AS 3.15: Molecular Scale Characterisation of Aerosol and Cloud Particles
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Which properties of adsorbed droplets can describe heterogeneous nucleation on carbonaceous surfaces? Insights from molecular simulations and theoretical models

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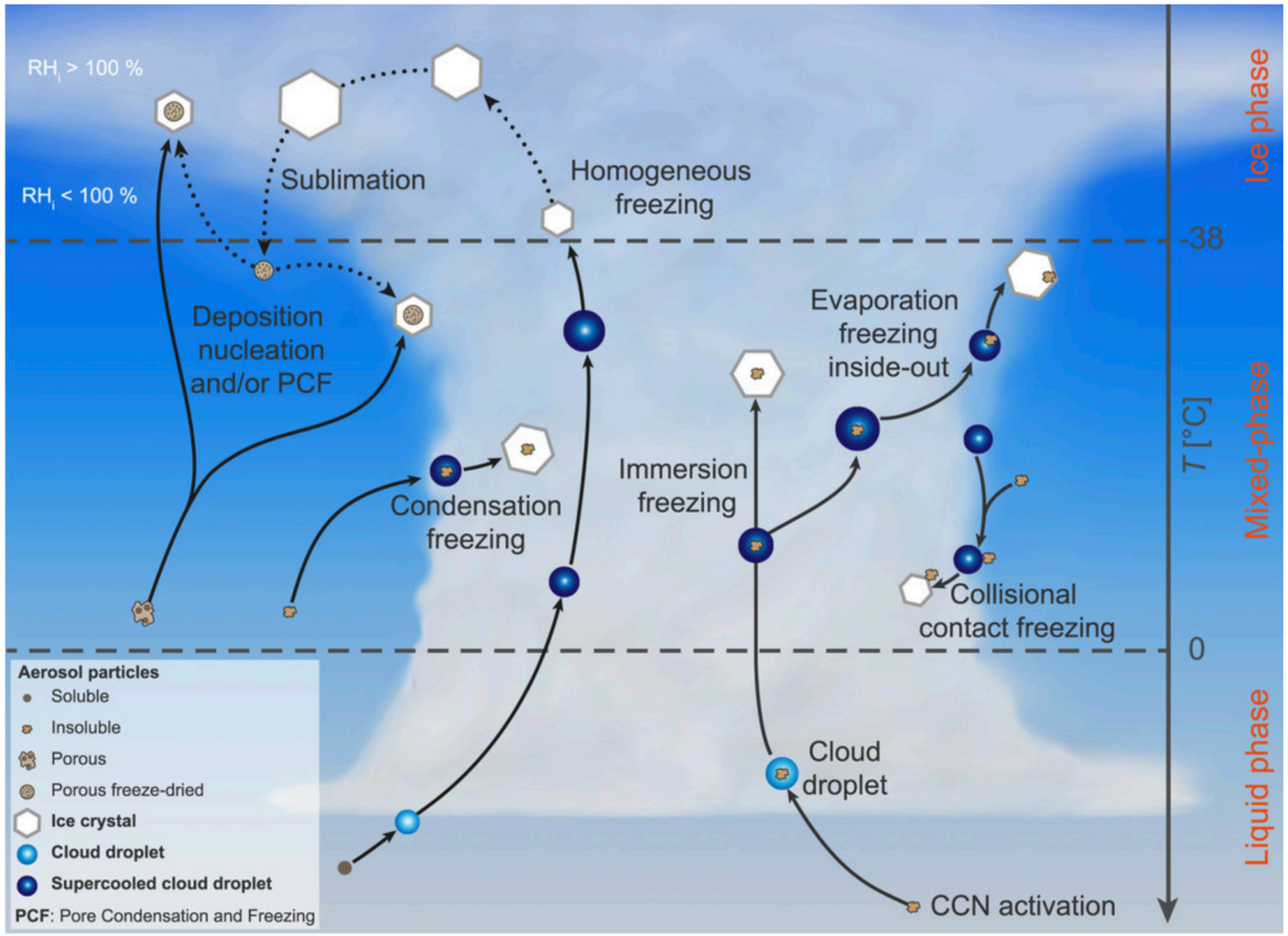
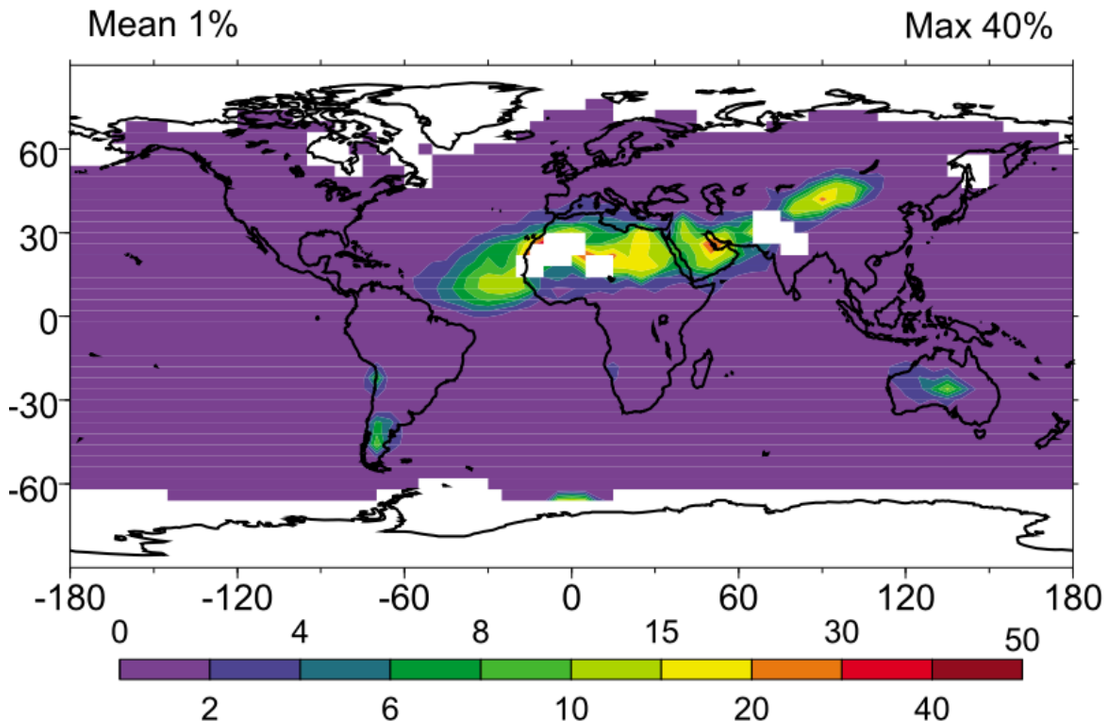
Heterogenous nucleation

