CIRCUMSTELLAR DUST AND CHEMISTRY

FORMATION AND DESTRUCTION OF DUST GRAINS IN CIRCUMSTELLAR REGIONS

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ABSTRACT. The existence of circumstellar dust in late-type stars is connected with stellar pulsations since periodic shocks accompanying pulsations seem to be the most probable mechanism of the gas density increase needed for condensation of dust particles in outer layers of the stellar atmosphere. Most abundant solid materials formed in O-rich stars are forsterite (or enstatite), silicon monoxide and iron, whereas in C-rich stars these are carbon, silicon carbide, magnesium sulphur and iron. Application of the homogeneous nucleation theory shows that condensation proceeds at extremely high departures from thermal equilibrium due to a very long time between collisions of condensable monomers. The most efficient mechanism of destruction of dust grains is thermal evaporation caused by variations of the stellar effective temperature.

1. INTRODUCTION

Circumstellar dust exists not only around cold late-type stars, but also around supergiants with higher effective temperatures. These are, for instance, R CrB stars, RV Tau (Gehrz and Woolf, 1970) and W Vir (Lloyd Evans, 1985) pulsating variables. Recent IRAS observations allow to suspect that even long-period Classical Cepheids are surrounded by dust shells (Deasy and Butler, 1985).

The main property of pulsating stars surrounded by dust shells is an extremely high luminosity to mass ratio. In Classical Cepheids and W Vir variables this ratio is of about 10^3 $L_\odot/M_\odot$, whereas in R CrB stars, RV Tau variables and pulsating red supergiants the luminosity to mass ratio is $L/M \sim 10^4$ $L_\odot/M_\odot$. A simple linear analysis shows that radial pulsations in the atmospheres of such stars can exist only in the form of running waves (Unno, 1965). This conclusion is confirmed by nonlinear calculations for the

I. Appenzeller and C. Jordan (eds.), Circumstellar Matter, 515–527.

models of pulsating asymptotic-giant-branch stars (Wood, 1974), R CrB variables (King, 1980), and low-mass yellow supergiants (Fadeyev, 1982). Moreover, nonlinear calculations show that periodic shock waves accompanying oscillations of such stars cause the mass ejection and seem to be the main mechanism of mass loss. On the other hand, dust grains cannot condense if the stellar atmosphere is in hydrodynamical equilibrium. This is due to the fact that gas density drops very fast with increasing radial distance, so that molecular compounds cannot be supersaturated. Thus, it seems to be most possible that it is the periodic shocks that cause increase of gas density needed for grain formation in outer layers of the stellar atmosphere.

Dust formation in outer layers of the stellar atmosphere results in another mechanism of mass loss connected with radiation pressure acting onto grains. So, mass loss from pulsating stars can proceed as it is shown in Fig. 1.

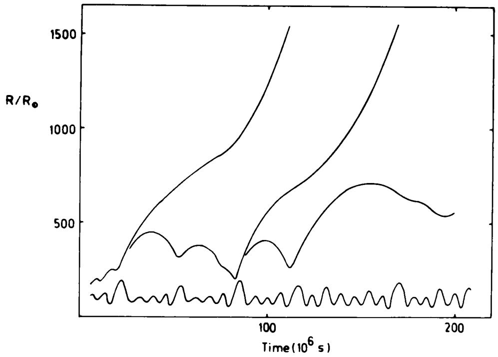

Figure 1. Temporal dependences of the outermost mass zones of the pulsating supergiant.

Each pulsation period the shock wave propagating through the stellar atmosphere causes expansion of gas with velocity comparable with the local escape velocity. As a result vapors of some compounds becomes supersaturated and further dynamical evolution of outer layers is governed by radiation pressure acting onto grains and momentum transfer from grains to gas molecules.

