Homogeneous Ternary H_2SO_4–NH_3–H_2O Nucleation and Diesel Exhaust: a Classical Approach

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Abstract

The classical nucleation theory was used to model ternary nucleation at temperatures and concentrations observed in diluting diesel exhaust. The nucleation rate does not markedly depend on the NH_3 concentration below the level of 0.8 ppb, with the binary H_2O–H_2SO_4 mechanism dominating. This rules out the effect of dilution air ammonia levels on nucleation mode formation in most cases. On the other hand, with high NH_3 concentration in the case of SCR (Selective Catalytic Reduction) technology, we predict a dependence between the ammonia slip and the nucleation mode concentration.

Keywords: Ternary nucleation; Diesel exhaust; Ammonia slip; Aerosol emissions.

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INTRODUCTION

Fine and ultrafine particles emitted by engines cause a significant risk to human health (e.g. Donaldson *et al.*, 1998), thus making the study of diesel particle emission a current topic for the last decade. Exhaust particle size distribution is typically formed by two modes. The solid soot mode, the particles of which may have adsorbed semi-volatile compounds, ranges between 40–150 nm. The dependence of the soot mode on engine parameters and its physical and chemical properties are understood quite well (e.g. Kittelson 1998; Tobias 2001). Nucleation mode particles are composed of more volatile material than the soot particles and usually have sizes below 30 nm. The chemistry and formation processes of nucleation mode have been studied somewhat less and are not yet fully understood. In many cases, the mode is formed due to the homogeneous nucleation of sulphuric acid and water, later followed by condensation of sulphuric acid, water and semi-volatile hydrocarbons. The nucleation occurs during the dilution of exhaust gas. Therefore, different dilution and cooling conditions greatly affect the particle formation (e.g. Mathis *et al.,* 2004). However, there are measurements reported in the literature where the nucleation mode concentration does not depend on sulphuric acid concentrations in the exhaust (e.g. Rönkkö *et al.,* 2006). In addition, using the classical nucleation theory, Lemmetty *et al.* (2006) infer that the nucleation mode observed by Vaaraslahti *et al.* (2004) cannot be caused by the sulphuric acid concentrations present in the exhaust stream.

The experimental evidence suggests that not all diesel exhaust nucleation can be explained by binary water–sulphuric acid mechanisms, therefore other nucleating species must be involved. In addition to water and sulphuric acid, one of the most important inorganic semi-volatile species in diesel exhaust and atmosphere is ammonia. In contrast, efforts in atmospheric science to explain observations have introduced a third nucleating component, most often ammonia (e.g. Kulmala, 2000). Its ternary nucleation with sulphuric acid and water has been modelled by Napari *et al.* (2002a and 2002b) and Anttila *et al.* (2005). The similarity of the basic processes governing diesel exhaust nucleation and atmospheric nucleation leads to a question of whether ammonia present either in the dilution air or in the exhaust may also influence nucleation in the diesel exhaust. Some experimental evidence supports such a hypothesis: Grose *et al.* (2006) measured the volatility of liquid diesel nanoparticles and observed that they behaved like neutral sulphate solutions. This is reminiscent of the current idea of atmospheric nanoparticles consisting of ammonium sulphate (e.g. Kulmala *et al.*, 2004).

The study of ternary nucleation in conditions relevant to the dilution of diesel exhaust has so far been hampered by problems in the classical model. The model published by Napari *et al.* (2002a) gave unrealistically high nucleation rates even in ambient conditions, which clearly made the study of diesel exhaust conditions unfeasible. The model proposed by Anttila *et al.* (2005), on the other hand, gives even more than 20 orders of magnitude lower nucleation rates than the

Napari *et al.* (2002b) model; the reason being that the new model takes into account the effect of stable ammonium bisulphate clusters. However, even this model suffers from numerical problems at high ammonia concentrations. In this paper, we use an improved version of the model to calculate the nucleation rate in conditions applicable to diesel exhaust.