Ice Particles



Kanji, 2017

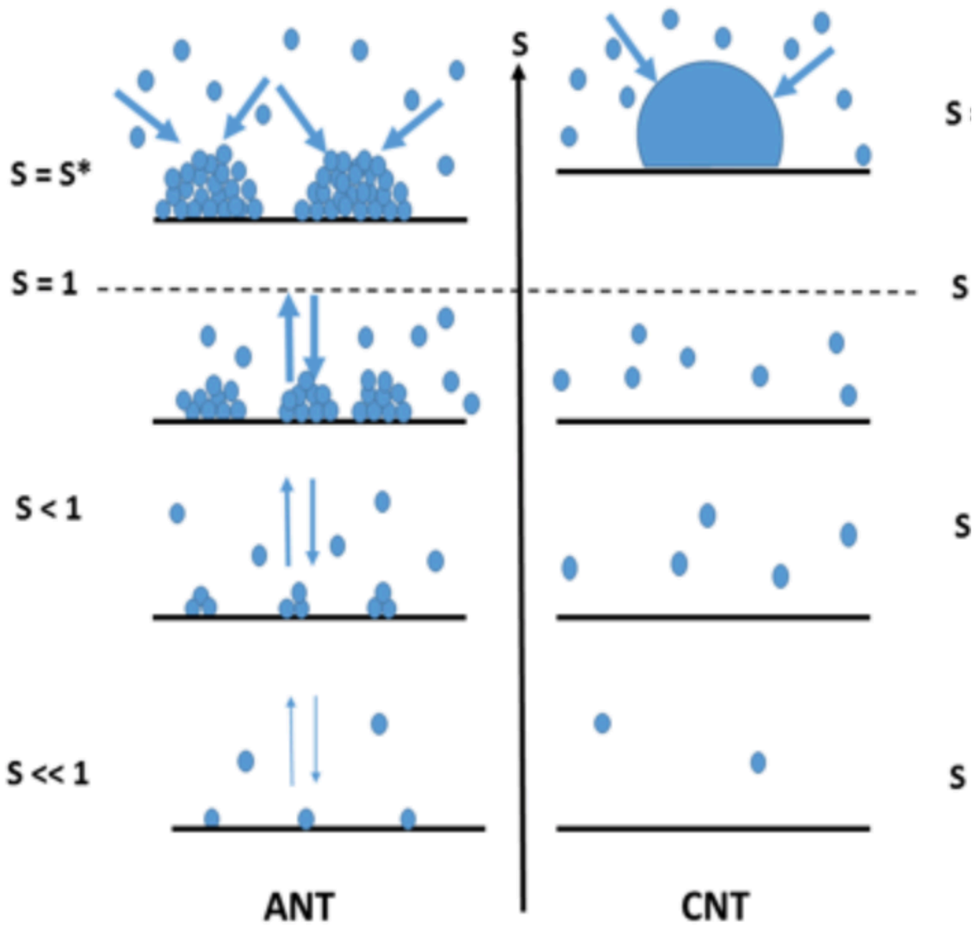
Cloud Droplets



Karydis et. al., 2011

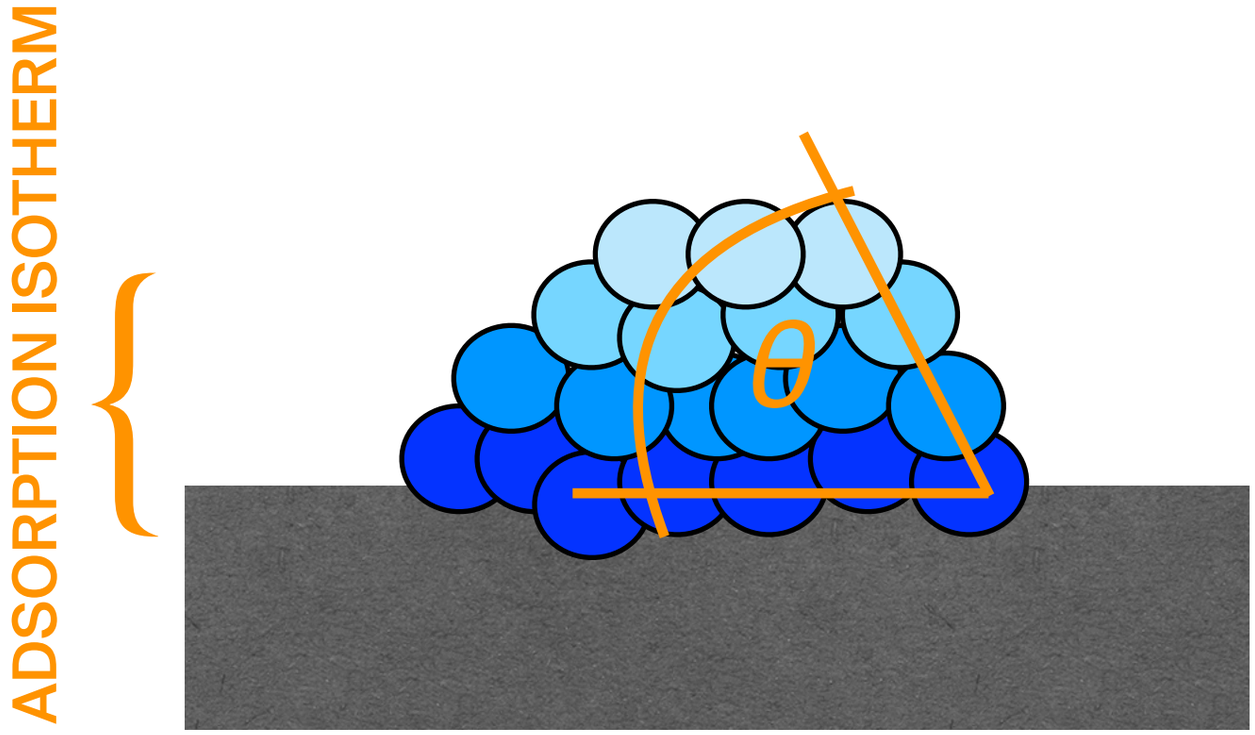
The role of the contact angle in theoretical models

ANT vs CNT



Laaksonen, Malila, Nenes, 2020

ANT at a glance



