Effect of ammonia on new particle formation: A kinetic H$_2$SO$_4$-H$_2$O-NH$_3$ nucleation model constrained by laboratory measurements

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[1] A clear understanding of the nucleation mechanisms is important to understand the lifecycle of atmospheric particles and to provide reliable predictions of climate change associated with aerosols. On the basis of the classical ternary homogeneous nucleation (THN) theory developed in recent years, the presence of ppt level NH$_3$ concentration significantly enhances nucleation rates. Here we compare the predicted NH$_3$ enhancement with that derived from several reported experiments. We find that the differences between results predicted and observed are very large. Compared to the binary homogeneous nucleation of H$_2$SO$_4$-H$_2$O (no NH$_3$), the classical THN theory predicts up to $\sim$30 orders of magnitude enhancement in the nucleation rates in the presence of ppt level NH$_3$, while the laboratory measurements show only one to two orders of magnitude enhancement in the presence of several ppt to several ppm level of NH$_3$. Furthermore, the classical THN theory predicts a decrease in nucleation rates as RH increases, but the measurements indicate an opposite trend. Since experimental results are probably more reliable than the theoretical model, we developed a kinetic THN model so that the nucleation enhancement effect of NH$_3$ derived from these experimental results could be included. The kinetic model assumes that H$_2$SO$_4$ is the principal specie dominating the cluster growth and nucleation, while H$_2$O and NH$_3$ are secondary species influencing the cluster compositions and hence the evaporation coefficient of H$_2$SO$_4$ from the clusters. The kinetic model is a new approach to simulating THN, and it can take into account the thermodynamic data of molecular clusters derived from density functional theory study and prenucleation cluster measurements. The preliminary simulations using the kinetic THN model constrained by the experimental results indicate a negligible contribution of THN to new particle formation in the boundary atmosphere. Our analysis suggests that the kinetic THN model is unlikely to underpredict the real ternary nucleation rates by much as long as there is no significant error in the experimental results. The implication of this finding and areas for further investigations are discussed.


1. Introduction

[2] The indirect effect of aerosols on climate provides the largest uncertainty in current climate change assessment. While the contribution of secondary particles to total particle mass is not significant, they usually dominate the number concentrations of atmospheric aerosols and those particles acting as cloud condensation nuclei (CCN) [Seinfeld and Pandis, 1998]. In order to provide reliable predictions of climate change associated with aerosols, the formation rates of new particles (secondary particles) in the atmosphere must be understood. Binary homogeneous nucleation (BHN) of sulfuric acid and water has generally been assumed to be the mechanism of new particle formation. However, it has been known in recent years that BHN theory cannot explain observed nucleation events in the boundary troposphere [e.g., Weber et al., 1996; Clarke et al., 1998]. One alternative mechanism proposed is ternary homogeneous nucleation (THN) involving H$_2$SO$_4$-H$_2$O-NH$_3$. Another alternative mechanism is the ion-mediated nucleation of H$_2$SO$_4$-H$_2$O [Yu and Turco, 2000, 2001]. The focus of this paper is on the possible role of ammonia in stabilizing the critical embryo and thus enhancing the nucleation rate. The effect of NH$_3$ on H$_2$SO$_4$-H$_2$O homogeneous nucleation has been investigated theoretically and the classical THN model has been developed [e.g., Coffman and Hegg, 1995; Korhonen et al., 1999; Napari et al., 2002a, 2002b].

[3] In the classical THN model, the rate of H$_2$SO$_4$-H$_2$O-NH$_3$ nucleation is calculated as

$$J = C \exp(-\Delta G^*/kT),$$

where $C$ is a kinetic factor and $\Delta G^*$ is the Gibbs free energy change to form a critical cluster. Here $k$ is the Boltzmann’s
constant, while $T$ is the temperature. The Gibbs free energy change to form a cluster containing $m_1$ H$_2$SO$_4$ molecule, $m_2$ H$_2$O molecules, and $m_3$ NH$_3$ molecules is

$$
\Delta G = -m_1 kT \ln(p_1/p_{i,1}) - m_2 kT \ln(p_2/p_{i,2}) - m_3 kT \ln(p_3/p_{i,3}) + \frac{4\pi r^2 \sigma}{C_0/C_1}.
$$

where $p_i$ ($i = 1, 2, 3$) is the ambient partial pressure of free molecules of species $i$ and $p_{s,i}$ is the equilibrium vapor pressure of species $i$ above the surface of a flat solution with same composition. Here $\sigma$ is the surface tension and $r$ is the radius of the cluster or droplet.

