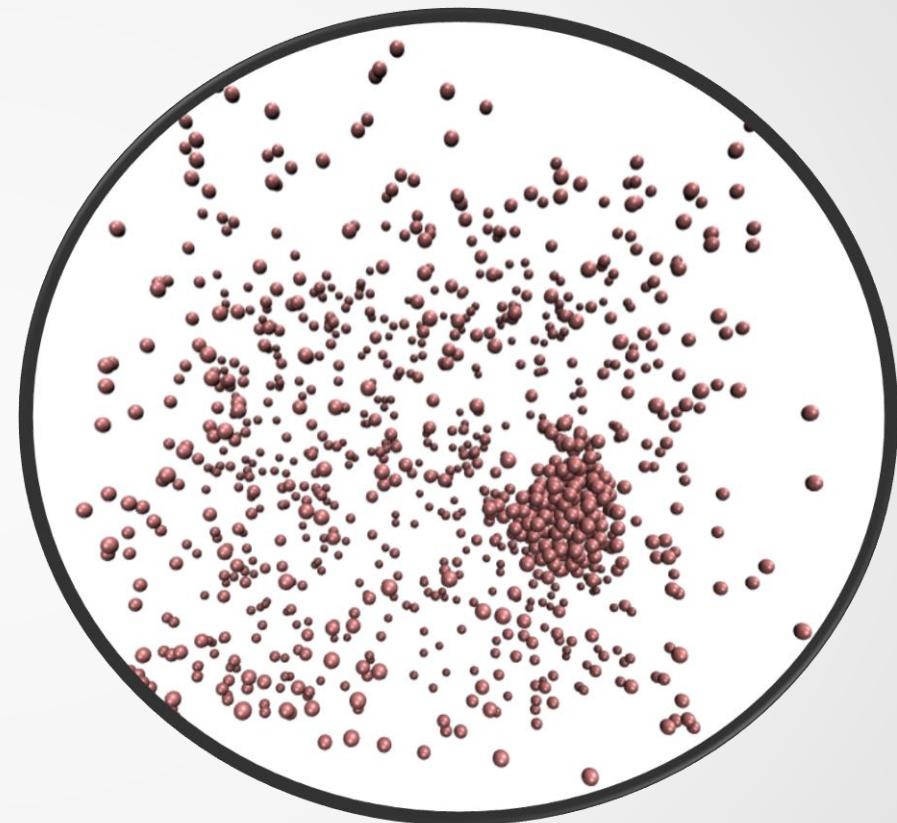


Molecular dynamics for homogeneous nucleation of H₂O and CO₂ in carrier gases

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The difference in composition between Natural Gas and LNG

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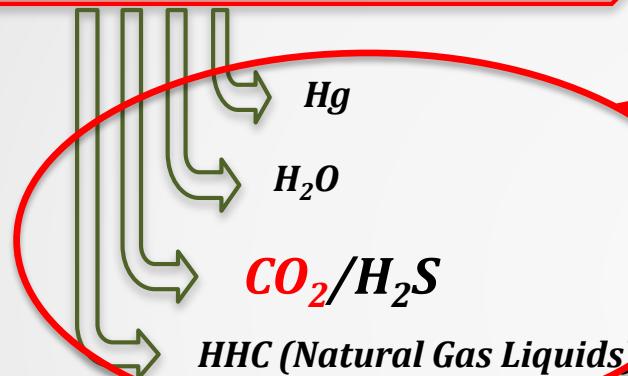
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Natural Gas Components		Fossil NG	Biogas	Before liquefaction	LNG
Methane	CH ₄	70 – 90%	45 – 60%	≈ 100%	81.57 - 99.73%
Ethane	C ₂ H ₆	0 – 20%			0.08 - 13.38
Propane	C ₃ H ₈	0 – 20%		1-10ppm	0.01 - 3.67
Butane	C ₄ H ₁₀	0 – 20%			
Carbon Dioxide	CO ₂	0 – 8%	4-60%	50-100ppm	
Oxygen	O ₂	0 – 0.2%	0.1 – 1.0%		
Nitrogen	N ₂	0 – 1%	2.0 – 5.0%		0.2 – 1.0%
Hydrogen Sulfide	H ₂ S	0 – 5%	0.0 – 1.0%	4ppm	
Mercury	Hg			0.01µg/Nm ³	
Water	H ₂ O			0.1-0.5ppm	
Ammonia	CH ₃		100ppm		
Various		H ₂ , Ar, He, Ne, Xe	H ₂ , CO, NH ₃		traces