2. COMPOSITION OF DUST GRAINS

The main quantity determining the composition of dust is the relative abundancy (by atoms) of carbon to oxygen [C]/[O]. The most stable molecular compound formed in gas cooling below of about 3000K is carbon monoxide CO. So, in the O-rich stars almost all carbon atoms are tied in molecules of CO, so that carbon cannot take part in phase transition. And vice versa, in C-rich stars all oxygen atoms are tied in CO molecules and formation of solid oxydes becomes impossible. The most abundant elements and their most abundant compounds existing in O-rich and C-rich stars are listed in Table I. Other elements such as natrium, aluminium, calcium etc. can be neglected due to their lower relative abundancy.

TABLE I

Element	Molecular compound O-rich stars	 C-rich stars
O	CO H_2O $(SiO)_s$	CO
C	CO	$(C)_s$ C_2H_2 CO $(SiC)_s$
Mg	Mg $(MgS)_s$	Mg $(MgS)_s$
Si	$(SiO)_s$	$(SiC)_s$
S	$(MgS)_s$	$(MgS)_s$
Fe	$(Fe)_s$	$(Fe)_s$

Some of the compounds listed in Table I can directly transform gas phase into solid state. In O-rich stars these are SiO, MgS and Fe. However, according to the thermochemical calculations done during last two decades (Wood, 1963; Lord, 1965; Gilman, 1969; Lewis et al., 1979) the most abundant solid materials formed in the atmospheres of O-rich stars are forsterite Mg_2SiO_4 and enstatite $MgSiO_3$. These compounds do not exist in gas phase and form due to reaction between gaseous cpecies. For instance, forsterite forms in the reaction

$$2Mg + SiO + 3H_2O = (Mg_2SiO_4)_s + 3H_2 \ . \qquad (1)$$

At lower temperatures solid forsterite reacts to solid enstatite according to the reaction

$$SiO + H_2O + (Mg_2SiO_4)_s = (2MgSiO_3)_s + H_2 \ . \qquad (2)$$

This conclusion is supported by the experimental studies of vapor-phase nucleation in the Mg-SiO-H_2 system (Day and Donn, 1978; Nuth and Donn, 1982; 1983a; 1983b). Abundant molecular compound which can directly transform from vapor into solid state is silicon monoxide. However, the experimental studies of avalanche nucleation in the SiO-H_2 system (Nuth and Donn, 1982) showed that SiO vapor condences rather into Si_2O_3 than into more stable oxides SiO, SiO_2. Unfortunately, these experiments were done at total pressures by 6-8 orders of magnitude higher than those typical for grain-forming regions in the stellar atmospheres. The presence of MgS particles in O-rich stars seems to be questionable since this solid material is extremely hygroscopic and can be rapidly destroyed via reaction with water molecules (Nuth et al., 1985).

The most abundant compounds which can transform into solid state in C-rich stars are carbon, silicon carbide, magnesium sulphur and iron. Because the principal bearers of gas phase carbon in typical C-rich stars are carbon monoxide CO and acetylene C_2H_2, only a very small fraction of gas phase carbon being in atomic form can take part in nucleation process (Hoyle and Wickramasinghe, 1962). Further growth of carbon particles can proceed due to the following exchange reaction:

$$C_n + C_2H_2 = C_{n+2} + H_2 , \qquad (3)$$

where n is the number of carbon atoms in the particle. The existence of MgS particles in C-rich stars was proposed for explanation of the 30 μm emission feature observed in some objects (Nuth et al., 1985; Goebel and Moseley, 1985).

3. INNER BOUNDARY OF CONDENSATION REGION

The main quantity governing the direction of the phase transition is the supersaturation ratio

$$S = P_v/P_s(T) , \qquad (4)$$

where P_v is vapor partial pressure, $P_s(T)$ is the equilibrium vapor pressure. The condition S=1 means that the flux of molecules evaporating from the solid surface is exactly the same as the flux of molecules incident onto this surface, that is solid material is in equilibrium with vapor. For S>1 vapor transforms into solid state since the flux of incident molecules exceeds that of evaporating molecules. And vice versa, solid material evaporates and condensation is impossible for S<1.

