Condensation Kinetics of N_2 at Cryogenic conditions from atomistic simulations

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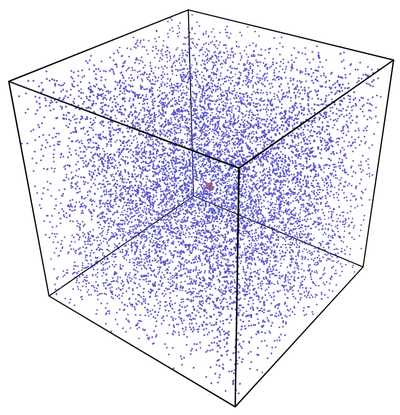
Motivation

Accurate prediction of condensation rates is critical for cryogenic liquefaction, thermal management, and safety in cryogenic systems. Traditional models derived by the kinetic theory use oversimplified assumptions, such as hard-sphere molecules, and neglect intermolecular forces, leading to large errors in the predicted condensation rates.

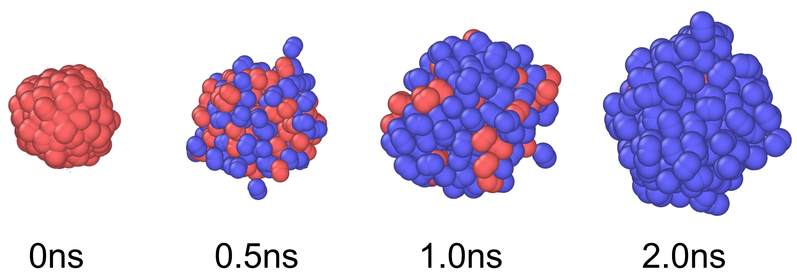
In this study, molecular dynamics (MD) simulations are used to explore N_2 condensation kinetics and derive rates at 30–80 K and droplet radii 0.8–6 nm. The *ab initio* obtained rates are compared to the kinetic theory, revealing sources of error in such classical theories. The proposed MD-derived rated can be directly incorporated into computational fluid dynamics simulations for improved design applications.

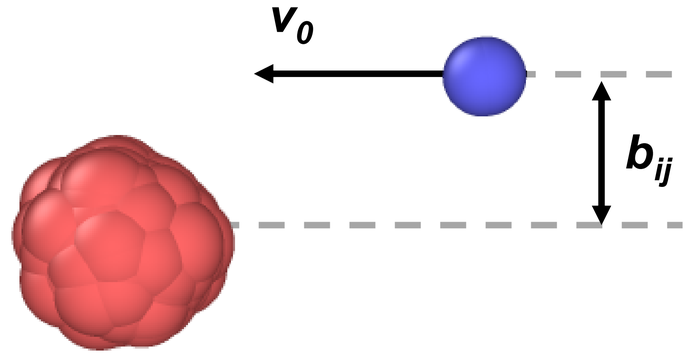
Methods



Surface condensation:

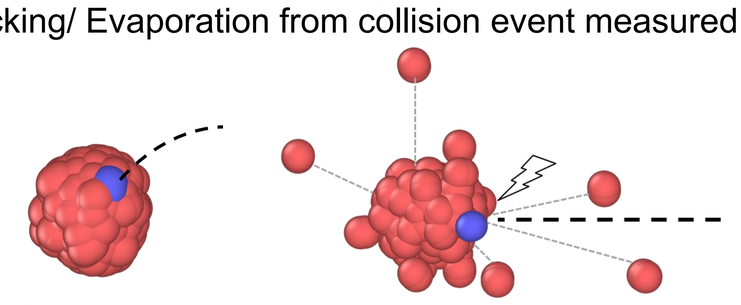
Droplet grows due to condensing vapour
Temporal evolution of the particle size is recorded





Single molecule-droplet collision:

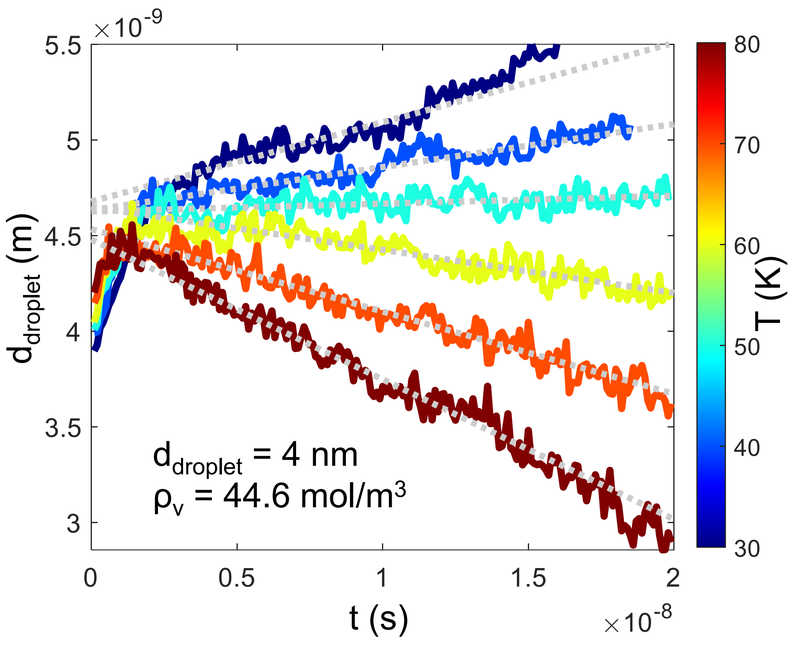
Droplet collides with **single vapour molecule**
Sticking/ Evaporation from collision event measured



