

NUCLEATION AND GROWTH OF A SOLID PHASE IN A GAS EXPANDING INTO VACUUM

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We study kinetics of homogeneous nucleation in over-saturated vapor expanding from a reservoir through a long channel into vacuum. Assuming adiabatic conditions for the gas, we derive an equation of state which accounts for the phase transformation of vapor into the condensed phase. To describe the growth rate of particles of the new phase gas kinetic theory is employed. We find the size-distribution of these particles, the temperature and flux velocity along the channel. Calculations are performed for the particular case of water vapor expanding to vacuum from its equilibrium state at the triple point. These conditions correspond presumably to the formation of the gas-dust plume, recently detected at Enceladus – the icy moon of Saturn. Our results, therefore, shed some light on this interesting astrophysical phenomenon.

Keywords: nucleation and growth; equation of state; gas expansion into vacuum.

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1. Introduction

In a large variety of natural and technological processes one encounters nucleation and growth of a new stable phase (e.g. solid, liquid) in an existing phase which becomes unstable (e.g. overcooled liquid, over-saturated vapor). The phase transformation kinetics sensitively depends on the thermodynamic conditions of the system, such as temperature and over-saturation. This defines, in its turn, the size distribution of particles of the new stable phase, which is the important characteristic of the process. If the phase transition occurs adiabatically, the excreted latent heat changes the temperature and over-saturation of the system and hence affects the nucleation and growth. In some cases, e.g. as in a gas expanding through a pipe into vacuum, the latent heat partly transforms into kinetic energy of the moving gas. Still, the major part of the latent heat raises the vapor temperature and diminishes its over-saturation; this eventually drives the system to a new phase equilibrium, where the nucleation and growth cease. One may ask, how large is the fraction of

the material transformed into the new phase and what is the size distribution of particles of the stable phase.

In the present study we address this problem in the context of an adiabatic expansion of a saturated vapor into vacuum through a long pipe. Due to the expansion out of the reservoir the vapor abruptly cools down and condensation into the solid phase begins. This however rapidly ceases, since the latent heat of condensation drives the system back to equilibrium so that an equilibrium gas-ice mixture is formed. Here we develop a model of this process and quantify the properties of the icy spray.

The relevance of the problem is related to recently observed dust-gas plume on Enceladus, the icy satellite of Saturn^{1,2}. A plausible explanation of the plume is based on the assumption that deeply under the icy shell in the south polar region of the moon, there exists a heat source of unknown nature^a, which keeps a large part of the ice near the triple point, where solid, water and vapor are in thermodynamic equilibrium. This region, beneath the satellite surface, is connected with the surface, i.e. the vacuum, via a system of cracks or channels. The saturated vapor from the under-surface gas reservoir thus expands to vacuum through these channels, cools down and partly transforms into the solid phase. As the result an icy spray is produced, which, shooting out of the channels, forms the observed dust-plume. Our model predicts, sofar, the velocities of particles in the Enceladus plume and their size distribution.

2. Adiabatic expansion of a gas with phase transformation

2.1. Flux velocity of an adiabatically expanding gas

Here we address a problem of a steady-state expansion of a gas from an infinitely large reservoir into vacuum through a long channel. We assume that the channel is wide enough and the motion of the gas is very fast, so that the effects of the gas interaction with the walls may be neglected, that is, we assume that the gas expands adiabatically. Naturally, when the gas starts to expand, its internal energy (or enthalpy) transforms into the energy of the flux, i.e. the energy of the hydrodynamic motion; for the adiabatic expansion the gas velocity u_g obeys the Bernoulli equation

$$w + \frac{u_g^2}{2} = w_0, \quad (1)$$

where w is the gas specific enthalpy, while w_0 refers to this quantity for the gas at rest in the reservoir. This can be expressed in terms of the speed of sound in the

^aTidal heating of the moon together with radiogenic heat can account only for a part of the power emanating from the south pole. In particular the concentration of the heat near the south pole remains a mystery to date.

gas c ,

$$w = \frac{c^2}{\gamma - 1}, \quad c^2 = \frac{\gamma RT}{\mu}, \quad (2)$$

where γ is the polytropic exponent ($\gamma = 4/3$ for water vapor), R is the gas constant, T is the temperature and μ is the molar mass.

