Homogeneous nucleation of carbon dioxide by molecular simulation

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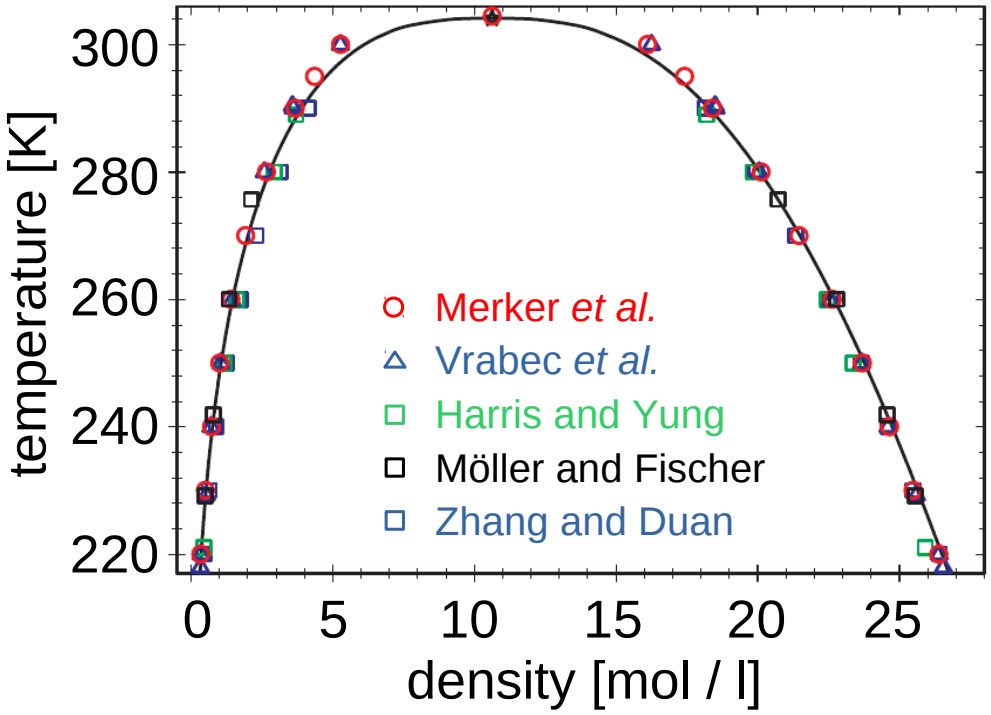
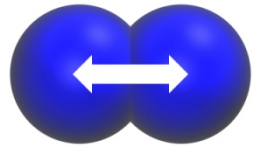
Molecular modelling of carbon dioxide

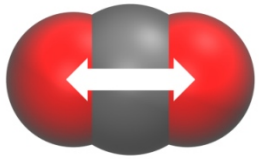
Comparison of literature models

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





CO_2 (Vrabec *et al.*)



CO_2 (Merker *et al.*)

Multicriteria optimization requires characterizing a whole class of models.

Molecular modelling of carbon dioxide

Comparison of literature models

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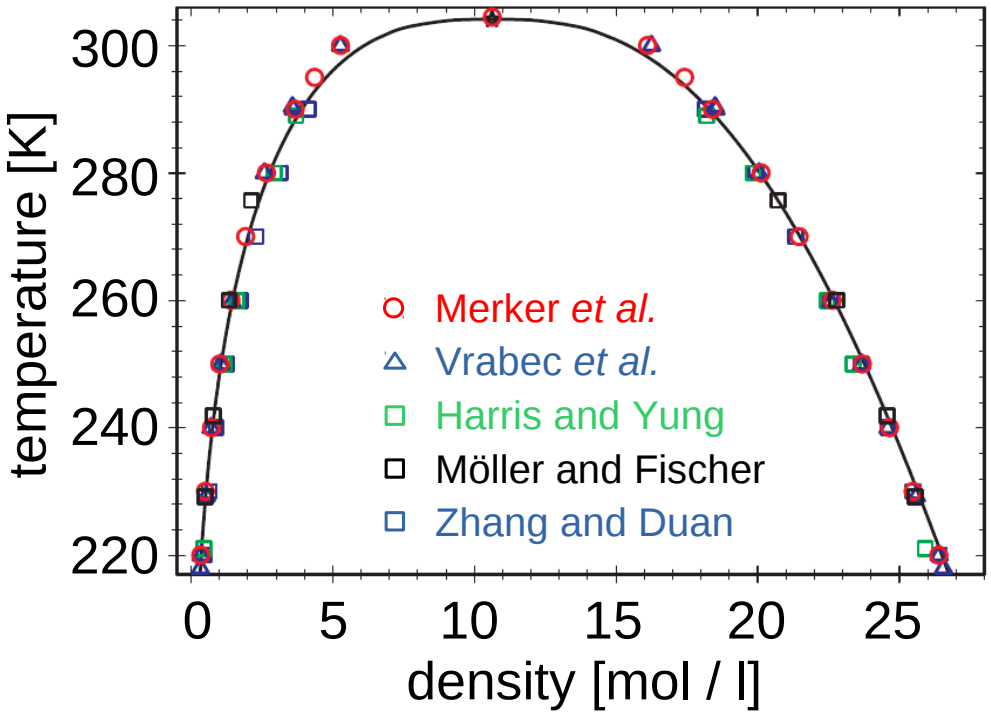
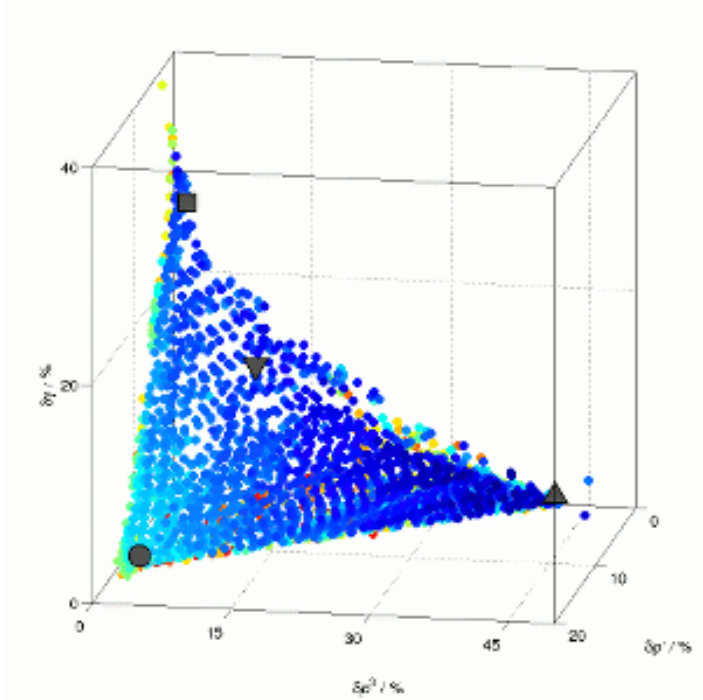