Extensive pre-treatment required

Focus on Natural Gas pre-treatment

NG pre-treatment



NG components suitable for Cryogenic Separation
> Focus on CO₂ removal <

Research question

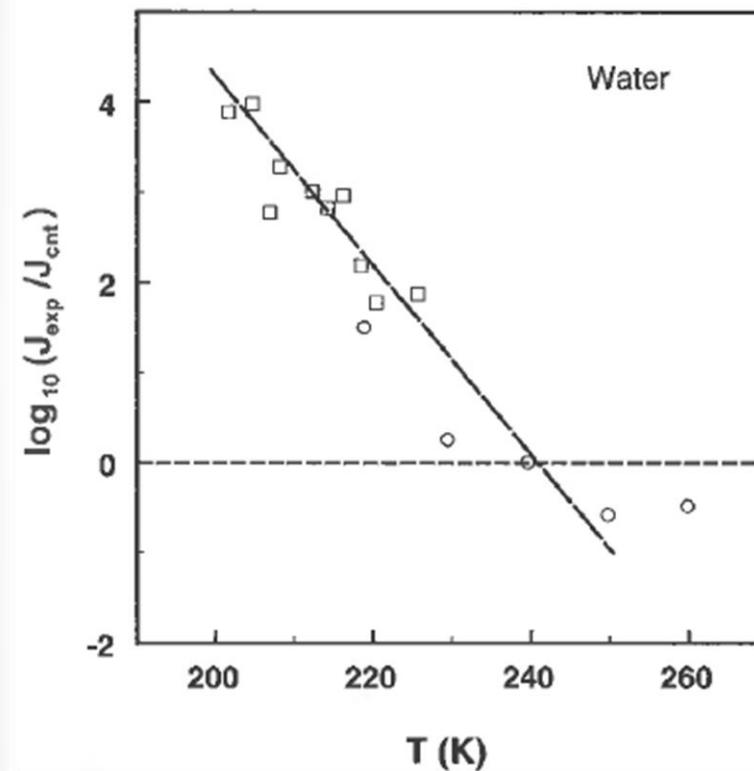
Condensate or crystallize all phase-changing components in the Natural Gas feed stream in a controlled and from the feed separable way?

Why we do MD simulations?



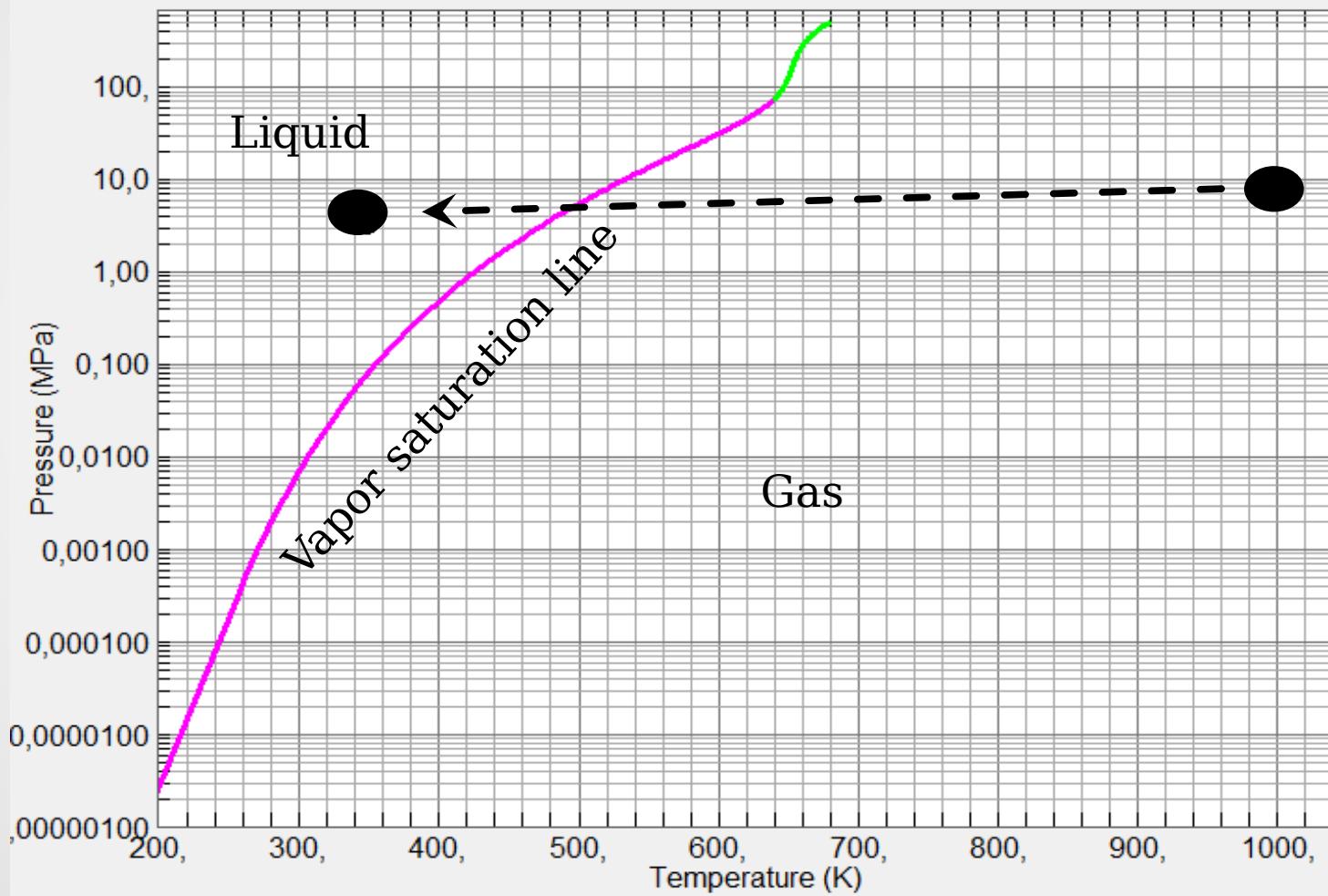
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Analyze properties of time dependent concentration of contaminants and determine the exact required physical process conditions.



