

General comments

In this work the authors extend a recently formulated theory of adsorption to describe the heterogeneous nucleation of water on curved surfaces. The authors use data from the literature to demonstrate the skill of the new theory in predicting the critical supersaturation of selected materials. Three nucleation regimes are proposed depending on the distance between different droplets on the substrate surface. Nucleation of water droplets is of importance for atmospheric processes and the topic of this work is of relevance to the atmospheric community. However, the authors need to greatly improve the description of the theory and make the paper readable to a more diverse audience before it can be published in ACP.

In several places there are gaps in the description that make it very difficult to understand what is new in the theory compared to Laaksonen (2015). I have tried to point out where things are most confusing but in general the authors must strive to explain the theory and its application in a lot more detail. It is never clear that how the equations developed here and those of Laaksonen (2015) are applied. This work cites over and over the work of Laaksonen (2015), which is justified since it is an extension of such theory, however in doing the authors make big jumps in the description that are hard to follow. This paper must be complete in itself without having to constantly refer to Laaksonen (2015).

We thank the referee for careful reading of the ms and the questions below, making it possible for us to improve the readability of the paper.

The authors also need to justify why the average height of the droplet and not the droplet volume was selected to describe the coverage, and, why the curvature of the nanoparticles is not taken into account when analyzing the literature data.

Regarding the coverage, the answer is simple. The FHH theory is based on the idea that “there is a potential field at the surface of a solid into which adsorbate molecules “fall”” (Adamson and Gast, Physical Chemistry of Surfaces, John Wiley & Sons, 1997). In the FHH equation $\ln S = -AN^{-B}$, the term N^{-B} describes how the potential field decays with distance (see e.g. the paper of Halsey, 1948). This is the reason why we define the coverage as $N = \delta/\delta_m$ (where δ is thickness of adsorption layer – or distance between the solid surface and the surface of the adsorption layer - and δ_m is monolayer thickness) rather than in terms of volumes. With uniform adsorption on a flat surface this of course makes no difference. We have added an explanation on the revised ms.

Regarding the second point, apparently the referee means our analysis of adsorption data (as we certainly account for nanoparticle curvature when analyzing the literature data of nucleation). None of the adsorption data we analyze has been measured with nanoparticles but either with flat surfaces or with powders having grain sizes of microns or larger. We now explain this on the revised manuscript.

Specific comments

Page 21886, Lines 2-6. It is not clear that the approximation can be obviated in the case of nucleation. After all, the average is taken over the curvature of the adsorbed droplet, not over different droplets on the substrate. Please clarify.

One of course wants to avoid approximations if possible. What we are saying is that with nucleation calculations one already knows the value of B , and it is not necessary to make the approximation as the average over N_d^B can be computed numerically for a single droplet. However, when one is determining the

value of B by fitting the equations to an adsorption data set (where the experimental coverage is a macroscopic average over a collection of droplets), the approximation has to be made. We will make this clearer in the revised ms.

Page 21886, Line 10. An assumption of the proposed theory is that $\overline{N_d^B} \approx \overline{\delta_d^B} / \delta_M^B$. However, this may lead to an underestimation of the number of “adsorbed” molecules. Why did the authors preferred this assumption over a volume-based approximation, i.e. $N_d \approx$ volume of spherical cap/volume of monolayer $\approx V / (\delta_M \sigma)$? This is particularly troubling since this is the form of the original FHH isotherm and is more consistent with the data and definition of Laaksonen (2015) also used in the work. Please explain.

See response to general comment above. Regarding Laaksonen (2015), in a situation with spherical caps on a flat surface, the volume-based definition of coverage can be used as it is equivalent to the thickness-based definition. We have now clarified this in the revised ms.

Page 21886, Lines 16-20. It is not clear what this means. Isn't the thickness of a monolayer always a molecule? Why would it be different in a curved surface? Please clarify.

If one assumes that the monolayer volume per unit surface area remains constant, then the monolayer thickness has to decrease with increasing curvature of the substrate. Admittedly, the explanation in the manuscript s can be made simpler. If a monolayer covers a spherical particle having a radius R_p , it's volume is $4\pi R_p^2 \delta_m = (4/3\pi)[(R_p + \delta_m)^3 - R_p^3]$, from which Eq. (7) of the manuscript follows.

However, answering the question of why we use thickness based definition of coverage rather than volume based, made us realize that we have lost the sight of the forest from the trees here. As explained above the B -term of the FHH equation describes the decay of the potential field as a function of distance, and the functional form needs to be the same regardless of particle curvature. The δ_m in $N = \delta/\delta_m$ used in the nucleation calculations thus needs to be the same as that used when the values of the FHH parameters A and B are determined from adsorption data, i.e. that determined for a flat substrate. We have removed the equations concerning size-dependent monolayer thickness, and re-done all nucleation calculations using a constant value for δ_m . The results changed noticeably only with the coalescence nucleation curve in Fig. 6, which came closer to experiment at the largest size, but at the same time flattened somewhat. We consequently added the word “somewhat” to the sentence on P4 L343 (revised ms).