- CNT : thermodynamic parameter that describes the effect of the surface in an average manner
- ANT: geometrical parameter that describes the amount of adsorbed water at any phase

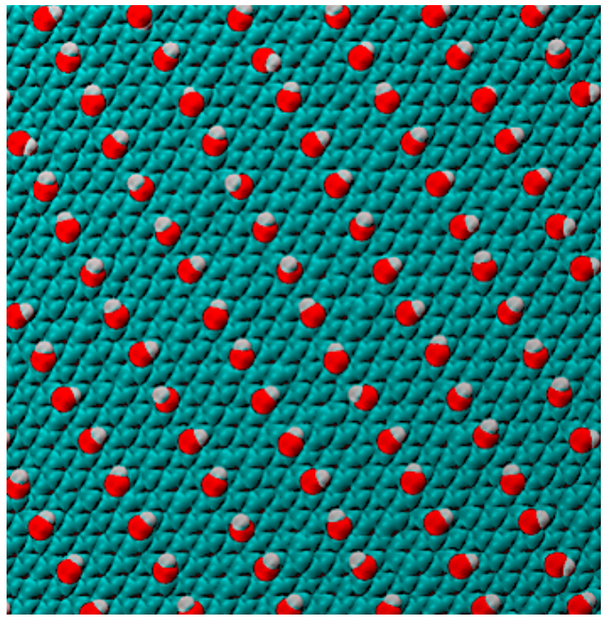
Is the contact angle really sensitive to surface properties?

