

Temperature dependence of cloud drop activation of insoluble particles

A. A. PIEDEHIERRO¹, A. WELTI¹, Y. VIISANEN¹, and A. LAAKSONEN^{1,2}

ana.alvarez.piedehierro@fmi.fi

¹ Finnish Meteorological Institute, Helsinki, Finland. ² Department of Applied Physics, University of Eastern Physics, Kuopio, Finland.

INTRODUCTION

The critical supersaturation of cloud droplet activation by water-soluble aerosols increases at lower temperatures. This is due to the proportionality to $1/T$, surface tension and molecular volume of water inherent to the Kelvin formulation. Less is known about the **temperature dependence** of **critical supersaturation** when the cloud condensation nuclei (CCN) are **water-insoluble**. In this case, the Kelvin term-induced temperature dependence is the same as for water-soluble particles. However, the influence of the adsorption term on critical supersaturation as a function of temperature remains unclear. The typical temperature dependence of water vapour adsorption is such that an increase in the adsorption layer thickness is expected with decreasing temperature at constant saturation ratio. Nevertheless, it is known that some adsorbent materials behave differently, adsorbing water vapour more efficiently at higher temperatures, while a third class of adsorbents show no temperature dependence at all. In this study, we investigate the temperature dependences of critical supersaturations for water-insoluble particle types that exhibit diverse temperature responses in adsorption measurements. We interpret the results in terms of the FHH adsorption activation model.

WHAT IS THE FHH ACTIVATION THEORY (FHH-AT)?

The FHH adsorption activation theory (Sorjamaa and Laaksonen, 2007) describes the CCN activation of insoluble particles by combining the FHH (Frenkel-Halsey-Hill) **adsorption isotherm** and the **Kelvin equation**.

