APPLICATION OF KOHLER THEORY: MODELING CLOUD CONDENSATION
NUCLEI ACTIVITY

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Introduction
Small solid or liquid particles suspended in air known as aerosols have adverse impacts on global climate through direct interactions with incoming solar radiation, as well as their ability to form clouds via water uptake processes. It is established that cloud condensation nucleus (CCN) activity is a complex function of aerosol size, shape, and chemical composition\(^1\), and is an important metric for investigating aerosol impacts on climate and the environment\(^2\). While empirical CCN measurements on ambient aerosol have been recently conducted\(^3-7\), the extent to which size and/or composition drives the CCN activity of a given aerosol is still unclear. The current study utilizes classical Köhler Theory to interrogate effects of mass, solubility, and composition on the CCN activity of atmospheric aerosols.

Köhler Theory is a comprehensive approach to modeling CCN activity by incorporating various physicochemical properties of aerosols, such as surface tension, density, and ionic contributions of soluble components\(^8\).

\[
e^{(r, n_{\text{sol}})} = (1 - \frac{b}{r^2}) \exp \left( \frac{a}{r} \right)
\]

Equation 1

Here, coefficients must be defined to incorporate size-dependent changes in surface curvature and tension, as well as compositionally-dependent contributions of soluble ionic components. The size dependence of surface curvature can be modeled via the Kelvin Effect, with a coefficient defined as follows:

\[
a = \frac{\sigma_{lv}}{\rho_l R_v T}
\]

Equation 2

where \(\sigma_{lv}\) is the surface tension of water at a liquid-air interface, \(\rho_l\) is the density of liquid water, \(R_v\) is the gas constant for moist air, and \(T\) is temperature. Dissolved ionic species will decrease the equilibrium vapor pressure for water via the Raoult effect, with a coefficient defined as follows:

\[
b = \frac{3i M_v n_s}{4\pi \rho_l}
\]

Equation 3

where \(i\) is the van’t Hoff factor, \(M_v\) is the molar mass of water, \(n_s\) is the moles of solute and \(\rho_l\) is the density of liquid water.

While this theory is well-suited for soluble species of a given size, atmospheric aerosol commonly exist as compounds with both soluble and insoluble components. Because these mixed-component aerosols can still act as cloud condensation nuclei, extending Köhler Theory to model them is of interest.
Model Description

To modify the Köhler equation in order to account for insoluble materials, we considered the case of a wet particle with a soluble component and an insoluble component. The following assumptions were made: (1) the soluble compound is perfectly soluble, disassociates completely and does not contribute the total volume of the particle significantly; (2) the insoluble compound is perfectly insoluble; (3) no internal mixing of the soluble and insoluble components; (4) the wet particle is a sphere; (5) the surface tension does not change with added solute and hence the Kelvin effect does not need to be modified; (6) the temperature is constant at 273 K (0°C); and (7) thermodynamic processes are ignored.

Our model used a modified Köhler equation (see supplemental information for the derivation) to calculate the water saturation over a range of wet radii:

\[ \frac{e_s(r, n_{salt})}{e_s} = \left(1 - \frac{b}{r^3 - r_i^3}\right) \exp \left(\frac{a}{r}\right) \]

Equation 10

The local maximum of the saturation curve determined the values of the critical supersaturation and critical radius. In order to validate the accuracy of our model, we used the assumptions described previously to replicate Table 5.1 and maintained these assumptions throughout.

Three sensitivity tests were conducted which represent atmospherically relevant scenarios mixed-component aerosols may undergo during their lifetimes. The first test examined the explicit role of particle mass on the critical radius for CCN activation by maintaining a constant soluble mass fraction, \( \chi_s \), and varying the total mass, \( m_{tot} \), which equals the sum of masses of the soluble and insoluble components. Throughout the model the insoluble component was hexane, for consistency. This modification changed the value of the variables \( b \) and \( r_i \) to include the respective solute mass and volume of insoluble component. This sensitivity test mimicked the aggregation of small aerosols of same composition to form larger aerosols. Although it is unlikely for aerosols of totally identical composition to aggregate without the addition of a dissimilar component, this result shows the general dependence of particle size to saturation ratio.

The second sensitivity test investigated the effect of soluble mass fraction on critical supersaturation. Total mass was held constant, mimicking the aging of an aerosol as the fraction of insoluble component increases over time without contributing to the total particle mass. Fixing total mass equal to \( 10^{-19} \) kg, the mass fractions 0.1, 0.5, and 1.0 were investigated which changed the value of both \( b \) and \( r_i \) in our modified Köhler equation. From these results we determined the approximate dependence of water uptake on mixed-component particles.

