

# From Molecules to Grains

*Erwin Sedlmayr*

Institut für Astronomie und Astrophysik  
Technische Universität Berlin  
Hardenbergstr. 36, D-10623 Berlin, Germany

## 1 Introduction

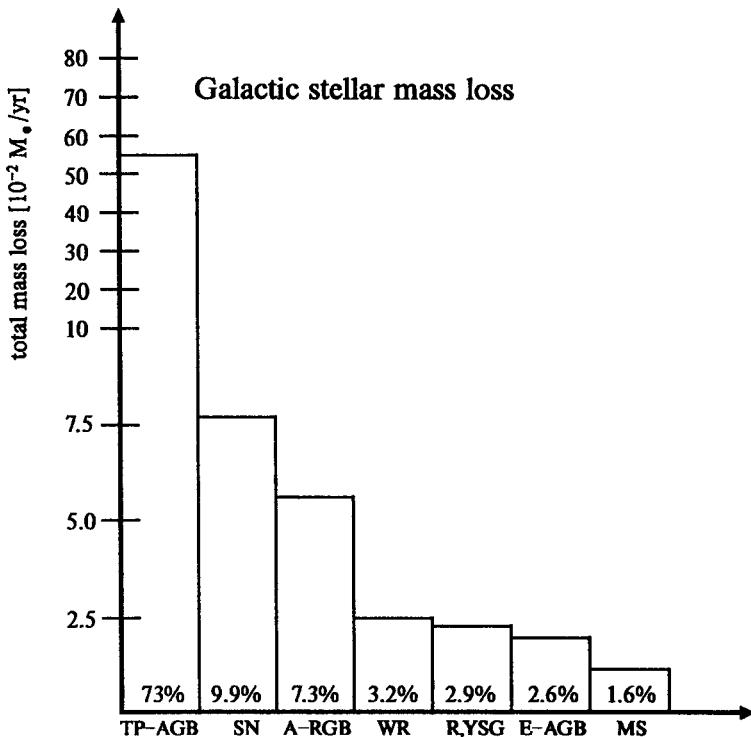
Cosmic dust is an ubiquitous component of the interstellar medium, the presence of which has severe bearings both upon the observations and upon the physical description and realistic modelling of astronomical objects. In most dusty objects, the grain component is intimately interwoven with the gas component and the radiation field, and, hence strongly affects the thermodynamical, the hydrodynamical and the chemical structure of the object. Therefore any consistent description of the astrophysical dust complex has to rely upon a treatment where these aspects are properly taken into account. In general this complex comprises the following problems:

- Formation of small stable molecular clusters out of the gaseous phase
- Growth of these clusters to macroscopic specimens (primary condensates: grains, plates, etc.)
- Destruction of grains (e.g. thermal evaporation, sputtering, shattering), and
- Physical and chemical processing of already existing grains (e.g. coagulation, chemical and thermal transformation, etc....).

In this contribution, the basic concepts for treating astrophysical grain condensation are surveyed by discussing the potentials, limitations and shortcomings of the various approaches. As it is especially dedicated to the question of the *molecule-solid-transition*, particular emphasis is given to the aforementioned first and second problem, by which a physical two-step process is suggested, involving the gas phase formation of small stable clusters and their subsequent growth to macroscopic specimens, which according to their specific shape result in 3-dimensional solid grains, two-dimensional (flat or curved) plates or even in fractal like structures. We confine our scope to the investigation and physical description of *primary grain condensation*, i.e. the formation of the first condensates emerging in astrophysical environments. As in the context of grain formation, the other problems – *grain destruction* and *grain processing* – are of secondary nature, in a sense that they concern already existing dust particles, we refrain from a discussion of these important subjects (e.g. Greenberg 1989; Jenkins 1989).

## 2 The astronomical objects of dust formation

In order to give some frame for the dust forming objects and the range of system parameters which determine the general conditions of astrophysical dust formation (see Gehrz 1989), Fig. 1 displays the total average mass loss rate of various astronomical objects in the disk of our galaxy showing dust formation.



**Fig. 1.** Total galactic mass loss (solar masses per year) of various classes of stellar objects: TP-AGB: tip-AGB objects, SN: supernovae, A-RGB: asymptotic red giant branch, WR-stars, R, YSG: red and yellow supergiants, E-AGB: early AGB objects, MS: main sequence stars. The indicated numbers are collected from the literature and are inferred from a rather inhomogeneous material (Weinzierl 1991). Despite these inherent uncertainties, they provide a confidential order of magnitude and a clear trend which is expressed at the percentage of their relative contribution to the total mass loss.

Inspection of Fig. 1 clearly shows that nearly 90 % of the total stellar mass loss originates from cool high luminosity stars, i.e. red giants and supergiants, in particular from AGB objects, which provide by far the largest contribution to the stellar mass injection rate into the interstellar medium. The winds of TP-

AGB-stars show a large fraction of condensates, with average values of the mass loss ratio

$$\frac{\dot{M}_{dust}}{\dot{M}_{gas}} = 10^{-3} \cdot \begin{cases} 6.3 & M - stars \\ 4.5 & C - stars \\ 2.0 & S - stars \end{cases}$$

for the different spectral types (e.g. Knapp 1985; Jura 1986).

Beside these main sources of galactic dust production also supernovae and novae outflows, B[e]-stars and even some WR-stars exhibit circumstellar dust formation. As these phenomena, however, are episodic or of minor importance in our context (cf. Fig. 1) we focus the further discussion on the problem of grain formation in the expanding circumstellar shells of cool late giants and supergiants (in this context see the excellent review on the mass loss mechanisms in evolved stars of Lafon & Berruyer 1991).

This restriction is also motivated by model calculations including dust condensation applied to various dusty systems.

**Table 1.** The condensation timescale for different astrophysical situations.  $n_{<H>}$  total density of hydrogen in the gas,  $t_{typ}$  typical hydrodynamical timescale in the system,  $t_{cond}$  condensation timescales for SiO, Fe and C.