To calculate the nucleation rate based on equation (1), one must decide the composition and size of critical clusters which needs composition-dependent thermodynamic data including surface tension, solution density, and equilibrium vapor pressure of H$_2$SO$_4$, H$_2$O, and NH$_3$ over the surface of the flat ternary solution. Currently, the experimental information on these parameters is not available. The thermodynamic data needed in the classical THN model has been calculated using the thermodynamic multicomponent solution model via integrating various extrapolations, approximations, and assumptions [Coffman and Hegg, 1995; Korhonen et al., 1999; Napari et al., 2002a]. On the basis of the classical THN theory, NH$_3$ at ppt level can significantly enhance the H$_2$SO$_4$-H$_2$O nucleation and THN can lead to significant formation of new particles in the boundary atmosphere. THN rates are very sensitive to the thermodynamic data. As a result, the THN rates calculated based on the classical THN model are expected to have large uncertainties due to the uncertainties associated with the thermodynamic data.

The exact role of NH$_3$ in enhancing nucleation and the validity (or uncertainties) of the classical THN theory must be assessed by comparing model predictions with experimental results. While there exist some experimental investigations on the possible role of NH$_3$ in enhancing H$_2$SO$_4$-H$_2$O homogeneous nucleation [e.g., Ball et al., 1999; Kim et al., 1998], the classical THN theory has never been assessed quantitatively against the experimental results. In this paper we compare the NH$_3$ enhancement derived from reported experiments with that predicted by the classical THN model. As we show in section 2, the differences between results observed and predicted are very large. With the understanding that experimental results are probably more reliable than the theoretical model, we develop a kinetic THN model with the NH$_3$ enhancement effect constrained by the experimental results (section 3).

Using this kinetic THN model, we explore the possible contribution of ternary nucleation to the production of new particles in the boundary atmosphere. Summary and discussion are given in section 4.

2. Comparisons Between Classical THN Model Predictions and Experimental Results

Sulfuric acid is the principal specie controlling the nucleation rates both in binary and ternary nucleation theories. Figure 1 shows a comparison between predicted and observed nucleation rates as a function of [H$_2$SO$_4$] for both binary and ternary nucleation at (a) RH = 4.6%, and (b) RH = 15%. The observed nucleation rates for binary (filled circles) and ternary (diamonds) are from Ball et al. [1999]. Predicted nucleation rates for binary (dot-dashed lines) and ternary (dashed lines for [NH$_3$] = 1 ppt, solid lines for [NH$_3$] = 10 ppt) are based on the parameterization of classical binary [Vehkamäki et al., 2002] and ternary [Napari et al., 2002a, 2002b] nucleation models, respectively.

Figure 1. A comparison between predicted and observed nucleation rates as a function of [H$_2$SO$_4$] for both binary and ternary nucleation at (a) RH = 4.6%, and (b) RH = 15%. The observed nucleation rates for binary (filled circles) and ternary (diamonds) are from Ball et al. [1999]. Predicted nucleation rates for binary (dot-dashed lines) and ternary (dashed lines for [NH$_3$] = 1 ppt, solid lines for [NH$_3$] = 10 ppt) are based on the parameterization of classical binary [Vehkamäki et al., 2002] and ternary [Napari et al., 2002a, 2002b] nucleation models, respectively.

The symbols are the binary (filled circles) and ternary (diamonds) nucleation rates reported by Ball et al. [1999]. The error bars indicate possible range of [H$_2$SO$_4$] in the nucleation zone. The ammonia vapor concentration ([NH$_3$]) in the experimental THN study as indicated in the figure was calculated from the ratio of flows in the NH$_3$ dilution system and the total flow. The actual [NH$_3$] in nucleation zone may be substantially less but is expected to be larger.
than 1 ppt [Ball et al., 1999]. Theoretical binary nucleation rates (dot-dashed lines) and ternary nucleation rates (dashed lines for [NH3] = 1 ppt, solid lines for [NH3] = 10 ppt) are calculated with the parameterization of the most recent version of classical binary [Vehkamäki et al., 2002] and ternary [Napari et al., 2002b] nucleation models, respectively. It is clear from Figure 1 that there exist huge differences between the observed and predicted enhancement in the nucleation rates due to the presence of NH3 at ppt level. Within the ranges of T and RH considered in Figure 1, the experimental results indicate one to two orders of magnitude enhancement in the nucleation rates. However, classical THN theory predicts an enhancement of ~30 orders of magnitude. For T = 295 K, [H2SO4] = 10^8 cm^-3, and RH < 15%, the nucleation rate calculated with binary homogeneous nucleation model is less than 10^{-30} cm^-3 s^-1 but with 1 ppt of [NH3] the classical THN model predicts a nucleation rate of >10^7 cm^-3 s^-1.