$$S = \exp \left(-AN^{-B} + \frac{2\gamma v}{kTR} \right)$$

RESULTS

Experimental isotherms

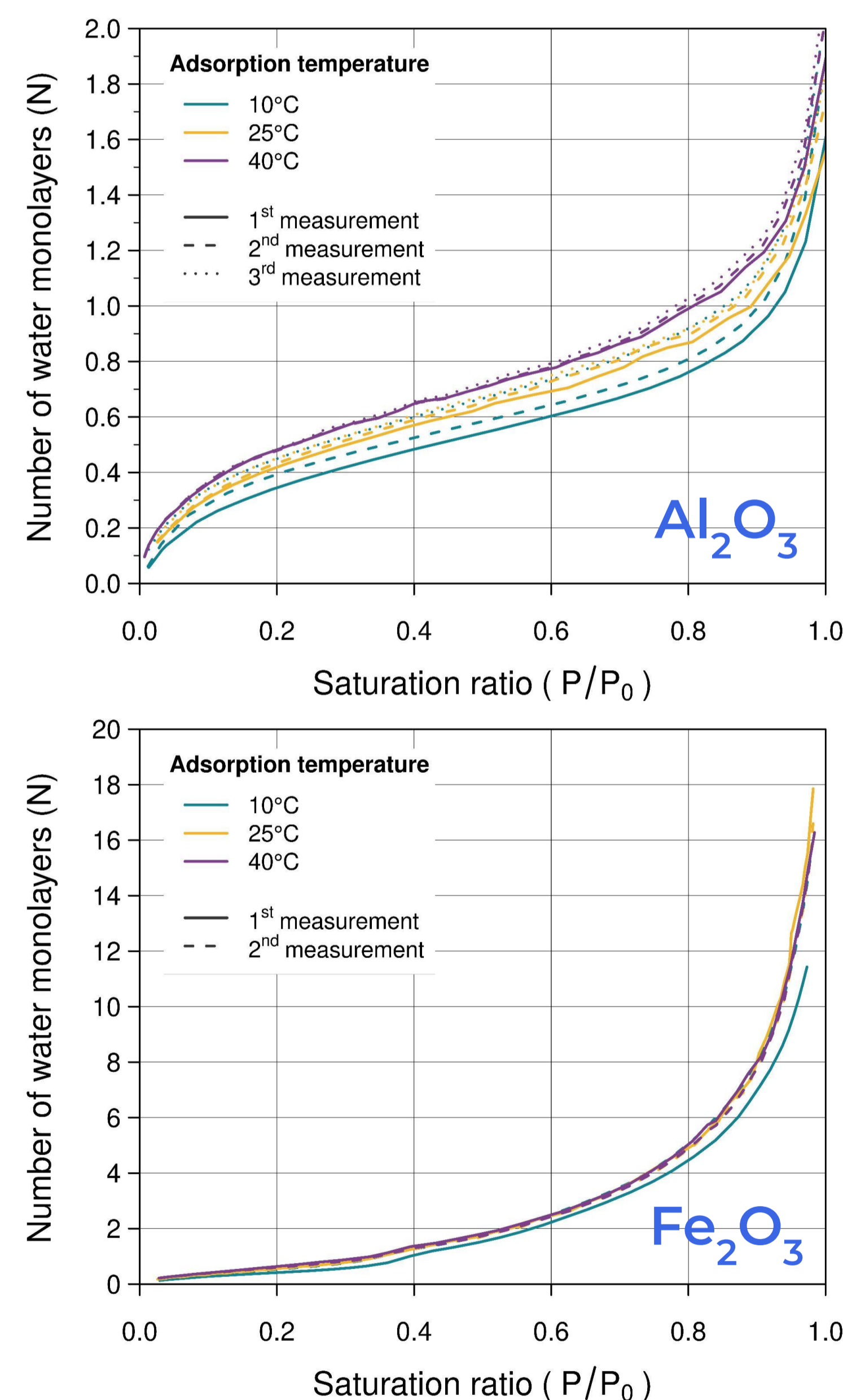


Fig 1. Experimental adsorption isotherms data for Al_2O_3 (top) and Fe_2O_3 (bottom). Al_2O_3 shows enhanced adsorption with increased temperature, while Fe_2O_3 presents a weaker temperature dependence.