Object	Temperature [K]	$\log n_{<H>}$ $[cm^{-3}]$	$\log t_{typ}$ [s]	$\log t_{cond}$ [s]		
				SiO	Fe	C
<i>interstellar medium</i>						
H II regions	10000	2 – 3	$\approx 12$	$\infty$	$\infty$	$\infty$
Intercloud medium	10000	$\approx -1$	?	$\infty$	$\infty$	$\infty$
Diffuse clouds	100	$\approx 2$	?	$> 18$	$> 18$	$> 18$
Dark clouds	10 – 20	$\approx 4$	?	$> 18$	$> 18$	$> 18$
Molecular clouds	50	$\approx 6$	$\approx 15$	$> 18$	$> 18$	$> 18$
Compact H II reg.	100 – 1000	3 – 4	$\approx 11$	$\approx 13$	$\approx 14$	13 – 14
<i>explosive ejection of matter</i>						
Novae	from 10000 down	$\leq 8 - 10$	6 – 7	$\approx 6 - 8$	7 – 8	7 – 8
Supernovae	from 10000 down	7 – 9	7 – 8	$\approx 7 - 9$	8 – 10	8 – 10
<i>massive winds of giant stars</i>						
Cool winds	from 2000 down	7 – 10	$\approx 8$	$\approx 7 - 9$	$\approx 8$	$\approx 8$
Hot winds	from 20000 down	6 – 8	$\approx 6$	$\approx 8 - 10$	$\approx 9 - 10$	$\approx 9$

Table 1 displays the typical system parameters and timescales which for each object determine the possibility and the efficiency of grain formation. For significant condensation of a species to take place, its characteristic condensation

time  $t_{\text{cond}}$  has to be shorter than the time-period  $t_{\text{typ}}$  for which favourable conditions for grain formation hold during the evolution of the considered object. From this table one concludes that only winds of cool stars, and novae and supernovae fulfil the condition  $t_{\text{cond}} < t_{\text{typ}}$  necessary for effective condensation of species like {SiO, MgO, Fe, ...} and {carbon compounds}, which are expected to play a key role in primary grain formation in oxygen rich and carbon rich environments, respectively (see Sect. 4.2).

### 3 Astrophysical dust condensation

#### 3.1 Embedding of the dust formation problem in physics and chemistry

Like any process of physical structure formation, also the problem of cosmic dust formation is closely related to various physical and chemical processes which either determine the physical and chemical initial and boundary conditions for the considered molecule-grain transition or are influenced by the local and global feed back of the grain formation process to the overall system. For this reason any reliable description of astrophysical grain formation basically has to refer to the couplings sketched in Fig. 2, from which the necessary methodical ingredients and the induced physical effects can be inferred.

In a general situation, many of these aspects are still unsufficiently explored or even unknown. Thus, a real improvement of this unsatisfactory situation requires extensive future work, in particular

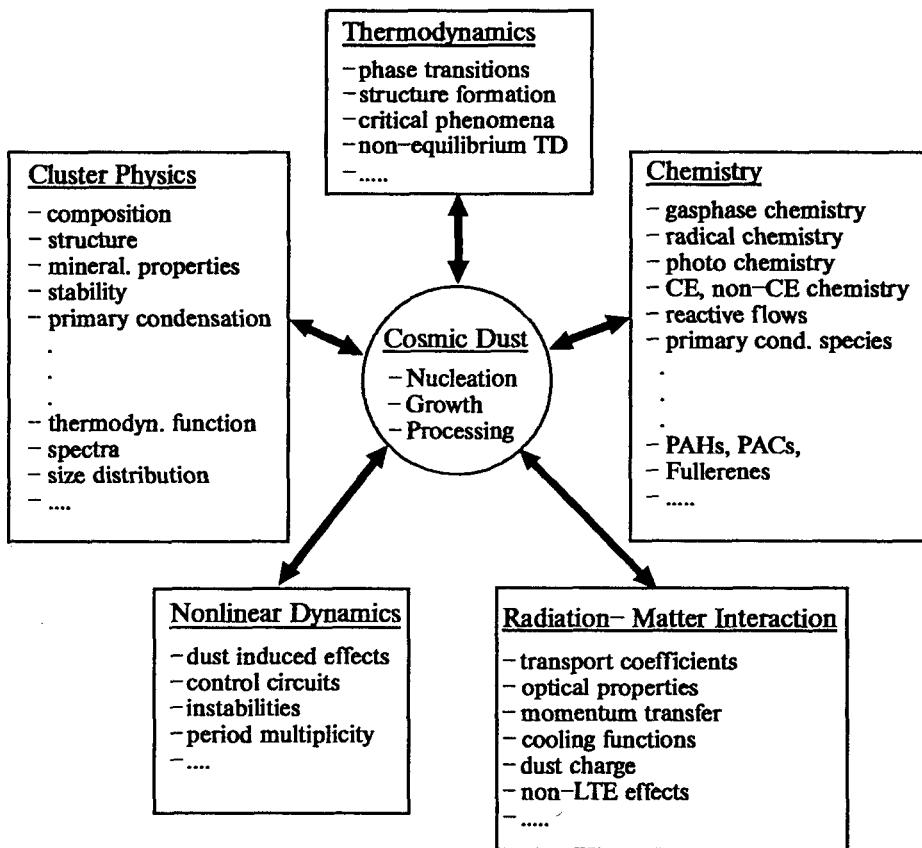
- specific laboratory experiments,
- detailed theoretical calculations, and
- suitably designed astrophysical observations.

Regarding these aspects, at several places important work is going on which supports the hope that significant progress in the reliable description of astrophysical dust formation and the consistent quantitative modelling of dust forming objects will be on line in the near future.

#### 3.2 The wind scenario

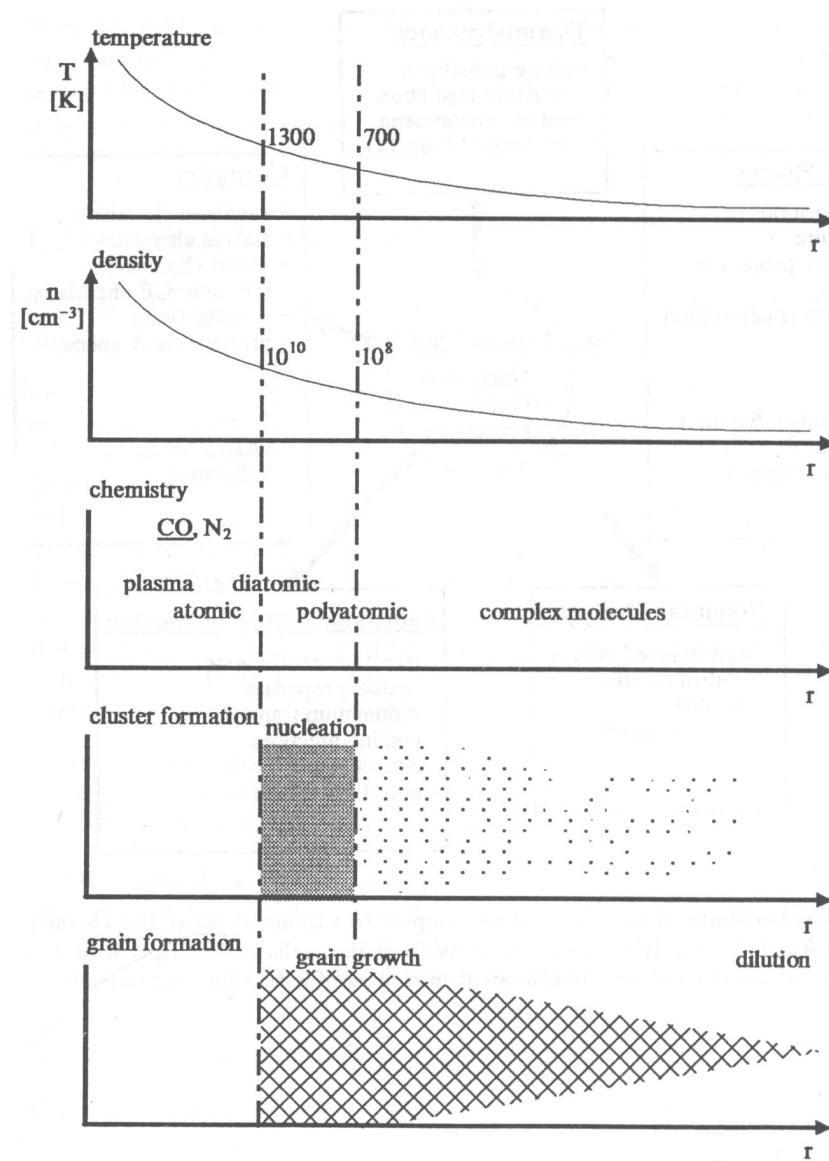
The basic situation of primary grain condensation can be best illustrated for a stellar outflow, where initially hot matter expands and subsequently cools and dilutes along its way outwards. Hence, both the gas temperature and the matter density show a monotonic decrease which causes the plasma to recombine and at increasing distance diatomic, polyatomic and finally complex molecules to form. At some distance, where the temperature is well below 1500 K certain atoms and molecules combine to stable clusters which by further addition of similar or different species grow to homogeneous or heterogeneous macroscopic specimens.