Lemmetty *et al.* (2006) used water and sulphuric acid concentrations estimated from stoichiometry to calculate the total nucleated particle concentration as a function of different dilution–cooling conditions. However, this approach becomes impractical with the introduction of ammonia into the model, requiring us to set fixed ammonia levels in order to study different dilution and cooling conditions. Yet, with the exception of Selective Catalytic Reaction (SCR) technology, exhaust ammonia concentrations are unknown. It is even conceivable that ammonia levels in urban dilution air are higher than in raw exhaust. In this case, ammonia in dilution air might have an effect on exhaust nucleation. In response to these observations, we use the classical nucleation model for a large number of different, equally possible concentration combinations of the reacting species to obtain an overall view of the effect of ammonia on the diesel exhaust nucleation.

MODEL

We used the model of Anttila *et al.* (2005) to study the ternary nucleation of the H_2O–H_2SO_4–NH_3 system. Details of this model can be found in Napari *et al.* (2002b). We will only outline here the main features of the model and the improvements introduced to apply it to the diesel exhaust nucleation.

First, the composition and radius of the critical cluster is solved from three simultaneous Kelvin equations, one for each component. According to the classical nucleation theory, the nucleation rate is given by equation:

$$J = \frac{|\lambda|}{\sqrt{-|\mathbf{D}|\pi}} F^e \exp\left(\frac{-\Delta G^*}{k_b T}\right) \tag{1}$$

where ΔG^* is the work of formation of the critical cluster, k_b is the Bolzmann constant, T is temperature. F^e is a normalization constant;

$$F^e = \rho_k^f \exp\left(\frac{-\Delta G_{0,1,0}}{k_b T}\right) \tag{2}$$

where $\rho_k{}^f$ is the number concentration of the free sulphuric acid molecules in the system and $\Delta G_{0,1,0}$ their Gibbs free energy of formation, non-zero according to the classical theory. This choice of parameter F^e ensures that the model gives a correct number concentration for free sulphuric-acid molecule concentration. The matrix **D** in equation (1) is a product of a matrix formed from the second derivatives of the formation energy evaluated at the critical cluster size, and a matrix containing kinetic growth rates. λ is the negative eigenvalue of matrix **D**. In the earlier work, λ was assumed to have the smallest absolute value of the three eigenvalues of matrix **D**. In the improved model, a numerical error in the calculation procedure of λ was corrected to actually find the negative eigenvalue, if one exists.

Classical nucleation theory assumes macroscopic thermodynamic parameters to describe molecular size clusters. The predictive power of classical nucleation theory is known to be somewhat limited; especially since the temperature dependency of the nucleation rates is often stronger than what experiments suggest. However, it still presents a general and usable theory for predicting nucleation rates in a highly non-ideal system such as a water-sulphuric, acid-ammonia mixture. Apart from being compromised by the assumptions inherent in classical nucleation theory, the validity of our results relies on the correctness of the activity, density and surface tension fits. These fits have been extrapolated from a fairly limited amount of experimental data. The models may not be strictly applicable to highly concentrated solutions and, since some of the clusters predicted by the nucleation model are practically dry, we carefully tested the behavior of the thermodynamic model from dilute solutions up to where only a very small amount of water is present. The resulting activity curves show no discontinuities or sudden changes of slope, which could indicate a break-up of the model.

It is crucial for any modelling effort to have a good estimate of the component species concentrations. From the fuel and lubricant sulphur contents, we can have a good estimate on the overall sulphur concentration of diesel exhaust, most of which will exit the engine as SO_2. However, an oxidizing exhaust after-treatment system can convert part of the SO_2 into H_2SO_4, and store part of the H_2SO_4 for release at a later time. The extent of these processes at different engine loads is unknown. The lower limit of the H_2SO_4 concentration is estimated from the commercial fuels used presently in Nordic countries, which may have fuel sulphur contents as low as 1 ppm. For the lower limit, we assume a SO_2-to-H_2SO_4-conversion factor of 1%, with no contribution from lubricant oil. This corresponds to the lower limit of the conversion factor measured by Sorokin *et al.* (2004) for aircraft plumes. The higher limit is obtained from a fuel sulphur content of 400 ppm (representing a high sulphur concentration) with a theoretical conversion factor of 100%. From the stoichiometry, we conclude that sulphuric acid concentrations are between 100 ppt and 10 ppm.

