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Interactive comment on "On the derivation of particle nucleation rates from experimental formation rates" *by* A. Kürten et al.

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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.

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

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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.
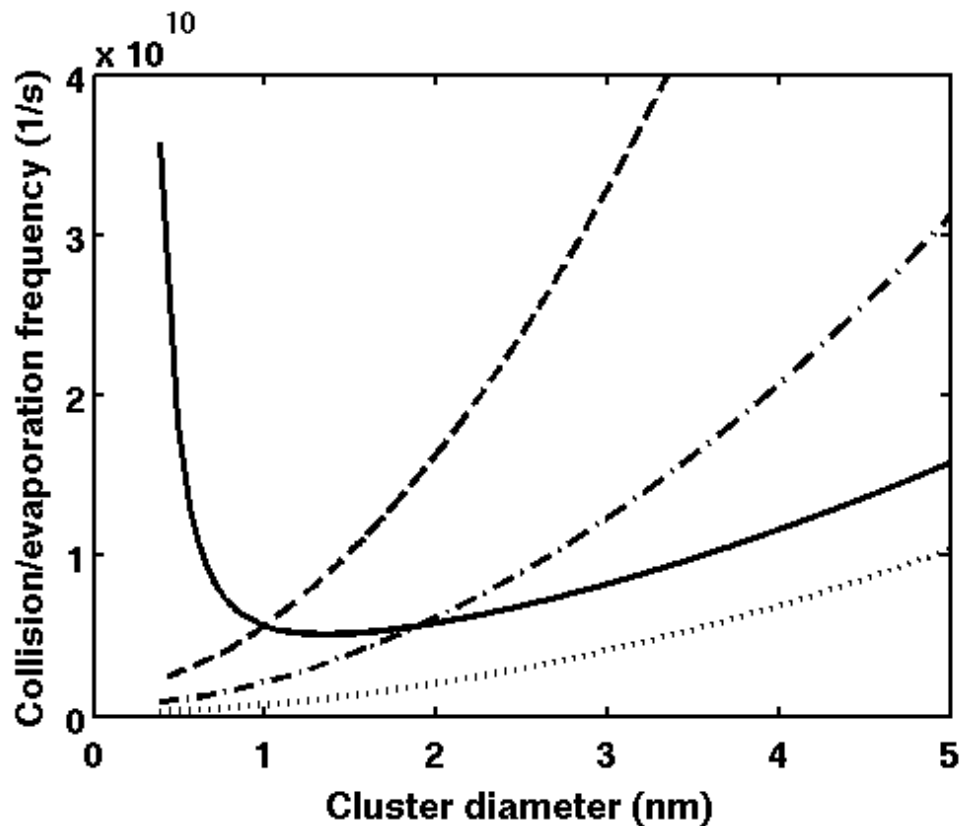
In the extrapolation method presented in the manuscript "the underlying assumption is that growth above this size is purely kinetic (no evaporation), which is fulfilled due to the assumption that d_{p1} is above the critical size" (page 27244, lines 6–8). This reasoning is in general not valid – on the 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 $\rho = 997.0$ kg/m³, $\sigma = 71.68 \times 10^{-3}$ N/m and $p_{\mathrm{sat}} = 3.169 \times 10^3$ Pa, respectively.

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.

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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.