Fig. 3 shows a schematic sketch of this basic situation encountered in the flows of cool giants and supergiants, novae and supernovae. Though, Fig. 3 refers



**Fig. 2.** Basic couplings of the cosmic dust complex to various physical and chemical disciplines which in principle have to be considered in a reliable description of dust nucleation and growth and for the consistent modelling of a dust forming object.

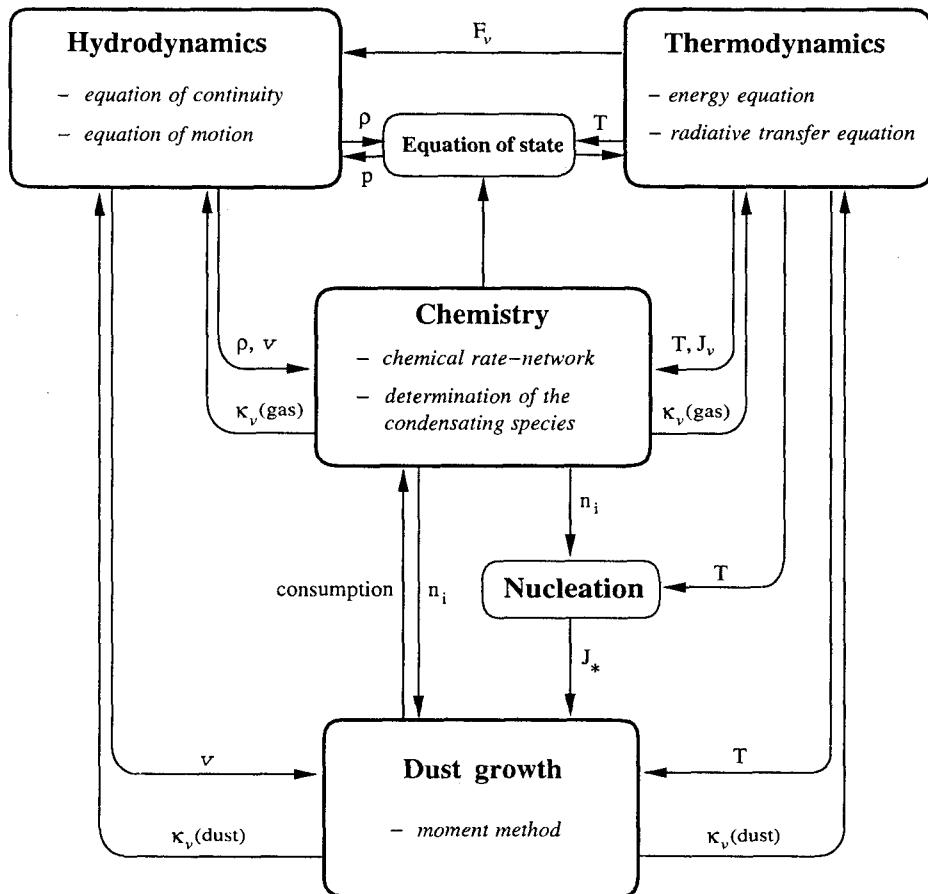
to the case of stationary outflows (e.g. stationary stellar winds, novae and supernovae expansions) similar scenarios hold for non-stationary expansions (e.g. circumstellar shells of Miras and LPVs). As cluster formation and grain growth are local phenomena, the efficiency of which is controlled by the local thermodynamical and chemical conditions, dust condensation in these objects depends strongly e.g. upon their specific shock structure and the related time scales (see Fleischer et al. 1992).



**Fig. 3.** Schematical radial course of temperature and density of an expanding stellar wind (cool stationary stellar winds, novae and supernovae) showing the evolution of a complex chemistry, and dust nucleation and growth. The nucleation regime is confined to a rather narrow zone with temperature between 1300 K ... 700 K having a relatively sharp inner edge. The growth regime extends from the nucleation regime outwards to a distance where either the condensable material will be totally consumed by grain growth or where it becomes too diluted for having still significant collision rates.

### 3.3 The selfconsistent wind model

The basic ingredients and couplings for the selfconsistent modelling of a dust forming stellar wind are depicted in Fig. 4.

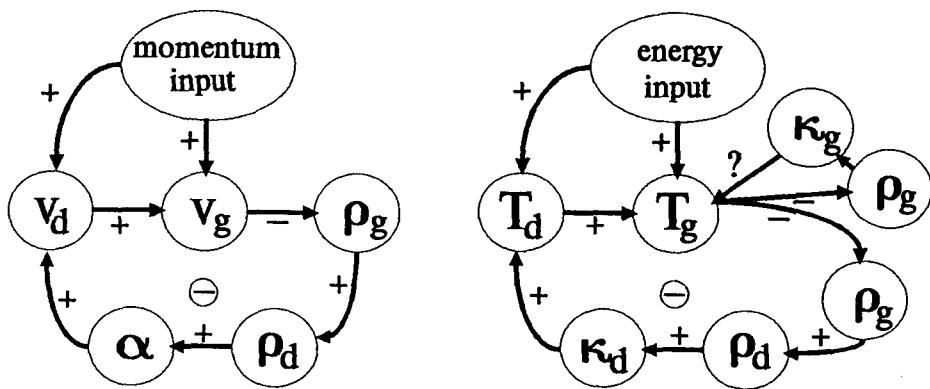


**Fig. 4.** Basic couplings for the selfconsistent description of dust forming stellar wind.

The upper part comprises the usual stellar atmosphere problem, whereas the lower part represents the dust formation complex, consisting of (i) a chemical subsystem which determines the dust forming species and their consumption due to condensation, and two complexes describing (ii) the formation of stable

clusters out of the gas phase, and (iii) the subsequent growth of these clusters to macroscopic particles. Besides the specific physical nature of the primary dust components and their size distribution function, this box also includes the calculation of realistic transport-coefficients which provide the coupling to the hydrodynamical and the thermodynamical structure of the shell.