The ammonia naturally present in raw exhaust is a by-product of secondary reactions occurring in the cylinder. Some may also be inherently present in the engine intake air. Since ammonia is

not considered an important emission for diesel vehicles, the actual gas-phase ammonia concentrations in raw exhaust have not been measured for engines without a urea catalyst. In combustion processes, nitrogen compounds figure only in the secondary reactions. Even in these reactions, the main product species are nitrogen oxides (Seinfeld and Pandis 1998, pp. 70–71 and 74–75). Therefore, stoichiometry cannot be used to estimate exhaust ammonia concentrations. It is quite possible that the exhaust ammonia concentration is at the same level, or even below, atmospheric concentrations, which in a clean environment, range from 0.1-10 ppb. In this case, even ammonia from polluted dilution air might play a role in the nucleation process. On the other hand, with SCR (Selective Catalytic Reduction) technology, urea injected into the catalyst is used to reduce NO_x into nitrogen. The urea is first converted into ammonia, which then reduces NO_x. For nitrogen monoxide, the reactions are:

$$
\begin{aligned}
H_2N - C(O) - NH_2 + H_2O &\rightarrow 2NH_3 + CO_2 \\
4NH_3 + 4NO + O_2 &\rightarrow 4N_2 + 6H_2O
\end{aligned}
\tag{3}
$$

In a phenomenon called ammonia slip, some ammonia always escapes into the exhaust (Schnelle, 2001, Ch. 17.2.2.2). In a study considering current technology, Koebel *et al.* (2004) observed an ammonia slip of 3–10 ppm. Therefore, exhaust ammonia concentrations are between 1 ppt and 10 ppm.

   Water concentration in the exhaust can be estimated from stoichiometry. For the stoichiometric air excess ratio of 1.36, which represents a realistic load, water concentration is around 8%. Choosing the water concentration is somewhat problematic because the cooling and dilution experienced by the exhaust change it constantly; but it is between 10^{22} and 10^{24} m^{-3}. After the tailpipe, ammonia originating from the engine, and sulphuric acid and water concentrations are reduced by the dilution, which is a complicated dynamical process. Nucleation takes place during this process locally, most likely in the micro-scale boundary layer of cool air and hot exhaust (Lamminen *et al.*, 2005). However, water and ammonia are especially present even in the dilution air, and their introduction into the exhaust stream may affect nucleation.

RESULTS AND DISCUSSION

   We studied the nucleation rate as a function of ammonia concentrations between 10^{13}/m^3 and 10^{19}/m^3, sulphuric acid concentrations between 10^{15}/m^3 and 10^{19}/m^3, and water vapor concentrations between 10^{22}/m^3 and 10^{24}/m^3. These ranges represent approximately the limits outlined in the preceding section. As noted by Lemmetty *et al.* (2006), the nucleation mainly takes place at fairly low temperatures, around 300–320K. Conveniently, this falls into the upper