[7] Ball et al.’s [1999] measurements are not the only measurements that indicate a rather modest enhancement in the nucleation rate by the addition of NH3 to H2SO4-H2O or SO2-H2O system. In their study of the nanoparticle formation from SO2/H2O or SO2/H2O/NH3 air mixtures by ionization irradiation, Kim et al. [1998] found that the presence of 0.71–3.6 ppm NH3 increases the number concentration of neutral nucleated particles by a factor of less than 10. These neutral particles were believed to be mostly formed via binary or ternary homogeneous nucleation. Diamond et al. [1985] and Christensen et al. [1994] observed similar modest increases of particle number concentration in their experimental nucleation study when NH3 was added to SO2/H2O system. In his laboratory investigation of particle formation by photo-oxidation of SO2 with OH radical, Nolan [1987] found that the difference in the values of nucleation rates for the cases without NH3 and with the NH3 (~50 ppb to 1 ppm) is less than a factor of 10. Nolan [1987] also observed no obvious change in the measured new particles when the added NH3 mixing ratio increased from ~50 ppb to 1 ppm. All these experimental investigations on the effect of NH3 on nucleation indicate that the presence of NH3 (mixing ratio range from a few ppt to more than 100 ppm) only slightly enhances the nucleation rates, which is significantly different from the calculations based on the classical THN theory as shown in Figure 1.

[8] In addition to the large differences in the absolute values of nucleation enhancement due to the presence of NH3, classical THN theory and experimental observations also give quite different dependence of nucleation rates on RH. Figure 2 shows the dependence of nucleation rates on RH. The unfilled and filled symbols are the experimental results for binary and ternary nucleation, respectively. The lines are the ternary nucleation rates at three different [NH3] (10, 30, and 100 ppt for Figures 2a and 2b, and 0.1, 0.3, and 1 ppt for Figure 2c) calculated based on the classical THN model of Napari et al. [2002b]. The data in Figures 2a and 2b are the experimental formation rates of neutral particles derived from the measurements of Kim et al. [1998]. The data in Figure 2c are from Ball et al. [1999] for [H2SO4] of 10^{11} cm^-3. The experimental conditions (T, [SO2], and [NH3]) and parameters used in the model calculations (T, [H2SO4], and [NH3]) are indicated in each panel.

Figure 2. The dependence of nucleation rates on RH. The unfilled and filled symbols are the experimental results for binary and ternary nucleation, respectively. The lines are the ternary nucleation rates at three different [NH3] calculated based on the classical THN model of Napari et al. [2002b]. The data in Figures 2a and 2b are the experimental formation rates of neutral particles derived from the measurements of Kim et al. [1998]. The data in Figure 2c are from Ball et al. [1999] for [H2SO4] of 10^{11} cm^-3. The experimental conditions (T, [SO2], and [NH3]) and parameters used in the model calculations (T, [H2SO4], and [NH3]) are indicated in each panel.
neous nucleation [Kim et al., 1998]. There is no direct measurement of $[\text{H}_2\text{SO}_4]$ in the work of Kim et al. The experimental data corresponding to $[\text{H}_2\text{SO}_4]$ of $10^{11}$ cm$^{-3}$ from Ball et al. [1999] (see Figure 1) are shown in Figure 2c. The experimental conditions (T, $\text{SO}_2$, and NH$_3$ concentration) are marked in each panel.