In this way both for momentum and energy, control circuits are induced which explain why in case of stationary winds, the dust forming shell remains stable (see Fig. 5 in Goeres & Sedlmayr 1992), in contrast to non-monotonic situations, like Miras and LPVs or RCrB stars where dust induced instabilities develop. It is just this strong interaction between the evolving dust complex and the shell structure which introduces a pronounced nonlinear behaviour and which makes the selfconsistent modelling of most dust forming systems so difficult.



**Fig. 5.** Stabilising control circuits for momentum and energy induced by dust condensation in a stellar wind. Quantities with index g(d) refer to the gas (dust)-component, respectively. The negative sign of the product of the influences (symbolised by the arrows) in a closed loop guarantee dynamical and thermal stability of the system. The side chain of the energy circuit indicated by ? depends strongly on the actual form of  $\kappa_g$ . Thus, its influence upon  $T_g$  can be positive or negative. However, this fact does not alter the above general conclusion.

## 4 The role of chemistry

### 4.1 The primary condensates

Basically grain formation can be conceived as a chain of chemical reactions which result finally in macroscopic products. This is at least true for the first phase of the molecule-grain transition where suitable molecules combine to form small clusters which by additional chemical reactions grow to their critical size (see Sect. 5.2).

In order to find out which molecules are important for this initial step of cluster condensation, usually three heuristic criteria are applied to the system considered (e.g. Gail & Sedlmayr 1986; 1987):

- i) The clustering molecules have to be abundant species in the gas phase

This criterion is motivated by the observational fact that circumstellar dust shells show large optical depths caused by appropriate dust components. Then the observed large mass loss ratios (cf. Sect. 2) can only be explained if a large fraction of the heavy elements take part in the condensation process.

- ii) The clustering molecules must not be blocked by high bond energies

As a chemical process cluster formation involves reactive species. Thus all molecules having a bond energy larger than the reaction energy required for cluster formation behave inert and can be excluded. This concerns especially CO and N<sub>2</sub> which due to their exceptionally high bond energies are blocked for the condensation process.

- iii) The resulting clusters have to allow for high temperature condensates

This criterion is motivated by the observations from which a temperature range from 1300 K to 700 K for the dust formation zone is deduced.

Applying these criteria to a dust forming shell having a reliable chemical composition (e.g. M-stars or C-stars) only a very small number of species remains as possible primary condensates (see Sect. 4.2).

## 4.2 The CO-molecule

Most important in this context is the role of the CO-molecule. Due to its exceptionally high bond energy ( $E_{bond} \sim 11.09\text{eV}$ ) it can only be dissociated by rather energetic photons. Thus in the absence of dissociating UV-fields for an element compositions  $\epsilon_O > \epsilon_C$  ( $\epsilon_O < \epsilon_C$ ) ( $\epsilon_X$  denotes the abundance of element X) nearly all *carbon* (*oxygen*) is consumed by CO formation with the consequence that in the case of M-stars (C-stars) practically no additional carbon (oxygen) compounds can be formed. This fact does not only determine the possible type of chemistry developing in such shells but also again reduces the number of possible primary condensating species, the most important of which are (e.g. Gail & Sedlmayr 1986; 1987):

- SiO, MgO, MgS, Fe for oxygen-rich compositions (M-stars)
  - C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H,... MgS, SiC, Fe for carbon rich compositions (C-stars)

This clear picture is considerably modified if UV photons capable to dissociate CO are present. In this case in both *carbon and oxygen* rich environments always significant amounts of C atoms, C<sup>+</sup> ions *and oxides* are found, which give rise to a complex carbon-oxygen chemistry (see Beck et al. 1992). Such cases, however, have not been sufficiently studied in the context of circumstellar grain condensation.

### 4.3 The state of equilibrium

The last remark about the role of the CO molecule raises the question of the appropriate level of description for the chemistry. If the shell chemistry is dominated by kinetic reactions detailed balancing holds and consequently the assumption of chemical equilibrium (CE) is justified. Hence CE is a reasonable assumption for all situations where UV-photons can be neglected and where the expansion velocities are sufficiently low that the local expansion time scale  $t_{exp}$  is large compared to the reaction rates involved. This is true for the innermost regions of the shells of chromosphere free C- and M-stars inside the sonic point. Outside the sonic point the increasing supersonic velocity field causes a significant decrease of  $t_{exp}$ , which requires expansion effects to be taken into account in the chemical reaction network, causing pronounced non-equilibrium effects, which in the extreme case of free expansion result in a frozen chemistry. If chromospheres are present in any case photoreactions dominate. In these situations the entire shell departs from chemical equilibrium and the full dynamical reaction network has to be solved to obtain reliable molecular concentrations (Beck et al. 1992; Goeres et al. 1988).

## 5 Cosmic grain formation

From a microscopic point of view grain formation out of the gaseous phase can be conceived as a network of chemical reactions which under favourable conditions leads to molecules of increasing complexity which finally grow to macroscopic specimens.

Such a fundamental microscopic description of grain formation is currently far from being tractable, not only due to the huge reaction network required to produce grains up to size of  $1 \mu m$ , but also because of the lack of most relevant input data (see for instance the set of kinetic equations in Donn et al. 1981).

However, detailed inspection of the thermodynamic functions and of the properties of the small clusters involved shows, that under the usual conditions of astrophysical grain formation a well defined condensation barrier exists given by a corresponding *critical cluster size*. This condensation barrier allows the molecule-solid phase transition roughly to be considered as a two-step process:

1. *the formation of critical clusters*
2. *the growth of these clusters to macroscopic grains.*

### 5.1 The critical cluster

When molecules of a condensating species in a supersaturated situation combine to small clusters by subsequent molecule addition finally a *first* thermodynamically stable configuration is achieved (see Feder et al. 1966). This first marginally stable product is called the *critical cluster*. Along the coordinate axis  $N$  in cluster space ( $N$  is the number of monomers, i.e. the number of the basic constituents of the particle) the critical cluster is defined as that cluster of size  $N_*$  for which

the *enthalpie of formation*  $\Delta_f G_N^\ominus$  has its maximum value for given temperature and density. Hence, by definition all clusters being smaller than  $N_*$  are thermally unstable and thus preferentially will evaporate and all clusters being larger than  $N_*$  are thermally stable and thus preferentially will grow. In this way, the critical cluster naturally devides the cluster space into two disjunct regions  $N < N_*$  and  $N > N_*$ , respectively, separated by a *nucleation barrier*, usually referred to as the *nucleation regime*, and the *growth regime*, respectively. The physical description of each requires different assumptions and theoretical techniques.