Systems and simulations

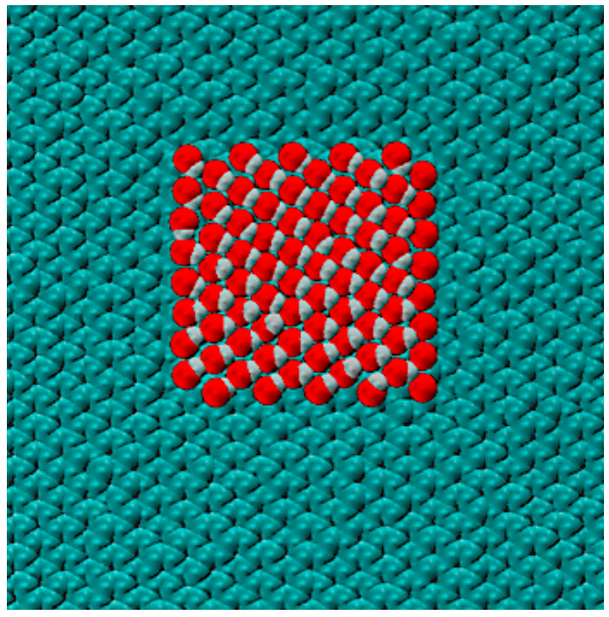
		$\varepsilon_{C\text{-}Ow}$ / kJmol^{-1}	OH	Coverage (area)	Coverage (C number)
PURE GRAPHENE (GRA)	eps_0.1881	0.1881	––	0	0
	eps_0.313	0.3135	––	0	0
	eps_0.392	0.3920	––	0	0
	eps_0.438	0.4389	––	0	0
	eps_0.460	0.4600	––	0	0
	eps_0.490	0.4900	––	0	0
	eps_0.550	0.5500	––	0	0
GRAPHENE OXIDE (GO)	1P_750	0.3920	2.5	100%	50%
	1P_500	0.3920	3.4	100%	33%
	1P_220	0.3920	5.5	100%	13%
	1P_110	0.3920	6.3	100%	7%
	2P_75	0.3920	2.5	10%	5%
	2P_150	0.3920	2.5	25%	10%
	2P_200	0.3920	2.5	35%	13%

- NVT, 300 K,
- OPLS+SPC/E
- 100ns (50 equilibration, 50 production)
- 6x6 nm graphite slab, 4 layers (system 1P_110 repeated with 12x12 graphite slab)
- 1000 water molecules (R_d~2.5 nm) , S<1

even GO (EGO)

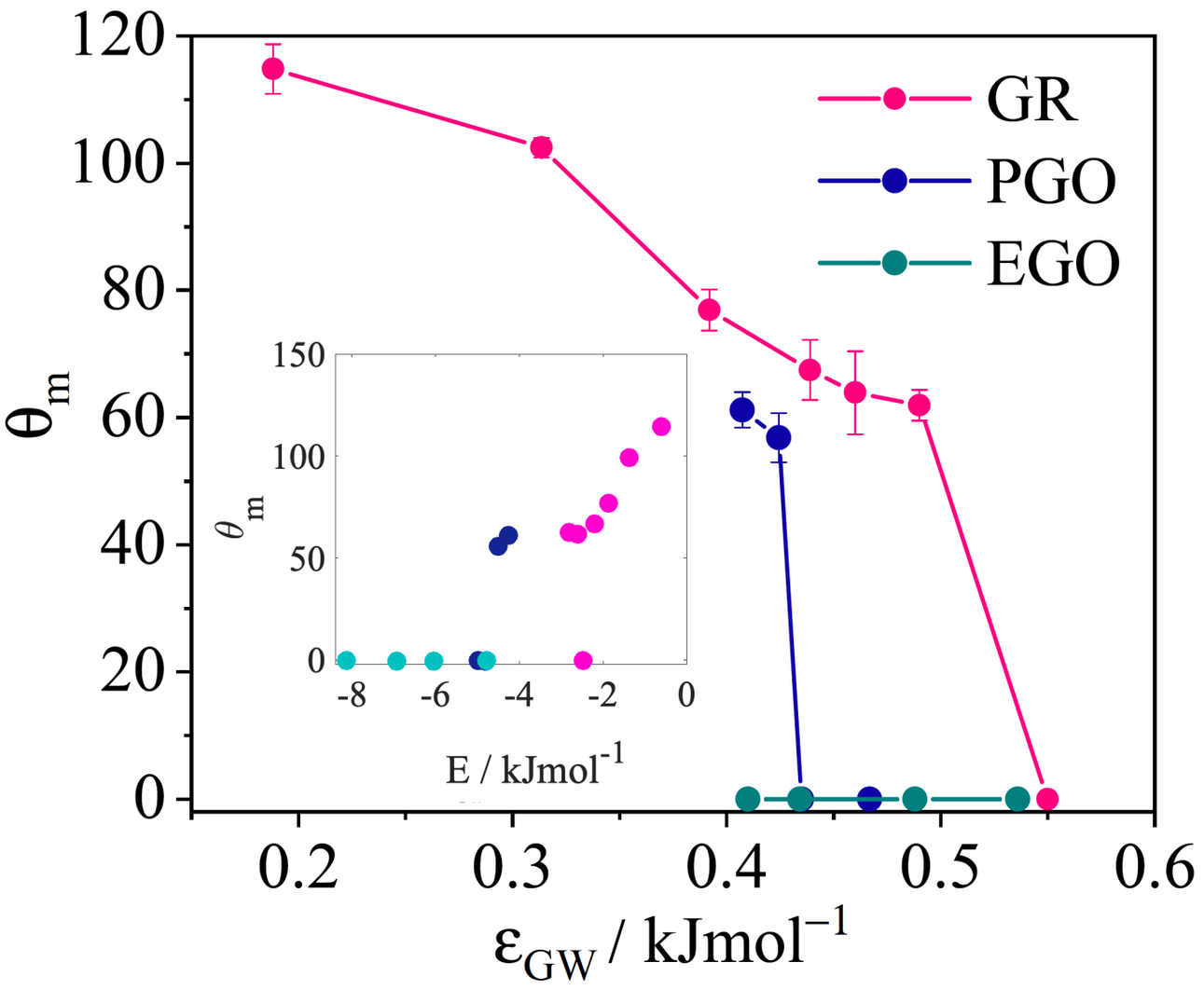


patchy GO (PGO)

