Tholin Aggregation in Titan's atmosphere: Developing a probabilistic model

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***Abstract*— Titan's climate is dominated by a reddish haze in its atmosphere made of the organic aerosol tholin. This haze is known to influence the climate through temperature control, hydrocarbon production and atmospheric circulation. Because of continuing interest in Titan's tropospheric activity, it is important to understand the production and growth of tholin through the atmospheric layers. The coagulation of tholin is influenced by the cross-sectional area, relative velocity and charge on the aggregates. The aggregates become charged through plasma produced primarily by galactic cosmic rays (GCR) and UV radiation during the nighttime and daytime, respectively. The purpose of this study is to model the formation of tholin molecules in the lower atmosphere of Titan, approximately 100 to 300 km above the surface, using different charging schemes for daytime and nighttime ion production. This is simulated by numerically modeling the growth of three generations of aggregates using different conditions and charging based on the altitude of production for each generation. The preliminary results for the first generation charged by UV radiation are given and compared with measured characteristics of tholin in Titan's atmosphere.**

***Index Terms*—Titan, tholin production, fractal aggregates, dust coagulation**

I. Introduction

INTEREST in Titan, the largest satellite of Saturn, stems both from its being frozen early in its developmental stage due to its immense distance from the sun [1] and its optically thick, hazy reddish-orange atmosphere [2]. This interest was increased when the Huygens probe entered Titan's atmosphere in January 2005 and sent back data on the atmosphere taken during its descent and landing on the surface as part of the Cassini-Huygens mission launched in 1997 [1], [3].

Its similarities and differences to Earth make Titan uniquely appealing to study [1]. Similar to Earth, Titan has an atmosphere and a complex surface geomorphology that has many features common on Earth and other icy satellites, but also many that are unique to Titan [4]. Titan's surface is composed of tectonic, cryovolcanic, and impact cratering features, but also shows evidence of "fluvial erosion" resulting from a hydrological cycle like Earth's but with liquid methane instead of water and aeolian features that result from Titan's thick and dynamic atmosphere [4]. It is these last two characteristics that make the study of Titan's atmosphere of interest to so many. Titan has a "surface modification process" [4] that is, so far, unique in planetary exploration experience. Its terrain is being thinly coated by a gradual, perpetual rain of complex-organic particles from its atmosphere [4]. Thus, much of Titan's weather and surface features are controlled by these aerosol particles, called tholins from the Greek word θόλος meaning "muddy" but also from θολός meaning "dome" because the aerosol forms a muddy or opaque dome over Titan [5]. The production of these tholins is the object of this study.

The production of tholin has been studied from many different perspectives including atmospheric dynamics, chemistry, climatology, and optical properties starting in the late 1970's [5], around the time of the first flyby of Saturn by Pioneer 11. Since then many studies of tholin have been conducted including the aforementioned observations by the Huygens probe, laboratory synthesis, and theoretical models of tholin aggregation in Titan's atmosphere [6].

II. The Tholin Production

Tholin is a polycyclic aromatic hydrocarbon formed by photolysis [7]. Tholin formation begins at high altitudes, around 1000 km above Titan's surface [8]. At this altitude, a concentration of methane and nitrogen molecules is the defining characteristic of the atmosphere [8]. These molecules are bombarded with UV radiation, galactic cosmic rays and free energetic particles which charges the nitrogen and methane molecules [8], [9]. The now charged molecules undergo a series of chemical reactions with the molecules already present in the atmosphere and form distinct species of organic compounds which are further photolyzed by long wave UV rays [8],[10]. This results in a polymerization of C_2H_2 and HCN producing benzene [8]. Benzene continues to react with other complex organic compounds that remain as these compounds become more negatively charged through reactions with free electrons and other ions [8], [10], [11].

These aerosols are then further processed into tholin particles [7], which begin to form at about 400 to 500 km above the surface [11]. The suggested formula for tholin, $(C_{11}N_4H_{14})_n$, compares well with optical properties as observed on Titan [12].