In astrophysical problems the critical clusters for the condensates to be expected are rather small, with  $N$  being typically 5 ... 20 at temperature where efficient nucleation takes place. Then,  $N_*$  gives also the order of magnitude for the number of chemical reactions required for a cluster to surmount the nucleation barrier.

For the conditions encountered in the innermost regions of the stellar outflows, the chemical reaction timescales usually are very small compared to the timescales governing the hydrodynamical and thermodynamical evolution of the medium. Thus, the formation of critical clusters in stellar outflows usually can be considered as a stationary process (Gail & Sedlmayr 1988; Rossi & Benevides-Soares 1988). This statement even holds for Miras and LPVs where avalanche nucleation occurs in the postshock region, where the chemical reaction timescales are small compared to the oscillation period (Gauger et al. 1990; Fleischer et al. 1992).

As by definition every critical cluster has the tendency to grow, its local growth rate  $J_*$  determines the number of grains emerging in a given environment. Thus, it is a central aim of all condensation theories to find out the critical clusters for a given thermodynamical situation and to give a quantitative expression for their growth rates.

In case of thermal equilibrium the partial pressure  $p_N$  of homogeneous clusters of size  $N$  is simply given by the law of mass action

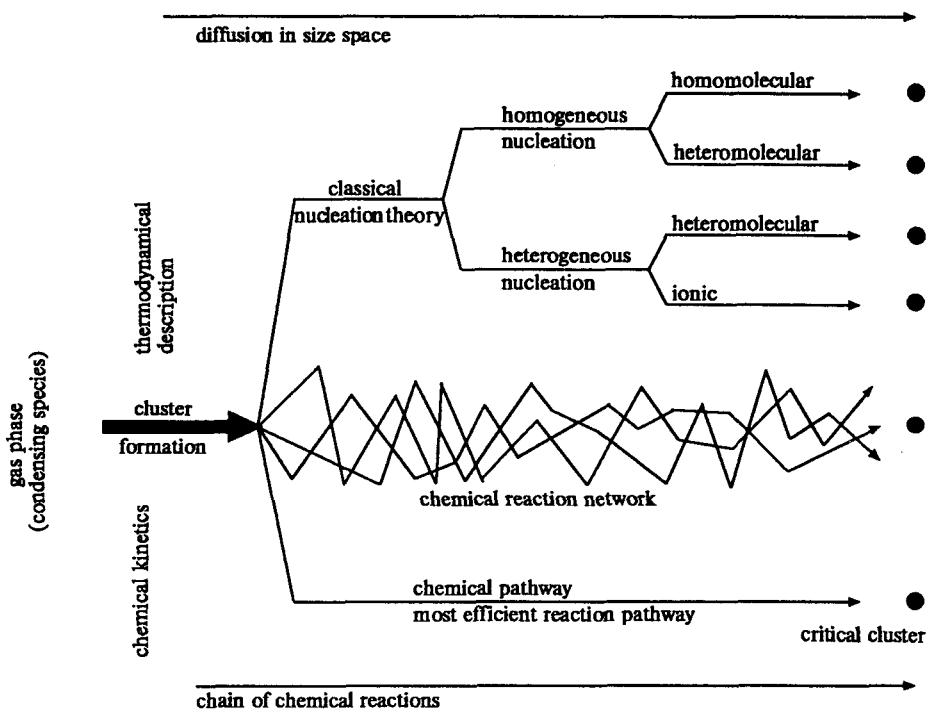
$$p_N = p_1^N \exp\left\{-\frac{\Delta_f G_N^\ominus}{kT}\right\}$$

with  $p_1$  being the partial pressure of the monomers in the gaseous phase (in units of standard pressure),  $T$  the gas temperature, and  $k$  the Boltzmann constant. Under the conditions prevailing in circumstellar environments the actual value  $p_N$  is dominated by the exponential function, which at  $N = N_*$  has a pronounced minimum. For this reason, the critical cluster can be seen as a narrow *bottle neck* which the basically unstable small clusters have to surmont along their way of formation, in order to arrive at the growth regime. It is just these properties – *marginal stability* and *minimum number density* – which give the critical cluster a key role in all theories describing dust formation.

## 5.2 The nucleation regime

No generally applicable physical treatment of the nucleation process in astrophysical environments is yet available. Thus, depending on the actual situation

and on the specific nature of the clusters to be expected, methodically different descriptions have been suggested for an approximate modelling of the nucleation regime.



**Fig. 6.** Basically alternative descriptions of the nucleation regime.

Fig. 6 displays the main lines according to which the various approaches applied today in this regime can be classified with regard to the adopted physical mechanism:

#### 5.2.1 The chemical network approach

Straightforward, one could aim to construct a *chemical reaction network* which finally results in the critical clusters. This way, however, faces the principal dif-

ficulties

- that it is not really known to which *minimum size* this network has to be extended along the evolution of specimens of increasing complexity in order to give a realistic quantitative description and how to *confine* it to such a size that it is still numerically treatable, and
- that many necessary input quantities (e.g. cross sections, reaction rates, etc..) are not available.

Therefore, at this time, the chemical network formulation is only applicable to situations where the way of cluster formation is well defined and is limited to a set of reactions, where the input quantities are known from laboratory experiments or from theory. For example, such a network has been worked out by Frenklach & Feigelson (1992), and more extended in the very important thesis of Cherchneff (see Cherchneff et al. 1991; 1992; Cherchneff & Barker 1992), who describes the first steps of the formation of *polycyclic aromatic hydrocarbon* molecules (PAHs) in the outflows of C-stars up to aromatic molecules containing five rings. But even in this narrow molecular domain such a large variety of possible reactions and products evolves, that one is finally forced to introduce *lumping*, a procedure where the reaction network is artificially reduced by fusing approximately similar reaction channels. Since immediately before effective nucleation starts the critical cluster is very large, truncated reaction networks in any case result in much too large nucleation rates. Thus the required selfregulation of the nucleation zone in its specific thermodynamic situation cannot be simulated within those rate networks.

An additional inherent difficulty of this method is, that due to the fast increase of the number of reaction channels with increasing complexity of the evolving aggregates, no obvious criterion is provided by the network of how to select the most efficient pathways leading to the critical cluster.

These basic difficulties of the chemical network approach strongly motivate alternative methods for the quantitative description of the nucleation regime, which avoid the above principle short-comings. These procedures, however, are rather schematic or highly specialized and can be classified as being to some extent asymptotic descriptions of the real problem.