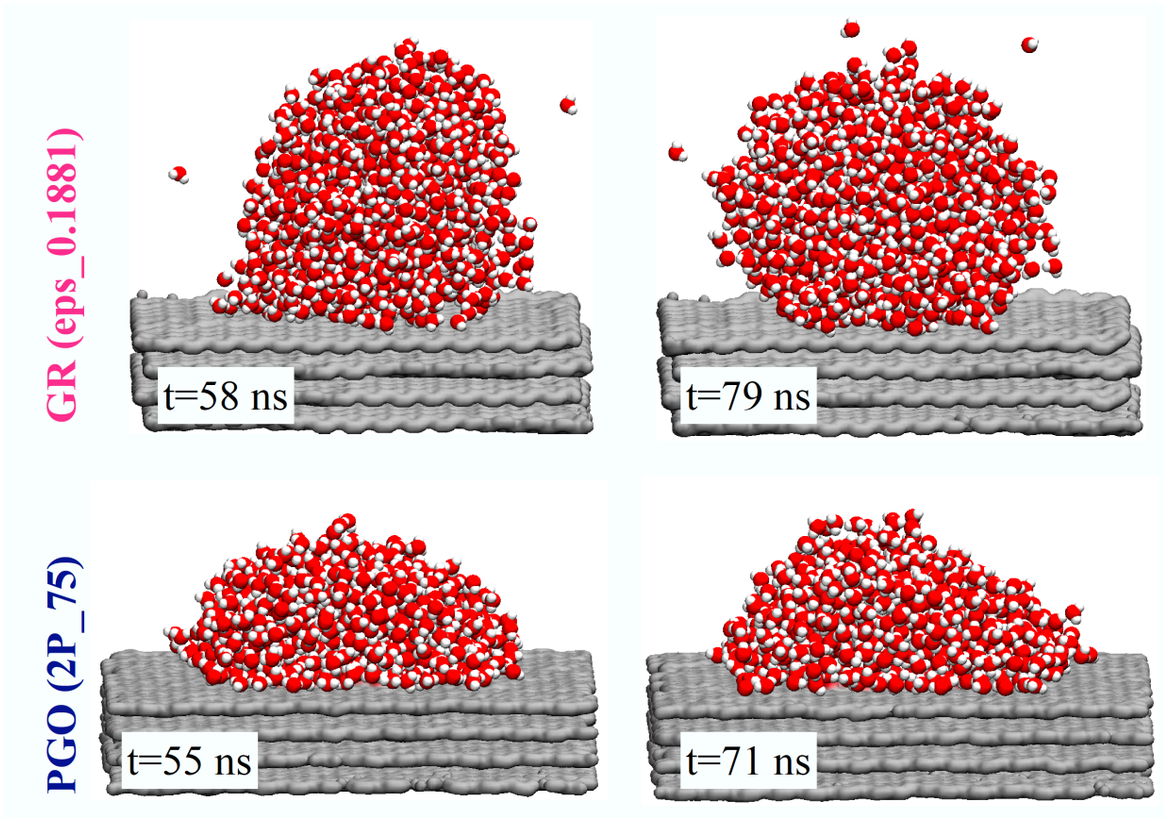


Avegare contact angles

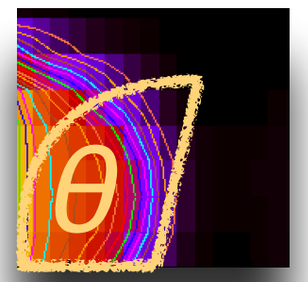
Surface properties and energetics



Droplet shape fluctuations

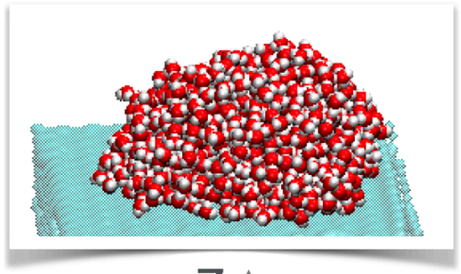


- θ is not a unique function of the surface properties or the surface water interaction energy
- The droplet shape fluctuates on the timescale of ~10-20 ns

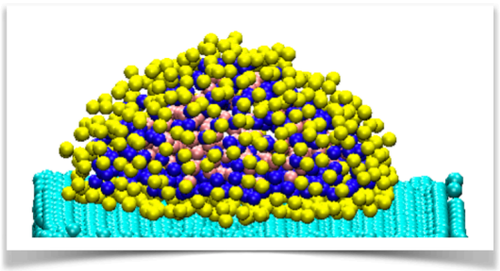


If the contact angle is not sensitive to surface properties then what is?