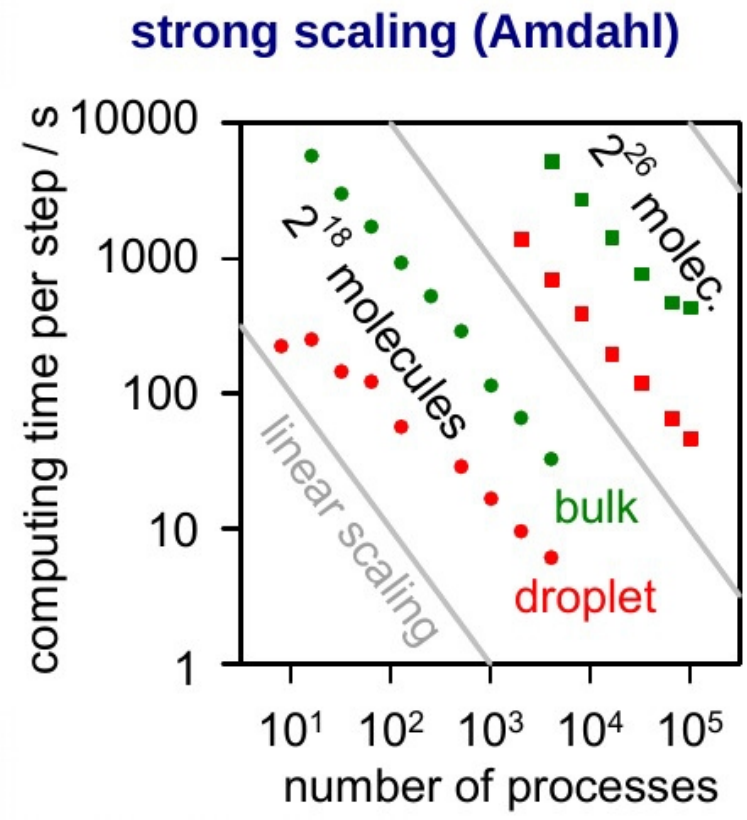
Pareto set for 2CLJQ models

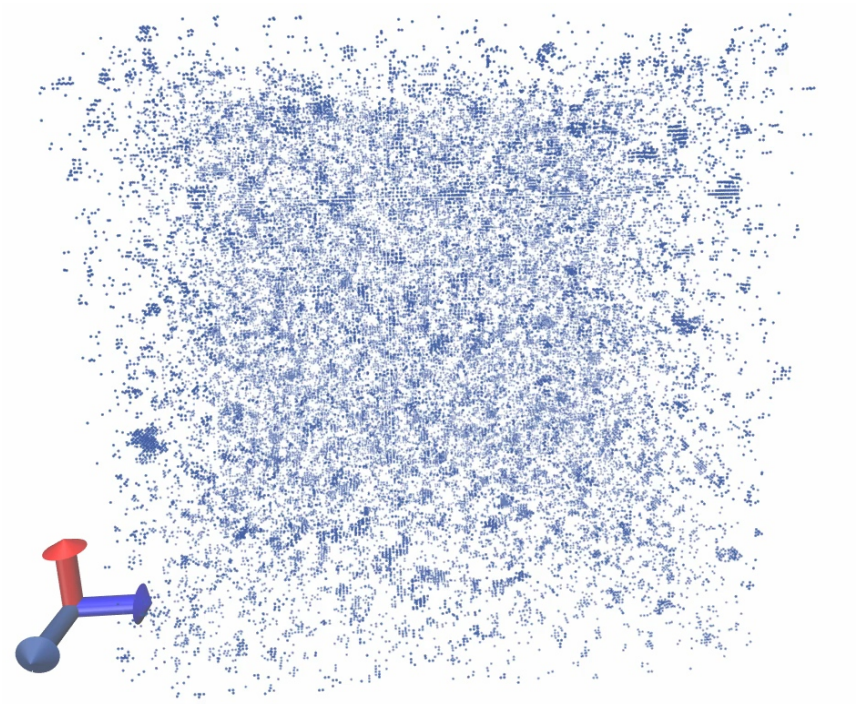


2CLJQ model by Vrabec *et al.*

Multicriteria optimization requires massively-parallel molecular modelling.

Massively-parallel MD on *hermit* (Stuttgart)





CO_2 (T = 280 K and ρ = 17.2 mol/l)

