

Supplementary Information for “Homogeneous nucleation of carbon dioxide in supersonic nozzles I: Experiments and Classical Theories”

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Surface tension: The Lielmezs-Herrick Equation

Lielmezs and Herrick¹ proposed a phenomenological scaling law for the surface tension of liquids using the critical point (c) and the boiling point (b) as reference points. The reduced surface tension is expressed as

$$\sigma^* = aT^{*b}, \quad (1)$$

where a and b are fitting parameters. The reduced coordinates are

$$T^* = \frac{T_c/T - 1}{T_c/T_b - 1}, \quad (2)$$

and

$$\sigma^* = \frac{\sigma/T}{\sigma_b/T_b}. \quad (3)$$

For CO₂, the corresponding values are $T_c = 304.2$ K, $T_b = 216.6$ K, and $\sigma_b = 16.9$ mN/m. The experimental surface tension data of liquid CO₂ by Muratov and Skripov² can be parameterized, yielding the following relation:

$$\sigma^* = 1.004 \times T^{*1.21}. \quad (4)$$

It has been shown that the relation by Lielmezs and Herrick performs relatively well for simple liquids, yielding smaller root-mean-square (rms) errors than other commonly used methods¹. In the case of CO₂, the rms deviation between the data and Eq. (4) is about 5% (both the critical and boiling points are omitted from the rms calculation). The relation by Quinn³ has an rms error of 8%.

References

1. J. Lielmezs and T. A. Herrick, *Thermochim. Acta*, 1989, **141**, 113.
2. G. N. Muratov and V. P. Skripov, *TVT*, 1982, **20**, 596.
3. E. L. Quinn, *J. Am. Chem. Soc.*, 1927, **49**, 2704.

Supplemental Figures and Tables

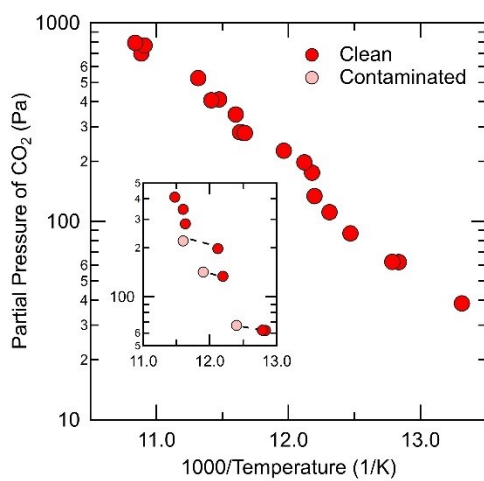


Figure S-1. Trace contaminants move the onset of condensation to higher temperatures and pressures and correspondingly lower supersaturations. Prior to establishing an adequate cleaning protocol, the onset of condensation occurred at temperatures and pressures up to ~ 3.7 K and 23 Pa higher than in the later, more controlled experiments. These changes decreased the maximum supersaturation reached by up to two orders of magnitude.