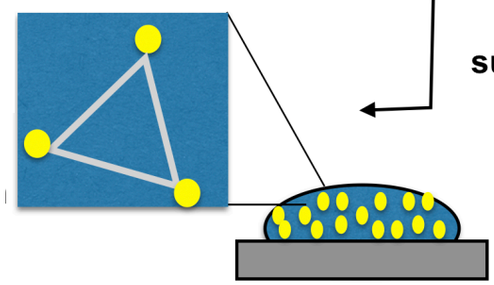
Contact angle distributions



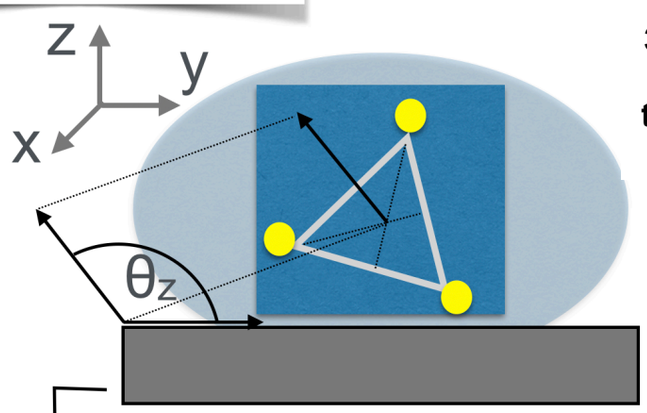
1. Select surface molecules



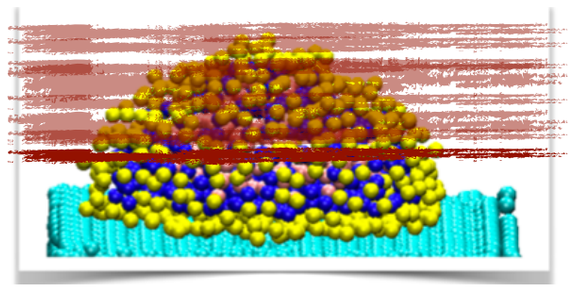
2. Exclude contacts, triangulate the surface



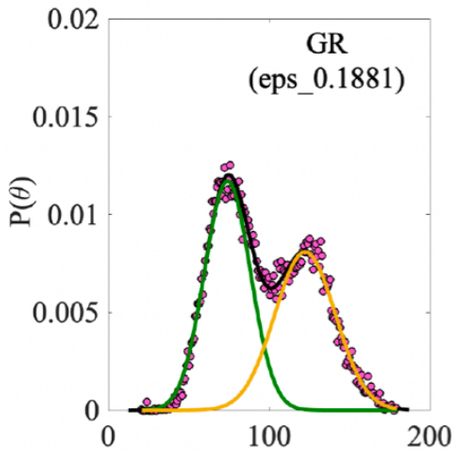
3. Calculate the angle between the triangle and the surface



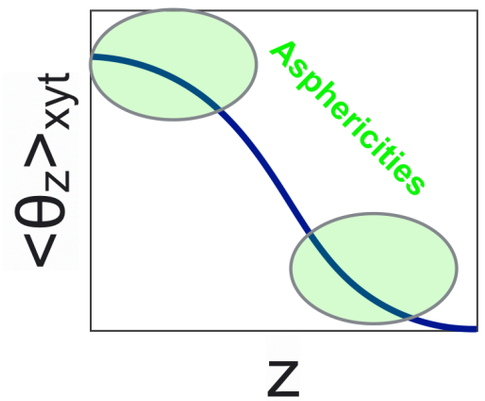
4. b. Select triangles near the surface



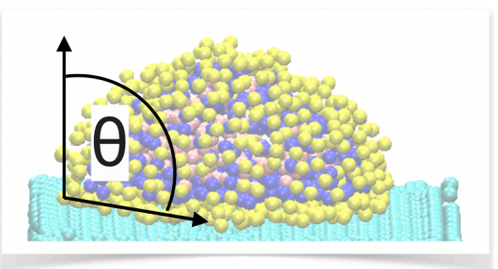
5. b. Generate histogram



4.a. Average in x,y,t distribution along z



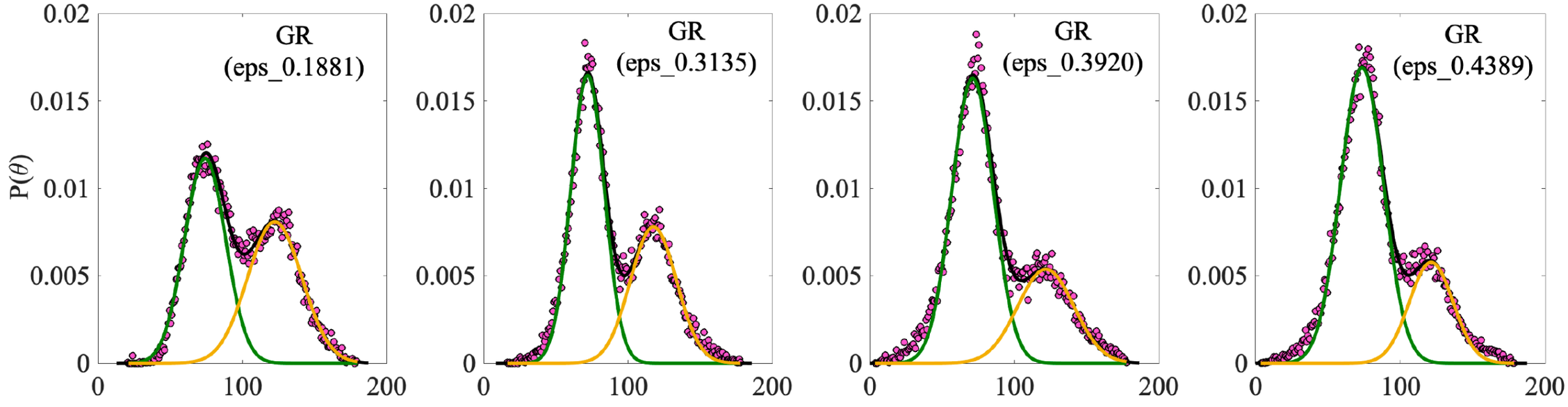
5. a. Extrapolate to z=0



Average nano-droplet contact angle

- A brand new method
- Explicit definition of the instantaneous surface
- No smearing due the thermal fluctuations

