

We thank Hanna Vehkamäki for commenting on our manuscript. Her comments are repeated in full below, with our replies indicated in blue font. Text which has been added to the manuscript is shown in red font.

5

Kürten et al. discuss the challenges involved in extrapolating observed particle formation rates down to sizes that are below the instrumental detection limit, especially down to a "critical size where nucleation occurs" (page 2734, lines 2–3). While the topic of the manuscript is important for understanding particle formation processes, there seems to be a major confusion in the kinetic definition of the thermodynamic critical size.

10

In the beginning of the Introduction it is stated that "the critical size is the smallest size at which the growth rate of a particle is faster than its evaporation rate" (page 27234, lines 19–20). If the growth rate is understood as the collision rate, this is indeed correct for a one-component system with a smooth ΔG -curve that exhibits a single local maximum: the collision and evaporation frequencies coincide at the critical size, and above it the collision frequency exceeds the evaporation frequency. However, there is no reason to assume that there would be no evaporation above the critical size, or even that evaporation would be negligible.

15

20

In the extrapolation method presented in the manuscript "the underlying assumption is that growth above this size is purely kinetic (no evaporation), which is fulfilled due to the assumption that d_{p1} is above the critical size" (page 27244, lines 6–8). This reasoning is in general not valid – on the contrary, even the widely used liquid drop model gives non-zero evaporation rates for all sizes. Figure 1 shows an example for water. The collision frequencies (collision rate constant \times monomer concentration) are calculated from kinetic gas theory assuming spherical clusters, and the evaporation rates are computed from Gibbs free energies of formation using the detailed balance condition. The cluster formation energies are calculated according to classical nucleation theory. The temperature is 25.0 °C, and the density, surface tension and saturation vapor pressure of water are set to $\rho = 997.0 \text{ kg/m}^3$, $\sigma = 71.68 \times 10^{-3} \text{ N/m}$ and $p_{\text{sat}} = 3.169 \times 10^3 \text{ Pa}$, respectively.

25

30

While the possibility of particle evaporation is brought up in the manuscript, the authors do not suggest how the evaporation processes would be taken into account in the extrapolation. They also do not even attempt to show whether their extrapolation method gives reasonable results for cases where clusters evaporate. As long as the effect of evaporation is not taken properly into account, the method cannot be called universal.

35

We agree, that the introduced method does not include the effect of evaporation on the clusters/particles with sizes between d_{p1} (size where the formation rate should be extrapolated to) and d_{p2} (size above which the size distribution is known). Therefore, we accept to drop the term "universal". Originally, we have used this term to express that the method can be used for any environment (ambient, chamber, or flow tube) as long as the loss processes are well characterized. Since the method takes into account the effect of self-coagulation it has an additional benefit compared to other methods. However, it is true that for more general cases evaporation can be an important effect, as demonstrated by the figure provided by Hanna Vehkamäki (Fig. 1). Nevertheless, the homogenous nucleation of water vapor is not representative for tropospheric new particle formation because of the very high vapor pressure of water. When applied to chemical systems, which are more relevant for the atmosphere, the particle formation rates measured at the CLOUD chamber have been reported at a particle mobility diameter of 1.7 nm. Several chemical systems have been investigated, i.e the system of sulfuric acid and water as well as sulfuric acid, water and ammonia (Kirkby et al., 2011), the ternary system of sulfuric acid, water and dimethylamine (Almeida et al., 2013) and the system involving sulfuric acid and oxidation products from α -pinene (Riccobono

40

45

50

et al., 2014). In none of these systems significant evaporation of particles above a size of 1.7 nm has been observed at the reported temperatures. Furthermore, the studies that are based on KK2002 do also neglect evaporation (Kerminen and Kulmala, 2002; Lehtinen et al., 2007; Anttila et al., 2010; Korhonen et al., 2014). For most conditions relevant to the atmosphere evaporation for clusters with $d_p > d_{p1}$ is therefore expected to have only a small effect. However, we agree that the method should not be called “universal” anymore and have consequently removed these statements from the manuscript. In addition, we have included the following sentence at the end of section 2.3 in order to raise awareness about the possible effect of evaporation:

“However, in future studies one could examine the effect of evaporation at sizes larger than the critical diameter on the method and attempt to implement it in a similar fashion as Olenius et al. (2014) in their study about the effect of monomer collisions on the growth rates.”