Source: V. I. Kalikmanov, Nucleation Theory, Lecture Notes in Physics, Volume 860, 2013

Applied method on H₂O-Ar mixture



Simulation validation model used in molecular dynamics

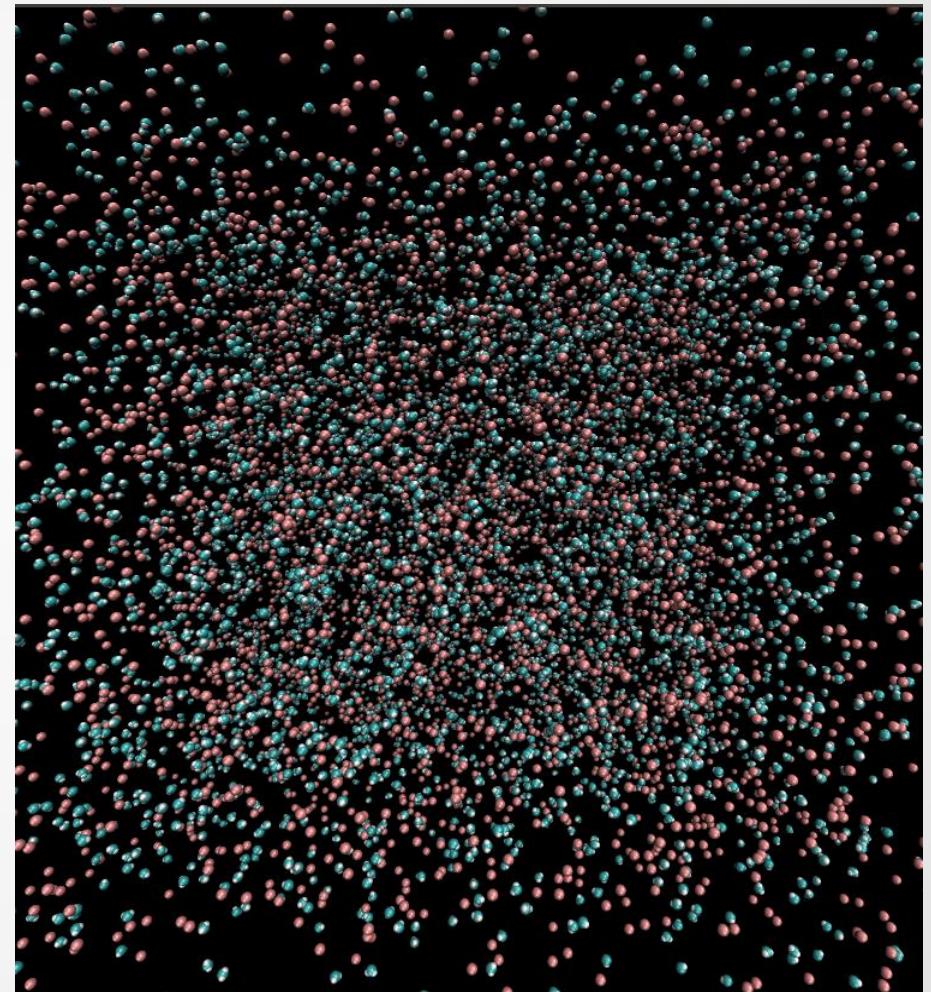


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Description of setup

- **5000 Water** molecules + **5000 Argon** atoms
- Box size of $28 \times 28 \times 28 [nm^3]$
for $\rho = 21.84 \text{ kg/m}^3$
- $T_{init} = 1000 [K]$
- $$U_{inter}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

Note: $\frac{\epsilon_{Ar}}{k_B} = 119.8 [K]$, $\sigma_{Ar} = 0.3405 [nm]$, $\frac{\epsilon_o}{k_B} = 78 [K]$, $\sigma_o = 3.154 [nm]$, $q_h = 0.520 [e]$.