[9] It is clear from Figure 2 that the trend of ternary nucleation rates on RH predicted by the classical THN model is opposite to that observed in laboratory studies. THN theory predicts a decrease in nucleation rates as RH increases, but instead, the measured ternary nucleation rates increase with increasing RH. The theoretical THN rates are very sensitive to [NH$_3$] and the overprediction of the effect of NH$_3$ on nucleation is obvious in Figure 2. To obtain nucleation rates in a similar range, the concentrations of H$_2$SO$_4$ and NH$_3$ needed in the classical THN theory are much lower than those used in the laboratory study. The observed decreasing effect of ammonia on nucleation with increasing RH may suggest that the effect of NH$_3$ on nucleation in the atmosphere is very limited because RH in the atmosphere is typically much larger than RH in these experiments (<~15%).

[10] The extraordinarily large deviation of ternary nucleation rates predicted based on classical THN theory from those observed experimentally, as we show in Figures 1 and 2, might suggest that substantial improvement in the current classical THN theory is needed and care should be taken when using the theory to predict particle formation in the atmosphere. It should be pointed out that the measurements of Ball et al. [1999] have been cited as evidence supporting the THN theory on the effect of NH$_3$ in enhancing the nucleation [Napari et al., 2002a]. As we shown here, Ball et al.’s [1999] measurements are actually against the classical THN theory with regard to the possible role of NH$_3$ in new particle formation in the boundary atmosphere.

3. A Kinetic Model of H$_2$SO$_4$-H$_2$O-NH$_3$

Ternary Nucleation

[11] On the basis of the classical THN theory, NH$_3$ significantly stabilizes the prenucleation clusters and leads to the enhancement of nucleation rates by up to ~30 orders of magnitude. However, as we described in the previous section, experimental studies indicate a much smaller enhancement in nucleation rates. That may suggest that the effect of NH$_3$ in stabilizing the small clusters is much less than that calculated based on classical THN theory. The formation of new particles in both binary and ternary system is actually a kinetic process involving forward and backward flux of clusters due to colliding of H$_2$SO$_4$ molecules with clusters and evaporation of H$_2$SO$_4$ from clusters. H$_2$O and NH$_3$ participate in the nucleation through influencing the composition of clusters and hence stability and evaporation coefficient of H$_2$SO$_4$ molecules.

[12] Recently, Yu [2005a, 2006] showed that the binary homogeneous nucleation (BHN) of H$_2$SO$_4$-H$_2$O can be treated as quasi-uniary nucleation of H$_2$SO$_4$ in equilibrium with H$_2$O vapor and developed a kinetic H$_2$SO$_4$-H$_2$O nucleation model. In the kinetic model, the growth/shrinking of clusters through the uptake/evaporation of H$_2$SO$_4$ molecules is simulated explicitly by solving the following equations:

$$\frac{dn_i}{dt} = \delta_{i-1,i} n_i - \gamma_i n_i - \gamma_{i+1} n_{i+1} + \gamma_{i-1} n_{i-1} \quad \text{if } \text{RH} \geq 2$$

$$\frac{dn_1}{dt} = P - \sum_{i=2}^{\infty} \beta_i n_i + 2\gamma_2 n_2 + \sum_{i=2}^{\infty} \gamma_i n_i,$$

where $n_i$ is the number concentration of clusters containing $i$ H$_2$SO$_4$ molecules ($i$-mers) and $n_1$ is the total concentration of H$_2$SO$_4$ monomers. Here $\delta_i$ is the average forward (rate) coefficient which can be calculated from the kinetic collision rate of hydrated monomers with $i$-mers, and $\gamma_i$ is the average reverse (or evaporation) rate coefficient or escape frequency of H$_2$SO$_4$ molecules from $i$-mers which can be calculated using the Kelvin equation [Yu, 2005a]. $P$ is the production rate of H$_2$SO$_4$ molecules.

[13] The nucleation rates based on the kinetic binary H$_2$SO$_4$-H$_2$O nucleation model ($J_{BHN}$) can be calculated as

$$J_{BHN} = \beta_i n_i - \gamma_i n_i + \gamma_{i+1} n_{i+1},$$

where $\beta_i$ is the number of H$_2$SO$_4$ molecules in the critical clusters ($i = i^* \text{ when } \beta_i = \gamma_i$). The nucleation rates reach a steady state value after certain time at a given (constant) [H$_2$SO$_4$] ($n_i = [\text{H}_2\text{SO}_4]$).