Adsorption

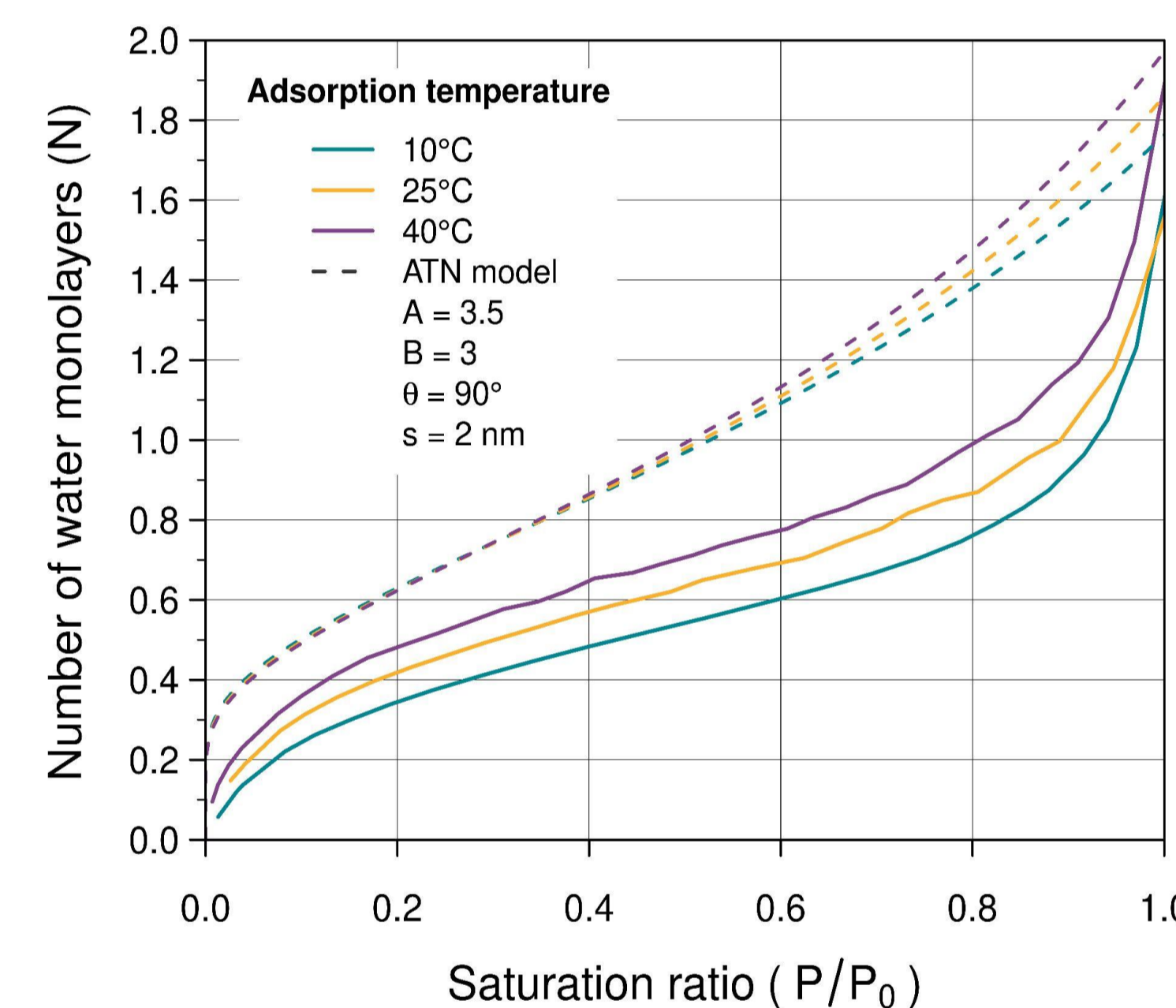


Fig 2. The adsorption nucleation model with $A(T)$ can capture the overall adsorption behavior of Al_2O_3 assuming values $A_{25^\circ\text{C}}=3.5$, $B=3$, contact angle $\theta=90^\circ$ and distance between clusters $s=2$ nm. Only towards higher saturation ratios (in the multilayer regime for this case), the model predicts thicker adsorption layers at higher temperatures.

Clausius-Clapeyron

$$\frac{d \ln S}{dT} = \frac{\Delta H_V}{kT^2}; \ln P_2^0 - \ln P_1^0 = \frac{\Delta H_V}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Film adsorption

$$\ln P_2 - \ln P_1 = \frac{\Delta H_A}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Rightarrow \ln S_2 - \ln S_1 = \frac{\Delta H_A - \Delta H_V}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Rightarrow \ln S = \frac{-(\Delta H_A - \Delta H_V)}{kT}$$

Cluster adsorption

$$P = P^F \exp \left(\frac{2\gamma v}{kTR} \right) \Rightarrow \ln S_2 - \ln S_1 = \frac{\Delta H_A - \Delta H_V}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \frac{2}{kR} \left(\frac{\gamma_2 v_2}{T_2} - \frac{\gamma_1 v_1}{T_1} \right)$$