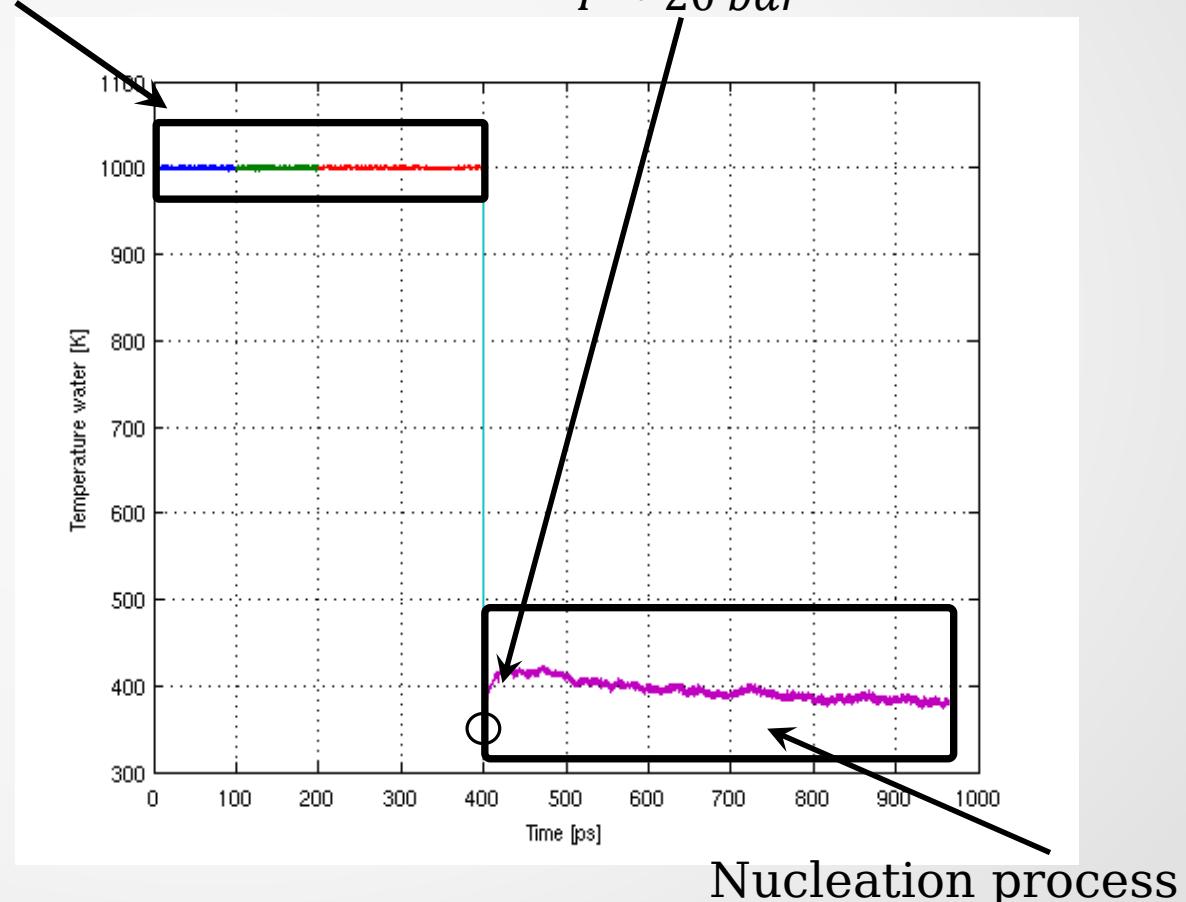


Applied method

$T \sim 1000 K$
 $TE \sim 185 MJ/mol$
 $P \sim 63 bar$

$T \sim 350 K$
 $TE \sim 64 MJ/mol$
 $P \sim 20 bar$