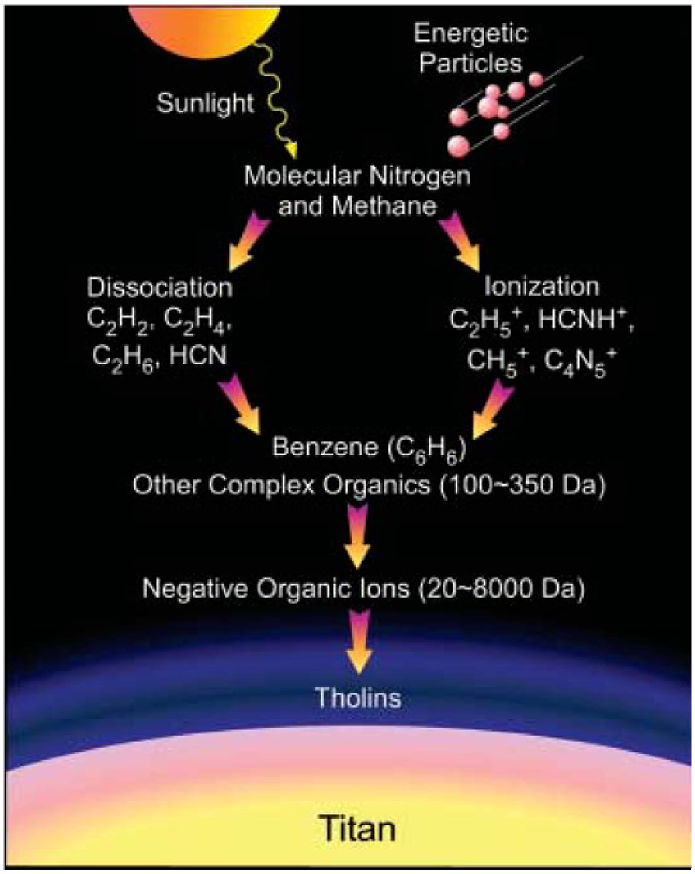

Fig. 1 An illustration of the chemical processes in the upper atmosphere of Titan that leads to the formation of tholin [8].

In Fig. 1 presented above, the steps in the upper atmospheric development of tholin are illustrated beginning with the initial charging of nitrogen and methane molecules by UV radiation and collisions with free particles [8].

Although the chemical process discussed above gives vital information about the tholin formation process, this study is concerned with the associated physical process. Following the model given by [11], we consider the development of tholin with respect to altitude and the aggregate's mass. The formation of tholin molecules is presented in three primary generations based on the size of the aggregate as defined by the number of components contained in the aggregate[6], [11].

The first generation is referred to as embryos. Embryos are the original product of the nucleation of the newly formed aerosols [6]. They are present in all levels of the atmosphere from about 1000 km and down [6], [9]. The term 'aerosol', for the purposes of this work, is interchangeable with the term monomer. Monomers are spherical masses that approximate the smallest tholin aerosols and are assumed to be 0.04 to 0.05 microns in radius [6]. Monomers build up the embryos which are shown to have radii from 0.05 to 0.1 microns [6].

As the embryos grow they naturally begin to settle lower in the atmosphere and collide with other embryos forming larger and heavier aggregates. It has been proposed that these aggregates continue to collide and coagulate with each other and eventually form the last two classes as follows [6]. A second generation is proposed to exist at an altitude of 500 km with a size up to about 800 to 1,800 monomers. Finally, a third generation at an altitude of 200 km consists of aggregates of size up to about 1,500 to 5,000 monomers. It should be noted that some would suggest that the primary production zone for tholin is about 270 ± 40 km which shifts the generation altitudes down to 270 km (first generation/embryos), 200 km (second generation), and about 100 km (third and final generation) [6].

Once the third and final tholin generation has settled into the lower atmosphere, it condenses into a thick layer at about 80 km [6], [7]. Here it dominates the atmospheric activity by filtering UV rays (thus controlling the temperature) and controlling the atmospheric circulation [7]. Because tholin also influences the amount of methane present in the atmosphere, methane clouds are influenced by the distribution of tholin concentrations. The diagram in Fig. 2 shows the atmopheric activity in Titan's lower altitude with respect to height, temperature, and pressure.