[14] Capillarity approximation is implied in the kinetic model as the Kelvin equation is used to calculate the compositions and evaporation coefficients of small clusters. Capillarity approximation may be not valid for clusters containing a few molecules. Nevertheless, the appropriateness of treating binary H$_2$SO$_4$-H$_2$O nucleation as quasi-uniary nucleation and using Kelvin equation to calculate evaporation coefficient appears to be supported by the good agreement of the nucleation rates predicted based on the kinetic quasi-uniary model with recent experimental results [Yu, 2005a, 2006].

[15] In the kinetic quasi-uniary nucleation model, the contribution of H$_2$O to nucleation is through the hydration of H$_2$SO$_4$ clusters (or modification of the cluster compositions) that reduces the H$_2$SO$_4$ vapor pressure over the H$_2$SO$_4$-H$_2$O clusters and hence the evaporation coefficient of H$_2$SO$_4$ from clusters. Similarly, the role of NH$_3$ in nucleation is also to stabilize the cluster and reduce the evaporation coefficient of H$_2$SO$_4$ from clusters by changing the cluster compositions. Thus we can incorporate the effect of NH$_3$ on nucleation in the kinetic model by modifying the evaporation coefficient,

$$\gamma_{THN} = \frac{\gamma_{BHN}}{\gamma_{FNH}},$$

where $\gamma_{BHN}$ and $\gamma_{THN}$ are the evaporation coefficient of H$_2$SO$_4$ molecules from binary H$_2$SO$_4$-H$_2$O and ternary
H$_2$SO$_4$-H$_2$O-NH$_3$ clusters, respectively. $F_{\text{NH}_3}$ is the NH$_3$ stabilizing factor.

With evaporation coefficient calculated based on equation (6), we develop a kinetic quasi-unary H$_2$SO$_4$-H$_2$O-NH$_3$ nucleation model that simulates the ternary nucleation kinetically by solving equations (3)–(5). The kinetic model is a new approach to simulate THN, and it captures the main physics of the THN that H$_2$SO$_4$ is the principal nucleation specie dominating the cluster growth (condensation and evaporation), while H$_2$O and NH$_3$ serve as secondary species influencing the evaporation coefficient of H$_2$SO$_4$ from clusters.

The difficult task of the kinetic model is to determine $F_{\text{NH}_3}$, which is likely a function of cluster size ($i_a$), composition, T, RH, [NH$_3$], etc. To properly define $F_{\text{NH}_3}$, one needs to know the thermodynamic data regarding the ternary system and small molecular clusters.

As a preliminary investigation, we derive the possible range of $F_{\text{NH}_3}$ by constraining the model-simulated nucleation enhancement with those observed in the experimental studies. Here we define nucleation enhancement (NE) as the ratio of steady state nucleation rates (at a given fixed [H$_2$SO$_4$]) in the presence of NH$_3$ (ternary) to those in the absence of NH$_3$ (binary). Figure 3 shows the values of NE as a function of [H$_2$SO$_4$] corresponding to the conditions in the laboratory study of Ball et al. [1999] (T = 295 K, RH = 5% and 15%). The symbols are NE values derived from experimental data of Ball et al. [1999]. The lines are NE calculated based on our kinetic ternary and binary models, representing three different values of $F_{\text{NH}_3}$, (1.1, 1.3, and 1.5). It is clear from Figure 3 that $F_{\text{NH}_3}$ value of ~1.3 gives nucleation enhancement close to the observed values. In other words, the experimental studies suggest that at the presence of NH$_3$, the mean evaporation coefficient of sulfuric acid molecules from clusters is reduced only by a factor of around 1.3.

With the NH$_3$ stabilizing effect derived from experimental studies, we can explore the nucleation rates in the presence of NH$_3$ in the boundary atmosphere. We should emphasize that $F_{\text{NH}_3}$ in ambient atmosphere may be quite different from that derived via experiments as $F_{\text{NH}_3}$ may depend on T, RH, and [NH$_3$]. To be conservative, we use $F_{\text{NH}_3}$ = 1.5. Figure 4 is the kinetic quasi-unary H$_2$SO$_4$-H$_2$O-NH$_3$ nucleation rate contours in the RH versus [H$_2$SO$_4$] planes at T = 280 K and T = 295 K. In the boundary atmosphere, [H$_2$SO$_4$] is generally lower than 10$^4$ cm$^{-3}$. It is clear from Figure 4 that the ternary nucleation rates with NH$_3$ stabilizing factor ($F_{\text{NH}_3}$) derived from experimental results are negligible in the boundary atmosphere.

