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Supersaturation on Pluto and elsewhere

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ABSTRACT

The atmosphere of Pluto contains a global thin haze layer, possibly clouds and a variety of gaseous species which may be supersaturated under some conditions. Studies of Pluto climate necessitate a fairly good knowledge of the interactions between gases and aerosols since it has an impact on the vertical profiles of these species and on the fluxes of matter at the planetary scale. In this paper we use the laws of cloud nucleation to evaluate the supersaturation which is needed to trigger condensation. HCN and H_2O can supersaturate by factor from several thousand to several billions depending on the type of nucleation which is used. Other species can supersaturate, but with smaller values of saturation. Gaseous species also found as ices at the surface (e.g., CO, N_2, CH_4) are of special interest. At a surface temperature of 37 K, they can be supersaturated with S between 1.5 to 2 even if condensation nuclei are available in large number. Such supersaturation factors have an impact on fluxes of these species from the surface to the atmosphere.

1. Context of the study

In planetary science, it is frequently assumed that condensation is triggered as soon as saturation is reached. (The saturation rate, S, of a species is the ratio of its partial pressure relative to its saturation pressure). This statement can be a convenient approximation but is not always true. When full microphysical models are used, they can give valuable predictions that differ from simplistic rules. Such models give a self-consistent estimate of droplet size, precipitation, aerosol scavenging and a rigorous evaluation of the actual saturation ratio of species. All these elements further act on the fluxes and budgets that can be studied on a column model or at planetary scale (e.g., Montmessin et al., 2004).

Recent observations of Pluto with New Horizons revealed a tenuous but complex atmosphere, a thin and global layer of haze (Gladstone et al., 2016) and a complex composite surface. Several chemical species, N_2, CH_4, C_2H_2, C_2H_4 and C_2H_6 were observed by the spacecraft (Gladstone et al., 2016; Young et al., 2018) while CO, HCN and also CH_4 were detected with telescopes or radiotelescopes (Young et al., 1997; Lellouch et al., 2011; Lellouch et al., 2017). Photochemical models (Luspay-Kuti et al., 2017; Mandt et al., 2017; Wong et al., 2017) explain observations relatively well and predict additional molecules. A haze microphysical model (Gao et al., 2017) was used to match optical properties of the haze with aggregates of 10 nm-radius spherical grains with a bulk radius of 0.15 µm (Cheng et al., 2017). Aerosols on Pluto are presumably formed by photochemistry in a similar way to those in Titan's atmosphere and are governed by dynamical processes (Bertrand and Forget, 2017; Gao et al., 2017) and, below a certain level, cloud processes are assumed to take place (Wong et al., 2017; Luspay-Kuti et al., 2017). The cloud effect is manyfold : It removes gas and modifies its vertical distribution, it also changes the vertical size distribution of particles by scavenging. These differences induce a modification of the radiative field and of the budget and fluxes of matter at the planetary scale. The models developed so far to understand Pluto microphysics (Gao et al., 2017; Wong et al., 2017; Mandt et al., 2017; Luspay-Kuti et al., 2017 are associated with a cloud model which does not follow the canonical laws of cloud microphysics (Pruppacher and Klett, 1997) and probably has different functional responses than a real cloud microphysical model. Mandt et al. (2017) and Luspay-Kuti et al. (2017) make a clear distinction between a process that they call incorporation of gas molecules by aerosols and condensation that concerns phase change for gases exceeding their vapor pressure. Incorporation is the process that best explains the gas vertical profiles observed by New Horizons. It assumes sticking with Van der Waals forces and then could be associated to physical adsorption. But they do not use the related constraint about the number of available adsorption sites on aerosols, which is limited. If other non-reversible pro-

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cesses are involved instead, this limitation may become irrelevant. Their condensation laws do not follow the canonical laws, but they use a proportionality factor between the loss by condensation and $S-1$ assuming that condensation is triggered for $S>1$. Notably, what Wong et al. (2017) name condensation is related to incorporation. However, classical equations for nucleation and condensation are valid for Pluto and, for instance, are used to describe CO_2 clouds on Mars, in an environment comparable to Pluto's stratosphere, with pressure levels between 10^{-2} and 1 Pa and temperatures between 80 and 120 K (Listowski et al., 2013; Listowski et al., 2014).

A major issue arising from recent works is the radiative equilibrium of Pluto's atmosphere which produces an unexpected temperature profile. At the surface, the temperature was thought to be around 40 K, rising rapidly to 110 K at 50 km and remaining around 100 K at higher altitudes before decreasing to about 70 K at a few Pluto radii (e.g., Zhu et al., 2014). Instead, the temperature drops above 50 km to reach 67 K above 400 km. To explain this temperature profile, an unknown coolant was needed (Gladstone et al., 2016).

A part of the solution may be given with the recent observation of a large amount of *HCN*, that is several orders of magnitude beyond the saturation level (Lellouch et al., 2017). However, this is shown to be not sufficient. From their data, Lellouch et al. (2017) were able to show that *HCN* should be found in two separate layers : In the warm layer of $\simeq$ 110 K around 50 km and at high altitudes above 400 km. At high altitude, the amount of *HCN* needed to explain observations is consistent with very high supersaturations ($S>>1$). This can easily occur above the haze layer, where atmosphere is free of particles (Lellouch et al., 2017). We can then infer that *HCN* condenses onto the aerosols when it is transported downward. In this work we demonstrate that a large supersaturation ratio of *HCN* is expected in Pluto's atmosphere, due its low vapor pressure, even when condensation nuclei are available in abundance. This is consistent with a sharp removal of *HCN* due to aerosols as proposed by Lellouch et al. (2017) if the supersaturation found above 400 km exceeds the supersaturation rate allowed by heterogeneous nucleation.