Contact angle distributions

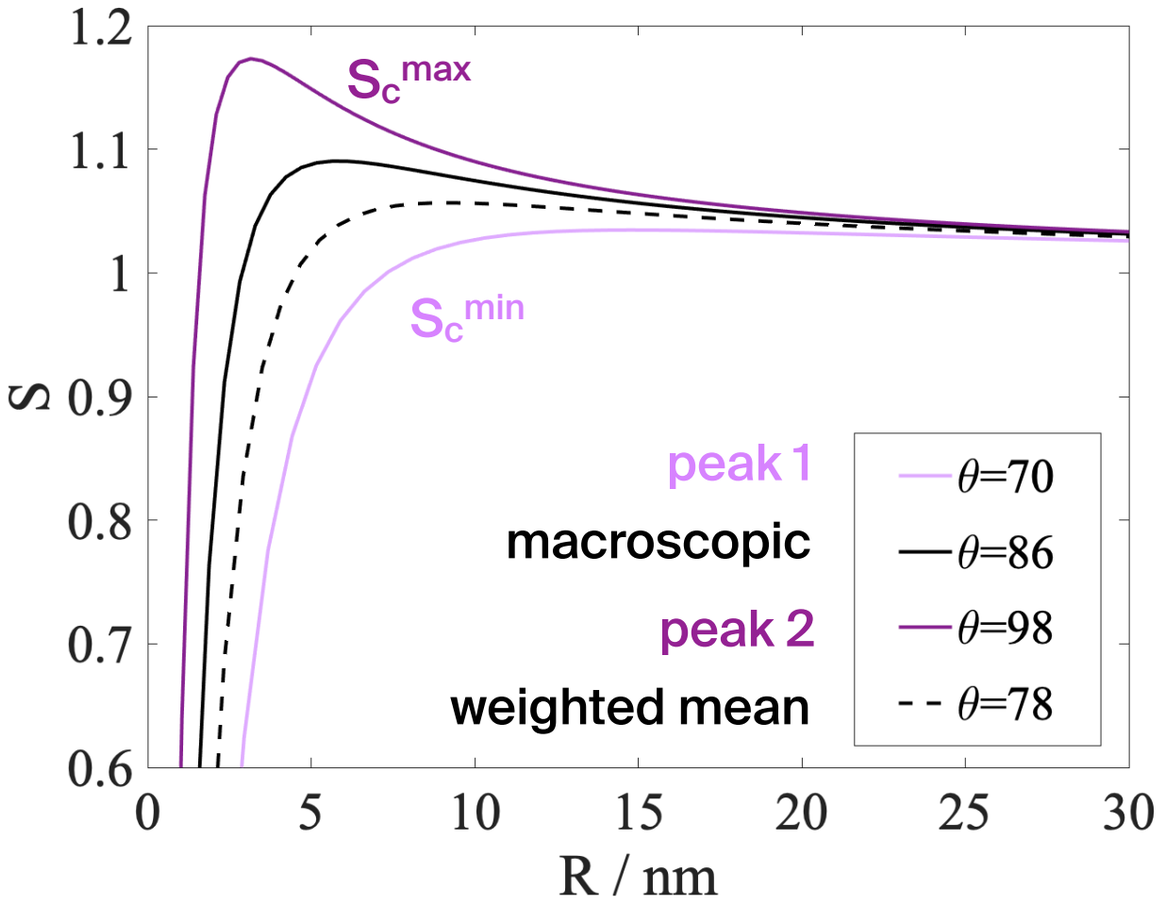


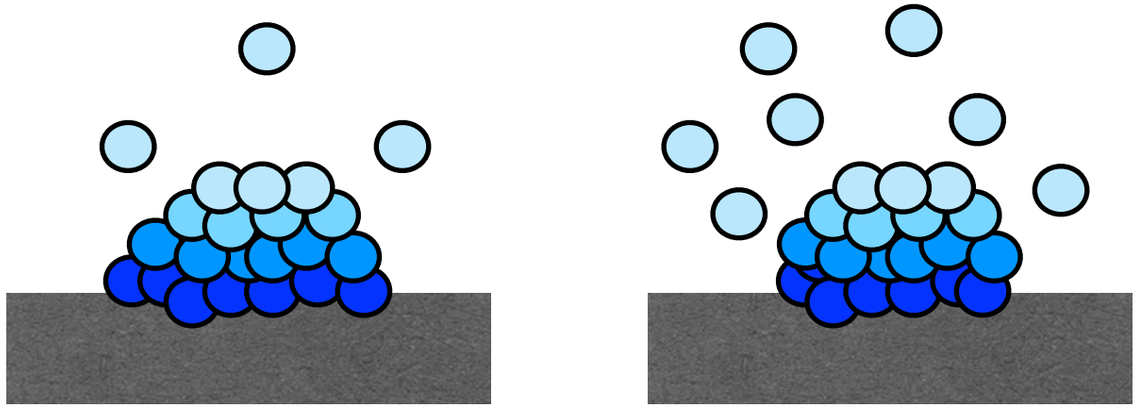
- Unique bimodal/trimodal distributions for each surface

What do they imply for heterogeneous droplet nucleation?