Obviously, there exist uncertainties in the calculated nucleation rates in Figure 4 as a result of uncertainties in $F_{\text{NH}_3}$. In the ambient atmosphere, [NH$_3$] can range from sub-ppt level to ppb level. While the effect of [NH$_3$] on $F_{\text{NH}_3}$ remains to be investigated, existing experimental studies [Nolan, 1987; Kim et al., 1998; Ball et al., 1999] indicate that the nucleation enhancement is not very sensitive to [NH$_3$]. For example, there is no significant difference in the nucleation rate enhancement between the measurements of Ball et al. [1999] and Kim et al. [1998], though one used ppt level [NH$_3$] while the other used ppm level [NH$_3$] (see Figure 3). No obvious change in the measured new particles for NH$_3$ concentrations range from ~50 ppb to 1 ppm was observed in the laboratory investigation of Nolan [1987] of particle formation by photo-oxidation of SO$_2$ with OH radical in the presence of H$_2$O and NH$_3$. In the ambient atmosphere, RH is generally higher and [H$_2$SO$_4$] tends to be much lower than what used in the laboratory studies shown in Figure 3. The evaporation coefficient of H$_2$SO$_4$ molecules from ternary H$_2$SO$_4$-H$_2$O-NH$_3$ clusters should be independent of [H$_2$SO$_4$]; thus the difference in [H$_2$SO$_4$] should not cause change in $F_{\text{NH}_3}$. As to RH, both measurements of Ball et al. [1999] and Kim et al. [1998] indicate the effect of NH$_3$ is reduced as RH increases. Thus using the $F_{\text{NH}_3}$ derived at lower RH may overpredict the NH$_3$ enhancement at higher RH. On the basis of these analyses about the possible difference between $F_{\text{NH}_3}$ derived from experiments and in the real
atmosphere, we may conclude that the nucleation rates shown in Figure 4 are unlikely to underpredict too much the real ternary nucleation rates as long as there is no significant error in the experimental results which indicate less than two orders of magnitude enhancement in the nucleation rates and a smaller enhancement at larger RH. The density functional theory (DFT) study of Ianni and Bandy [1999] suggests that NH$_3$ is not able to neutralize and stabilize H$_2$SO$_4$ dimers. As a sensitivity study, we simulate the effect of ammonia stabilization on nucleation for two different cases: Case 1 assumes that clusters of all sizes are stabilized by the same $F_{\text{NH}_3}$ while case 2 assumes that only clusters containing more than 10 H$_2$SO$_4$ molecules (i.e., $i_a > 10$) are stabilized (by $F_{\text{NH}_3}$).

Figure 6 presents the simulated nucleation enhancement factor under different values of $F_{\text{NH}_3}$ (3, 30, 300; corresponding to different degree of neutralization, see Figure 5) for the two cases at RH = 5% (Figure 6a) and RH = 15% (Figure 6b). The values observed by Ball et al. [1999] are also shown for comparison. It is obvious from Figure 6 that the nucleation should be enhanced significantly if the small clusters are neutralized and stabilized same as bulk solution (case 1). The nucleation enhancement is dramatically reduced if we assume that small clusters (in this case $i_a \leq 10$) are not neutralized and stabilized by ammonia (case 2). Comparison with the observation of Ball et al. [1999] (and those of Kim et al. [1998], Christensen et al., [1994], and Diamond et al. [1985] as well) suggests that

![Figure 4](image1.png)

**Figure 4.** The contours of kinetic H$_2$SO$_4$-H$_2$O-NH$_3$ nucleation rates in the RH versus [H$_2$SO$_4$] planes at (a) T = 280 K and (b) T = 295 K. The nucleation rates are calculated with the kinetic quasi-unary H$_2$SO$_4$-H$_2$O-NH$_3$ nucleation model with ammonia stabilizing factor constrained by experimental results.