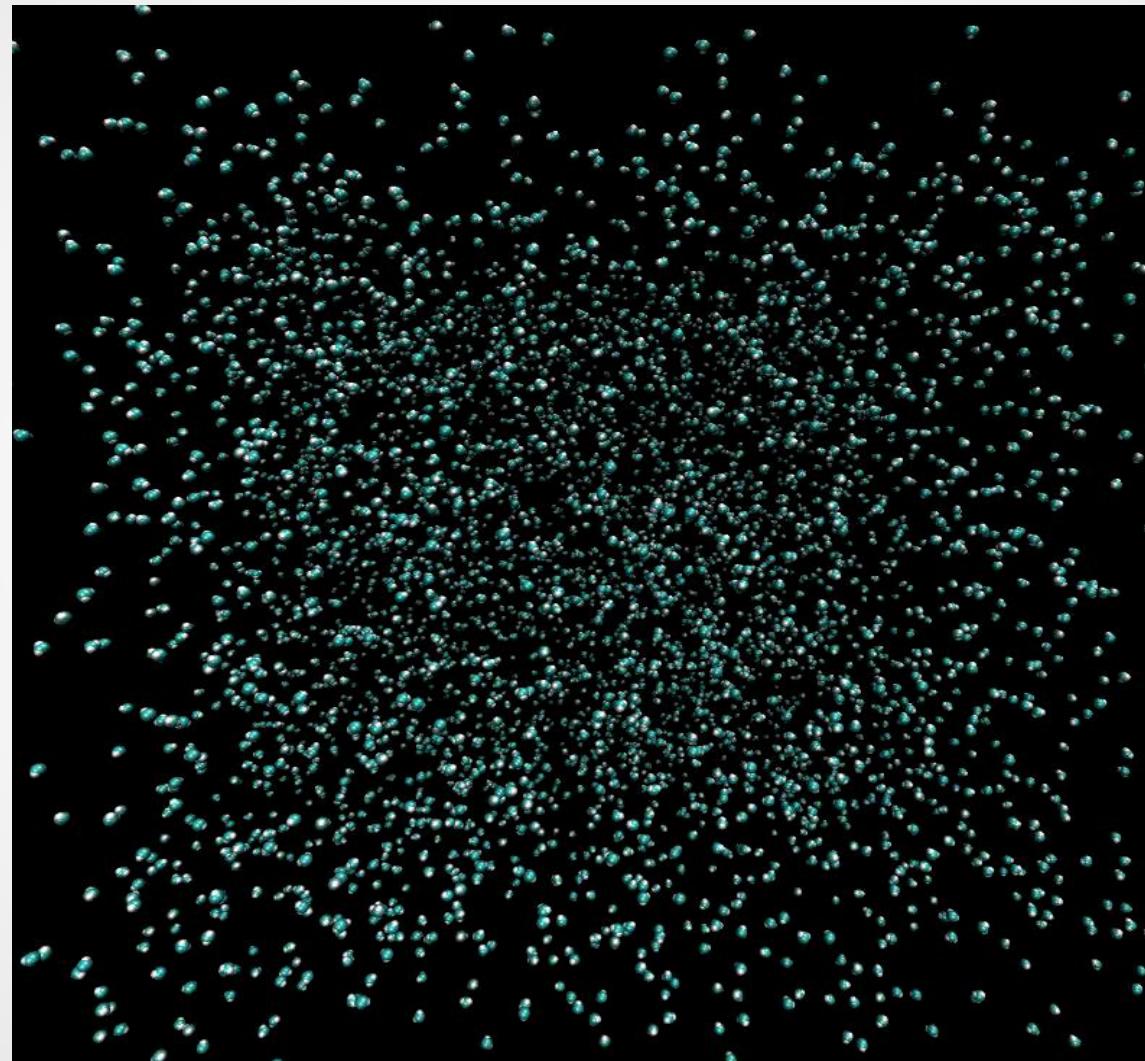
1. Equilibrate system
2. Reduce temperature
3. Production of dynamics,
by keeping carrier gas at
constant T.