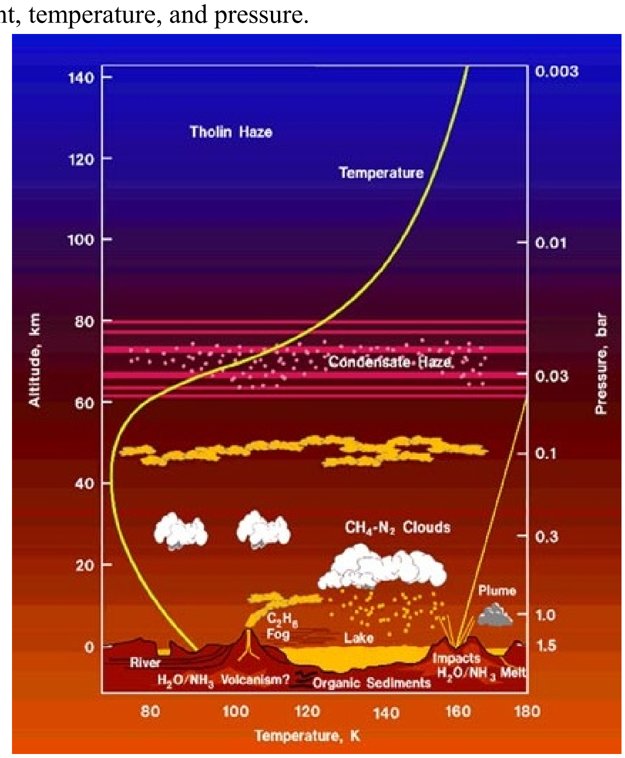

Fig. 2 A diagram illustrating the atmospheric activity in Titan's lower atmosphere with respect to height, temperature and pressure. Also shown are tholin concentrations and suspected topographical features of the surface. [http://www.jpl.nasa.gov/media/cassini-102504/visuals.html]

III. Numerical Model

The model used to simulate the growth process is a version of Aggregate Builder, a computer model developed by Matthews to investigate early stages of planetesimal formation, modified to include height as a parameter value that influences initial plasma parameter values, relative velocities, and particle characteristics appropriate for modeling tholin development on Titan [13].

The general process for aggregate formation follows a simple procedure. An aggregate or monomer with a fixed mass and charge is placed at the origin as defined by its center of mass. An incoming aggregate or monomer is then introduced into the frame with similar set characteristics such as mass, charge, and initial velocity, but with a randomly determined entry position and orientation and a predetermined time step which is based on the velocity. The particles travel towards each other but the reference frame is fixed on the initial aggregate. The program tracks the incoming particle throughout its motion in the frame and as it nears the initial aggregate it checks for a collision. If there is no collision the program then introduces a new aggregate or monomer and the process repeats.

If the particles collide, then they coagulate and are connected. When this happens the new aggregate's characteristics, including the fractal dimension and charge, are calculated. The fractal dimension is calculated using the Hausdorff method whereby the aggregate is placed in a subsectioned cube, and the fractal dimension is calculated by dividing the logarithmic values of the number of subboxes containing portions of the aggregate by the logarithmic value of the quotient of the original cube length with the length of the subboxes.

The charge calculation is done by a modified orbital motion limited theory with a line-of-sight approximation (OML_LOS) [14]. This technique takes into account the fractal aggregate structure, which cannot be approximated as a sphere. Orbital motion limited theory is founded in the assumption that energy and momentum are conserved for impinging current species and that ions and electrons that have encountered potential barriers have been removed from the background Maxwellian distribution [14]. But, as the fractal aggregates grow, OML_LOS uses a line-of-sight approximation determines the surface areas which are blocked by other monomers in the aggregate. Since aggregates are charges through collisions with electrons and ions, it is unnecessary to consider the areas of the fractal aggregate where charging is not possible due to the areas being blocked by parts of the structure [14].