The approximate temperature dependence of equilibrium vapor pressure over a flat solid surface is determined by Clapeyron-Clausius equation:

$$\frac{dP_s}{dT} \equiv \frac{h}{T(\Omega_g - \Omega)} , \qquad (5)$$

where h is the latent heat of the phase transition. Let us assume that the latent heat does not depend of temperature and the bulk molecular volume Ω is neglegible in comparison with that of gaseous phase Ω_g. Then the solution of Clapeyron-Clasius equation (5) can be written in the following form:

$$\ln P_s(T) = -h/(kT) + C \ , \tag{6}$$

where the integration constant C is determined from laboratory experiments. It should be emphasized that equilibrium vapor pressure is determined for the flat solid surface. This is a very strong shortcoming of the condensation theory since usually the grain radii do not sufficiently exceed the molecular sizes.

The problem of grain formation in circumstellar envelopes is complicated due to the existence of the two different temperatures: gas temperature T and temperature of dust particles T_p. In the first approximation dust temperature can be estimated from the radiation energy balance equation

$$4\pi r^2 Q_p(r,T_e) W \sigma T_e^4 = 4\pi r^2 Q_p(r,T_p) \sigma T_p^4 \ , \tag{7}$$

where W is a dilution factor, r is a dust particle radias, T_e is the stellar effective temperature, Q_p is the Planck-mean absorption efficiency factor. As it was shown by Lefevre (1979), the flat solid surface of temperature T_p is in equilibrium with vapor of temperature T at vapor partial pressure

$$P' = P_s(T_p)\ (T/T_p)^{1/2} \ . \tag{8}$$

Thus, the supersaturation ratio is determined from the following relation:

$$S = \frac{P_v}{P_s(T_p)} \left(\frac{T_p}{T}\right)^{1/2} \tag{9}$$

Let us consider the spherically-symmetric steady expansion of gas. In this case gas density ρ in the layer with radius R and expansion velocity v is determined from the continuity equation:

$$\dot{M} = 1/(4\pi R^2 \rho\, v) \ , \tag{10}$$

where $\dot{M}$ is the matter outflow rate. Because temperature of expanding gas gradually decreases with increasing radial distance R, it is important to find the radius of the saturation level where S=1. For the fixed stellar effective temperature T_e and matter outflow rate $\dot{M}$ this level represents an inner boundary of the grain-forming region because the condition $S > 1$ is fulfilled at larger radii. Fig. 2 shows the radius of the saturation level as a function of the effective ytemperature calculated for forsterite and silicon monoxide at matter outflow rates $\dot{M}=10^{-10}$ and 10^{-4} $M_\odot yr^{-1}$. The bolometric magnitude of the model is -5 mag.

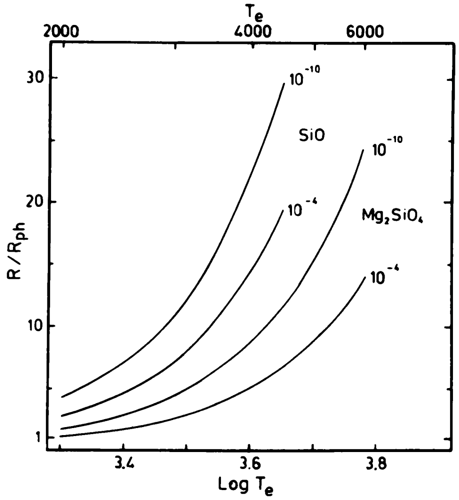

Figure 2. The radial distances of the saturation levels of forsterite and silicon monoxide as a function of the effective temperature at matter outflow rates 10^{-10} and 10^{-4} $M_\odot$ yr^{-1}.

As it is seen from Fig. 2, the radius of the saturation level exponentially increases both with increasing effective temperature and decreasing matter outflow rate. Such a behaviour of the inner boundary of the condensation region is connected with exponential temperature dependence of equilibrium vapor pressure (6).