100 000 000 interaction sites, 110 592 cores

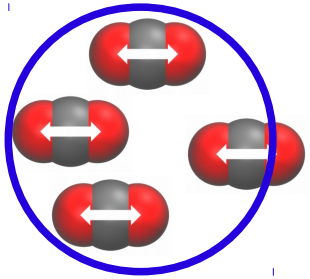
http://www.ls1-mardyn.de/

large systems “1”: molecular dynamics

Massively-parallel MD: Cavitation

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

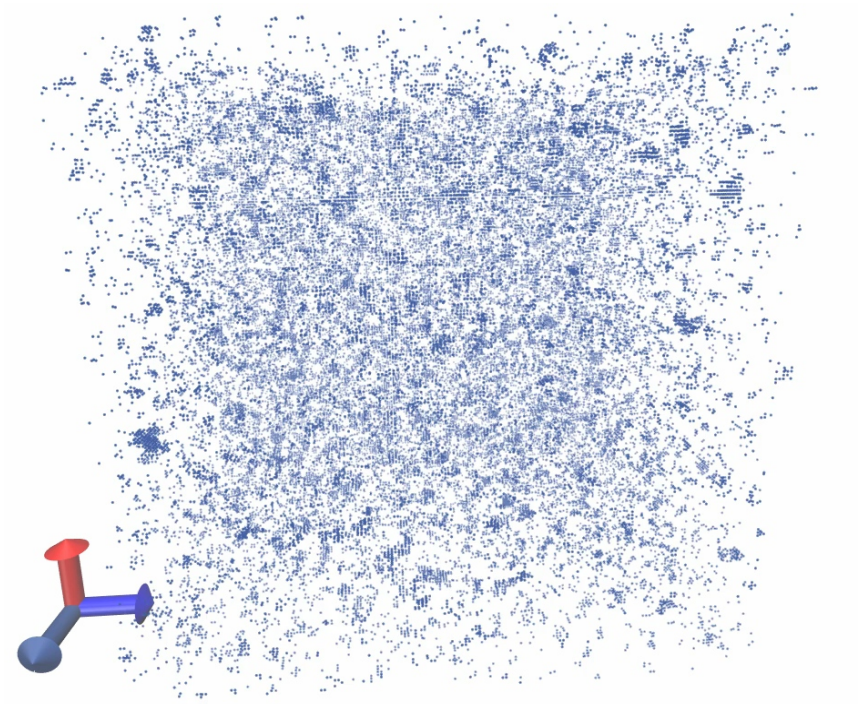
Evaluation of local density at 180 x 180 x 180 grid points:



≤ 5 ?

(6 mol/l)

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



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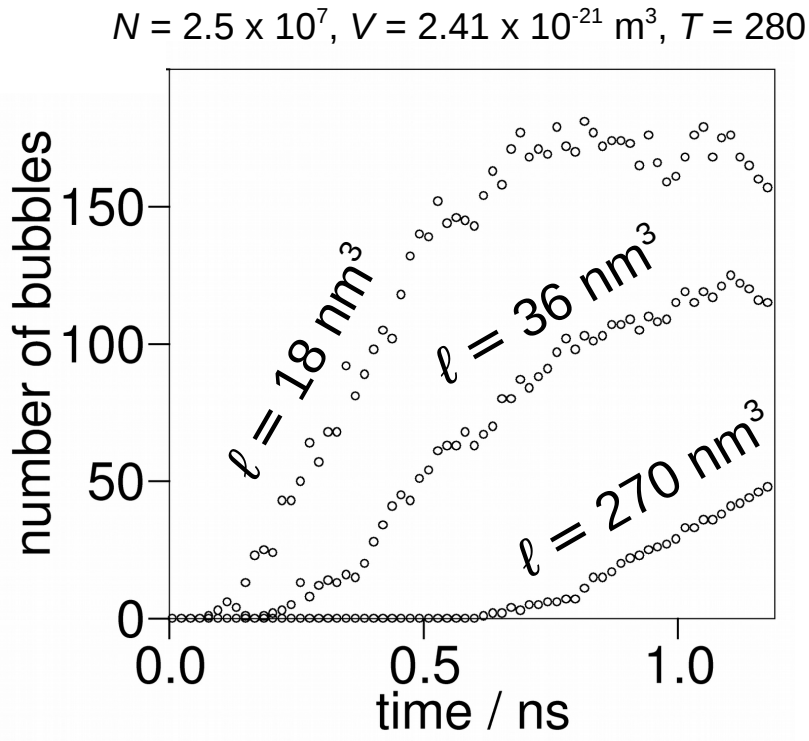
Cavitation in a subsaturated liquid

Yasuoka-Matsumoto method: Count nuclei exceeding a threshold size ℓ.