Expanding into vacuum in a channel of a constant width, the gas cools down and rapidly accelerates to a maximal possible speed, where its flow velocity u_g is equal to the speed of sound in the gas³. This critical velocity $u_g = c_*$ may be found from the equation, which follows from the conservation of energy:

$$\frac{c_*^2}{\gamma - 1} + \frac{c_*^2}{2} = \frac{c_0^2}{\gamma - 1}. \quad (3)$$

Solving the above equation, one finds c_* and then from Eq. (2) the corresponding temperature T_* . To obtain pressure and density of the gas, at the instant when its velocity reaches the critical velocity c_* , we use the equation of state for the adiabatic process of a polytropic gas³,

$$\rho = \rho_0 \left(\frac{T}{T_0} \right)^{\frac{1}{\gamma-1}} \quad p = p_0 \left(\frac{\rho}{\rho_0} \right)^\gamma. \quad (4)$$

As a result we obtain for this initial stage of the gas expansion³:

$$T_{*in} = \frac{2T_0}{1 + \gamma} \quad p_{*in} = p_0 \left(\frac{2}{1 + \gamma} \right)^{\frac{\gamma}{\gamma-1}} \quad \rho_{*in} = \rho_0 \left(\frac{2}{1 + \gamma} \right)^{\frac{1}{\gamma-1}}, \quad (5)$$

with $c_{*in} = c_0 \sqrt{2/(\gamma + 1)}$, where c_0 , T_0 , p_0 and ρ_0 refer to the quantities in the reservoir.

2.2. Phase transformation in a gas during adiabatic expansion

Up to now we assumed that the expansion of the gas happens so quickly that no phase transformation could occur. However due to the drastic decrease of the vapor temperature in the adiabatic expansion the gas becomes over-saturated. As a result, condensation of the vapor into the stable phase – ice, if the temperature is below the triple point temperature $T_{t,p}$, takes place. We assume that the condensation process develops slowly enough, so that the vapor and the originating solid phase have the same temperature. Then the specific latent heat of sublimation H , excreted through the vapor condensation will lead to heating of the gas and a further acceleration in the channel. If f is the fraction of vapor, which has been transformed into ice, the generalization of the Bernoulli equation reads,

$$(1 - f) \frac{c_*^2}{\gamma - 1} + f \left(\frac{c_*^2}{\gamma - 1} - H \right) + \frac{c_*^2}{2} = \frac{c_0^2}{\gamma - 1}. \quad (6)$$

Here we take into account that the fraction $(1 - f)$ of vapor remains in the gas phase, while the fraction f , which transforms into ice, has the specific enthalpy

smaller by H and that both phases move with the same velocity c_* . The solution to the last equation may be easily found and we arrive at the following expressions for the speed of the gas $u_g = c_*$ and its temperature corresponding to the nucleation fraction f :

$$c_* = \sqrt{\frac{2}{\gamma + 1}} \sqrt{c_0^2 + f H(\gamma - 1)} \tag{7}$$

$$T_* = \frac{2T_0}{\gamma + 1} \left[1 + \frac{f H(\gamma - 1)}{c_0^2} \right]. \tag{8}$$

Naturally, for $f = 0$ we recover the above result, Eq. (5).

As the gas moves along the channel, the nucleation fraction f grows. Hence, the speed of the gas u_g gradually increases and it simultaneously heats up. The pressure and density of the gas change accordingly. Usually, the initial pressure of the gas, p_{*in} , when it starts to expand significantly exceeds the saturated pressure $p_{sat}(T_{*in})$ at the gas temperature T_{*in} . In other words, the vapor is initially strongly over-saturated^b. As the condensation into the solid phase proceeds, the temperature of the gas increases. The pressure of saturated vapor $p_{sat}(T)$, however, increases with temperature much faster than the pressure of the expanding gas. As a result the over-saturation decreases, and eventually at some temperature T_{fin} the gas becomes saturated. At this moment the condensation into the solid phase ceases. If the equation of state of the expanding gas with condensation is $p(f, T)$, the condition for the temperature T_{fin} and solid phase fraction f_{fin} at which the condensation stops, reads,

$$p(f_{fin}, T_{fin}) = p_{sat}(T_{fin}), \tag{9}$$

where for the temperature dependence of the saturated vapor pressure, which is in equilibrium with ice, one can use the empirical relation ⁴:

$$p_{sat}(T) = \exp[(-2663.5/T + 12.537) \log[10]]. \tag{10}$$

Hence Eqs. (9, 10) give the maximal possible fraction of the gas condensed into the solid phase during the adiabatic expansion. Note that the final temperature T_{fin} can not exceed the triple point, when the condensation into the solid phase (ice) occurs.

2.3. Equation of state for a gas with phase transformation

As it follows from the above discussion, to obtain the final temperature of the expanding gas and the fraction of the condensed solid, one needs to know the equation of state $p(f, T)$. Here we derive this equation of state assuming that the process is reversible and adiabatic.