This study also deals with tholin production during the daytime. To accomplish this, UV charging has been added to the charging code with a specified photon flux. This UV aspect also utilizes the line-of-sight approximation since UV radiation cannot charge a blocked portion of the aggregate. UV charging is accomplished by the photoelectric effect and allows for electrons to escape from the aggregate structure or to be recaptured if its path is blocked by another monomer in the aggregate. For nighttime charging, the photon flux is set to zero to indicate no UV charging of the aggregates [15].

The current density for a given species of charged particles is

$$J_0 = n_{\alpha\infty} q_\alpha \int f v \cos\theta \, d^3\vec{v}, \tag{1}$$

where $n_{\alpha\infty}$ is the number density of the plasma species far from the grain, q_α is the charge of the particle species (ion or electron), f is the Maxwellian distribution function, v is the velocity of the particle species (electron or ion), and θ is the angle of incidence with the grain surface[14]. To calculate the photoelectric current, the potential of the grain is found using

$$q_e V_d = k_B T \ , \tag{2}$$

where k_B is Boltzmann's constant and T is the temperature of the plasma [15]. This gives the photoelectric current of

$$\begin{aligned} I &= 4\pi r_p^2 \mu \Gamma & V_d &\le 0 \\ I &= 4\pi r_p^2 \mu \Gamma \, e^{q_e V / k_B T} & V_d &\ge 0 \ , \end{aligned} \tag{3}$$

where Γ is the photon flux and μ is the photo emission efficiency [15].

Plasma conditions determine the velocity involved in the current density coefficient calculations. Therefore, the mass of the ions in the plasma was needed. The atmosphere of Titan is complex in that it contains several different ions which all have different masses but the same charge [16]. An effective ion mass was calculated for each altitude from the mass of the ions present (nitrogenated cations, short chain hydrocarbons and long chain hydrocarbons) and their relative abundances in the atmosphere [16].

Once the charge and fractal dimension have been calculated for the newly formed aggregate, another particle is initialized as the next incoming particle. The process repeats until either an aggregate of the specified size forms or a maximum number of missed collisions is reached.

The relative velocities between the aggregate and the incoming particle are due to Brownian motion and an approximate Maxwell distribution about this Brownian velocity based on the temperature and reduced mass. The mean speed from this distribution is

$$v_d = \sqrt{\frac{8 k_B T}{\pi \mu}} \, , \tag{4}$$

where k_B is Boltzmann's constant, T is temperature, and μ is the reduced mass for the two masses of the aggregates, m_1 and m_2, defined as

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)} \, . \tag{5}$$

The temperature is based on the altitude so that each generation has a different Maxwellian velocity distribution [9].

IV. Method

Using Aggregate Builder, aggregates are made in three generations. Beginning with 0.04 to 0.05 micron sized monomers, the first generation of aggregates is built up to 2 to 15 monomers in size. The growth is considered to take place at 270 km in the altitude and a temperature of 177.5 K. Each incoming monomer has a charge of one electron [6]. Assuming that as the embryos grow in size, they settle lower in the atmosphere, the monomer charge and plasma parameters are updated for the next generation of aggregates. This second generation consists of aggregates up to 200 to 300 monomers and is grown at 200 km with a temperature of 170 K. Repeating the general process, a third generation is assumed to be at 100 km with a temperature of 142 K and built up to size 2,000 to 3,000 monomers. In all cases the plasma parameters, including the ion masses and densities, are calculated from data given by [10] and the temperatures are given by [9].

During the nighttime, charging is accomplished only through plasma produced primarily by galactic cosmic rays (GCR), whereas daytime charging is accomplished by both GCR and UV radiation. The photon flux is taken to be 6.74 x 10^{13} $\frac{photons}{cm^2 \cdot s}$ as calculated for the distance of Titan from the sun.