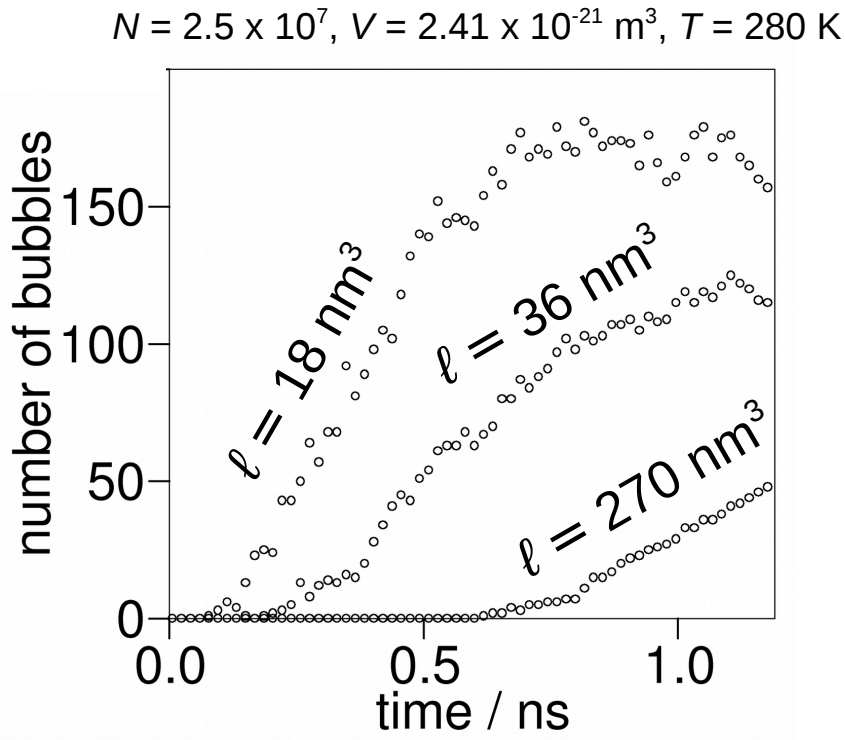


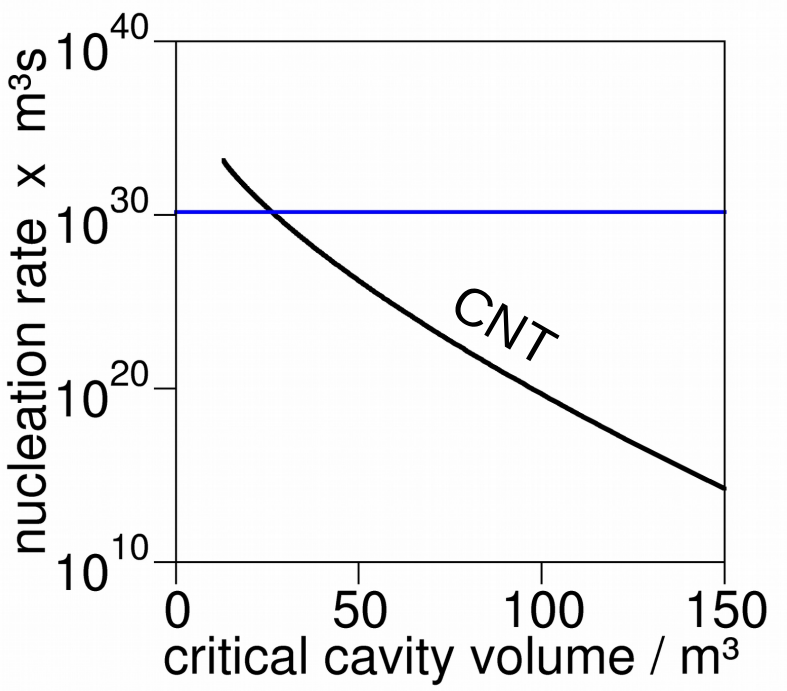
Three consecutive regimes:

- relaxation (equilibration)
- homogeneous cavitation
- growth and aggregation

Cavitation in a subsaturated liquid

Yasuoka-Matsumoto method: Count nuclei exceeding a threshold size ℓ.

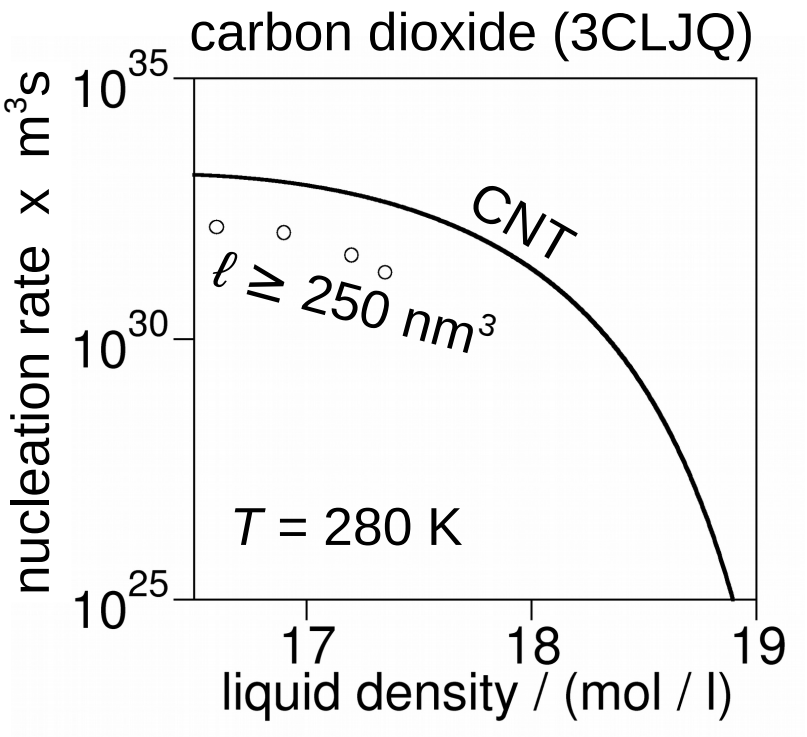


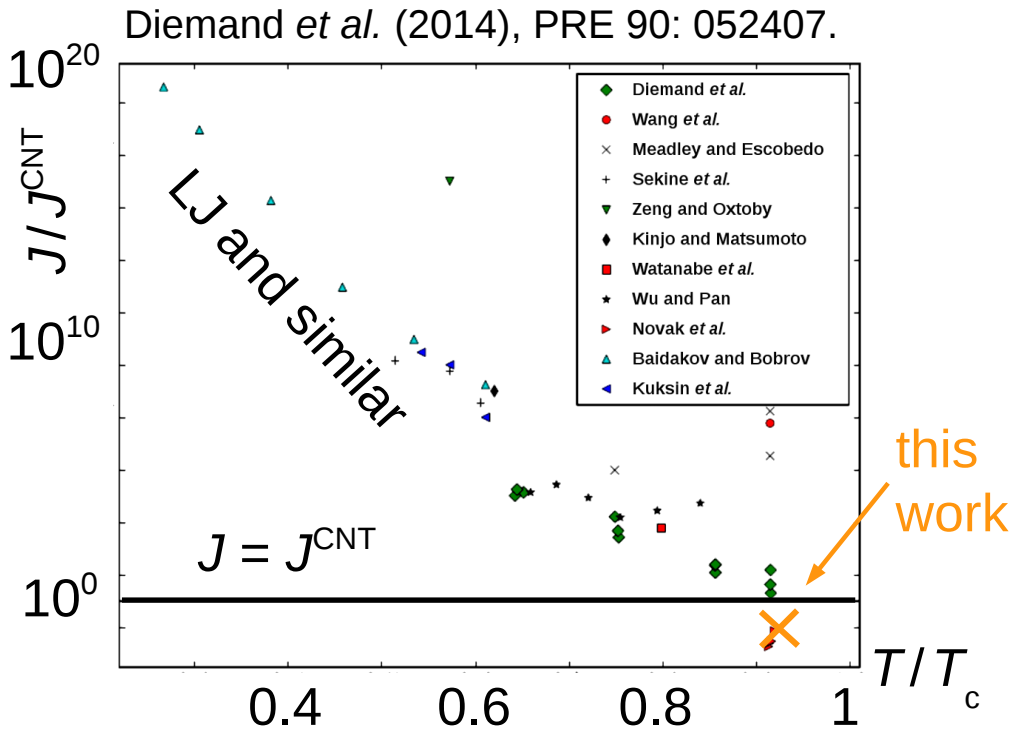


Classical nucleation theory predicts critical cavity sizes from 10 to 30 nm^3.

