Homogeneous nucleation of carbon dioxide by molecular simulation

Martin Horsch, Kai Langenbach, Katrin Stöbener, Stephan Werth, Zengyong Lin, Thorsten Windmann, Jadran Vrabec, Hans Hasse

Laboratory of Engineering Thermodynamics, University of Kaiserslautern
Thermodynamics and Energy Technology, University of Paderborn

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Molecular modelling of carbon dioxide

Comparison of literature models

Merker et al. (2010), JCP 132: 234512.

Multicriteria optimization requires characterizing a whole class of models.
Molecular modelling of carbon dioxide

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Pareto set for 2CLJQ models

Multicriteria optimization requires massively-parallel molecular modelling.
Massively-parallel MD on hermit (Stuttgart)

http://www.ls1-mardyn.de/

large systems “1”: molecular dynamics

CO₂ (T = 280 K and ρ = 17.2 mol/l)

100 000 000 interaction sites, 110 592 cores
Massively-parallel MD: Cavitation

Scale-up to the entire *hermit* cluster for canonical simulation of cavitation in carbon dioxide.

Evaluation of local density at 180 x 180 x 180 grid points:

Liquid phase detected for more than 5 neighbours within a radius of 6.9 Å around the grid point.

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100 000 000 interaction sites, 110 592 cores
Cavitation in a subsaturated liquid

Yasuoka-Matsumoto method: Count nuclei exceeding a threshold size \( \ell \).

\[
N = 2.5 \times 10^7, \quad V = 2.41 \times 10^{-21} \, m^3, \quad T = 280 \, K
\]

Three consecutive regimes:
- relaxation (equilibration)
- homogeneous cavitation
- growth and aggregation
Cavitation in a subsaturated liquid

Yasuoka-Matsumoto method: Count nuclei exceeding a threshold size $\ell$.

$N = 2.5 \times 10^7$, $V = 2.41 \times 10^{-21}$ m$^3$, $T = 280$ K

Classical nucleation theory predicts critical cavity sizes from 10 to 30 nm$^3$. 
Cavitation rates from simulation and CNT

Cavities with a volume greater than 250 nm$^3$ are certainly supercritical.

For cavitation at high temperatures, CNT is a good approximation.
Nucleation in supersaturated vapours

Cluster criterion:
Stillinger type, single neighbour within radius $1.5 \sigma + L/4$, i.e. 5.1 Å.

Critical size predicted by CNT in region of interest:
40 to 60 molecules.
Nucleation in supersaturated vapours

Cluster criterion:
Stillinger type, single neighbour within radius $1.5 \sigma + L/4$, i.e. $5.1 \text{ Å}$. 

CO$_2$  269 K  250.2 K  238.4 K  228.4 K

Cluster criterion:

- $\ell = 50$ molecules
- $\ell = 75$ molecules
- $\ell = 250$ molecules

2CLJQ
The carrier gas effect on nucleation

Scenario:
- Vapour contains \( k \) components
- Liquid phase approximately pure
- \( k - 1 \) components: Carrier gas

Carrier gas effect (Wedekind et al.):
- Thermalization → \( J \) increases
- Greater pressure → \( J \) decreases

\[
W(Y_0) = \frac{b_{PE}^2(Y_0) \left[ b_{PE}^2(Y_0 = 1) + q_{PE}^2(Y_0 = 1) \right]}{\left[ b_{PE}^2(Y_0) + q_{PE}^2(Y_0) \right] b_{PE}^2(Y_0 = 1)} \exp \left( \frac{\Delta G_{PE}^*(Y_0 = 1) - \Delta G_{PE}^*(Y_0)}{kT} \right)
\]

The air pressure effect on nucleation

Quaternary system

$\text{CO}_2$, $\text{N}_2$ and $\text{O}_2$ (2CLJQ)

$\text{Ar}$ (LJ)

Air components with relative mole fractions as in air.

rate in units of cm$^{-3}$s$^{-1}$

$-23^\circ\text{C}$ $S = 2.34$

$-34.8^\circ\text{C}$ $S = 2.8$

$-44.8^\circ\text{C}$ $S = 3.42$

$\ell = 50$

$\ell = 100$

$\ell = 150$
The air pressure effect on nucleation

Quaternary system

\( \text{CO}_2, \text{N}_2 \text{ and } \text{O}_2 \) (2CLJQ)

\( \text{Ar (LJ)} \)

Air components with relative mole fractions as in air.

-23 °C  \( S = 2.34 \)

-34.8 °C  \( S = 2.8 \)

-44.8 °C  \( S = 3.42 \)

rate in units of \( \text{cm}^{-3} \text{s}^{-1} \)

\( 10^{22} \)

\( 10^{24} \)

\( 10^{26} \)

\( 10^{28} \)

air density / \( \text{CO}_2 \) density

\( \ell = 50 \)

\( \ell = 100 \)

\( \ell = 150 \)
Is a carrier gas only present in the vapour?

Light boiling compounds (i.e. “carrier gases”) often adsorb at the interface:

For very small droplets, a bulk-like region (with little air) is absent.

The interfacial region contains great amounts of air due to *interfacial enrichment*.

Droplet growth and decay is dominated by heat and mass transfer through the interface.

*Interfacial enrichment* probably influences nucleation in fluid mixtures.
Adsorption and surface tension

Gibbs adsorption equation: \( dy = -\sum \Gamma_i \, d\mu_i - \zeta \, dT \).

Even small liquid mole fractions of a carrier gas can reduce \( \gamma \) significantly.
Conclusion

With optimized and validated molecular models, e.g. from multicriteria optimization, quantitatively reliable predictions can be made.

Massively parallel MD simulation of large systems makes activated processes like homogeneous nucleation directly accessible. In this way, over 100 000 cores of a supercomputer can be used efficiently.

For pure carbon dioxide, homogeneous nucleation of bubbles in a metastable liquid and of droplets in a metastable vapour is well described by CNT, without the need for a curvature correction.

The influence of a carrier gas cannot be reduced to its presence in the vapour phase, due to the possibility of interfacial enrichment.