Nucleation process visualization



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Note: Only water molecules are shown.

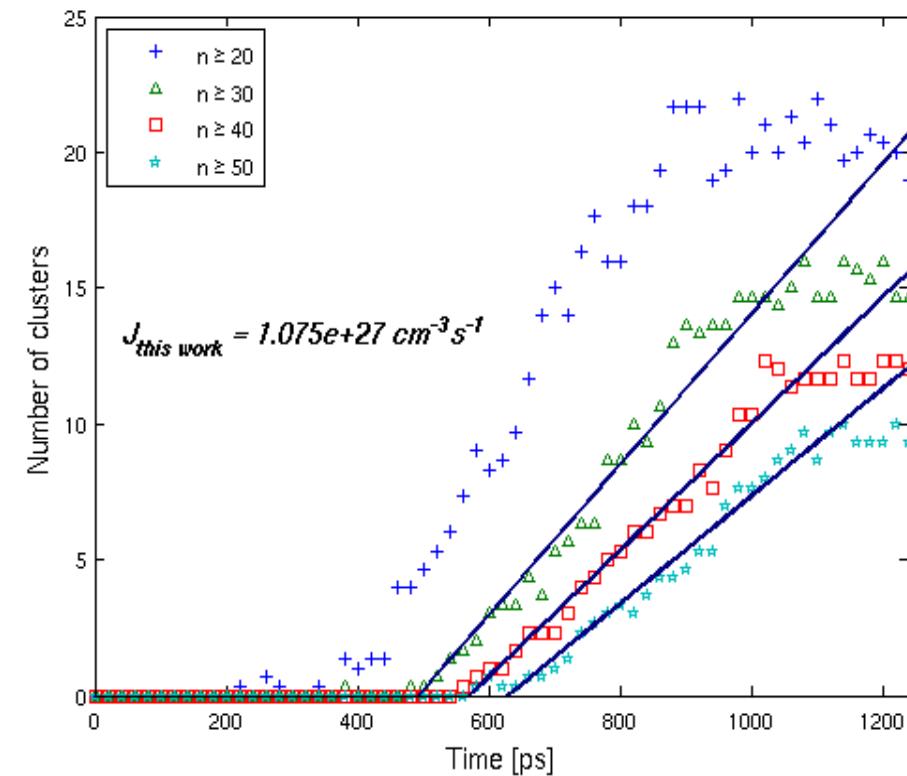
Model validation

Nucleation rate

$$J_{\text{this work}} = 1.07 \times 10^{27} (\text{cm}^{-3} \text{s}^{-1})$$