Cavitation rates from simulation and CNT

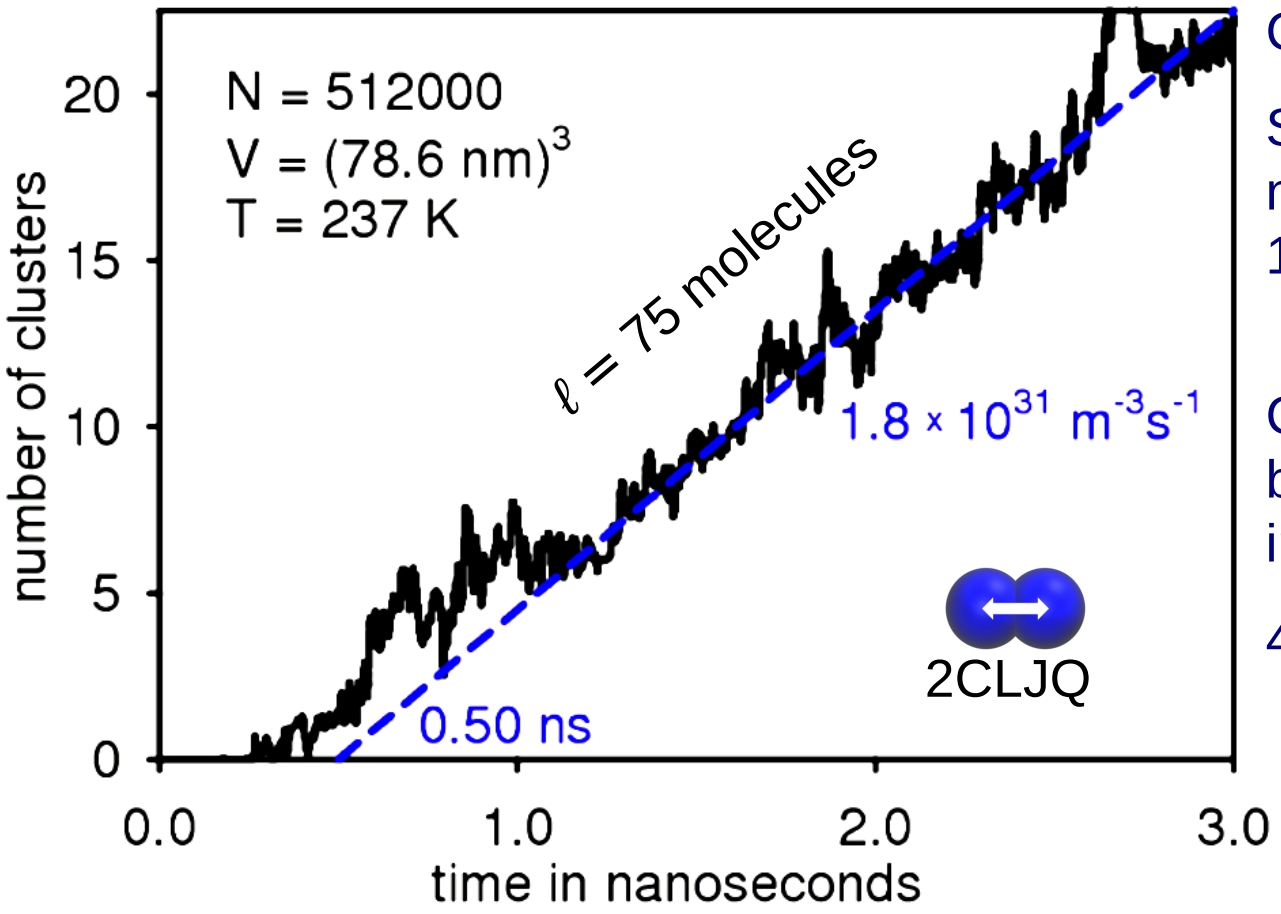
Cavities with a volume greater than 250 nm^3 are certainly supercritical.





For cavitation at high temperatures, CNT is a good approximation.

