquid mixtures predicted by the Parachor method.

Figure 4: Theoretical (CNT) nucleation rates (lines) vs. experimental nucleation rates (dots).

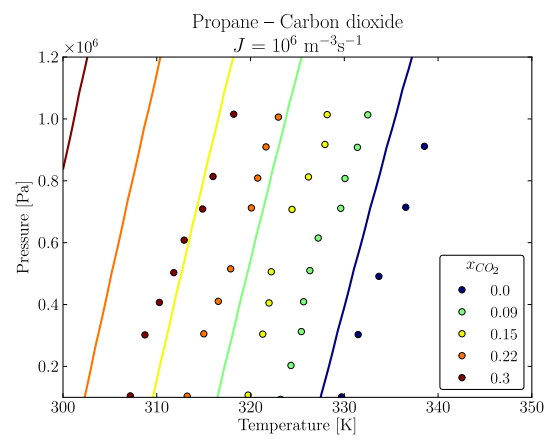
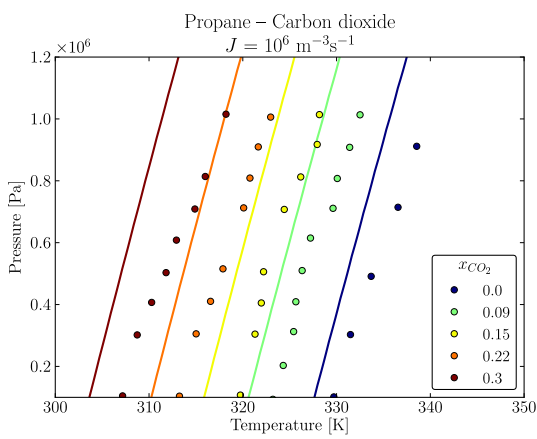