range of the thermodynamic model of Clegg *et al.* (1999), which was used in the nucleation model to calculate equilibrium partial pressures over the ternary mixture.
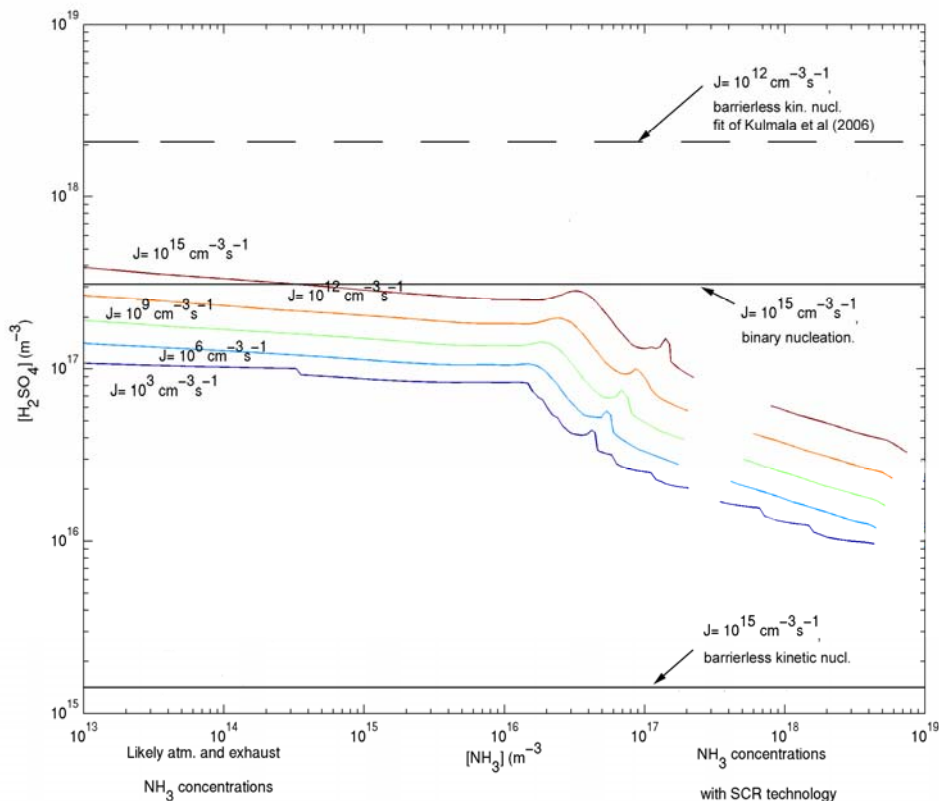

Fig. 1. The contours of nucleation rate at 310K and RH of 35%. The threshold H_2SO_4 concentrations start to decrease at a NH_3 concentration of $10^{16}/m^3$. The breaks in the contours result from the failure of the classical nucleation theory. The break around ammonia concentration $10^{17}/m^3$ is caused by the failure of the coinciding surface of tension and equimolar surface assumption, the break on the extreme right by the failure of the chemical model. The straight lines show the $J = 10^{15}/cm^3 *s$ threshold for the binary nucleation model of Vehkamäki *et al.* (2003) and the barrierless kinetic nucleation of Kulmala *et al.* (2006) assuming that the limiting step is collision between two sulphuric acid molecules. The dashed line represents the kinetic model with collision frequency fitted to atmospheric observations.