$$J_{\text{Yas}} = 9.26 \times 10^{26} (\text{cm}^{-3} \text{s}^{-1})^*$$

$$J_{\text{CNT}} = 3.70 \times 10^{28} (\text{cm}^{-3} \text{s}^{-1})$$

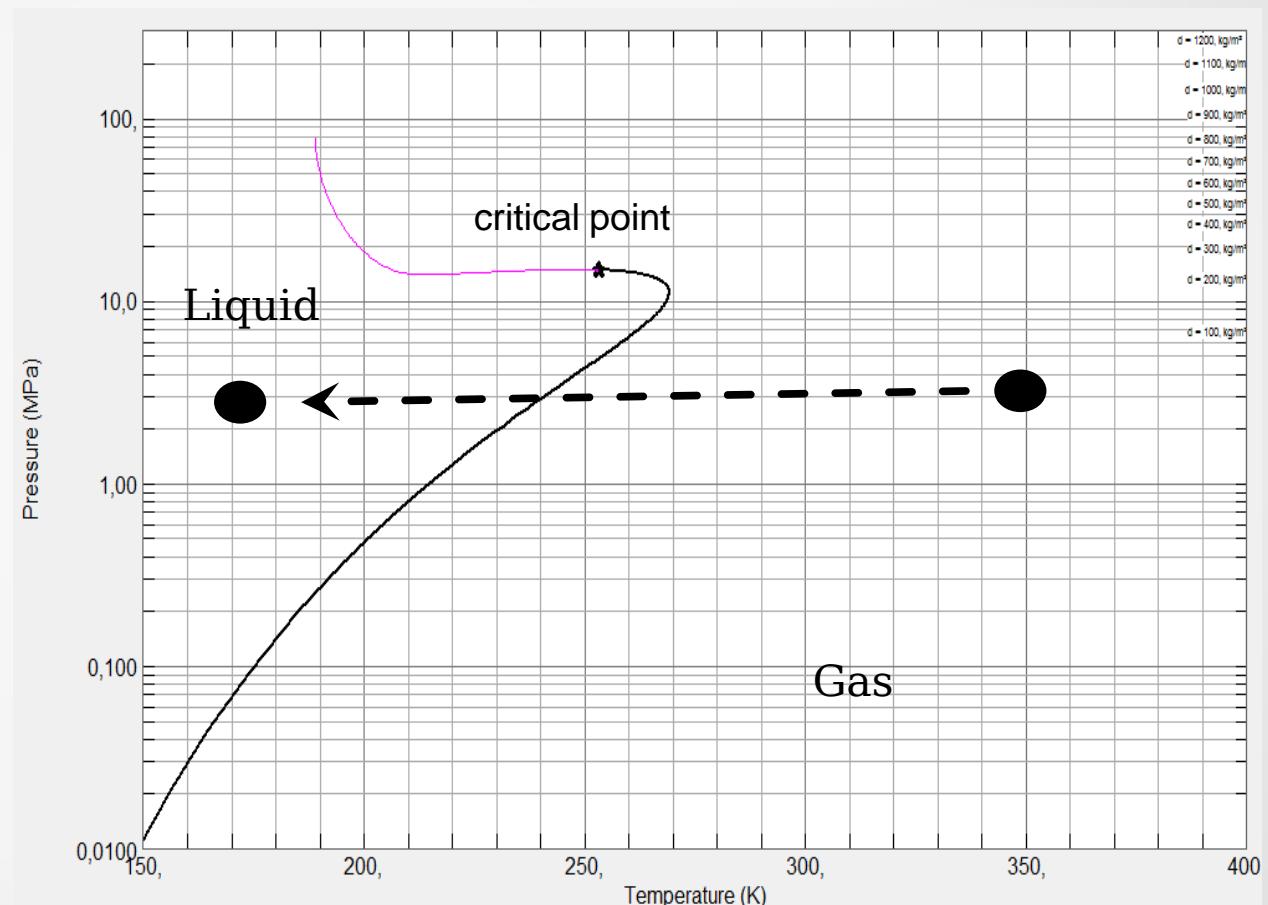


*K. Yasuoka and M. Matsumoto, J. Chem. Phys. 109, 8463 (1998)