The final test investigated the chemical compositional changes a particle has on the activation behavior. A totally soluble (\( \chi_s = 1 \)) and mixed-component (\( \chi_s = 0.5 \)) particle were compared, each with two different van’t Hoff factors which isolates the dependence of ionic behavior on CCN activation based on Köhler Theory approximations. The van’t Hoff factor accounts for the number of dissociated ions contributing to water uptake which is compositionally dependent, therefore the molecular weight value also changed for the particular
soluble compound. Therefore, this test essentially modeled the saturation dependence on the ratio of $i/M_s$ for solutes which have been found in atmospheric aerosols.

These modifications to Kohler Theory allow for a more complex modeling system. However, it does not consider components that have limited or partial solubility in water. It also neglects the effect of dissolved solute on the surface tension of the droplet. These omissions could serve to over or underestimate a particle’s critical radius and critical supersaturation, depending upon its composition.

Results and Discussion

The results of the first sensitivity test (Figure 1) show that increasing total particle diameter while keeping the mass fraction and identity of solute constant leads to a decrease in critical supersaturation. Essentially, larger particles are easier to activate.

The results of the second sensitivity test (Figure 2) show that for a constant mass a greater fraction of solute in the particle decreases the value of critical supersaturation. Based on this result, particles with a greater mass fraction of insoluble component are harder to activate.

The results of the third sensitivity test (Figure 3) were somewhat inconclusive regarding the effect of changing solute identity on critical supersaturation. It was recognized that the trend is dependent on the ratio of $i/M_s$ and not solely on $i$, thus the critical radius with a higher van’t Hoff factor will be larger than a particle with a smaller van’t Hoff factor if the molecular weight remained constant. The magnitude of this effect was less significant than those of the other sensitivity tests.

The three factors probed in the sensitivity tests can be ranked in accordance to their impact on critical supersaturation and critical radius. The total particle mass has the largest impact, the mass fraction of solute has the second largest impact, and the identity of the solute has the smallest impact. As is consistent with discussions of classical Köhler Theory, the size of the aerosol particle plays the largest role in determining critical supersaturation and critical radius of CCN, although the results show that the presence of insoluble component is significant. Furthermore, studies examining the impact of organic components on CCN activation verify the qualitative trend presented by the second sensitivity test, but quantitative values could not be confirmed.

Conclusions

This result is relevant to climate science because almost all aerosols found in nature contain insoluble components. Therefore, models that incorporate the presence of insoluble components in CCN are critical. Furthermore, calculations based on classical Köhler Theory, which does not take insoluble components into account, underestimate the critical supersaturation and overestimate the critical radius of mixed component aerosols. While the modified Köhler equation presented in this model relies on several assumptions and simplifications, the model provides a good starting point for development of further models that take insoluble components of CCN into account.
Figure 1: Saturation ratio as a function of particle diameter for varied total particle mass at a constant mass fraction of soluble component (left). Critical supersaturation and radius for each scenario are taken as the peak maxima (right).

Figure 2: Saturation ratio as a function of particle diameter for varied mass fraction of soluble component at a constant total particle mass (left). Critical supersaturation and radius for each scenario are taken as the peak maxima (right).

Figure 3: Saturation ratio as a function of particle diameter for varied van’t Hoff factor (solid vs. dashed) and mass fraction of soluble component (left). Critical supersaturation and radius for each scenario (i=2, solid; i=4, dashed) are taken as the peak maxima (right).
References
Raoult’s Law for an electrolytic solution states that:

\[ \frac{e_s(n_{\text{sol}})}{e_s} = 1 - \frac{in_{\text{sol}}}{n_{H_2O}} \]  
Equation 4

Since \( n = m/M \) and \( m = \rho V \) we can state that

\[ n_{\text{sol}} = \frac{m_{\text{sol}}}{M_{\text{sol}}} \]  
Equation 5

\[ n_{H_2O} = \frac{V_{H_2O} \rho_i}{M_v} \]  
Equation 6

For the purpose of our model in which an insoluble core is surrounded by an aqueous solution with a solute that contributes minimally to the total volume, we can describe the volume of water as:

\[ V_{H_2O} = V_{\text{tot}} - V_i \]  
Equation 7

Using the definition of volume for a sphere, we can write that

\[ V_{H_2O} = \frac{4\pi(r^3 - r_i^3)}{3} \]  
Equation 8

where \( r_i \) is the radius of the insoluble core. Substituting (5), (6) and (8) into (4) yields

\[ \frac{e_s(n_{\text{sol}})}{e_s} = 1 - \frac{3im_{\text{sol}}M_v}{4\pi M_{\text{sol}} \rho_i (r^3 - r_i^3)} \]  
Equation 9

(9) can be combined with the Kelvin effect to yield the modified Köhler equation:

\[ \frac{e_s(r, n_{\text{sol}})}{e_s} = \left(1 - \frac{b}{r^3 - r_i^3}\right) \exp \left(\frac{a}{r}\right) \]  
Equation 10