   The main features of the result can be seen from the Fig. 1 which presents the contour plot of the nucleation rate as a function of H_2SO_4 and NH_3 for the RH of 35% at a temperature of 310K. As in all other nucleation studies, we can see that the contours are concentrated in a small part of the whole Fig. 1. This is an indication of the steepness of the nucleation rate as a function of vapor concentrations. When the NH_3 concentration is below $10^{16}/m^3$, the contours are almost horizontal, suggesting that in this region, NH_3 has almost a negligible effect on nucleation.
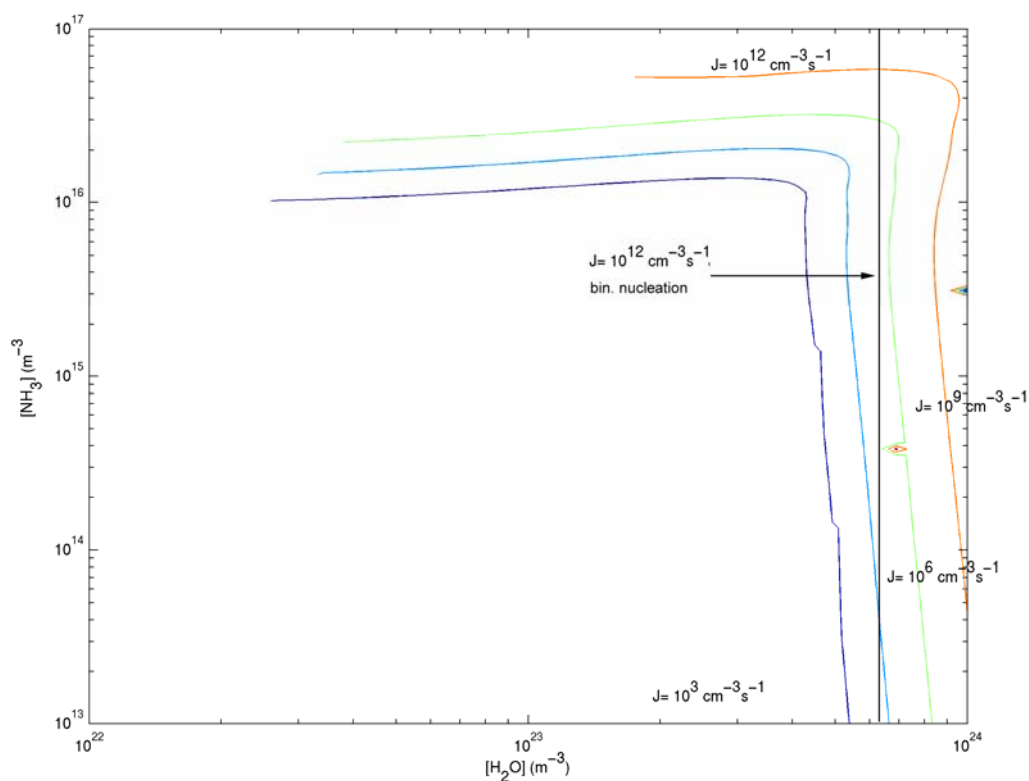
Fig. 2. The contours of nucleation rate at 310K and H_2SO_4 concentration of $1 \cdot 10^{17}/m^3$. The chemical model for the equilibrium partial pressures is not valid on the left-hand side of the figure due to the alkalinity of the critical cluster, so the contours are not drawn in this region. The straight line shows the $J = 10^{12}$ cm^3/s threshold for binary water-sulphuric acid nucleation model of Vehkamäki *et al.* (2003).

In Fig. 2, the sulphuric acid concentration is $10^{17}/m^3$ and NH_3 and H_2O concentrations are varied while the temperature is again 310K. In this case, we clearly see two areas: NH_3 is the controlling species of the nucleation for water concentrations below $4 \cdot 10^{23}/m^3$, and water is the controlling species at higher water concentrations. After 1:10 dilution with dry air, the exhaust has a water concentration of approximately 0.8%, which corresponds to a concentration of $1.8 \cdot 10^{23}/m^3$ at 310K. This shows that the ammonia-controlled region can be reached in realistic situations. In the transition region at the upper right-hand corner of the figure, NH_3 and H_2O both have an effect on nucleation rate, and water vapor concentration seems to have a slight inhibiting effect on the nucleation rate. The inhibiting effect arises from hydrate formation, with an increasing amount of water molecules binding acid and/or ammonia molecules effectively, and thus reducing their potential for nucleation. The nucleation enhancement due to increased water concentration does not always compensate for the hydration effect, as seen earlier also in binary sulphuric acid-water case (Noppel, 2002). In the regime where water is the controlling species,

the nucleation is essentially binary nucleation of water and sulphuric acid. In the area where the ammonia is the controlling species, the addition of ammonia molecules to the cluster is the limiting step for particle formation.

The contours in Figs. 1 and 2 have gaps in them: in these regions the classical model breaks down. The most important reason for the breakdown is the assumption that the two dividing surfaces—the surface of tension and the equimolar surface—coincide. This leads to negative molecular numbers for the critical cluster, and results in the model being unusable. The observed failure of the classical nucleation theory is a well-known phenomenon, and has been encountered in the literature before; the most notable example being the ethanol–water system (e.g. Viisanen *et al.*, 1994, further reviewed by Vehkamäki 2006, pp. 124–125). This mechanism of model breakdown dominates the breakdown regimes in the middle of Fig. 1. Another problem appears if the number of ammonia molecules in the critical cluster exceeds the number of sulphuric acid molecules by a factor of two. In this case, the equilibrium vapor pressure model of Clegg *et al.* (1999), which assumes an acidic solution, is not usable. This is the reason for the failure of the model on the extreme right of Fig. 1 and extreme left of Fig. 2.