### 5.2.2 *The chemical pathway*

The basic idea of this procedure is to reduce the immense variety of the different kinetically possible constructive reactions contained in the full network to the most efficient one which requires the minimum travel time in  $N$ -space for a small molecule to develop deeply into the growth regime and which thus essentially determines the grain formation rate.

Of course such a procedure requires

- i) that the mechanism of cluster formation basically occurs along few chemically well defined channels, and

- ii) that sufficient information is known about the reaction rates and branchings at every reaction step involved.

Then by detailed discussion of each reaction step, it is possible to select the *most efficient pathway*, i.e. that chain of cluster formation having maximum probability for bridging the molecule-cluster-region. If this pathway leads far enough into the domain of thermally stable clusters, there always exists a reaction step having minimum probability. This bottle neck, which controls the efficiency of the grain production is called the *critical reaction* with respect to the selected chemical pathway. Comparing this definition with the properties of the critical cluster introduced in Sect. 5.1 one confers that the critical reaction just defines the critical cluster  $N_*$  and its growth rate  $J_*$  along the pathway under consideration (see Gail & Sedlmayr, 1987; 1988; Goeres 1993).

In any case, the selection of a chemical pathway is a rather elaborate task which requires considerable physical and chemical insight into the actual nucleation mechanism. Therefore such a procedure is limited to specific problems, like PAH formation in C-star shells or the formation of *polyaromatic carbon* molecules (PACs) in RCrB-atmospheres (e.g. Goeres & Sedlmayr 1992). In these problems one is guided by laboratory chemistry and the wealth of data provided by pyrolysis experiments.

In this way carbon nucleation in C-star shells is described by a chemical pathway starting at acetylene (which is the most abundant condensable species) and leading via a series of polycyclic aromatic hydrocarbons of increasing complexity to flat and curved two-dimensional macroscopic structures (e.g. Keller & Sedlmayr 1983; Keller 1987; Gail & Sedlmayr 1987; Goeres 1993) which exhibit the characteristic emission features attributed to carbonaceous grains (Léger & Puget 1984; Allamandola et al. 1987)

An interesting application of this method is the formation of fullerenes in the Krätschmer-Fostiropoulos-Huffman experiment (Krätschmer et al. 1990), where according to our suggestion the nucleation pathway starts from the  $C_{10}$ -ring as monomer, leading by addition of monomers finally to closed  $C_{60}^-$  and  $C_{70}^-$  cages (Goeres & Sedlmayr 1991).

### 5.2.3 Classical nucleation theory

Classical nucleation theory describes the formation of critical clusters, like droplet formation in a supersaturated vapour, by means of thermodynamic quantities considering the clusters in the nucleation regime as macroscopic particles. The properties of these clusters are described either by extrapolation of the corresponding bulk phase quantities, even into the domain of very small clusters, by interpolation between the bulk phase and the corresponding molecular values, or by ab initio calculations for the actual equilibrium structure of the emerging small clusters from which their thermodynamic properties are derived (Köhler 1993). This latter procedure, however, is rather elaborate and hence is practically limited to chemically homogeneous clusters, where the internal interaction potentials are sufficiently well known (e.g. MgO-cluster formation).

In principle, classical nucleation is conceived as an evolution along the  $N$ -axis

in cluster space described by a master equation for the cluster size distribution function (see Yamamoto & Nishida 1977; Gail & Sedlmayr 1988) from which by arguments similar to those presented in Sects. 5.1. and 5.2.2. (– first reaction with a negligible inverse rate –) the critical reaction step and hence the critical cluster and its growth rate can be deduced.

In real astrophysical situations several basically different mechanisms of cluster nucleation have to be distinguished with regard to the kind of the primary condensating species and to the chemical composition of the emerging clusters:

#### *5.2.3.1 Homomolecular homogeneous nucleation*

This mechanism describes the formation of chemically homogeneous clusters by direct condensation of molecules of one kind (monomers). Adopting classical nucleation theory and chemical equilibrium, this most simple approach, hitherto has been applied to the formation of

- pure SiO-, MgO, MgS- and Fe-clusters in the outflows of M-giants and supergiants, and
- amorphous C<sub>N</sub>- clusters in the outflows of C-stars

(e.g. Gail & Sedlmayr 1986; 1987; 1988; Sedlmayr 1989)

#### *5.2.3.2 Heteromolecular homogeneous condensation*

This method describes the formation of homogeneous clusters by reactions with various kinds of molecules. For example the formation of pure amorphous carbon clusters from various contributing carbon compounds like C<sub>1</sub>, C<sub>2</sub>,..., C<sub>2</sub>H, C<sub>2</sub>H<sub>2</sub>,..., etc. Such a process can be easily treated with slight modifications in the frame of classical nucleation theory even in case of non-equilibrium conditions, (see Gail & Sedlmayr 1988; Gauger et al. 1990). Another important application is e.g. the formation of silicates (MgSiO<sub>3</sub>-, (Mg,Fe)SiO<sub>4</sub>-grains) in M-giant outflows. This formation mechanism is complicated by the fact that under circumstellar conditions only basic constituents, like MgO, SiO, Si<sub>2</sub>O, Fe, FeO, etc., are present in the gas phase, but the corresponding nominal molecules (like MgSiO<sub>3</sub>, Mg<sub>2</sub>SiO<sub>4</sub>, etc.) do not exist.

In the usual treatment of these situations thermal equilibrium between the various components in the gas phase and the individual constituents in the considered solid clusters is adopted, in this way calculating equilibrium abundances for the stable condensates as function of temperature and the partial pressures of the ambient condensating species. This method has been especially applied by the Japanese group in an impressive series of publications, e.g. Kozasa & Hasegawa (1987); Kozasa et al. (1989a,b).

Despite the widespread use of classical homogeneous nucleation theory in astrophysical dust formation problems (e.g. Salpeter 1977; Draine & Salpeter 1977; Draine 1979; Gail & Sedlmayr 1987; Kozasa et al. 1989 a,b), there exist some intrinsic shortcomings (see Sedlmayr 1989) which contemporary modifications aim to eliminate:

- The thermodynamical functions required in the small cluster domain, should

no more be adopted as smooth functions extrapolated from the macroscopic domain, but will be provided by laboratory measurements or ab initio calculations (Köhler 1993).

- Being basically a phase transition, grain formation requires conditions far from thermal equilibrium. In the last years, generalisations of classical nucleation theory have been developed, which straightforward allow to treat situations far from thermal and chemical equilibrium (Gail & Sedlmayr 1988; Gauger et al. 1990; Dominik et al. 1993).

#### *5.2.3.3 Heterogeneous nucleation*

In the frame of classical nucleation theory heterogeneous nucleation describes the formation of clusters by chemical reactions with already existing nucleation seeds, resulting in critical clusters of a new chemical composition. In principle heterogeneous nucleation can be described by the chemical network or by the chemical pathway approach, respectively, with all difficulties and shortcomings inherent in these methods already mentioned in Sects. 5.2.1 and 5.2.2. Their application to PAH-formation in C-star shells is in fact an important example for heterogeneous nucleation.