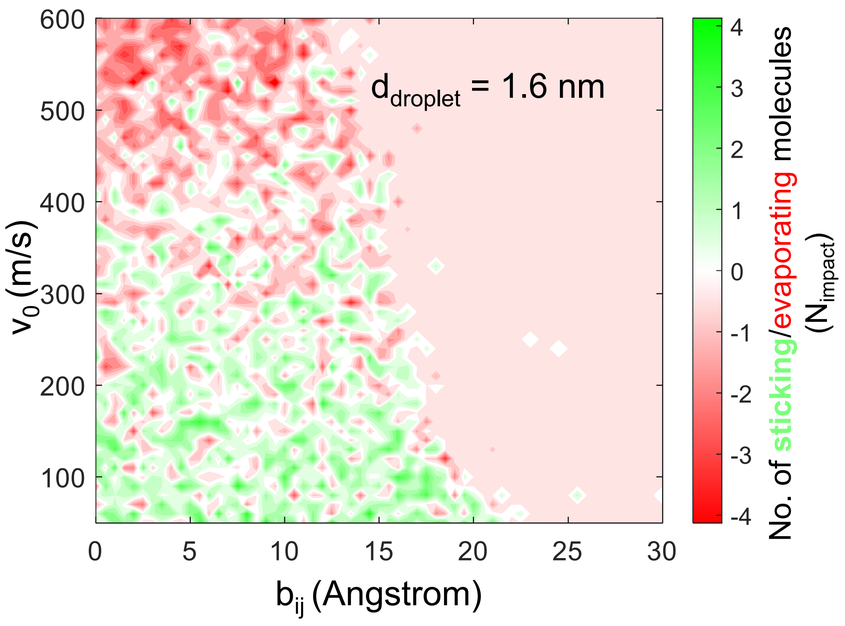
Sticking
Vapour attached

Vaporisation
Liquid Disassociated

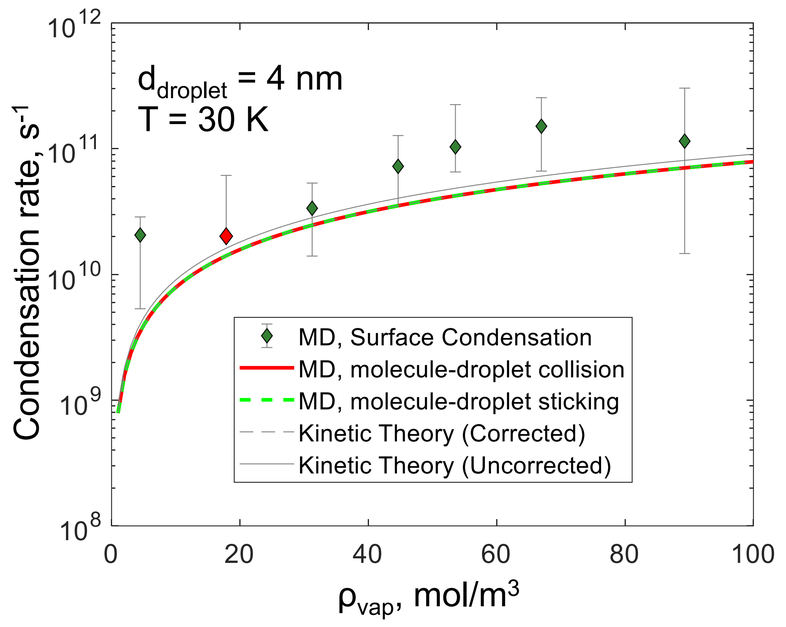
Results



Temporal evolution of droplet size during condensation. Steady-state condensation is denoted by broken lines.



Heatmap of droplet size change due to monomer collided with various v_0 and b_{ij}.



Condensation rate as a function of vapour density by MD and by kinetic theory.

Discussion

Condensation rates from two different MD simulation methods match well with each other, confirming the reliability of the proposed methodology. Monomers stick to the droplet due to attractive forces and direct collisions, while evaporation also occurs due to high impact velocity and thermal energy fluctuations. The flux of condensing particles, $n_{cond,MD}$, is obtained by the flux of particles sticking upon collision, $n_{z,imp}$, minus the flux of particles evaporating due to thermal fluctuations, $n_{evap,th}$:

$$n_{cond,MD} = n_{z,imp} - n_{evap,th}$$

where:

$$n_{z,impact} = 2\pi \int_0^\infty dv_0 \int_0^\infty v_0 f(v_0)\, b_{ij} N_{impact}(b, v_0) db\, \rho_{vap}$$

$\boldsymbol{b_{ij}}$: interparticle distance
$\boldsymbol{v_0}$: impact velocity
ρ_{vap}: vapour density
f: Maxwell-Boltzmann distribution probability density
N_{impact}: sticking/evaporation due to particle impact

Conclusions

- Highly accurate size- and temperature-dependent condensation rates are derived for the first time for N_2 nanodroplets with diameter of 0.8–6 nm at cryogenic temperatures (30–80 K).
- Two independent MD methods yield consistent condensation rates, validating the results.
- **Sticking** is driven by attractive forces and low impact velocity, while **evaporation** is induced by high-impact velocity collisions and thermal fluctuations.
- A new theoretical framework is developed that properly includes velocity- and impact-dependent sticking, collision-induced evaporation, and thermal evaporation.
- The new model provides reliable condensation rates across wide temperature and size ranges, offering an *ab initio* basis for improved design and safety assessments of cryogenic systems.

References

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