An alternative solution for the radiative cooling may come from H_2O molecules deposited in the atmosphere by the ablation from dust grains falling onto Pluto. Strobel and Zhu (2017) show that even a small amount of water, however highly supersaturated, may participate in the thermal equilibrium. Because H_2O vapor pressure is lower than *HCN* vapor pressure, we expect that its nucleation is even more difficult than for *HCN* and that high supersaturation may also be possible.

Although gases surely participate in the thermal budget, the most convincing explanation for this low stratospheric temperature involves thermal infrared cooling by aerosols in the stratosphere (Zhang et al., 2017). In previous radiative models, when haze is accounted for, the optical constants are generally assumed to be similar to those of Titan's tholin (e.g., Bertrand and Forget, 2017). But, departure from this initial guess provides a very powerful way to control the stratospheric temperature by changing the balance between heating by incoming solar energy and cooling by the outgoing thermal radiation. On Titan, the spatial coincidence between the altitude of the detached haze layer (Porco et al., 2005) and the strong vertical temperature inversion at 515 km (Sicardy et al., 2006; Fulchignoni et al., 2005) was quickly noticed (e.g., Lavvas et al., 2009). It was further shown that the optically thin detached haze locally controls the temperature profile through the direct diabatic heating (e.g., Cours et al., 2011; Larson et al., 2015). Therefore, adjusting the optical constants, which are unknown for Pluto's aerosols, is acceptable to explain the observed temperature profile. However, to further understand the respective roles of haze and gas, it is necessary to account for supersaturation of *HCN* and H_2O. Similarly, other molecules could also be supersaturated with various rates, but to a lesser extent. This may have consequences on the radiative budget and on the evaluation of exchange fluxes, for these species, between the surface and atmosphere.

Even in a warm atmosphere with a large number of solid and soluble aerosols, like on Earth, supersaturation frequently occurs and is the subject of climate studies (e.g., Gettelman et al., 2006; Gierens et al., 2012). Such events occur frequently at altitudes below the 200 hPa level in polar arctic and antarctic environments due to very low temperature and clean air, and at tropical latitudes around 200 hPa in convective overshoots. For instance, in arctic, they are observed more than 50% of the time and more than 70% of the time during southern winter. In the tropics, this occurs on average 2–5% of the time. But, supersaturation occurs up to 30% of the time in specific regions, essentially associated with the seasonal evolution of deep tropical convection. Supersaturation is then far from being an improbable or exotic event.

Supersaturation has been documented for the martian atmosphere as well. Microphysical models predicted that it should be moderate ($S\simeq 1.2$) in the case of heterogeneous nucleation (Määttänen et al., 2005) and may potentially reach a saturation ratio close to $S=1000$ with homogeneous nucleation, in the absence of available aerosols (Montmessin et al., 2002). Observation of supersaturation was reported between 20 and 50 km altitude with saturation ratio of water as large as $S\simeq 10$ (Maltagliati et al., 2011). These supersaturated layers appear because at some altitudes, water condenses on aerosols. This produces a complete removal of aerosols from these layers by scavenging and sedimentation. Then, the lack of available nuclei prevents any subsequent heterogenous nucleation from occurring, enabling large supersaturation. Navarro et al. (2014) made an exhaustive study, using the LMDGCM (Global Circulation Model from the Laboratoire de Météotologie Dynamique), with a sophisticated cloud microphysical model, including radiative feedback from the cloud droplets. They show that supersaturation is permanent above the 0.1 Pa and related to the seasonal and diurnal cycles between the 5 Pa level and 0.1 Pa. This model also confirmed that such supersaturations are due to the scarcity of aerosols above $\simeq$20 km. These results are consistent with the observations made previously (Maltagliati et al., 2011). Supersaturation was again confirmed in another recent work using CRISM (Compact Reconnaissance Imaging Spectral Mapper) onboard the Mars Reconnaissance Orbiter (MRO) observations, with saturation level possibly higher than $S=3$ (Clancy et al., 2017).

2. Classical theory of cloud nucleation

The theory of cloud microphysics describes the formation of condensation droplets in two steps: The nucleation and then the condensation. The nucleation deals with the transition of condensable gases from the state of clustered molecules (embryos) to growing droplets. Condensation deals with the growth of droplets which occurs under energetically favorable conditions. In this work, we only investigate the conditions related to nucleation because this is the key process to determine beyond which saturation level clouds can be produced in an atmosphere. We do not perform calculation of condensation since this is useful only in the frame of a complete microphysical model where gases and their condensates interact with aerosols and with the thermodynamical conditions through a thermal model. The core of the nucleation theory, as described here, is taken from the chapters 7, 9-§1 and 13-§2 of Pruppacher and Klett (1997). In this section we give successively a description of the homogenous nucleation (*HOM*), heterogenous nucleation (*HET*) and finally, of the heterogeneous nucleation with surface diffusion (*HSD*).