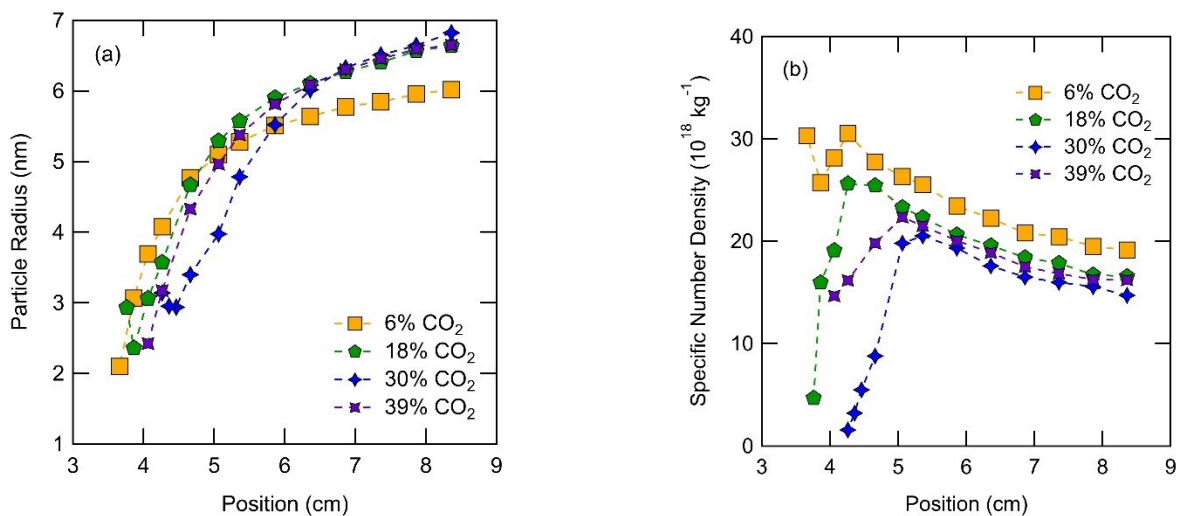


Figure S-2. (a) Position-resolved particle radii for 6, 18, 30, and 39 mol% CO_2 . (b) Position-resolved specific number density data for the same conditions. These data complement those shown in Figure 7(a) and 7(b) in the main text.