Nucleation in supersaturated vapours



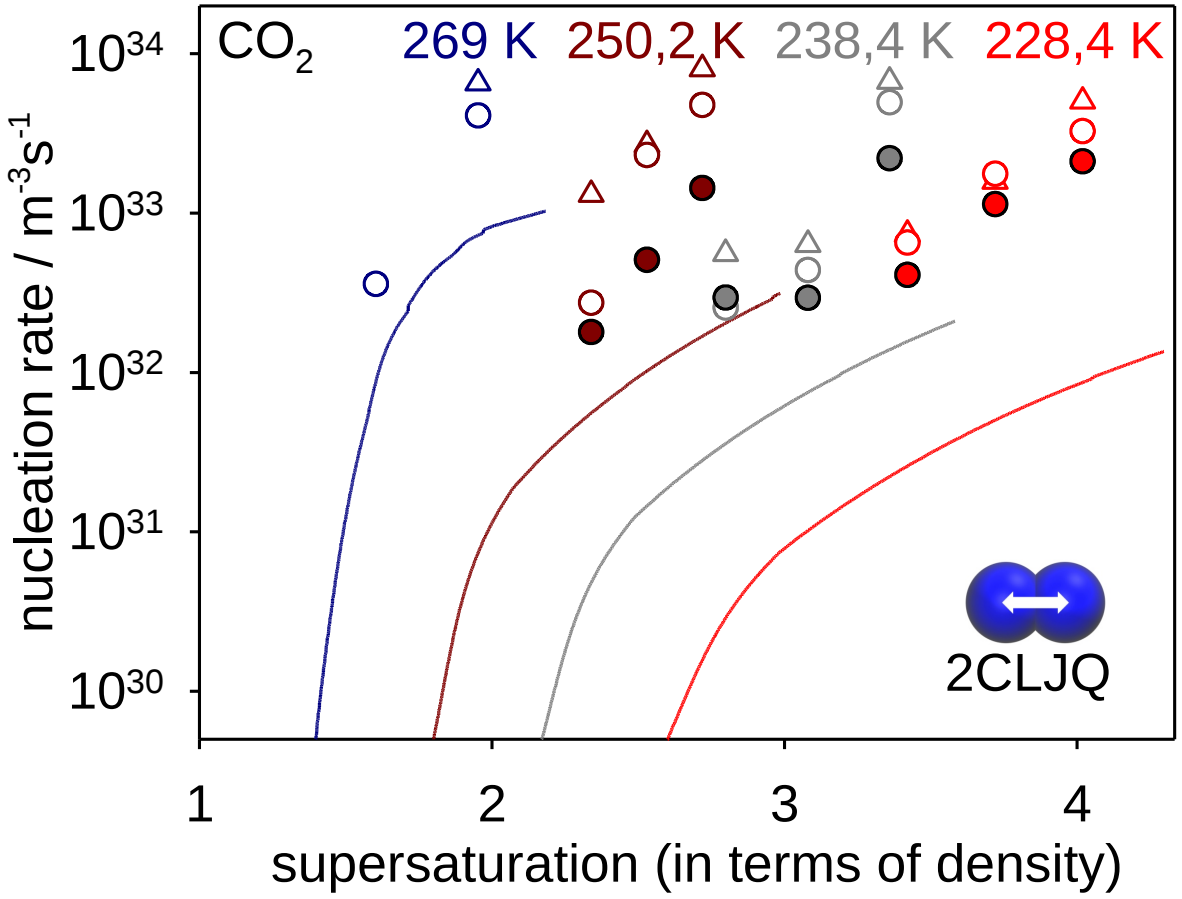
Cluster criterion:

Stillinger type, single neighbour within radius 1.5 σ + 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 Å.

— CNT (nonisothermal)

△ ℓ = 50 molecules
○ ℓ = 75 molecules
● ℓ = 250 molecules

The carrier gas effect on nucleation

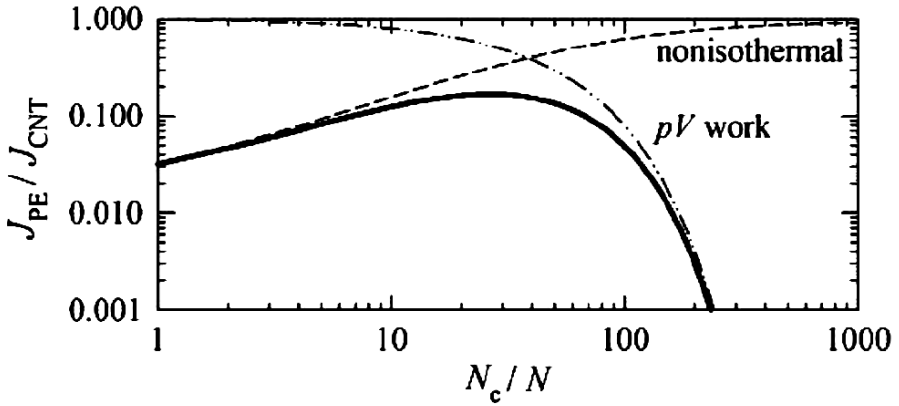
Scenario:

- Vapour contains *k* components
- Liquid phase approximately pure
- *k* – 1 components: Carrier gas

Carrier gas effect (Wedekind *et al.*):

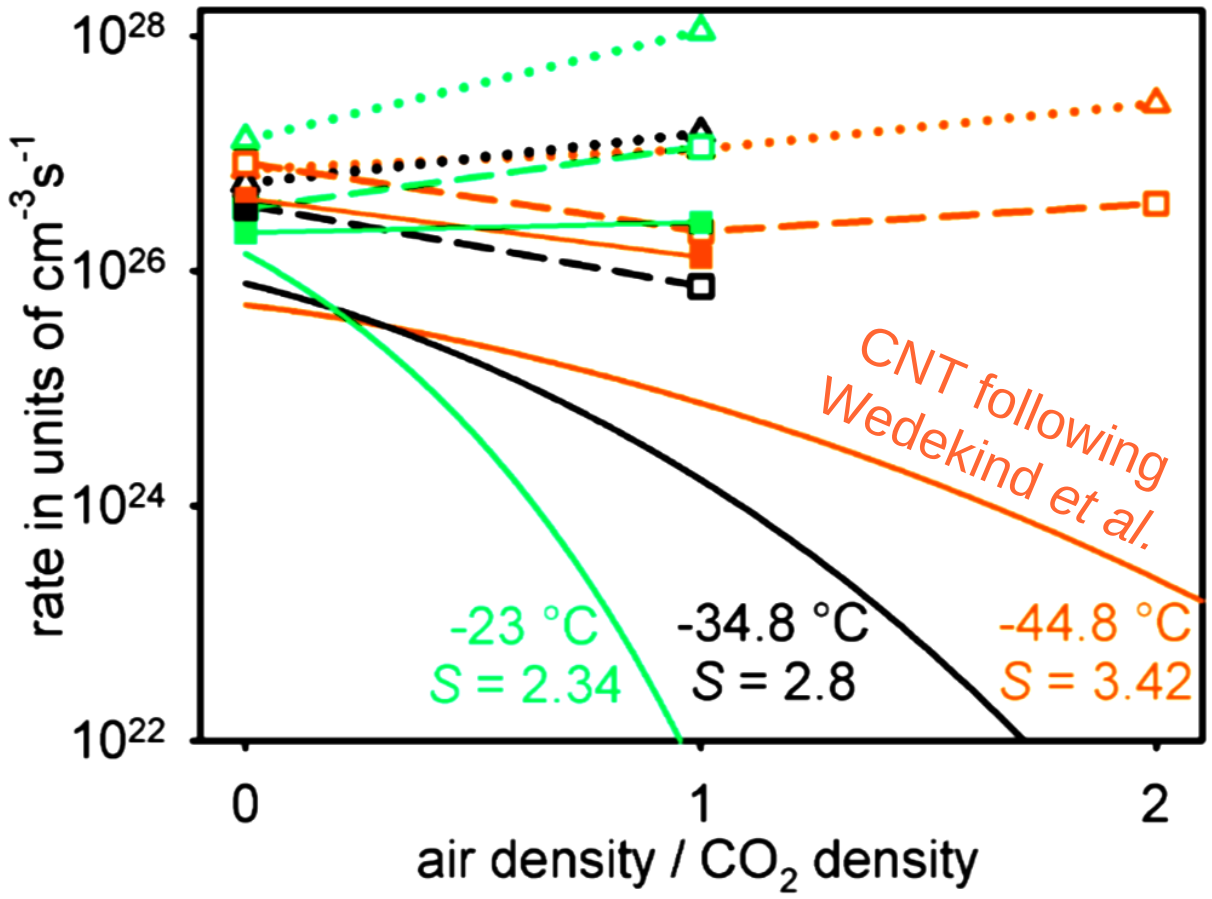
- Thermalization → *J* increases
- Greater pressure → *J* decreases