Finally, the collision data is collected from the aggregate formations. The collision data is a record of whether an incoming particle hit or missed the aggregate. This data is then used to calculate the coagulation kernel in the Smoluchowsky equation,

$$Q(m) = -\int_0^\infty K(m,m')f(z,m)f(z,m')dm' + \frac{1}{2}\int_0^m K(m',m-m')f(z,m')f(z,m-m')dm' \,, \qquad (6)$$

which describes the evolution of particles with a given mass at a specific altitude. Here, f is a function for the density of particles with given masses and altitudes, and K is the coagulation kernel. The coagulation kernel is important since it gives the probability of particles with masses m and m' coagulating [6]. The calculation of this kernel is the ultimate goal of this study.

V. Results and Discussion

Results are shown for only the first generation for the daytime charging class. In order to evaluate the general accuracy of the model, the radius, charge and collision probability of the aggregates are considered. The subsequent preliminary data is presented below in Fig. 3 - 6. The mass, shown in Fig 3, is linear as is expected. The mass is directly proportional to the size of the aggregate. Therefore in the Smoluchowsky equation size can be discussed instead of mass. Fig. 4 shows the expected trend of the radius and that the proposed size of 2 to 15 monomers fits the embryo radius given in [6].

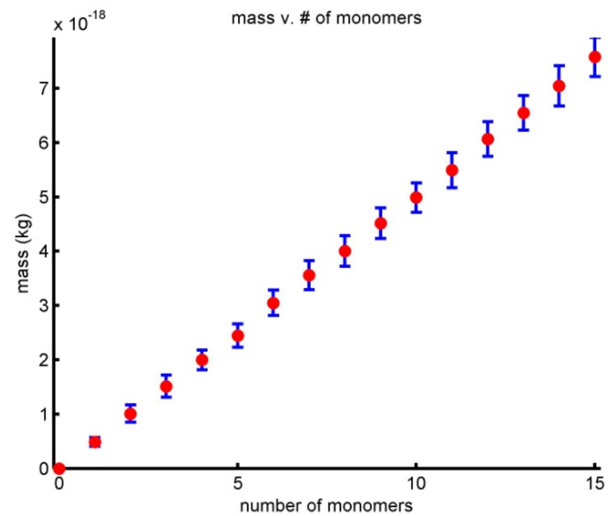

Fig. 3 shows the linear trend of the average mass of an aggregate v. the number of monomers in an aggregate

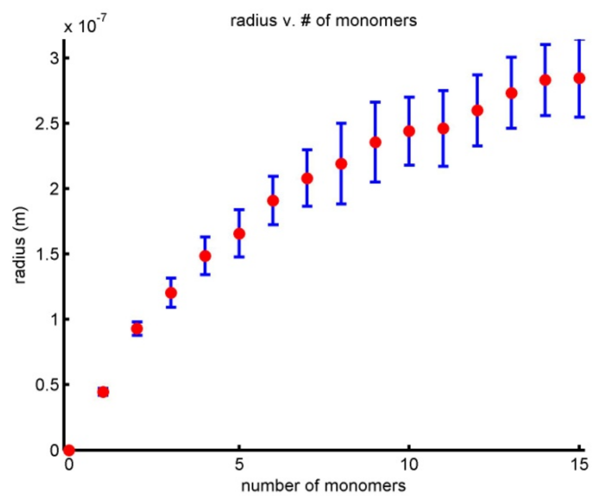

Fig. 4 shows the average radius v. the number of monomers in the aggregate

The charge exhibits interesting behavior as seen in Figs. 5a and 5b. The charge, though initially negative due to the ion charging, becomes less negative as the aggregates grow. Fig. 6 shows the probability that a monomer will collide with a certain size aggregate. Note that this collisional probability follows roughly the same trend as the charge.