Heterogeneous cluster formation is also expected in environments contaminated by UV-photons, where ions and charged clusters might play a major role in the condensation process. Then especially ion-neutral reactions could be important in the cluster formation process. However, until now, in the context of astrophysics, no reliable description of ionic cluster nucleation exists. In contrast to this unsatisfactory situation regarding the nucleation regime, powerful methods for treating heterogeneous *grain growth* have been developed. (see Castleman 1979; Draine 1979; and recently Dominik et al. 1993).

Heterogeneous grains are also widely discussed in the context of interstellar grain processing (see for instance the review of Tielens & Allamandola 1987 and references therein). This subject, however, is outside the scope of this contribution.

### **5.3 The growth regime**

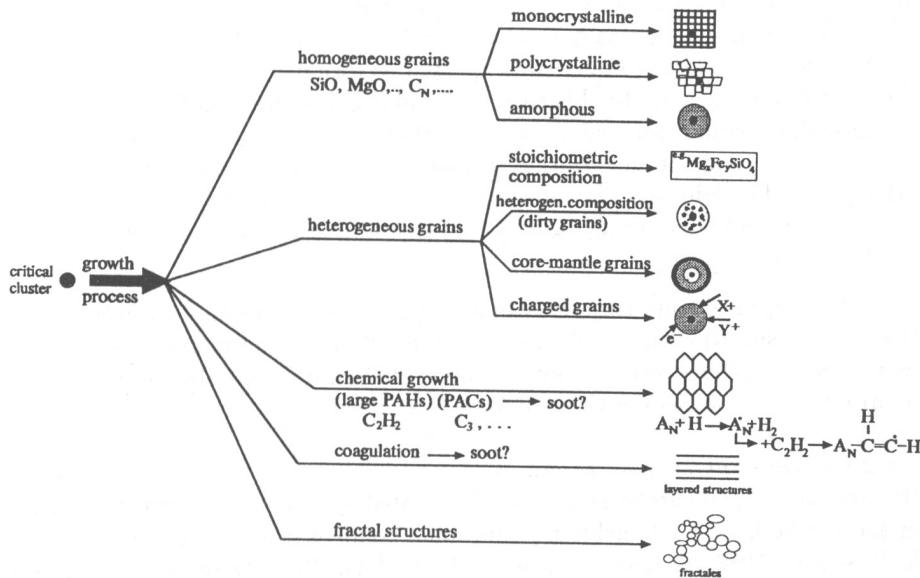
By definition (cf. Sect. 5.1), in a supersaturated environment every cluster larger than  $N_*$  has the tendency to grow at given temperature and density. In all cases of astrophysical interest, growth of critical and supercritical clusters is a thermodynamical process, which in principle can be described by the time evolution of the *local grain size distribution function*  $f(t, N)$  according to the corresponding master equation (e.g. Gail & Sedlmayr 1988; Dominik et al. 1989; 1993). In this regime, the relevant growth timescales, at least for sufficiently large particles, are comparable or larger than the timescales governing the hydrodynamical evolution of the system. Therefore, grain growth usually has to be treated as a time dependent problem, in contrast to cluster nucleation which in most cases is a stationary process.

In many astrophysical problems, it is not necessary to have the full information provided by the local size distribution function, but it suffices to use appropriately defined moments

$$K_j = \sum_{N=N_l}^{N_u} N^{\frac{d}{2}} f(t, N) , \quad j = 0, 1, 2, \dots$$

which directly enter into the model calculations (see Gail & Sedlmayr 1988).  $N_l$  and  $N_u$  are suitably chosen lower and upper limits of summation;  $d$  is the dimension of the considered grain with  $d = 2$  for two-dimensional,  $d = 3$  for three-dimensional particles, respectively.

Depending on the local chemistry and the thermodynamical conditions a large variety of resulting grain structures will evolve. Fig. 7 gives a sketch of the different types of grains which are expected to evolve in various realistic situations.



**Fig. 7.** Schematic sketch of different growth mechanisms and of the expected structures of the evolving grains. X<sup>+</sup> and Y<sup>+</sup> denote suitable ions contributing to the growth of charged grains.

### 5.3.1 Growth of chemically homogeneous grains

Homogeneous grain growth has been studied extensively both for C- and M-stars, where the formation of pure carbon grains and of SiO-, MgO-, MgS- and Fe-grains are discussed (Gail & Sedlmayr 1986; 1987; 1988).

As the applied methods only consider molecule addition controlled by a suitably defined growth timescale no answer can be given to the question concerning the real mineralogical structures of the resulting grains. To decide whether *monocrystalline*, *polycrystalline* or *amorphous* grains are produced by this condensation process four different timescales have to be compared:

- *the mean capture time*  $t_c$  for a condensating molecule to be adsorbed at the cluster surface,
- *the hopping time*  $t_h$  of this admolecule at the surface,
- *the time*  $t_n$  required for the admolecule to find a suitable lattice site to be built in, and
- *the characteristic evaporation time*  $t_{ev}$  of the admolecule.

According to the relations between these timescales different crystalline structures of the evolving grains have to be expected (Gail & Sedlmayr 1984):

- a)  $t_c < t_{ev}$ : This is the basic necessary condition for grain growth to take place. It defines the growth regime (see Sect. 5.1).
- b)  $t_n = n^2 t_h < t_c$ : The admolecule, after a random walk with  $n^2$  steps, always arrives at the energetically most favourable lattice site to be built in. In this case *monocrystalline* grains are expected to form.
- c)  $t_n \geq t_c$  and  $t_h < t_c$ : In this case grain addition occurs too fast for allowing growth via equilibrium configurations. However, due to the second inequality still short range order resulting in *polycrystalline specimens* is possible.
- d)  $t_h > t_c$ : The addition of condensating molecules to the grain occurs so fast, that even no short range order can develop. In this case *amorphous grains* have to be expected.