PRL **101,** 125703 (2008) Wedekind *et al.*



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

The air pressure effect on nucleation



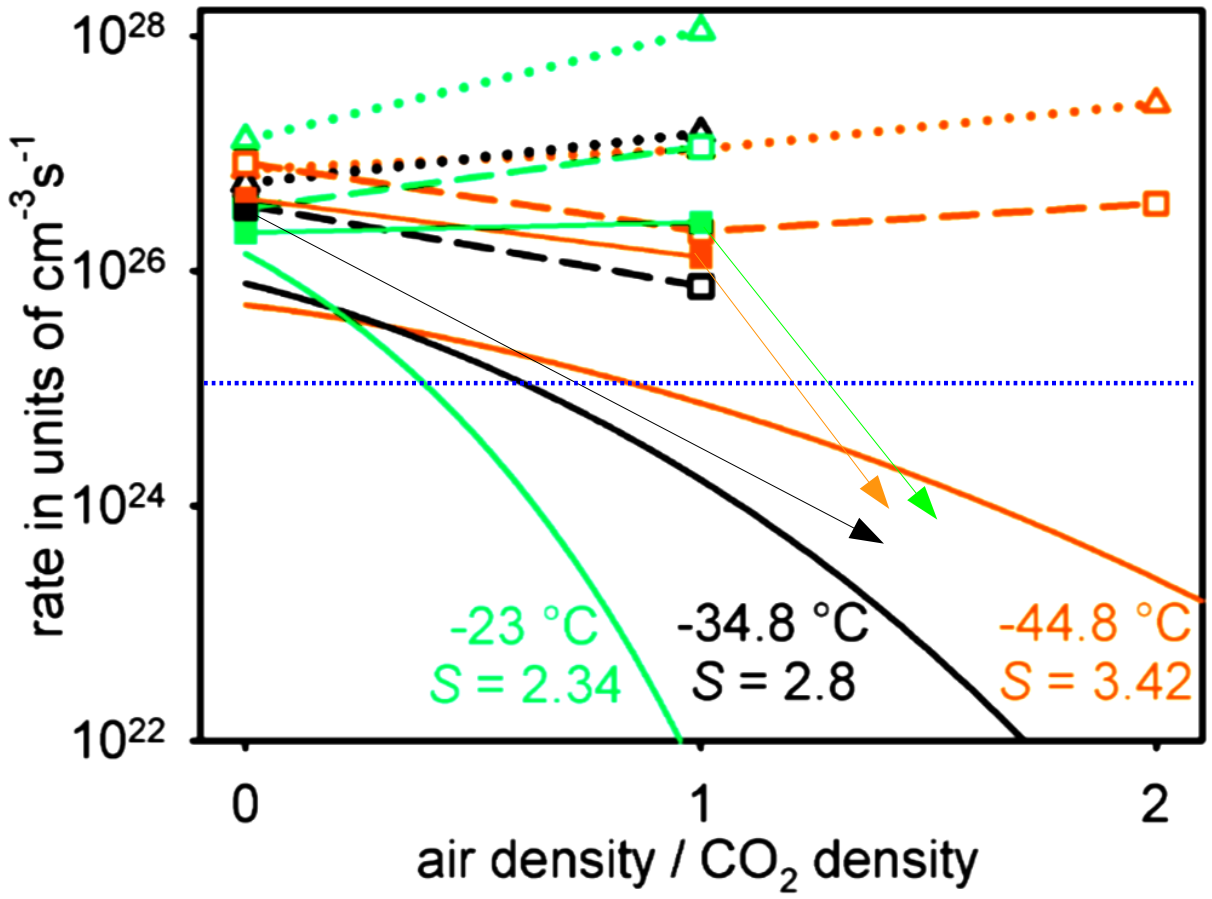
Quaternary system

CO_2, N_2 and O_2 (2CLJQ)
Ar (LJ)

Air components with relative mole fractions as in air.

