The air pressure effect on CO_2 nucleation by molecular dynamics simulation

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Nucleation theory

Classical nucleation theory (CNT) was recently applied to the formation of a pure liquid phase from a supersaturated vapor containing an inert carrier gas, discussing the influence of carrier gas partial pressure [1].

The effective chemical potential difference $\Delta\mu_e = \Delta\mu + v'(P_s - p)$ yields the bulk contribution to the free energy of formation for a droplet [1], cf. Fig. 1. Therein, $\Delta\mu$ is the chemical potential supersaturation and P_s is the saturated vapor pressure of the nucleating component.

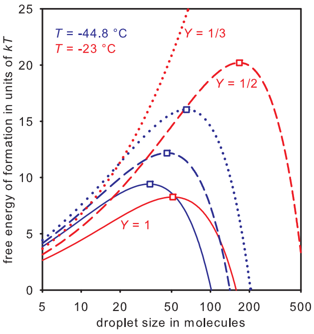

Fig. 1. Free energy of formation according to CNT for CO_2 droplets in supersaturated vapors at T = -44.8 °C with S = 3.42 (blue) and T = -23 °C with S = 2.72 (red) at CO_2 mole fractions of Y = 1 (solid lines), 1/2 (dashed lines), and 1/3 (dotted lines), reaching a maximum for the critical size (squares). The supersaturation S is given in terms of the CO_{20} density in the vapor phase.

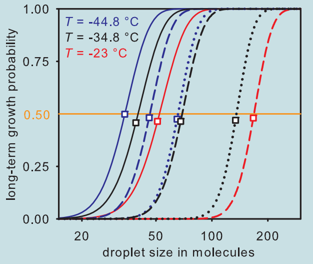

Fig. 2. Long-term growth probability over droplet size for CO_2 droplets in supersaturated vapors at T = -44.8 °C with S = 3.42 (blue), T = -34.8 °C with S = 3.08 (black), and T = -23 °C with S = 2.72 (red) at CO_2 mole fractions fractions of Y = 1 (solid lines), 1/2 (dashed lines), and 1/3 (dotted lines), calculated from the free energy of formation according to CNT. The supersaturation S is given in terms of the CO_2 density. The probability for the critical nucleus (squares) to reach macroscopic size (instead of evaporating completely) is slightly lower than 50 %.

Simulation method

MD simulation of nucleation, employing the Yasuoka-Matsumoto (YM) method [2], was conducted using the models of Vrabec *et al.* [3]. The long-term growth probability converges to unity above the critical size N^*, cf. Fig. 2. The droplet formation rate can be used to approximate J if only large droplets are taken into account [2], cf. Fig. 3.

VLE results from Grand Equilibrium simulation [4], cf. Tab. 1, confirm that air only accumulates to a limited extent in the liquid phase. It can therefore be treated as a carrier gas.

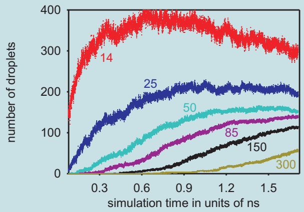

Fig. 3. Number of droplets containing more than M = 14, 25, 50, 85, 150, and 300 molecules over time from canonical ensemble MD simulation of pure CO_2 at T = -44.8 °C with S = 3.42 for a system of 300 000 molecules. According to the YM method, a linear fit of the droplet formation rate $J(M)$ during the nucleation stage of the condensation process is used to approximate the nucleation rate J.

T [°C]	$x(CO_2)$	p_s(MPa)	$y/x(N_2)$	$y/x(O_2)$	y/x(Ar)	ρ' [mol/l]	ρ'' [mol/l]	Δh^v [kJ/mol]
-90.3	0.969	2.53(8)	40(2)	24.5(9)	24.7(9)	29.24(1)	1.854(2)	17.092(9)
	0.941	3.9(1)	21.5(8)	13.9(5)	13.7(5)	29.13(1)	3.031(5)	16.27(1)
	0.910	6.0(2)	13.7(4)	9.1(3)	9.0(3)	29.01(2)	5.29(2)	15.12(1)
-40.3	0.941	4.38(5)	14.0(2)	10.8(1)	10.3(1)	24.94(3)	2.663(5)	13.30(1)
	0.910	5.30(4)	9.7(1)	7.72(8)	7.34(8)	24.47(2)	3.247(7)	12.64(1)
9.7	0.969	5.97(4)	5.6(1)	4.88(8)	4.72(7)	19.3(2)	3.90(1)	8.55(5)
	0.941	6.98(3)	4.31(5)	3.82(5)	3.67(4)	18.55(9)	4.63(2)	7.79(4)

Tab. 1. Bulk VLE data for the quaternary system $CO_2 + N_2 + O_2$ + Ar from Grand Equilibrium simulation [4] using the molecular models of Vrabec *et al.* [3]. The saturated liquid composition was specified to be equimolar in nitrogen, oxygen, and argon. The dew line mole fractions y_i are given as multiples of the bubble line mole fractions x_i of the respective components. Values in parentheses indicate the uncertainty in terms of the last given digit.

Pure carbon dioxide

Using the massively parallel MD program *mardyn*, condensation processes were simulated in systems with 300 000 CO_2 molecules, covering the regimes of relaxation, nucleation, and droplet growth, cf. Fig. 4.