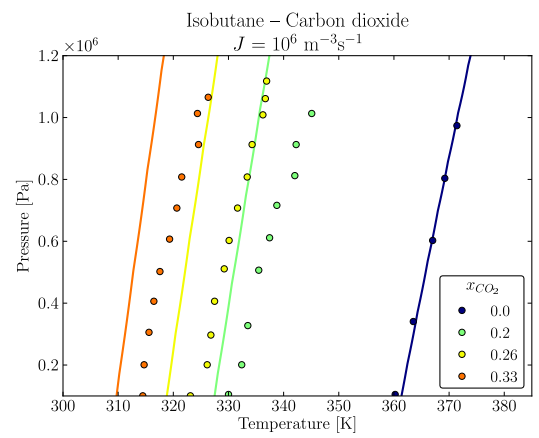
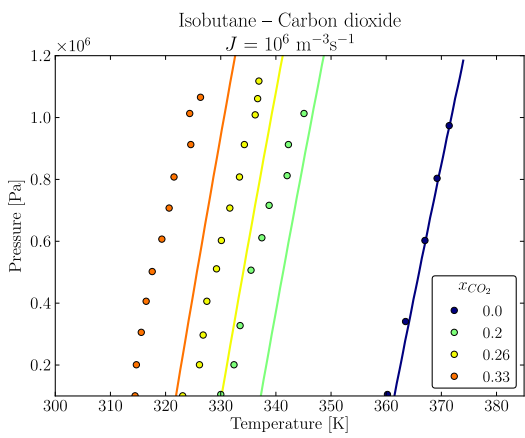
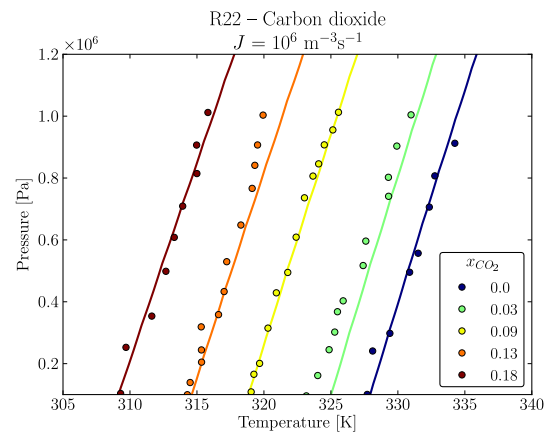
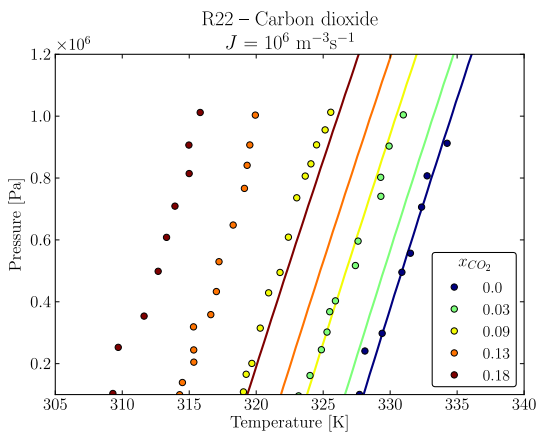
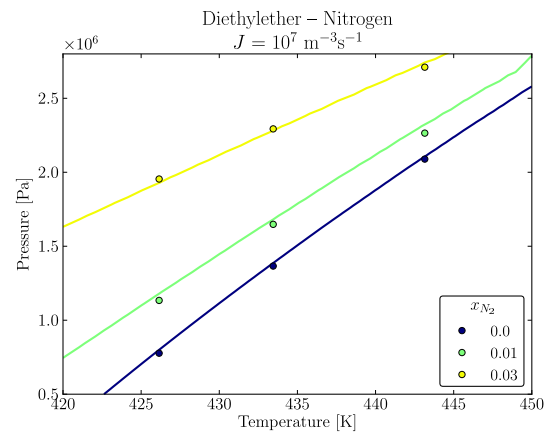
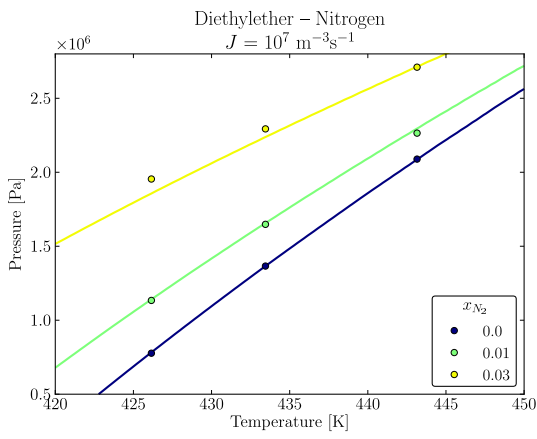