4. HOMOGENEOUS NUCLEATION AND GROWTH OF DUST GRAINS

The saturation level gives only a lower limit of the radius of the condensation region, whereas vapor has to reach the critical supersaturation when the perceptable fraction of vapor commences to transform into solid state. This critical supersaturation can be found from equations describing mass exchange between gaseous and solid states.

Supersaturated vapor is in metastable state, so that under equilibrium conditions vapor inevitably transforms into stable solid state. At the beginning of the phase transition the small droplets of the new phase appear in vapor. The probability of droplet formation due to thermodynamic fluctuations is

$$w \propto \exp(-\Delta G/kT) , \qquad (11)$$

where ΔG is the change of the free Gibbs energy connected with formation of a droplet. Formation of droplets is accompanied by the competition of the two mutually opposite effects: creation of a spherical boundary of new phase and lowering of the chemical potential due to phase transition. Let us assume that droplets are spherical macroscopic clusters of molecules, so that macroscopic thermodynamics can be applied. In this case the change of the free Gibbs energy is

$$\Delta G = 4\pi r^2 \sigma - \frac{4}{3}\pi \frac{r^3}{\Omega} kT \ln S , \qquad (12)$$

where σ is the surface tension energy, r is the radius of the droplet. The change of the free Gibbs energy as a function of the number of molecules in the cluster is shown in Fig. 3. The maximum of the free Gibbs energy is

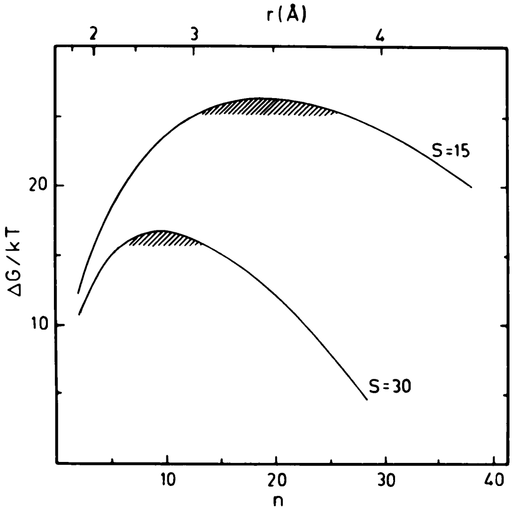

Figure 3. The free Gibbs energy as a function of the number of carbon monomers contained in the cluster. Dashed areas represent the critical regions.

reached at the radius of the cluster

$$r_* = 2\sigma\Omega/(kT \ln S) . \qquad (13)$$

For radii larger than the critical one r_* addition of a new molecule onto the surface of the cluster causes decrease of the free Gibbs energy, so that growth of such clusters is more favourable than destruction due to evaporation. However, more detailed analysis shows that the number of molecules contained in the critical cluster stochastically changes, so that there is the possibility that the critical cluster may become the subcritical cluster due to fluctuations (Zel'dovich, 1942). So, within the critical region where ΔG changes by of about kT the motion of the clusters in the space of their sizes is ibeyed to Focker-Planck type equation.

The nucleation rate, that is the number of critical clusters formed per unit time per unit volume is written as

$$J = \alpha_s (4\pi r_*^2) \beta Z N_* , \tag{14}$$

where α_s is a sticking coefficient,

$$\beta = P_v / (2\pi m\ kT)^{1/2} \tag{15}$$

is impingement flux of monomers, m is the mass of the monomer. The factor Z takes into account diffusion of the clusters through the critical region (Feder et al., 1966). The concentration of critical clusters is determined by

$$N_* = N_1 \exp(-\Delta G_*/kT) , \tag{16}$$

where N_1 is the concentration of monomers. According to Draine and Salpeter (1977) it is convenient to introduce the quantity

$$\Theta = 2(4\pi/3)^{1/3} \Omega^{2/3} \sigma / k , \tag{17}$$

whereby the expression for the free Gibbs energy may be written as

$$\Delta G_*/kT = 1/2\ (\Theta/T)^3\ (\ln S)^{-2} . \tag{18}$$

The most uncertain quantity of the nucleation theory is the surface tension energy σ. The review of the experimental data presented by Tabak et al. (1975) shows that the surface tension energy of solid carbon is in the range from 1000 to 3000 erg cm^{-2}. According to Draine (1979), the surface tension energy of small graphite particles is σ = 1400 erg cm^{-2}. The estimates of σ for silicates are also uncertain. Blander and Katz (1967) estimated the surface tension to be σ = 850 erg cm^{-2}. Nuth and Donn (1982) concluded that the surface tension energy of solid silicates is in the range from 500 to 650 erg cm^{-2}.