Droplet formation rates obtained for pure CO_2 according to the YM method are shown in Fig. 5. In general, a good quantitative agreement between theory and simulation was found. In the spinodal limit, the nucleation rate was determined to be about 10^{27} $cm^{-3}s^{-1}$ over the whole temperature range.

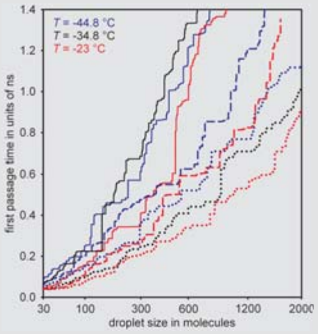

Fig. 4. First passage time, i.e. the temporal delay until the first droplet containing N molecules is formed, over droplet size N at T = -44.8 °C (blue) with S = 3.42 (solid line), 3.72 (dashed line), and 4.02 (dotted line), at T = -34.8 °C (black) with S = 2.80 (solid line) and 3.36 (dotted line), as well as T = -23 °C (red) with S = 2.34 (solid line), 2.53 (dashed line), and 2.72 (dotted line) for pure CO_2 from canonical ensemble MD simulation. The horizontal axis scales with the cubic root of N, so that the slope becomes linear for the growth dominated regime.

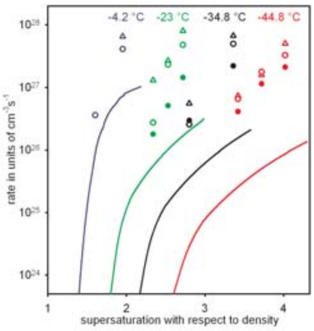

Fig. 5. Nucleation rate according to CNT (solid lines) and droplet formation rate according to the YM method for M = 50 (triangles), 75 (circles), and 250 molecules (bullets) from canonical ensemble MD simulation over supersaturation for pure CO_2 at T = -44.8, -34.8, -23, and -4.2 °C.

However, while the simulation results do not exhibit a temperature dependence for the spinodal value of J, CNT predicts it to increase with temperature, cf. Fig. 5. This may be due to a discrepancy concerning the free energy barrier ΔG^* of the nucleation process.

By definition, ΔG^* converges to zero in the spinodal limit, since spinodal decomposition is not an activated process. This qualitative transition is not reproduced by CNT, where a non-zero magnitude of ΔG^* is obtained for arbitrary supersaturations. Since the temperature occurs in the denominator of the Boltzmann distribution, the deviation due to that theoretical artifact decreases with T.

Air pressure effect

Results for homogeneous vapor to liquid nucleation in the quaternary system $CO_2 + N_2 + O_2$ + Ar are shown in Fig. 6. The mole fractions were specified to match the composition of the earth atmosphere, and 300 000 (Y = 1/2) or 600 000 (Y = 1/3) carrier gas molecules were present during MD simulation, wherein Y denotes the CO_2 mole fraction. A significant depression of J was found, in particular at high temperatures where no nucleation could be detected for Y = 1/3.

Qualitatively, the MD simulation results confirm CNT. For a quantitative comparison with theoretical predictions, the carrier gas contribution to p was approximated by an ideal term, i.e. $p = P + (1 - Y)\rho kT$, where P is the supersaturated vapor pressure of pure CO_2 at the same partial density.

It should be noted that a substantial deviation from ideality is present for the pressure at high supersaturations, cf. Fig. 7. This non-ideality alone, however, is insufficient to fully account for the deviations between CNT and MD simulation for the air pressure effect on the nucleation rate.

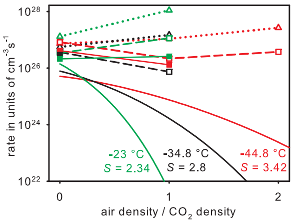

Fig. 6. Nucleation rate according to CNT (solid lines) and droplet formation rate according to the YM method for M = 50 (triangles), 100 (empty squares), and 150 molecules (filled squares) from canonical ensemble MD simulation at T = -44.8 °C with S = 3.42, T = -34.8 °C with S = 2.8, and T = -23 °C with S = 2.34 in dependence of $Y^{-1} - 1$, i.e. the ratio between air and CO_2 molecules in the system. In the latter two cases, no nucleation was detected during the entire MD simulation run for $Y^{-1} - 1$ = 1 and 2, implying $J < 10^{25}$ $cm^{-3}s^{-1}$.

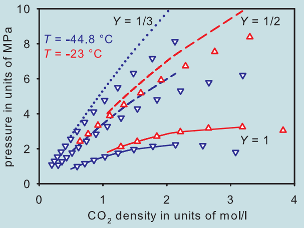

Fig. 7. Pressure over CO_2 density from canonical ensemble MD simulation of small homogeneous systems at T = -44.8 °C and -23°C in comparison with the metastable section of the vapor pressure isotherm for pure CO_2 (solid lines), correlated to the simulation results, increased by an ideal carrier gas contribution for carbon dioxide molar fractions Y = 1/2 (dashed lines) and 1/3 (dotted line).

References

[1] J. Wedekind, A.-P. Hyvärinen, D. Brus, and D. Reguera, *Physical Review Letters* **101**: 125703 (2008).
[2] K. Yasuoka and M. Matsumoto, *The Journal of Chemical Physics* **109**: 8451 (1998).
[3] J. Vrabec, J. Stoll, and H. Hasse, *Journal of Physical Chemistry B* **105**: 12126 (2001).
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