We start from the first law of thermodynamics,

$$dQ = dU + pdV = 0, \tag{11}$$

^bFor triple point conditions in the reservoir the over-saturation is about 22

where dQ is the transmitted heat, and dU is the change of the internal energy of the mixture of the gas with the fraction $(1 - f)$ and solid with the fraction f :

$$dU = (1 - f)c_v dT + f c_{ice} dT - Hdf. \tag{12}$$

Here we take into account that the vapor, with the specific constant-volume heat capacity $c_v = R/(\gamma - 1)\mu$ and the solid phase (ice) with the specific heat capacity c_{ice} change their temperature by dT , while the fraction of the solid increases by df . The pressure for the gas fraction is related to its temperature and volume in accordance with the ideal gas equation of state,

$$p = \frac{(1 - f)RT}{\mu V}, \tag{13}$$

where, as previously, all quantities refer to a *unit* mass. The temperature of the gas is related to the condensation fraction f according to Eq. (8), hence

$$\frac{dT}{df} = \frac{2H(\gamma - 1)\mu}{\gamma(\gamma + 1)R} \equiv 1/a. \tag{14}$$

Using $df = (dT/df)^{-1} dT = a dT$ together with Eq. (14) and substituting Eqs. (13) and (12) into Eq. (11) we obtain,

$$\frac{dT}{T} \frac{\mu [(1 - f)c_v + f c_{ice} - aH]}{(1 - f)R} = - \frac{dV}{V}. \tag{15}$$

To solve this equation we use the dependence $f(T)$, which follows from Eq. (8) and apply the initial condition T_{*in} and ρ_{*in} from Eq. (5) for $f = 0$. After a simple algebra we obtain for the density of the gas, $\rho = 1/V$,

$$\rho = \rho_{*in} \left(\frac{T}{T_{*in}} \right)^{A-B} \left(\frac{b - aT}{b - aT_{*in}} \right)^B, \tag{16}$$

where

$$a = \frac{\gamma(\gamma + 1)R}{2(\gamma - 1)\mu H} \tag{17}$$

$$b = 1 + \frac{\gamma RT_0}{\mu(\gamma - 1)H} \tag{18}$$

$$A = \frac{1}{\gamma - 1} \left(1 - \frac{c_{ice}}{c_v} \right) \tag{19}$$

$$B = \frac{\gamma(\gamma + 1)}{2b(\gamma - 1)} \left(1 - \frac{2}{\gamma(\gamma + 1)} \frac{c_{ice}}{c_v} \right). \tag{20}$$

Using Eq. (13) we find the temperature dependence of pressure,

$$p = p_{*in} \left(\frac{T}{T_{*in}} \right)^{A-B+1} \left(\frac{b - aT}{b - aT_{*in}} \right)^B. \tag{21}$$

Note that for the gas expanding into vacuum addressed here, the pressure effectively depends only on temperature, that is $p(f, T) = p(T)$, since the solid fraction f and temperature are related by Eq. (8).

Substituting the obtained Eq. (21) and Eq. (10) for the pressure of saturated vapor into Eq. (9), one can find the maximal fraction of the solid phase, temperature of the gas and other gas characteristics.

3. Kinetics of particle nucleation and growth

3.1. Growth rate of the solid particles

For the presently addressed conditions (vapor at the triple point expands into vacuum) the density of a gas is rather small. Moreover, as it follows from our analysis, the typical size of ice particles, arising in the gas is of the order of a few microns. It is much smaller than the mean free path of the gas molecules, which is about a few tens of microns. In other words, the Knudsen number for the particles is large and their growth occurs in the kinetic-transport regime. In this case the flux of gas molecules on the surface of a particle of radius R reads ⁵,

$$\Phi_+ = \pi R^2 \beta \langle v \rangle n_g$$

where β is the condensation coefficient ⁵, which defines the fraction of gas molecules hitting the surface, that are absorbed, $\langle v \rangle = \sqrt{8k_B T / \pi m_0}$ is the average velocity of the gas molecules with mass m_0 , and $n_g = \rho / m_0$ is the number density of the gas. At the same time there exists a backward flux Φ_- , due to evaporation of the molecules from the particle surface. This flux depends only on the temperature of the surface and may be found from the equilibrium condition, $\Phi_-(^{eq})(T) = \Phi_+^{(eq)}(T, n_{eq}(T))$, where $n_{eq}(T) = p_{eq}(T) / k_B T$ is the equilibrium number density of the vapor. Taking into account that the mass of a particle of radius R is $(4\pi/3)R^3 m_0 n_{ice}$, where n_{ice} is the number density of ice, while the mass growth rate is $(\Phi_+ - \Phi_-)m_0$, we obtain for the growth rate of the particle radius,

$$\frac{dR}{dt} = \sqrt{\frac{k_B T}{2\pi m_0}} \beta [n_g(z) - n_{eq}(z(T))] \frac{1}{n_{ice}}. \tag{22}$$