Critical supersaturation

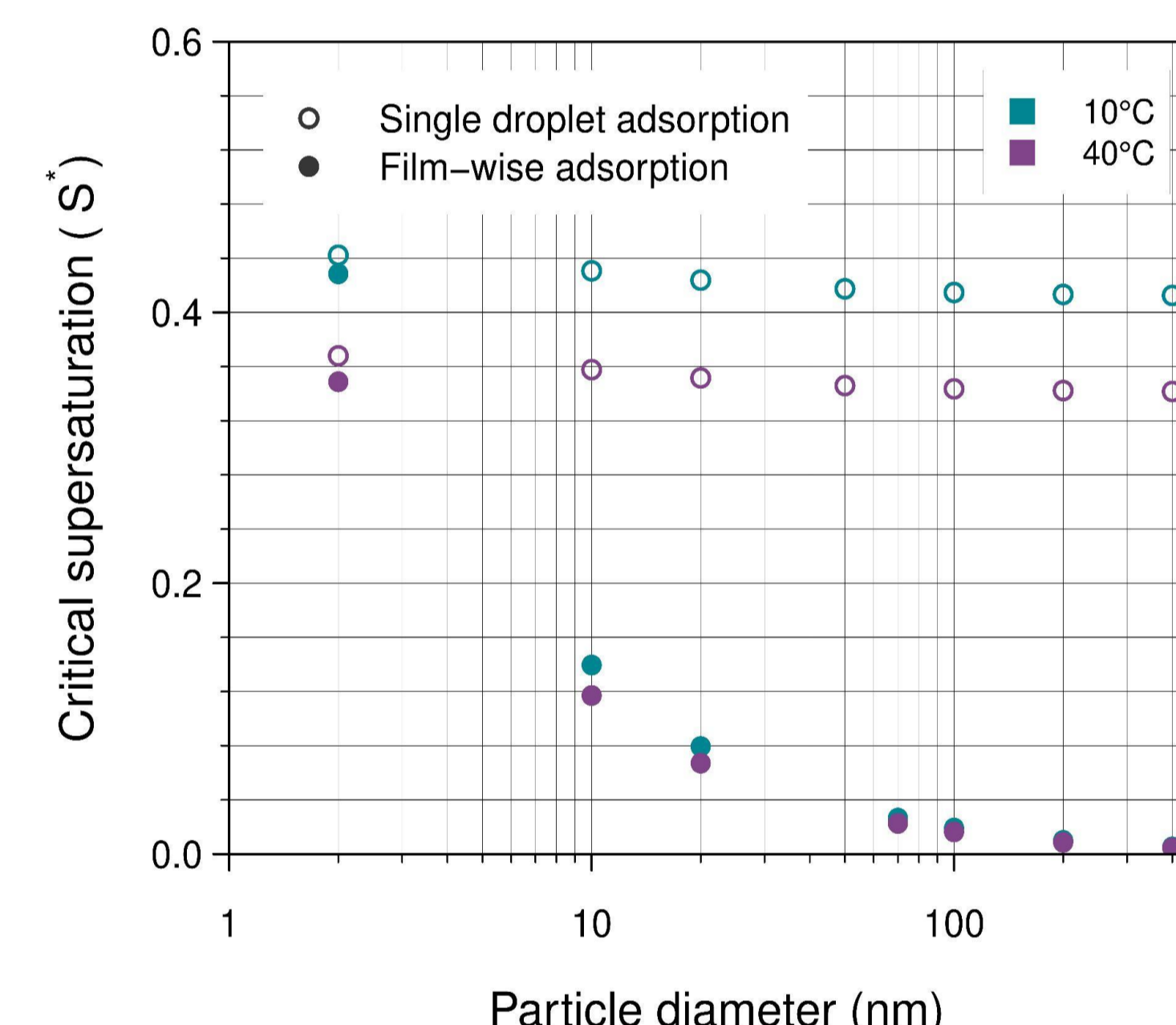


Fig 3. Critical supersaturation calculations using the adsorption nucleation model for **single droplet nucleation** (open symbols) and **filmwise adsorption** (solid symbols) for two different temperatures. The FHH A, B parameters used are the same as in Fig. 2.

FHH theory T-dependence

$$\ln S = -AN^{-B}; \ln S_2 - \ln S_1 = N^{-B} (A_1 - A_2)$$

$$\ln S_2 - \ln S_1 = \frac{A'}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) N^{-B}; A(T) = \frac{A'}{kT}$$

METHODS

Experimental

Water adsorption isotherms on insoluble powders were measured using a **Belsorp-Max II** (Microtrac). The volume of the water monolayer (V_m) was obtained from the BET (Brunauer-Emmett-Teller) analysis of nitrogen adsorption isotherm data using the same setup.

Substances Fe_2O_3 , Al_2O_3

Measurements 10°C, 25°C and 40°C water adsorption isotherms



Data analysis

- V_m (volume of water monolayer) BET analysis from nitrogen adsorption.
- FHH adsorption parameters (A, B) from FHH fitting of water isotherms.

Theoretical calculations

Critical supersaturation calculations using the standard FHH-AT formulation and a modified version in with $A = A(T)$ are used.

T-modified FHH-AT

$$S = \exp \left(-A(T)N^{-B} + \frac{2\gamma v}{kTR} \right) \quad A(T) = \frac{A_{25^\circ\text{C}} T}{298.15}$$

where S is the saturation ratio of water vapor, A , B are the FHH parameters, γ is surface tension of water, v is the molecular volume of water, k is the Boltzmann constant, T is temperature, and R is the droplet radius. The number of monolayers is given by V/V_m .

CONCLUSIONS

- Adsorption nucleation model has the potential to reproduce adsorption experimental data by parameter optimization. By introducing $A(T)$, the T-dependent adsorption is partially explained. This is only possible if droplet-wise adsorption is considered.
- The calculations of critical supersaturation for Al_2O_3 predict higher values for colder temperatures. For filmwise adsorption, the temperature dependence becomes relevant for nanosized particles. For single droplet nucleation, the temperature dependence remains constant for different particle sizes.