△	ℓ = 50
□	ℓ = 100
■	ℓ = 150

The air pressure effect on nucleation



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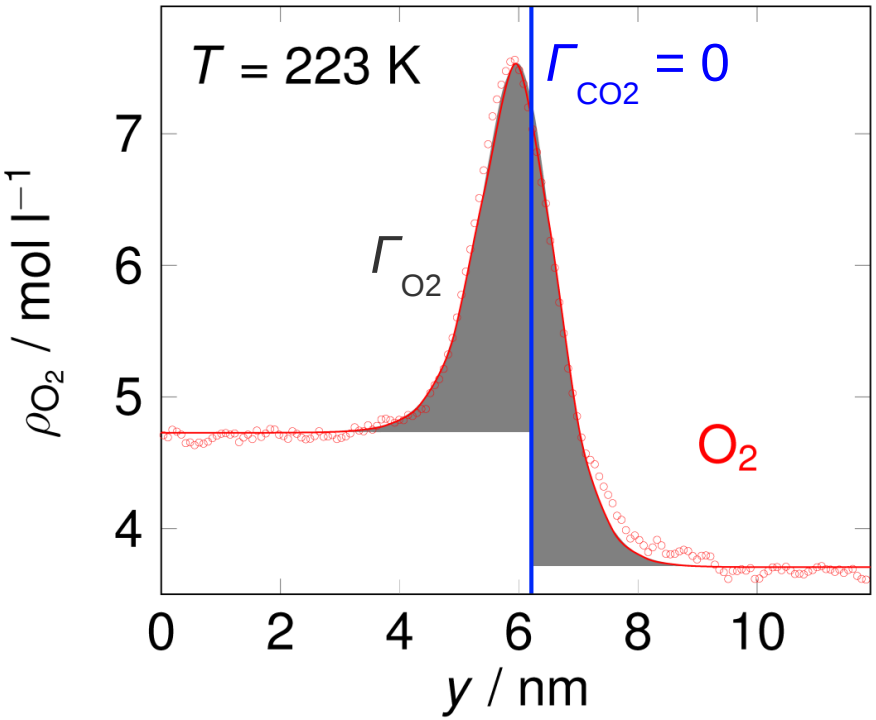
Is a carrier gas only present in the vapour?

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.

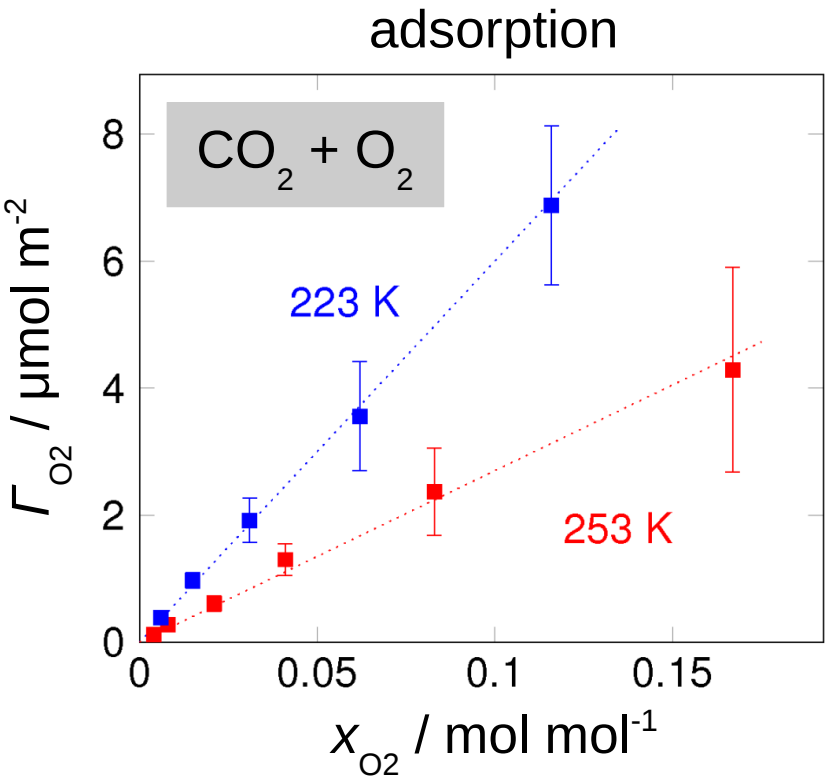
The interfacial region contains great amounts of air due to *inter-facial enrichment*.

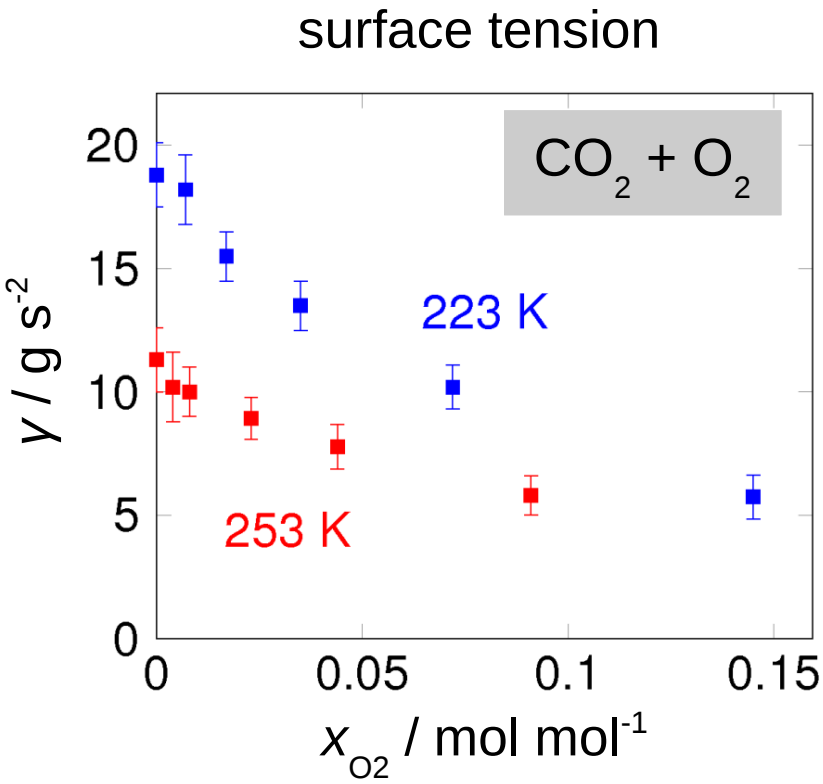
Droplet growth and decay is domi-nated by heat and mass transfer through the interface.

Interfacial enrichment probably influences nucleation in fluid mixtures.

Adsorption and surface tension

Gibbs adsorption equation: $dy = -\Sigma\, \Gamma_i\, d\mu_i - \zeta\, dT$.





Even small liquid mole fractions of a carrier gas can reduce *y* 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**.