Figure 5: Theoretical (Forest-Ward formula (5) with pure solvent surface tension) nucleation rates (lines) vs. experimental nucleation rates (dots).

Figure 6: Theoretical (CNT with the simplified nucleation work formula (6)) nucleation rates (lines) vs. experimental nucleation rates (dots).

We can see that the simplified nucleation work surface in Fig. 7 (top) shows its maximum (critical) value quite close to the saddle point of the complete nucleation work of Fig. 1; i.e. at $r^* = 3.22$ nm and $W^* = 188.9$ zJ as opposed to $r^* = 2.69$ nm and $W^* = 272.7$ zJ. Such a difference in the critical nucleation work results into a difference of roughly 10^{40} $\text{m}^{-3}\text{s}^{-1}$ in the nucleation rate which is what we see as a difference between Figs. 4 and 6 in the case of isobutane – carbon dioxide nucleation rate.

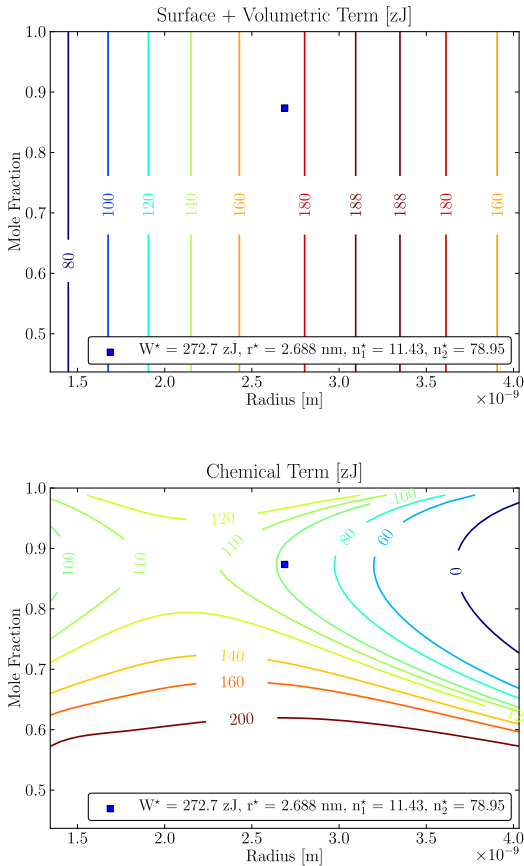


Figure 7: The partitioning of the nucleation work surface plotted in Fig. 1 into the surface/volume part $V(p - p_{sat}) + A\sigma$ and the chemical part $\sum_{i=1}^2 n_i \Delta\mu_i$.

The calculations with the simplified nucleation work formula (6) are less complex as only a maximum of a function of one variable (the bubble radius r) has to be found. Such calculations can be an option in cases where the nucleation parameters need to be calculated quickly, or where some thermophysical properties (saturation pressure and Henry constant) of the nucleating mixtures are not available. The calculations with the full form of the nucleation work (1) involve a more complex numerical estimation of the saddle point of a function of two variables (radius and concentration). On the other hand, they offer additional information about the composition of the nucleated bubble.

Let us proceed to the discussion of the deviations in the predictions of the nucleation rate in the case of propane – carbon dioxide mixture. Our results are surprisingly much worse than the nucleation rates presented in the work of Mori *et al.* calculated according to the Forest–Ward approach. The case of

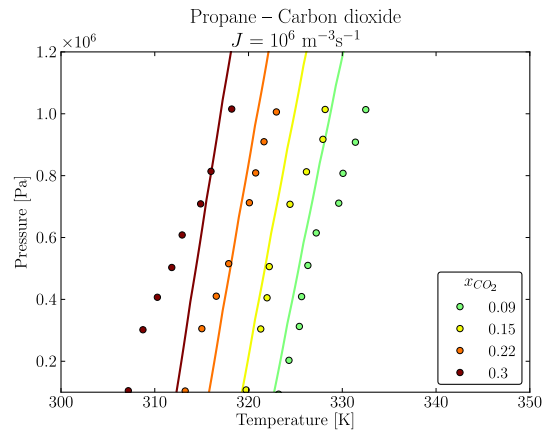


Figure 8: Theoretical (Mori [15]) nucleation rates vs. experimental nucleation rates in the propane – carbon dioxide mixture.

propane – carbon dioxide was the only one that was predicted theoretically in the work of Mori *et al.* In the other cases of R22 – carbon dioxide and isobutane – carbon dioxide only experimental data are presented due to the lack of thermophysical properties of those mixtures required for theoretical calculations. Although the details of the nucleation rate calculations are mentioned very briefly in the paper of Mori *et al.*, it can be deduced that they used the surface tension of pure propane in their calculation and also certain data for the Henry constant of carbon dioxide. We therefore used their two fits of the surface tension and the Henry constant in our model and calculated the nucleation rate; the results are plotted in Fig. 8. Surprisingly, the nucleation rates calculated with pure-propane surface tension are much closer to the experimental results of Mori *et al.*, than our calculations (Fig. 4) that use correct values of the surface tension. This strange result suggests that the experimental data of Mori *et al.* of the propane – carbon dioxide mixture should be reexamined.

CONCLUSION

In this work, the accuracy of the Classical Nucleation Theory predictions was investigated in the case of four cavitating binary mixtures, i.e. diethylether – nitrogen, propane – carbon dioxide, isobutane – carbon dioxide, and chlorodifluoromethane – carbon dioxide. The CNT was presented in a general multicomponent form and the resulting nucleation rates show very good agreement with experimental data. In comparison with previous theory[5] the fully multicomponent treatment shows higher accuracy. Also, an inconsistency in the nucleation-rate experimental data of the propane – carbon dioxide system[15] was identified.

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