The phase transition in expanding circumstellar gas is connected with competition of the two mutually opposite effects: lowering of gas temperature and increase of the mean collision time of monomers. So, at the beginning the nucleation rate exponentially increases with decreasing gas temperature. Simultaneously with formation of new critical clusters the dust grains formed before commence to grow due to accretion of vapor molecules onto their surface. As a result, the nucleation rate reaches the maximum and begins to diminish when growth of the dust grains causes the perceptable depletion of the vapor and, hence, decrease of the supersaturation. The calculations show that the maximum nucleation rate is reached when from 1 to 3 percent of vapor transforms into solid state.

The quantities describing phase transition of forsterite in the O-rich star with T_e=2000K, M_{bol}=-5 mag and $\dot{M}$=3.16·10^{-4} $M_\odot$ yr^{-1} are shown in Fig. 4. These calculations show that maximum of the nucleation rate is reached at extremely high supersaturation ($S \sim 10^5$) corresponding to the very small number of molecules in the critical cluster ($n_* \simeq 3$), so that the applicability of the liquid droplet approximation becomes doubtful. Such a high departure from thermal equilibrium is due to the fact that the mean collision time of condensable monomers ($t_c \approx 10^4$ s) exceeds the time interval of the nucleation burst by two orders of magnitude only. The final radius of the forsterite grains does not exceed 5·10^{-7} cm.

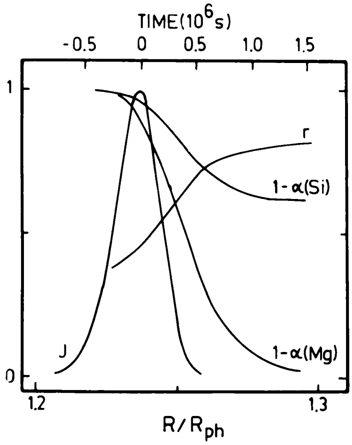

Figure 4. Nucleation rate J, mean grain radius r, relative fractions of gas-phase magnesium and silicon as a function of the radial distance from the stellar center.

Condensation of SiO proceeds at less favourable conditions since the nucleation peak occurs at $S \sim 10^6$ when the mean collision time of SiO molecules is $t_c \simeq 6 \cdot 10^4$ s. The final radius of SiO grains is of about 4·10^{-7} cm. It should be noted that in experimental studies the avalanche nucleation of vapor-phase SiO was observed also at very high supersaturations ranging from 10^3 to 10^5 (Nuth and Donn, 1982).

5. DESTRUCTION OF DUST GRAINS

Almost all late-type stars surrounded by dust shells are pulsating variables, so that the periodic variations of the effective temperature caused by stellar pulsations seem to be the most important mechanism of destruction of dust grains. Let us assume that the dust grains are spherical particles. In this case the rate of the change of the radius of grains is determined by the following relation:

$$dr/dt = \Omega \alpha_s \beta (1 - S^{-1}) \quad . \qquad (19)$$

So, when the supersaturation ratio increases above unit the growth rate of dust grains tends to its upper limit depending of the impinging flux of monomers β . On the other hand, decrease of S below unit is accompanied by increase of the evaporation rate without any limit. This means that the evaporation rate depends only on the rate of increase of the stellar effective temperature.