![Figure 5](image2.png)

**Figure 5.** The values of $F_{\text{NH}_3}$ for bulk ternary solution derived from the data of Marti et al. [1997]. $F_{\text{NH}_3}$ is $\sim 3$ when ionic ratio is less than 0.5 but increases to $\sim 30$ and $\sim 300$ when ionic ratio reaches 0.8 and 1.0, respectively. Figure 5 also indicate that $F_{\text{NH}_3}$ tends to decrease as RH increases. It should be noted that $F_{\text{NH}_3}$ shown in Figure 5 is for bulk solution and it is not clear if ammonia can neutralize and thus stabilize small sulfuric acid clusters in a similar way.
the neutralization and stabilization of small prenucleation sulfuric acid clusters by ammonia are probably very limited. Otherwise, much more significant enhancement in nucleation rates at the presence of ammonia should be detected in the laboratory experiments.

4. Summary and Discussion

[23] On the basis of the classical THN theory, the presence of ppt level NH3 concentration significantly enhances the nucleation rates. Several experimental investigations on the possible role of NH3 in enhancing the H2SO4-H2O homogeneous nucleation were reported in the literature; however, the classical THN theory has never been assessed quantitatively against these experimental results. In this study we compare the NH3 enhancement derived from reported experiments with that predicted based on the recent version of the classical THN model.

[24] We find that the differences between results observed and predicted are huge. The classical THN theory predicts up to around 30 order of magnitude enhancement in the nucleation rates when ppt level of ammonia is added to the binary system. However, the existing laboratory measurements indicate only one to two orders of magnitude enhancement in the nucleation rates when NH3 at concentrations ranging from several ppt to several ppm is added to H2SO4-H2O or SO2-H2O system. To predict nucleation rates in similar range to those observed in the laboratory, the THN theory requires much lower concentrations of H2SO4 (about 3 orders of magnitude smaller than the corresponding [H2SO4] used in the experiments). The other significant difference between the THN theory and measurements is the opposite dependence trends of ternary nucleation rates on RH. THN theory predicts a decrease in nucleation rates as RH increases but to the contrary, the measurements indicate an increase in nucleation rates with increasing RH.

[25] Since experimental results are probably more reliable than the theoretical model, we develop a kinetic THN model so that the NH3 enhancement effect derived from the experimental results can be taken into account. Our preliminary investigations using the kinetic THN model constrained by the experimental results indicate a negligible contribution of THN to new particle formation in the

Figure 6. Simulated nucleation enhancement factor under different values of $F_{NH3}$ (3, 30, 300; corresponding to different degree of neutralization as shown in Figure 5) for two cases at (a) RH = 5% and (b) RH = 15%. Case 1 assumes that clusters of all sizes are stabilized by the same $F_{NH3}$, while case 2 assumes that only clusters containing more than 10 H2SO4 molecules are stabilized (by $F_{NH3}$).
boundary atmosphere. While there exists uncertainty in the calculated nucleation rates based on the kinetic THN model, our analysis suggests that the kinetic nucleation rates are unlikely to underpredict too much the real ternary nucleation rates as long as there is no significant error in the experimental results which indicate less than about two orders of magnitude enhancement in the nucleation rates and a smaller enhancement at larger RH.

[28] Our conclusion about the negligible contribution of THN to new particle formation in the boundary atmosphere is consistent with the density functional theory (DFT) study of Ianni et al. [1999], who found that NH3 is not able to stabilize H2SO4 dimers and concluded that NH3 appears to have no role in the initialization of new particles in the atmosphere. On the other hand, equilibrium thermodynamic study based on liquid droplet model indicates that in the presence of small ammonia concentrations, H2SO4 vapor molecules in the lower atmosphere may be bound to stable ammonia-bisulfate clusters [Vehkamäki et al., 2004]. It remains to be investigated whether H2SO4 molecules in the lower atmosphere are bound to stable ammonia-bisulfate clusters or not. Nevertheless, Vehkamäki et al. [2004] suggest that the formation of stable ammonia-bisulfate may actually inhibit the participation of H2SO4 in nucleation.