We calculated the nucleation rates also at temperatures 320K and 300K. At 320K, the contours of constant nucleation rates move towards higher, and at 300K towards lower species concentrations, but the qualitative properties of contours are retained. The level of ammonia concentrations where the theory breaks down due to the dividing surface assumption moves similarly with the temperature.

For comparison the nucleation rate was also calculated with the binary water and sulphuric acid model behind the parameterization of Vehkamäki *et al.* (2003) and the kinetic nucleation model, assuming that the limiting step in nucleation is the collision of two sulphuric acid molecules. At low ammonia concentrations ($10^{13}/m^3$), the predictions of the ternary model and the binary nucleation model of Vehkamäki *et al.* (2003) agree quite well, as can be seen in Figs. 1 and 2. When we calculate the nucleation rate from barrierless kinetic nucleation of sulphuric acid (e.g. Kulmala *et al.,* 2006), we get unrealistically low threshold concentrations. However, by fitting the collision frequency to experimental data, even the kinetic theory can be modified to give more reasonable nucleation rates, and the dependency of the nucleation rate on vapor concentrations will not be as sharp as in the classical nucleation theory. Such fittings have been done, for example, by Vouitsis *et al.* (2005) and Kulmala *et al.* (2006). In this paper, such a fit was not attempted, owing to the lack of experimental data applicable to concentrations present in diesel exhaust; however, for comparison we also plotted the kinetic theory results using the atmospheric collision frequency (10^{-18} m^3/s) of Kulmala *et al.* (2006)

Our results thus indicate that below the ammonia concentration of $2 \cdot 10^{16}$ molecules/m^3 (0.8 ppb), changes in the ammonia concentration do not change the sulphuric acid concentrations required for a certain nucleation rate by more than a factor of 2. At higher concentrations,

ammonia has a marked effect, decreasing the H_2SO_4 threshold concentration by an order of magnitude at ammonia concentrations of approximately 10^{19} m^{-3} (0.4 ppm). These concentration limits mean that the ammonia concentrations usually present in urban dilution air have little or no effect on the nucleation of H_2SO_4 and H_2O, if the ammonia output of the engine is negligible. On the other hand, when using SCR technology the ammonia concentrations are in the ppm range due to the catalyst ammonia slip and the nucleation rate may be affected by the exhaust ammonia.

CONCLUSIONS

The ternary model based on classical nucleation theory and presented by Anttila *et al.* (2005) was numerically refined to work at relatively high temperatures and vapor concentrations relevant to diluting diesel exhaust. The results show that the ammonia levels usually present in dilution air have little effect on the nucleation in the exhaust. The same is true for the low exhaust ammonia levels of the traditional diesel engine technology. On the other hand, with concentrations typical when using Selective Catalytic Reduction (SCR) technology, ammonia clearly decreases the nucleation threshold concentrations of H_2SO_4. On the basis of classical nucleation theory, experimental dependence between ammonia slip and nucleation mode number concentration should be detectable. In very polluted environments, the effect of atmospheric ammonia may also become important for exhaust nucleation. These predictions provide a way to test the validity of the current classical ternary nucleation theory in conjunction with other dynamometer experiments. For engines without SCR, ammonia should have only little significance to the nucleation rate.

In a general dynamic model of diesel exhaust aerosol, the uncertainties of the nucleation rate calculations are large in any case. At ammonia concentrations likely in the exhaust of engines without SCR after-treatment technology, the dependence of nucleation rates on ammonia is only slight. On the basis of this study, we believe that in general dynamic models, the introduction of ammonia as a nucleating species is not essential to make the model predictions realistic.

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