The simple criterion of the survival of forsterite grains in the expanding circumstellar envelope can be obtained with use of the diagram shown in Fig. 5. The constant supersaturation of forsterite is maintained at

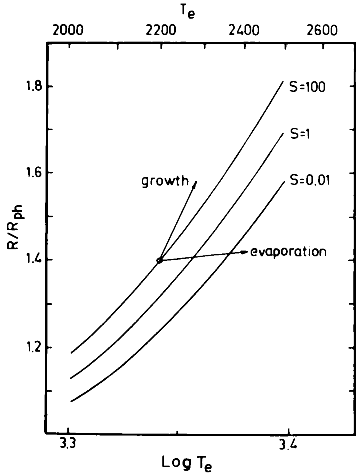

Figure 5. The radial distances of the layers with constant supersaturation of forsterite as a function of the effective temperature.

the radial distance obeying to the relation

$$\frac{d \log x}{d \log T_e} = 1.8 \ , \tag{20}$$

where $x=R/R_{ph}$, R_{ph} is the radius of the photosphere. The motion of the dust grains on this diagram can be represented by the following relation

$$\frac{d \log x}{d \log T_e} = \frac{T_e v}{R} \Big/ \frac{d\ T_e}{dt} \ . \tag{21}$$

Let us approximately assume that $dT_e/dt = 2\Delta T_e/P$, where ΔT_e is the amplitude of the change of the effective temperature, P is the pulsation period. Then the condition of the survival of forsterite grains may be written as

$$T_e vP/(2R\Delta T_e) > 1.8 \ . \tag{22}$$

For instance, for the red supergiant with T_e=2200K, R_{ph}= $622R_\odot$ and dust velocity v=20 km s^{-1} the relation (22) may be rewritten as

$$P/\Delta T_e > 4 \cdot 10^4 \ .$$

So, if the amplitude of effective temperature variation is ΔT_e=800K, the dust grains can be destroyed at pulsation periods less than 370 days.

Another mechanism of grain destruction which in principle may occur in circumstellar envelopes is sputtering caused by the drift of dust grains through gas. According to Wickramasinghe (1972) there is a few regimes of sputtering. Firstly, the energy of incident particles (atoms or molecules) E has to exceed the threshold energy E_t since at lower energies the collision does not cause escaping the atoms of lattice. If the energy of incident particles is less than a few tenth of keV, sputtering proceeds in the hard sphere collision regime and the sputtering yield (i.e. the number of atoms escaping the solid surface per one incident particle) is determined by the following empirical relation (Wehner, 1958):

$$Y = K\ (E - E_t) \ .$$

According to numerous studies reviewed by Barlow (1978) the threshold energy is approximately related to the sublimation energy of lattice H_s as $E_t=4H_s$, whereas the sputtering yield slope is $K=S_i/H_s$. The quantity S_i is constant for fixed solid material and incident particles. The values of S_i are given by Barlow (1978).

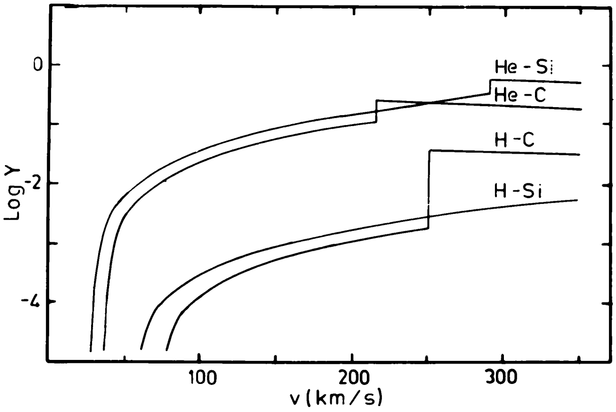

Figure 6. The sputtering yield Y calculated for solid carbon and solid silicates colliding with atoms of hydrogen and helium as a function of the velocity of the incident particle.

As it is seen from Fig. 6 sputtering occurs at too high drift velocities which seem to be improbable in late-type stars. For instance, destruction of silicate grains due to sputtering by incident helium atoms commences at the drift velocity of about 30 km s^{-1}.

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