Fig. 5a

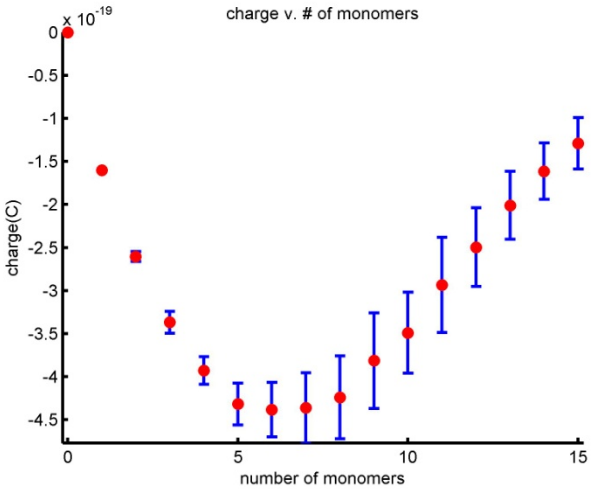

Fig. 5b

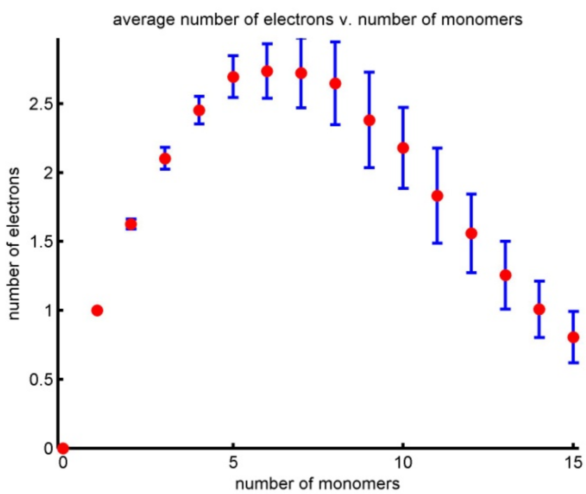

Fig. 5a) shows the average charge of an aggregate v. the number of monomers in an aggregate. b) shows the average number of electrons on an aggregate v. the number of monomers in the aggregate. Note that in a) the charging becomes more positive as the aggregate grows past 6 or 7 monomers.

VI. Conclusions and Future work

The mass and radius act as expected in Fig. 3-4. The UV charging for the first generation is dominant over the ion and electron charging as shown in Figs. 5a and 5b. Fig. 6 shows that the charge of the aggregate is related to the collisional probability. When the aggregate is more positive, the charges repel each other less, which increases the probability of a having a collision. Currently only single monomers are introduced as the incoming particles. For further generations, the collision probability will be plotted against the aggregate size and the incoming particle size.

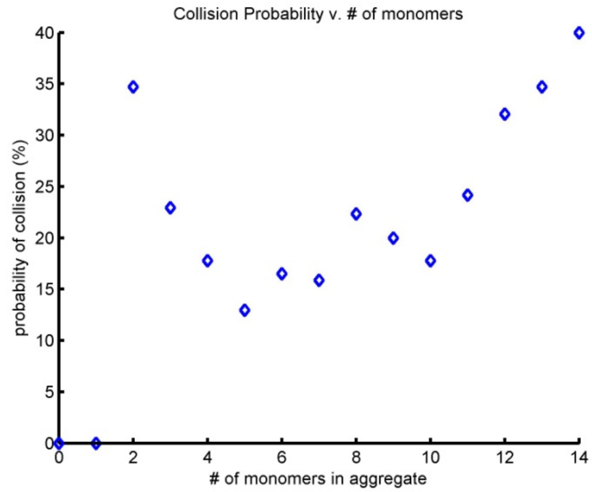

Fig. 6 shows the collision probability v. the number of monomers in the aggregate. Note that it follows roughly the same trend as the charge.

Tholin is an interdisciplinary study in which further research must be done to understand the role it plays in Titan's tropospheric activities. So far in this development of a probabilistic model of the production of tholin, only the first generation in the daytime charging class has been produced. In future works, the second and third generations for daytime charging will be built. Also, we are considering the problem of a nighttime charging class which will require something other than simple Brownian motion to coagulate. Any atmosphere has turbulence which results eddy diffusion. More research will be done regarding the eddy diffusion coefficient and its use in producing higher relative velocities [6]. With these new initial velocities, the first, second, and third generations of nighttime charged tholins will be produced and used to calculate the coagulation kernel in the Smoluchowsky coagulation equation.

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