For the stationary gas flow one can relate the time derivative to the derivative with respect to the coordinate z along the channel (note that for a long narrow channel we have an effectively one-dimensional problem). This may be done using the local gas velocity $u_g(z)$, which follows from Eqs. (7, 8) where $u_g(z) = c_*(z)$. In these equations the local temperature $T(z) = T_*(f(z))$ and the local condensation fraction $f = f(z)$ are to be used:

$$u_g(z) = \sqrt{\frac{\gamma R T(z)}{\mu}} = \sqrt{\frac{\gamma k_B T(z)}{m_0}}. \tag{23}$$

Taking into account that $d/dt = u_g(z) d/dz$ and that the phase transformation starts when the gas was in the thermodynamic state with the number density n_{*in} and temperature T_{*in} , we arrive at the following equation,

$$\frac{dR}{dz} = \frac{\beta}{\sqrt{2\pi\gamma}n_{ice}} [n_g(z) - n_{eq}(T(z))], \tag{24}$$

where

$$\frac{n_{\text{eq}}(T(z))}{n_{*\text{in}}} = \frac{T_0}{T(z)} \exp \left[-A_p \left(\frac{1}{T(z)} - \frac{1}{T_0} \right) \right] \left(\frac{1 + \gamma}{2} \right)^{\frac{1}{\gamma-1}}, \tag{25}$$

with $A_p = 2663.5$, as it follows from Eq. (10), $n_{\text{eq}}(T) = p_{\text{eq}}(T)/k_B T$, and

$$\frac{n_g(z)}{n_{*\text{in}}} = \left(\frac{T(z)}{T_{*\text{in}}} \right)^{A-B} \left(\frac{b - aT(z)}{b - aT_{*\text{in}}} \right)^B, \tag{26}$$

as follows from Eq. (21) for the expanding gas with condensation.

3.2. Nucleation rate and solid phase fraction

For the homogeneous nucleation rate γ_{nuc} we use the functional dependence which follows from the classic nucleation theory ^{6,7},

$$\gamma_{\text{nuc}} = B_n n_g^2 \exp \left[-\frac{A_n}{T^3 [\log(n_g/n_{\text{eq}}(T))]^2} \right],$$

with the constants $A_n = 8.0 \cdot 10^5$ and $B_n = 5.1 \cdot 10^9$, which yield the nucleation rate $\gamma_{\text{nuc}}(T_{*\text{in}}) = 1.0 \cdot 10^{10} \text{ m}^{-3} \text{ s}^{-1}$ in agreement with the experimental data obtained for thermodynamically close states ⁷.

Let $R(z)$ be the size of particles at point z , which have nucleated at the initial point $z_0 = 0$, then Eq. (24) implies that the radius of particles at point z , which have nucleated at $z_0 > 0$, reads

$$R(z, z_0) = R(z) - R(z_0). \tag{27}$$

To obtain the number density of particles of different size we notice that the number of germs nucleated during a time interval dt in a small volume $S dz_0$ with the rate $\gamma_{\text{nuc}}(z_0)$ (S is the channel cross-section) is $\gamma_{\text{nuc}}(z_0) S dz_0 dt$. For a stationary flux this quantity is equal to $n(z_0) u_g(z_0) S dt$. Hence the number density of germs nucleated at point z_0 is $n(z_0) = \gamma_{\text{nuc}}(z_0) dz_0 / u_g(z_0)$. Therefore, if $n(z, z_0)$ is the number density of particles at point z , which have nucleated at z_0 , the continuity equation,

$$n(z, z_0) u_g(z) = n(z_0) u_g(z_0) = \text{const},$$

implies

$$n(z, z_0) = \frac{\gamma_{\text{nuc}}(z_0) dz_0}{u_g(z)}. \tag{28}$$

Note that the latter equation gives the number density of particles of size $R(z, z_0)$.

