

ON THE THERMODYNAMIC CONSTRAINTS ON DUST RELEASE: IMPLICATION TO THE STRUCTURE AND SIZE OF DUST PARTICLES IN COMETARY COMAS. L. V. Starukhina, Astronomical Institute of Kharkov National University, Sumskaya 35, Kharkov, 61022, Ukraine, Larissa.V.Star@mail.ru

Introduction: Detachment of particles from the surface of a comet nucleus is the initial stage of dust distribution in the comet coma and all over the Solar system. In theoretical modeling of dust production by comets (e.g., [1]), processes in contacts between a particle and the surface were not considered, in particular, cohesion between the particles was neglected. However, the attachment of the particles to the surface was shown to be dominated by the forces in the contacts between the particles even for the Moon [2]. On the comets, where gravity is much weaker, the processes in the contact between a particle and the surface should control the size and structure of the released dust particles. Here the thermodynamic conditions of dust release are considered.

Thermodynamics of ice evaporation from the contact of a particle with a surface: Consider a refractory, e.g., silicate, particle frozen to a silicate surface by thin ice “bridge” of a radius $r_c \ll R$, R being the local curvature radius of the particle in the contact point (Fig.1). The evaporation of the ice “bridge” may occur either when the free energy G of the ice-silicate system decreases during this process ($dG/dr_c < 0$) or if the energies ΔG are low (less than about $10kT$) and can be provided by thermal fluctuations. The change of the free energy after evaporation of all the ice from the contact is:

$$\Delta G = \Delta\mu V/\omega + \Delta\alpha S \approx \Delta\mu\pi r_c^4/4\omega R + 2\Delta\alpha\pi r_c^2, \quad (1)$$

where V and S are the volume and the surface of the ice “bridge”, ω is the volume per one water molecule in ice, so that V/ω is the number of water molecules in the contact zone. $\Delta\mu$ is the difference in chemical potentials of the vapor and solid phases:

$$\Delta\mu = kT \ln(p/p_0), \quad (2)$$

where $p \approx nkT$ is water vapor pressure at the surface, p_0 is its equilibrium value at surface temperature T , k is Boltzmann constant, and n is the number density of

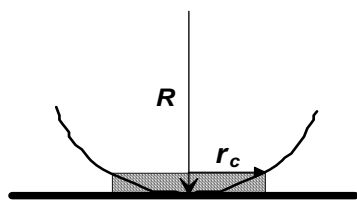


Fig.1. A scheme of the contact zone for a particle frozen to a surface by thin ice “bridge” of a radius $r_c \ll R$, R being the local curvature radius of the particle in the contact point. The substrate is supposed to have much lower curvature than the particle.

water molecules near the nucleus surface. As $p < p_0$, $\Delta\mu < 0$, so that the volume component of the free energy decreases in evaporation. However, its surface component may increase, if the change in specific energy of the surface after ice evaporation $\Delta\alpha = \alpha_s - \alpha_{s-i} > 0$, α_s and α_{s-i} , being specific energies of bare silicate surface and silicate-ice boundary respectively. Silicates are known to be wettable by polar water molecules, i.e., the energy per unit of their surfaces increases after water molecules are removed. If a few nanometer layer of liquid water remains on silicate (which is possible at T close to 0°C), then $\Delta\alpha = \alpha_{\text{ice}} - \alpha_{s-i}$, which can still be positive. For the examples shown in Figs.2 and 3, $\Delta\alpha = 10 \text{ erg/cm}^2$ was taken, which is rather intermediate value (compare $\alpha_s \approx 700 \text{ erg/cm}^2$ and $\alpha_{\text{ice}} \approx 70 \text{ erg/cm}^2$).

In Fig.2 the change of free energy after evaporation of ice “bridge” of radius r_c is given for different contact curvature radii R (at $T = 300 \text{ K}$ and $n = 10^{13} \text{ cm}^{-3}$). It shows maximum

$$\Delta G_{\text{max}} = 4\pi R(\Delta\alpha)^2\omega/|\Delta\mu| \quad (3)$$

similar to that known from theory of nucleation of new phases. Eqs. (1), (3) and (4) for ΔG , ΔG_{max} , and r_c^* differ from those in phase transition theory due to special contact geometry. The maximum ΔG_{max} characterizes the energetic scale for contact evaporation and is achieved at

$$r_c = r_c^* = (2\alpha\omega R/|\Delta\mu|)^{1/2} \quad (4)$$

E.g., $r_c^* \approx 5$ and 16 nm at $R = 1$ and $10 \mu\text{m}$.

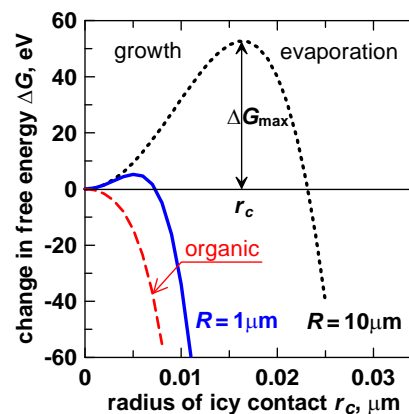


Fig.2. Examples of the change of free energy as water ice evaporates from the contact of a radius r_c between silicate (black and blue lines) particle and a substrate for different local curvatures R in the contact point. Typical case for organic particle is shown by red line: evaporation is allowed in all the ranges of contact sizes.