Page 21887, Lines 15-20. It is not clear how these three regimes are related or how the authors discriminate between them. In the figures of the Section 4, S^* is shown for all three regimes which makes things more confusing. Please clarify and show how the equations would differ in each case.

The criterion for the coalescence transition is that the combined surface area of the liquid caps equals the surface area of the seed particle. In practice, our computer code calculates the equilibrium RH for a spherical cap whose size is increased slightly at each step until a maximum RH is reached; this point represents cluster nucleation. However, at each step the computer code also checks whether the coalescence transition takes place. If that happens, the code then checks whether the RH is above or below the critical supersaturation for uniform film nucleation. If above, we report both the critical supersaturation for the uniform film nucleation and that for the coalescence nucleation. If below, we only report the critical supersaturation for the uniform film nucleation.

We have added the explanation as well as the relevant equations on the revised ms, and improved the notation for the critical supersaturations.

Page 21887, Line 24. Again, this assumption could have been used to develop Eq. (6) and it would be more consistent with the data. Moreover, in a curved surface the definition of coverage should not change.

See replies above.

Page 2188, Lines 1–5. Wouldn't the most complete theory presented here, accounting for the curvature of the substrate, be more appropriate to find the adsorption parameters? This seems contradictory.

In practice, vast majority of adsorption data have been measured with flat surfaces (often the samples are powders but with grain size so big that the curvature effects are completely insignificant). This is true also for the systems tested in this paper, which is the main reason for presenting the flat interface equations. We agree with the referee that if adsorption measurements are carried out with nanoparticles, the curvature effects need to be accounted for when determining the FHH parameters. However, there is no reason *per se* to assume that A and B would be curvature dependent, so in that sense we disagree with the referee about the (in)appropriateness of using the flat interface equations. We have clarified the issue in the revised ms.

Page 21888, Lines 14-15. What parameters exactly need to be found?

A , B , and s . Also Θ if it is not known from separate measurements. We have clarified this on in the revised ms.

Page 21889, Lines 19-20. Please say exactly what the multilayer portion of the data is?

We have added an extensive clarification of the sub-monolayer and multilayer portions and how they are distinguished in FHH plots, on page 3 of the revised ms.

Page 21890, Lines 5-9. What equations are being applied here? How do they differ for cluster and uniform nucleation?

For cluster nucleation we used Eqs. (1) – (7), and for uniform nucleation those given in Sorjamaa and Laaksonen. In principle, the latter are obtained from Eqs. (1) – (7) at the limit $\Theta \rightarrow 0$. The equations are now given on pages 2 and 3 of the revised ms.

Page 21890, Line 10. What form of classical nucleation theory is applied here? What parameters are used? If the authors criticize the use of the classical theory it must be clear, including equations used, how it is applied.

We use basically Fletcher's original form on nucleation rate, with the kinetic pre-factor set to a constant value of $10^{29} \text{ m}^{-2}\text{s}^{-1}$. This makes only a very small difference compared to using full form of the pre-factor. In order to calculate the critical supersaturation, we use a formula for nucleation probability that accounts for the experimental nucleation time. A subsection devoted to the Fletcher's theory with relevant equations are now given in the revised ms.

Page 21890, Lines 13-15. This would also apply to the author's theory presented here since non-sphericity is not taken into account.

Granted that the theory is approximate in this sense, but the implication is not necessarily the same as with the measurements. With measurements, the question is about mobility diameter vs. volume equivalent diameter, whereas with the theory, the question is about making a correction to the nanoparticle curvature. Romakkaniemi et al. (J. Phys. Chem. A, 105, 8183, 2001) have discussed both effects in the case of cubic particles. As an example, consider a cubic particle that is measured with a DMA to have a diameter of 10 nm. Making a correction for its cubic shape reveals that the actual volume equivalent diameter is 9.6 nm, and thus the data points would shift to the left in an S^* vs. diameter plot. Regarding the effective curvature of the particle (that is needed to calculate the Kelvin effect), the particle radius needs to be multiplied by 0.8 in the case of cubic particles, and thus the theoretical curve would be shifted upward. As we do not know the actual shapes of the particles, we cannot do any corrections for either the measurement data or for the theory. The point we want to make, however, is that increasing discrepancy between data and theory at small sizes may well be a sign of increasing non-sphericity. We have added discussion on this issue in the revised ms.

Page 21890, Section 3.2. The authors need to clarify this a lot. It is not clear how the new theory can predict these things. How do the authors know that cluster coalescence takes place at subsaturation or above the uniform line? Please refer to specific equations showing this.

See our explanation above about how our computer code works. We have clarified this in the revised ms.