To obtain the total mass of particles at point z , with radii ranging from the radius of a germ, R_{germ} , to $R(z, 0)$ one has to integrate over all possible nucleation points z_0 from the interval $(0, z)$. Therefore the mass fraction $f(z)$ of the gas, initially being at state $T_{*\text{in}}, n_{*\text{in}}$, which has been transformed into the ice at point z reads,

$$f(z) = \frac{n_{\text{ice}}}{n_{*\text{in}}} \frac{1}{u_g(z)} \int_0^z \gamma_{\text{nuc}}(z_0) \frac{4}{3} \pi [R(z) - R(z_0)]^3 dz_0, \tag{29}$$

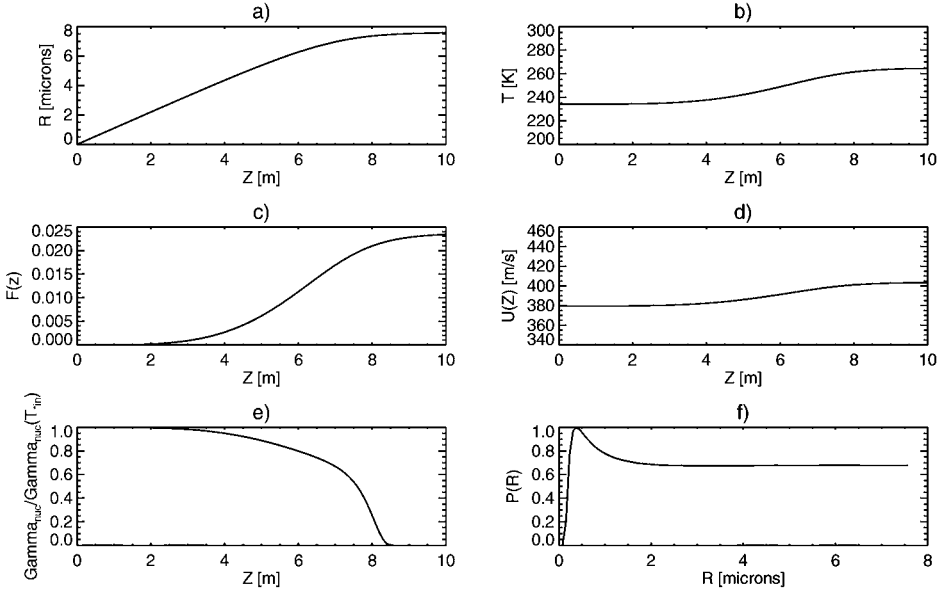


Fig. 1. The main characteristics of the nucleation process along the channel coordinate z : (a) the radius of the ice particles, (b) temperature, (c) solid phase fraction, (d) the gas speed, (e) the ratio of the initial nucleation rate to the current rate along the channel, (f) size distribution of the grains.

where we approximate $R_{\text{germ}} = 0$. Eqs. (24) and (29) supplemented by Eq. (23) and Eq. (8) which relates temperature and the solid fraction,

$$T(z) = \frac{2T_0}{\gamma + 1} \left[1 + \frac{f(z)H(\gamma - 1)\mu}{\gamma RT_0} \right], \tag{30}$$

form a closed system.

3.3. Distribution of temperature and particle size-distribution along the channel

We solve the above system numerically with an iterative scheme and obtain the space dependence of temperature and of the particle size distribution, Fig. 1.

It is found that the temperature rises along the channel (Fig. 1b) until the nucleation ceases (Fig. 1e) since the equilibrium conditions between the ice and vapor are fulfilled. The temperature (Fig. 1b) the gas speed (Fig. 1d) and the solid phase fraction (Fig. 1c) saturate at T_∞ , u_∞ and f_∞ , respectively, when the maximal particle size R_∞ is reached (Fig. 1a).

For the maximal size of particles nucleated at z_0 we can write,

$$R(\infty, z_0) = R_\infty - R(z_0) \equiv r(z_0).$$

The inverse function $z_0(r)$ (found numerically) gives the asymptotic size distribution $P(r)$:

$$P(r)dr = \frac{\gamma_{\text{nuc}}(z_0(r))}{u_\infty} \left| \frac{dr}{dz_0} \right|^{-1} dr. \quad (31)$$

The obtained size distribution is shown in Fig. 1f.

4. Conclusion

We develop a theory which describes the phase transformation into the solid phase in a gas expanding from equilibrium into vacuum. Assuming that the process is adiabatic and reversible, we derive the equation of state for the expanding gas which relates the density of the gas with its temperature and the fraction of the solid phase. Using gas kinetic theory we obtain an equation which describes the growth kinetics of a particle of the new (stable) phase. Combining the derived equation of state with the kinetic equation for the particle growth, we find numerically the distribution of temperature, flux velocity and the fraction of the solid phase along the channel. We also obtain the size distribution of the particles formed in the channel. The results of our study shed some light on the physical processes that take place in the dust-gas plume recently observed on Enceladus – the icy moon of Saturn. In particular, it allows to explain the origin of the ice particles in the plume and to predict the size-distribution of particles. These particles presumably support the E-ring of Saturn.

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