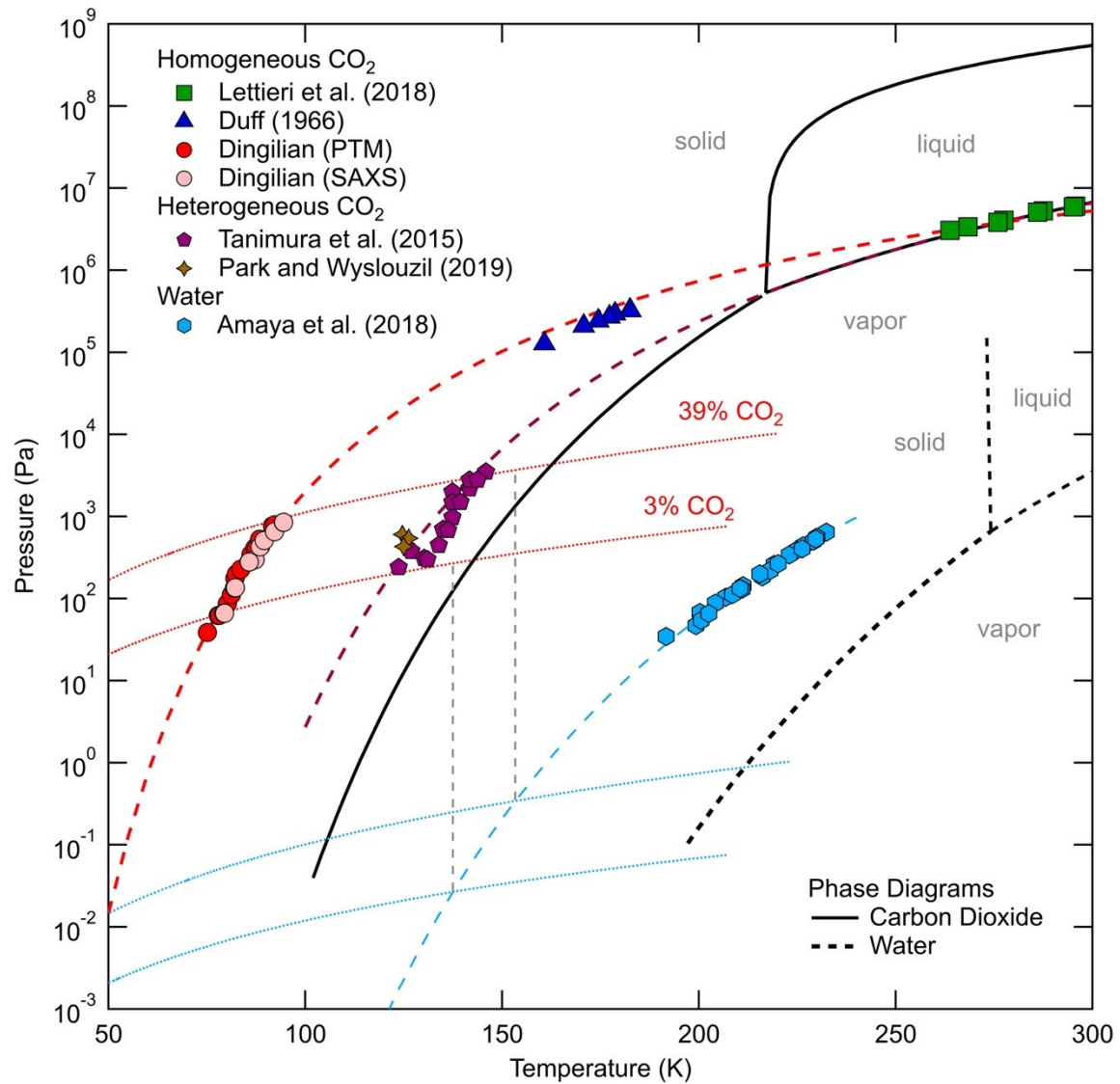


Figure S-3. A combined phase diagram for CO₂ and H₂O. For CO₂, both the homogeneous and heterogeneous nucleation data are included. The red dotted lines indicate the isentropic expansions expected for CO₂ concentrations of 39 mol% and 3 mol%. The red circles correspond to the conditions for J_{max} determined by pressure trace measurements (PTM), and the pink points are those consistent with the SAXS measurements. Both are clearly separated from the heterogeneous onset data. The blue dotted lines indicate the isentropic expansions of water for the two CO₂ conditions considered above, and assuming 10 ppm water in the bone dry CO₂. If contamination from water vapor were an issue in these experiments, water particles should have formed when the water isentropes crossed the blue dashed line that extrapolates the homogeneous nucleation limit for water (blue circles). If water particles had formed at these temperatures and CO₂ partial pressures, CO₂ should have condensed close to the heterogeneous nucleation line rather than close to the homogeneous nucleation line. The references are those given in Figs. 5(a) and 5(b) of the main text.

Table S-1. The non-isothermal factors used to correct the nucleation rates. The parameters b^2 and q are calculated via **Eq. (9)** and **(10)** in the main text, respectively, and the correction factor f is calculated via **Eq. (8)**. Application of this correction factor suggests that intrinsic nucleation rates are one to two orders of magnitude higher than the values obtained experimentally.

mol %	$p_{J_{\max}}$	$T_{J_{\max}}$	N_c/N	b^2	q	f
2.0	38	75.1	49.0	1.127-40	2.38E-20	0.17
3.0	61	77.8	32.3	8.06E-41	2.4E-20	0.12
3.0	63	78.2	32.3	8.15E-41	2.41E-20	0.12
4.0	87	80.2	24.0	6.42E-41	2.41E-20	0.10
4.5	110	80.5	21.2	5.75E-41	2.39E-20	0.10
5.0	110	81.2	19.0	5.26E-41	2.41E-20	0.083
6.0	130	82.0	15.7	4.47E-41	2.4E-20	0.072
8.00	176	82.1	11.5	3.36E-41	2.37E-20	0.056
9.00	198	82.5	10.1	3.01E-41	2.37E-20	0.051
10.0	227	83.6	9.0	2.78E-41	2.37E-20	0.047
12.0	281	86.0	7.3	2.45E-41	2.39E-20	0.041
12.0	278	85.7	7.3	2.43E-41	2.39E-20	0.041
15.0	345	86.2	5.7	1.97E-41	2.37E-20	0.034
18.0	411	87.2	4.6	1.68E-41	2.37E-20	0.029
18.0	408	87.6	4.6	1.70E-41	2.38E-20	0.029
21.0	448	88.2	3.8	1.47E-41	2.38E-20	0.025
24.0	528	88.4	3.2	1.29E-41	2.36E-20	0.026
27.0	572	89.6	2.7	1.17E-41	2.38E-20	0.020
31.2	701	91.9	2.2	1.07E-41	2.4E-20	0.018
33.0	695	90.8	2.0	9.84E-42	2.38E-20	0.017
36.0	757	91.4	1.8	9.13E-42	2.38E-20	0.016
38.9	770	91.7	1.6	8.49E-42	2.38E-20	0.015
39.0	782	91.9	1.6	8.51E-42	2.38E-20	0.015
39.3	793	92.3	1.5	8.49E-42	2.39E-20	0.015