Added reference:

Olenius, T., Riipinen, I., Lehtipalo, K., and Vehkamäki, H.: Growth rates of atmospheric molecular clusters based on appearance times and collision–evaporation fluxes: Growth by monomers, *J. Aerosol Sci.*, 78, 55–70, 2014.

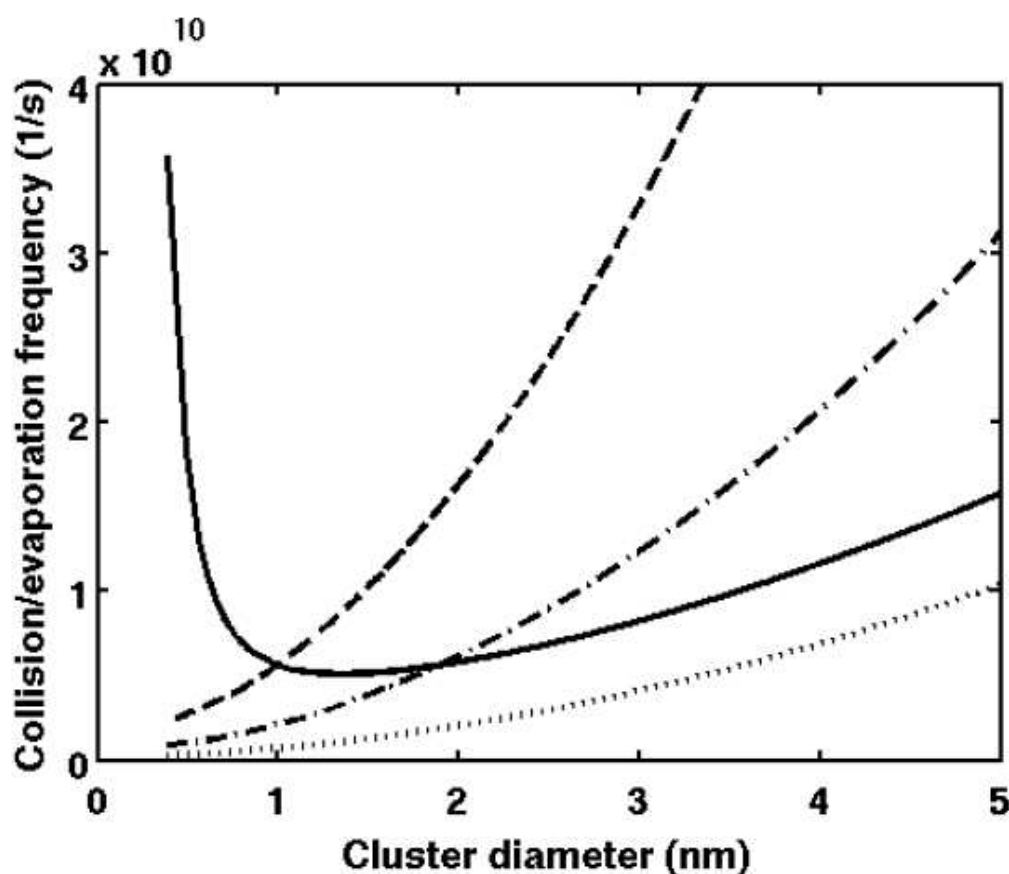


Fig. 1. Collision frequencies of water molecules with water clusters at saturation ratios $S=1$ (dotted), $S=3$ (dash-dotted) and $S=8$ (dashed), and evaporation frequencies as a function of cluster diameter.