[27] The classical THN theory has been applied to interpret some observed nucleation events in the boundary atmosphere. For example, significant nucleation events were frequently observed during the 1999 New Particle Formation and Fate in the Coastal Environment (PARFORCE) coastal field campaign at Mace Head [O’Dowd et al., 2002a], and Kulmala et al. [2002] concluded that all particle formation events observed at coastal sites can be initiated by ternary nucleation of H2SO4-H2O-NH3. More recently, frequent regional scale particle nucleation events were observed during the Pittsburgh Air Quality Study (PAQS) [Sturin et al., 2004; Zhang et al., 2004a], and Gaydos et al. [2005] argued that classical THN model gives excellent model-measurement agreement. However, our conclusion about the negligible contribution of THN to new particle formation in the boundary atmosphere, if confirmed, may suggest that mechanisms other than THN are responsible for these observed nucleation events. It appears that the new particle formation observed during PARFORCE is associated with the nucleation involving iodine-containing vapors [O’Dowd et al., 2002b]. Using an updated version of ion-mediated nucleation (IMN) model, Yu et al. [2004] found that IMN mechanism appears to be able to explain the nucleation observed during PAQS. Our updated IMN model (F. Yu, manuscript in preparation, 2006) simulates explicitly the growth and evaporation of both charged and neutral clusters with size dependent growth and evaporation coefficient calculated with recently developed schemes [Nadykto and Yu, 2003; Yu, 2005a, 2005b, 2006]. In addition to ions, certain organic species may also enhance the nucleation rates [Zhang et al., 2004b]. Further investigations are needed to determine the relative contributions of various nucleation mechanisms to new particle formation under different atmospheric conditions.

[28] With regard to the role of NH3 in stabilizing H2SO4-H2O clusters, there is another experimental study reported by Hanson and Eisele [2002] who found the enhancement in the formation of small clusters (clusters containing 2–6 H2SO4 molecules) at the presence NH3. Since the nuclelated particles were not directly measured in the study of Hanson and Eisele [2002], and due to the limitation and uncertainties of the measurements, it is hard to determine to what degree the presence of NH3 enhanced the nucleation rates. Nevertheless, a careful analysis of Hanson and Eisele’s [2002] measurements may provide important information to constrain $F_{\text{NH3}}$ (especially the dependence of $F_{\text{NH3}}$ on the cluster sizes).

[28] The lack of reliable thermodynamic data is a problem for both classical and kinetic ternary nucleation model. The classical model uses the thermodynamic data of bulk solution calculated from thermodynamic multicomponent solution model. It is not clear how accurate the approximation to apply bulk properties to small ternary prenucleation clusters tends to be. Since the kinetic model explicitly simulates the evolution of clusters starting from monomers, it has the capability to take the advantage of bonding thermodynamic data of small clusters, which can be derived from density functional theory study [Ianni and Bandy, 1999] and prenucleation cluster measurements [Hanson and Eisele, 2002]. The kinetic model also enables us to make use of the experimental results to constrain the model. For example, instead of evaluating the Kelvin equation to calculate the evaporation coefficient for small molecular clusters, the thermodynamic data can be derived from DFT or other molecular level computations or experimental results [e.g., D’Auria et al., 2004]. It will be difficult for the classical nucleation model to take into account such particular information about small cluster formation because the classical model assumes that the equilibrium concentrations of critical clusters are achieved instantaneously at given conditions, and it does not explicitly consider how these critical clusters are formed.

[30] While ammonia is known to be able to efficiently neutralize the acid solution, the efficiency of ammonia in stabilizing the small acid clusters and thus enhancing the nucleation rates remains to be investigated. As we illustrate in this paper, classical THN predictions conflict with experimental results. Comparison of our simulations based on the kinetic model with the observation of Ball et al. [1999] (and those of Kim et al. [1998], Christensen et al. [1994], Diamond et al. [1985] as well) suggests that the neutralization and stabilization of small prenucleation sulfuric acid clusters by ammonia are probably very limited. Obviously, more research is needed to quantify the real role of NH3 in nucleation. Well-controlled laboratory experiments are the most useful tool to determine the magnitude of enhancement in nucleation rates when NH3 is added to the binary system. Measurements of prenucleation clusters as well as DFT study of ternary clusters can provide important data to constrain $F_{\text{NH3}}$ and to improve the kinetic quasi-unary H2SO4-H2O-NH3 nucleation model. It should also be noted that NH3 molecule interacts strongly with ions due to its high dipole moment and is likely to be a key component of small ion clusters in the boundary atmosphere. Since NH3 can stabilize small clusters, it could also enhance the ion-mediated nucleation. The possible role of NH3 in nucleation via ion-mediated nucleation of H2SO4-H2O-NH3 remains to be investigated.
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References


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