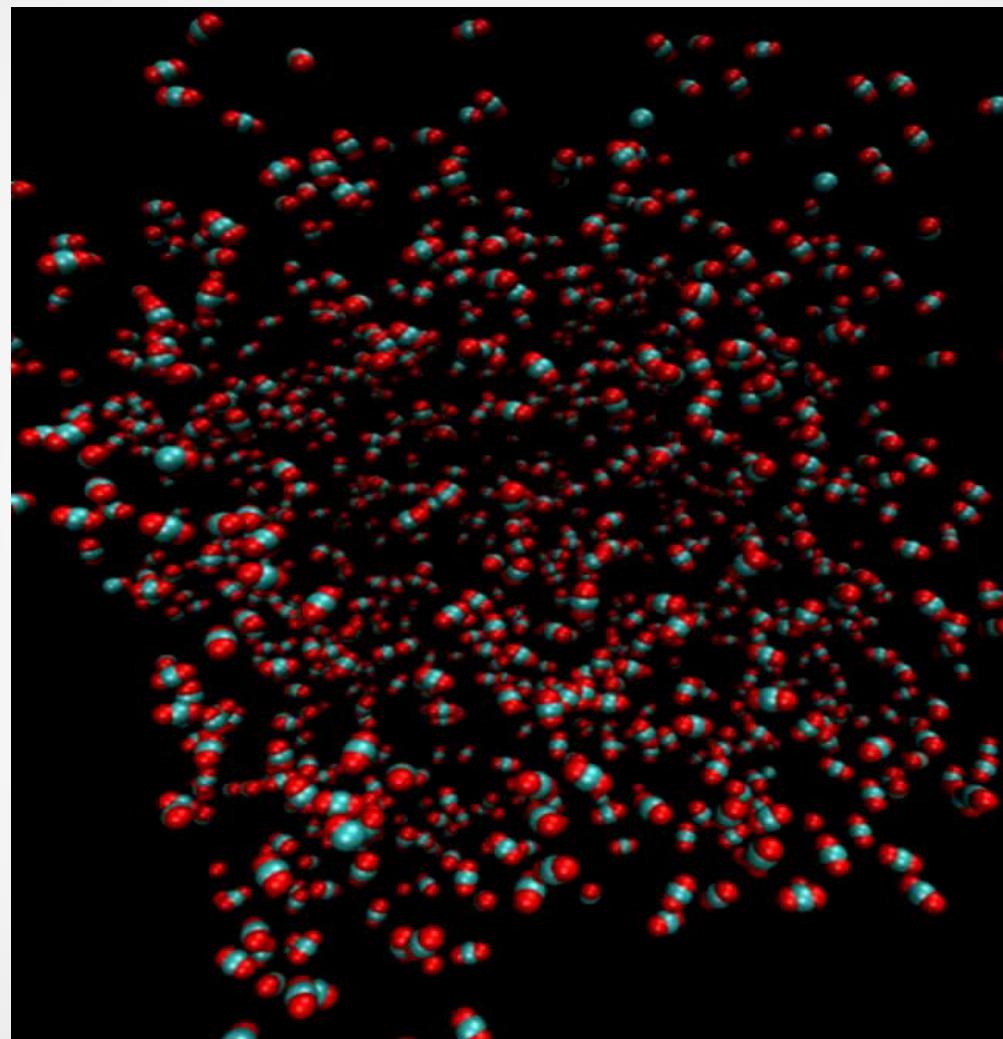
Setup description

- 1000 CO₂ molecules + 1000 Ar atoms
- Box of 16 x 16 x 16 [nm³]
- $T_{init} = 350$ [K]
- EPM2 intermolecular model¹⁾

$$1) \frac{\varepsilon_o}{k_B} = 80.507 \text{ [K]}, \sigma_o = 3.033 \text{ [nm]}, \\ \frac{\varepsilon_c}{k_B} = 28.129 \text{ [K]}, \sigma_c = 2.757 \text{ [nm]}, q_c = 0.6512 \text{ [e]}$$



Nucleation process visualization



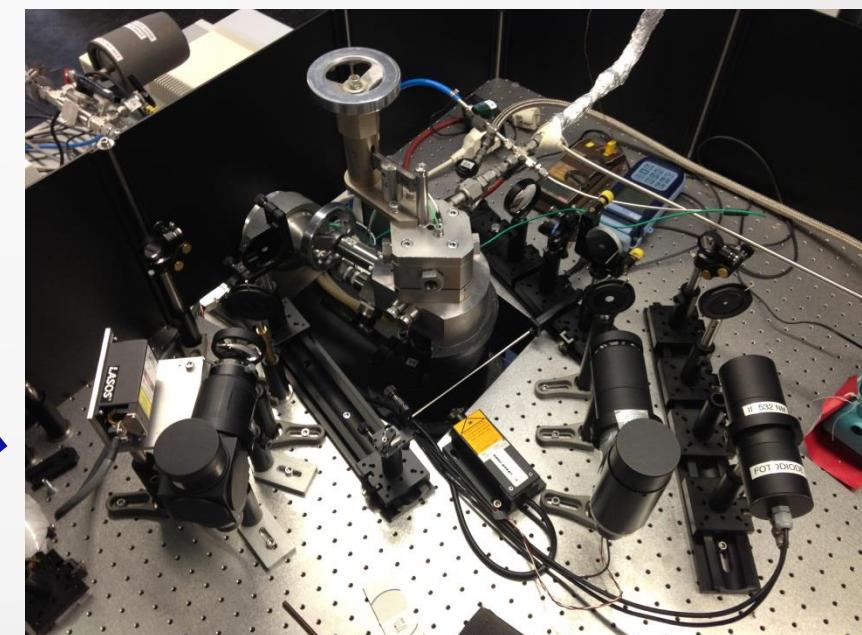
Note: Only carbon dioxide molecules are shown.

Conclusions & Future work

- Both systems (argon-water and argon-carbon dioxide) behaviour in equilibrium corresponds to EOS values;
- Nucleation has been successfully triggered by rapid cooling method;
- Validated a large molecular model;
- The method applied is feasible for other mixtures.

Next steps:

- More complex CO₂ intermolecular models
- Study pure CH₄ system
- Study CO₂ - CH₄ mixture
- Experimental validation



Research resources sponsored by:

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Questions?

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