Along a typical wind trajectory of a cool giant, we therefore expect an evolution via the situations a) → b) → c) → d), finally resulting in grains, consisting of a monocrystalline core, a polycrystalline shell and eventually an amorphous mantle (see Gail & Sedlmayr 1984; Williams 1989)

### 5.3.2 Growth of heterogeneous grains

Heterogeneous grain growth can easily be treated by a straight forward extension of the methods of 5.3.1 including additional condensating species (e.g. Kozasa & Hasegawa 1987; Tielens 1989; Sharp & Huebner 1990; Dominik et al. 1993). Different situations have to be distinguished with regard to the evolving grain structures:

#### a) Stoichiometric compositions

These descriptions assume that grains of a well defined stoichiometric composition are formed in a given chemical environment. The necessary condition for this process to occur is that the gas phase partial pressures of

the individual grain constituents are larger than their corresponding vapour pressure. Thus, by definition of suitably defined *supersaturation ratios* equilibrium grain structures are calculated from a given chemistry (e.g. Kozasa & Hasegawa 1987; Sharp & Huebner 1990). A generalisation of these methods which allows to treat also non-equilibrium growth is given by Dominik et al. (1993).

b) *Heterogeneous compositions (dirty particles)*

Evolution of dirty particles simply can be treated by the method of Dominik et al. (1993) if chemically different condensating species are present having a supersaturation ratio larger than unity with regard to the considered clusters. Then, these molecules are considered to be deposited at the grain surface, which in this way (according to their individual constructive collision rates), form a chemically heterogeneous particle having a non-stoichiometric composition.

c) *Core-mantle grains*

The general condition for a species to condense is that its local partial pressure is larger than its corresponding vapour pressure in the solid. This condition is a very sensitive function of the local temperature and the chemical composition. Thus, the monotonic course of these quantities in a stellar wind defines a time order with respect to the condensation of certain species in a mass element moving outwards. As different regions in the shell usually correspond to different chemical conditions, – i.e. different abundances of the condensating species – grain growth in a stellar wind proceeds along a sequence of changing chemical environments, thus leading quite naturally to an onion-shell like grain structure (see Dominik et al. 1993).

d) *Charged grains*

In environments where ionising UV-photons are present a considerable fraction of the molecules and atoms become ionised thus producing free electrons. Calculations of the charge of clusters present in such situations show, that due to their large electron affinity macroscopic specimens usually become highly negatively charged, easily achieving values of the order  $\langle Z \rangle \simeq 100e$ , where  $e$  denotes the electron unit (Gail & Sedlmayr 1975; Augustin 1990). This gives rise to an effective Coulomb-coupling between clusters and ions which should cause a considerable increase of the rate of constructive collisions contributing to grain growth. As this process may involve a large variety of positive ions having very different chemical nature heterogeneous grains with compositions much apart from those formed by neutral growth are expected to evolve. Until now, however, no quantitative description of this basically important growth mechanism is available, and the question about the chemical composition and the mineralogical structure of these grains is still open.

### 5.3.3 Chemical growth

This growth mechanism basically can be conceived as a straightforward continuation of the chemical pathway (see Sect. 5.2.2) into the growth domain. It is best illustrated by the example of PAH-formation in the expanding wind of a C-star.

In this case the growth of the critical clusters simply proceeds via a two-step process basically defined

- by formation of a radical site (marked by a dot) by hydrogen abstraction according to the reaction



and

- by addition of an acetylene molecule due to the reaction



where  $A_N$  denotes a polycyclic aromatic molecule consisting of N (hexagonal and pentagonal) rings. By further addition of  $C_2H_2$  and quasi spontaneous ring closure or by a rearrangement process an aromatic molecule with size  $A_{N+1}$  results.

By repetition of this process large two-dimensional flat or curved polycyclic structures are generated (see Keller 1987; Gail & Sedlmayr 1987; Goeres 1993). For large PAHs this growth process can be described by suitably defined moment equations (see Gail & Sedlmayr 1987), the solution of which yields the total amount of the condensed material and the mean size of the resulting particles, from which by functional derivation also the corresponding grain size distribution function follows (Dominik et al. 1989, see Sect. 5.4).

### *5.3.4 Grain coagulation*

In the context of stellar winds until now grain coagulation has not been taken into account. A first investigation of this process (Krüger 1992) applying the moment method proposed by Pruppacher & Klett (1978) suggests, that due to the large grain-grain collision timescales coagulation processes should be rather ineffective in stellar wind situations and, thus, have only a minor effect upon the emerging size distribution function. Despite this result, which has been obtained by rather severe mathematical simplifications, in particular regarding the adopted initial size distribution functions, coagulation deserves further studies. This concerns especially the formation of graphitic (layered) grains from large PAHs, where the adhesive forces seem to become relevant for specimens having more than hundred C-atoms.

### *5.3.5 Fractal structures*

Fractal structures are likely to evolve by grain-grain collisions and thus should be of minor importance in circumstellar shells (cf. Sect. 5.3.4). However, as the question of PAH-coagulation, in particular if curved structures are involved, is still open, the formation of fractal like geometrical shapes deserves further investigation. Under the conditions prevailing in the interstellar medium, Wright (1989) has demonstrated that fractal grain structures are likely to evolve and could be important in particular for the interpretation of the far-infrared and the sub-mm emissivity ( $\lambda > 100\mu m$ ) of the cold components of the interstellar medium, which would provide a critical test on the existence of fractal dust grains in interstellar space.

### 5.4 The grain size spectrum

As the growth regime generally can be described thermodynamically by means of suitably defined moment equations (Gail & Sedlmayr 1988; Gauger et al. 1990; Dominik et al. 1993) the actual grain size spectrum in a dust forming stellar wind can be directly calculated by a functional derivative of the equation for the 0-th moment of the grain size distribution function, which describes the time evolution of the grain number density (Dominik et al. 1989; 1993). From these calculations one infers that, in case of dust-driven winds, selfconsistent solutions always result in a power law like size distribution function

$$f(a) \sim a^{-\beta}$$

for the large particle wing of the final grain component, with  $a$  being the particle size and  $\beta$  the spectral index, which for the large variety of calculated models ranges between 4 and 5. Such a power law, however, only shows up, if dust driven winds, i.e. selfconsistent solutions of the system sketched in Fig. 4 are considered. (see Dominik et al. 1989). In situations where the stellar outflow is not primarily dust induced, but generated by some different process, like mechanical energy input, etc..., asymmetric Gaussian like grain size distribution functions are produced (Dominik et al. 1993). This should be the case for objects situated in the HR-diagram below the critical line for the possibility of dust driven winds (see Dominik et al. 1990).

In recent years considerable progress has been achieved for obtaining reliable size distribution functions for specific primary condensates. Nevertheless, much work remains to be done, in particular regarding the various processes of heterogeneous grain growth, the resulting grain sizes and grain geometries, which are most important ingredients for the calculation of reliable optical properties of the emerging grain components (see Alexander & Ferguson this volume).

## 6 Conclusions

Though considerable progress has been achieved in the last decade regarding cosmic dust condensation a number of important open questions still remain, e.g.:

- What is the true geometrical shape of the grains ? In all calculations adopting classical nucleation theory spherical grains are assumed to evolve.
- What is the true mineralogical structure of the emerging grains, in particular in case of heterogeneous growth ?
- What are the optical constants of these particles ?
- What is the nucleation mechanism in a partially ionised chemistry and what are the critical clusters to be formed ?
- What grain size distribution functions evolve in non-monotonic situations, like Miras and LPVs ?
- etc....

Much work addressing these questions is currently under way. Hence one can be confident, that within the near future the complex physical and chemical problem of astrophysical grain formation, which provides the key for a reliable understanding of many astrophysical objects, can be treated in a quantitatively more adequate manner for the various situations encountered.

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