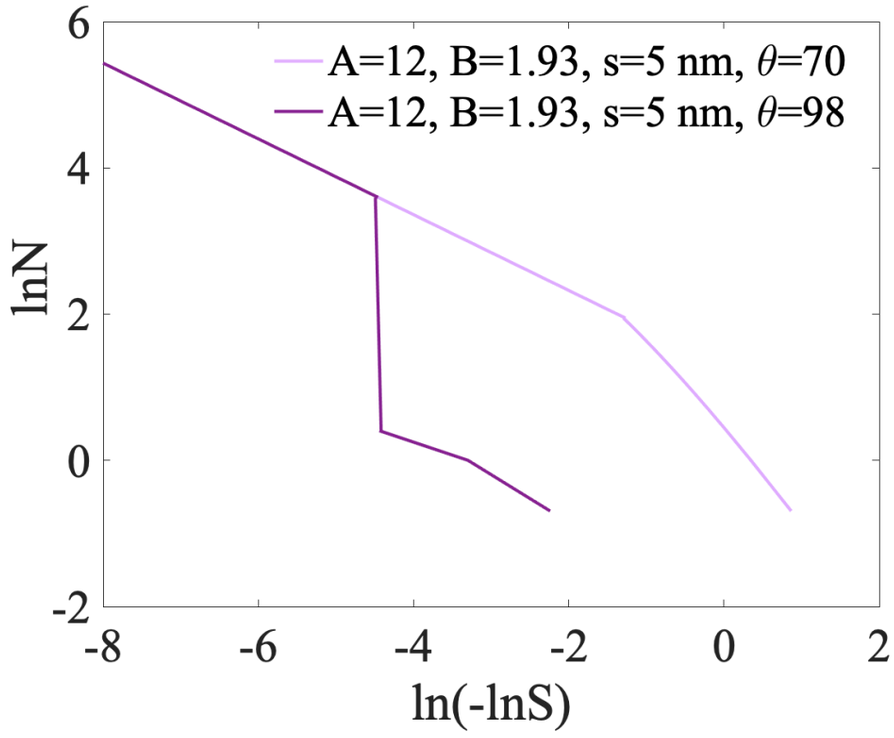
Implications for modelling

Single droplet

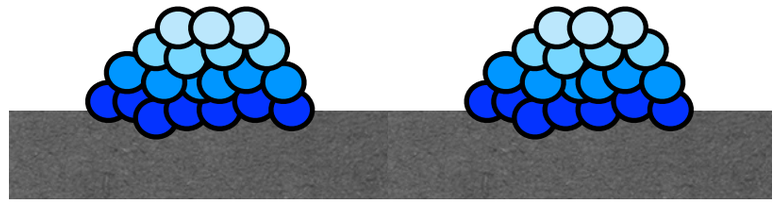




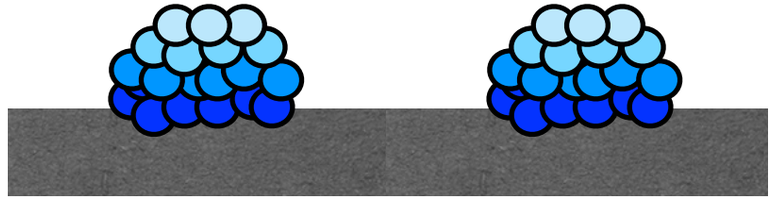
Ensemble of droplets



Film formation before critical droplet formation



Film formation after critical droplet formation



Because of droplet shape fluctuations,
only a range of critical conditions can be defined

Conclusions

- The average contact angle of the droplet is not a unique function of neither the surface properties nor the surface water interactions. Contact angle distributions that contain both temporal and spatial fluctuations of the droplet can be uniquely related to the surface properties.

- In CNT the contact angle is a thermodynamic parameter that describes the overall impact of the presence of a surface on the free energy of critical droplet formation.

- In ANT the contact angle is a geometric parameter that is used to relate the adsorbed amount to the geometry of the adsorbing phase instantaneously at any stage of the nucleation process.

- Therefore in ANT it is possible to predict the impact of the droplet shape fluctuations on the accuracy with which critical conditions can be predicted using the distributions obtained from the MD simulations.

- For a single droplet a range of critical conditions will be accessible whose limits are defined by the hydrophobic and hydrophilic peaks of the CA distribution.

- For droplet ensembles with a small number of coexisting droplets - typical for precritical systems - the mechanism and conditions of activation becomes uncertain because of the droplet shape fluctuations.

EPFL

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C·STACC
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Thank you!