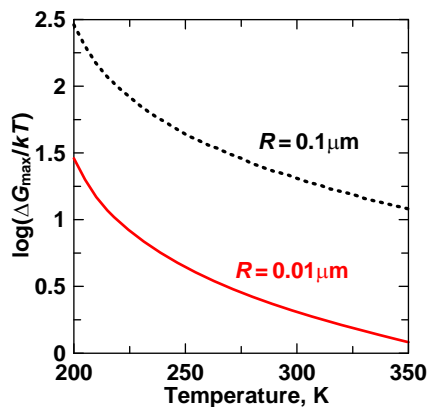


Fig. 3. Estimates of the temperature dependence of the characteristic scale of energy barrier ΔG_{\max} for evaporation of water ice from the contact between silicate particles for different local curvatures R in the contact.

At $r_c < r_c^*$ further evaporation in the contact is not favored by thermodynamics. The energy barrier may be overcome due to by thermal fluctuations. In Fig. 3 the energy scale ΔG_{\max} is compared to characteristic thermal energy kT , since the probability of defrosting is proportional to $\exp(-\Delta G/kT)$. Fig.3 demonstrates that ice removal from the contact is possible only for extremely small R ($\sim 0.1\mu\text{m}$ or less).

As follows from Figs. 2 and 3, dust detachment from an icy nucleus surface is favored in the cases, when the local curvature radii $R < 0.1\mu\text{m}$. These cases are: (1) small particles, (2) larger particles with sharp surface details, in particular, needle-like grains, (3) aggregates of small particles. The case (1) is consistent with the maximum particle number densities observed for this size range in cometary comas and the lack of cutoff in the dust mass spectra at $M < 10^{-14}\text{g}$ [3,4].

Implication to organic substance: Most of organic substances are not wettable by polar water molecules, so that $\Delta\alpha < 0$ and free energy of such organic-ice system always decreases in ice evaporation (red line in Fig.2). This favors removal of water ice in the vicinity of such substances, in particular, ice mantles around nonwettable organic materials cannot be preserved.

Many organic molecules have hydrophilic groups (polar radicals such as $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, $-\text{CN}$, $-\text{NO}$, $-\text{CHO}$, $-\text{SO}_2\text{H}$) on the end of a hydrophobic hydrocarbon chain. The possibility of ice mantles for these organic materials depends on the structure of molecular clusters on the periphery of organic particle (Fig. 4). If the hydrophilic groups are directed to the surface (Fig. 4a) ice mantles around such particles can be formed.

The above considerations equally apply to the contacts of volatile organics with silicates that also have polar atomic structure and are not wettable by nonpolar

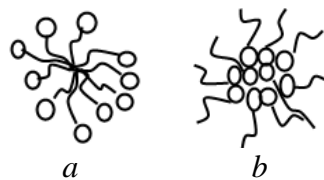


Fig. 4. Two types of structure of clusters of organic molecules: with hydrophilic groups outside (a) and hydrophobic groups outside (b). In case (a) the organic substance can be surrounded by water ice; in case (b) no ice mantles are possible.

organic molecules. Thus stable silicate-organic configurations are not favored by thermodynamics, and organic particles without hydrophilic groups on the periphery tend to be isolated from any materials surrounding them at a cometary surface.

However, in case of refractory organics, silicate-organic contacts may exist for very long time because of kinetic restrictions: there are no mechanisms to break a contact of two nonvolatile materials in an aggregate particle except fast collisions with the other particles.

Conclusions: Thermodynamic calculations show that silicate and other inorganic refractory dielectric particles which are released from the cometary surfaces should be either very small ($R < 0.1\mu\text{m}$, $M < 10^{-15}\text{g}$) or be aggregates with fluffy structure and large porosity, the grains in the aggregates being “cemented” by thin ice “bridges” of radii $r_c \sim 0.01\mu\text{m}$. Small sizes and porous structure were either observed or generally accepted; both statements follow from thermodynamic constraints. Further evolution of the structure of the released dust is controlled by kinetic constraints.

However, mantle-core model of an interplanetary dust particle is not validated by thermodynamics, especially for organic substance. The volatile organic substances may remain in a stable contact with water ice and silicates only by their hydrophilic groups, if any. The refractory hydrophobic organics may be in long contact with silicates only.

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References: [1] Shulman L. M. (1987) Comet nuclei. Nauka publ., Moscow, 1987. [2] Starukhina L.V. (2000) *Solar System Res.*, 34, 295-302. [3] Mazets E. P. et al. (1987) *Astron. Astroph.*, 187, 699-706. [4] Hörz F et al. (2006) *Science* 314, 1716-1719.