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Dust formation in stellar winds

VII. Kinetic nucleation theory for chemical non-equilibrium in the gas phase

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Abstract. We present a new theoretical formulation of the nucleation process of solid particles from the gas phase with special emphasis on the effects of chemical non-equilibrium in the gas phase and thermal non-equilibrium between the gas and the clusters or dust grains. In the derivation of the nucleation rates from kinetic theory and from thermodynamic arguments thermal and chemical non-equilibrium are straightforwardly included. A hierarchy of expressions for the stationary nucleation rate is given, ranging from a system of equations, which determines the rate, to an approximate analytic expression in the case of a single dominating growth species, which requires only the time scales of the growth processes and the Gibb's free energy change for the formation of clusters.

Key words: molecular processes – dust, extinction – circumstellar matter – stars: late-type

1. Introduction

Small solid particles, which are found to be generally distributed throughout the interstellar medium (ISM), are not formed in the ISM itself, but in the more dense outflows from stars, especially the winds of Red Giants and Supergiants, and the ejecta of Novae and Supernovae (e.g. Gehrz 1989). The dust forming regions of these objects are characterized by complex dynamical and chemical processes, and substantial non-equilibrium effects are to be expected, whenever velocity fields or sufficiently strong UV radiation are present.

In the ejecta of Novae, for one example, the cluster temperatures are usually controlled by the radiation field and do not equal the kinetic gas temperature. In addition the molecular composition of the gas and also the very small clusters are not in chemical equilibrium, because the conditions change too quickly for the molecular abundances and for the cluster distribution as well to remain in equilibrium (e.g. Beck 1993; Johnson et al. 1993).

Consequently, thermal non-equilibrium between the clusters and the gas and chemical non-equilibrium in the gas phase have to be taken into account in the theoretical description of the dust formation process.

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The most general description of the formation of dust grains from the gas phase is given by the time evolution of the local size distribution function of the dust particles, which is determined by the microscopic gain and loss processes changing the size of the clusters. Balancing these processes results in a master equation, which is in principle restricted only by the assumptions regarding the microscopic processes taken into consideration. A generalized master equation for particle formation in a dilute vapor, which accounts for arbitrary chemical reactions was presented by Gail & Sedlmayr (1988) (henceforth Paper IV). In general, such an approach is unfortunately intractable, because each reaction coefficient of all chemical reactions involved in the process has to be known and the number of different reaction channels increases dramatically with the size of the particles. Therefore, this method is limited by the availability of the basic data for the reactions and the necessary numerical effort. The latter problem can be reduced by splitting the range of cluster sizes into two regions: the region of small clusters up to a few ten monomers, where the kinetic equations are solved for each discrete size, and the region of larger clusters up to radii of the order of 1 μm, where the discrete particle sizes are lumped together into sections of geometrically increasing size (e.g. Girshick & Chiu 1989; Johnson et al. 1993).

Many of the previous approaches to describe the nucleation process of seed particles in astrophysical environments rely on classical nucleation theory or at least on its fundamental assumptions (e.g. Salpeter 1974; Yamamoto & Hasegawa 1977; Draine & Salpeter 1979, Gail et al. 1984, henceforth Paper I). The classical theory assumes, that

- the free energy of formation of small clusters can be approximated in terms of macroscopic parameters such as the surface tension of the bulk solid,
- the cluster vibrational temperature is equal to the gas temperature (thermal equilibrium, TE),
- small clusters are present in equilibrium concentrations,
- chemical equilibrium (CE) prevails in the gas phase.

(see McDonald 1962; Feder et al. 1966; Abraham 1974). Predictions of the classical nucleation theory mostly agree well with the results of nucleation experiments for low supersaturation, low nucleation flux systems (cf. Nuth 1986) for which it has

been developed originally, such as the formation of raindrops in supersaturated air. But the predictions fail for materials with relatively strong covalent or metallic bonds (e.g. Nuth & Donn 1982, 1983). This is also the case for experiments on the nucleation of organic compounds (e.g. Strey et al. 1986; Hung et al. 1989; Peters & Paikert 1989). The problems related to the application of classical nucleation theory to the non-equilibrium conditions found in stellar environments and the uncertainties inherent in this approach have often been discussed, for example by Donn & Nuth (1985), who reject all four assumptions for astrophysical objects based on theoretical arguments.

Therefore, it is the aim of this paper to develop a new formulation of the nucleation process under the conditions of chemical non-equilibrium in the gas phase and of thermal non-equilibrium between the gas and the clusters or dust particles. We use the methods of kinetic nucleation theory and thermodynamic arguments, which refer to a true, physically realizable equilibrium state. In this way non-TE and non-CE effects are straightforwardly included in the derivation of the nucleation rate.

In Sect. 2 we formulate the master equation describing nucleation and grain growth, and introduce the reference equilibrium state and its application to the characteristic time scales of the microscopic processes. This is the foundation for the derivation of expressions for the stationary nucleation rate in Sect. 3, which despite some approximations all include the non-TE and non-CE effects. In Sect. 3.1 the most general case is considered, where several equally important growth species are involved in nucleation. For the special case of a single dominating growth species an analytic form of the nucleation rate is given in Sect. 3.2. With additional assumptions an approximate analytic relationship is derived depending essentially on the growth time scale and the Gibbs free energy of formation of the critical cluster, for which several approximations are discussed in Sect. 3.3. We finish the paper with a summary in Sect. 4.

2. The master equation in the case of chemical and thermal non-equilibrium

In the following we consider solid particle formation for pure substances, i.e. the formation of grains, which consist only of monomers of one kind (e.g. the C-atom in case of pure carbon grains or the SiO molecule in the case of unmixed silicon monoxide dust particles). In addition, we assume for simplicity of presentation that all clusters are compact and have the same shape.[1] Such particles are fully characterized by their size, which is measured by the number of monomers N contained in the particle.

The ensemble of dust particles of different sizes is described by the respective particle densities $f(N,t)$ at time t, and the time evolution of f is determined by the microscopic gain and loss processes changing the particle size N. These processes can be considered in general as chemical reactions between the grain and a molecule, where i-mers of the nucleating species are associated to or dissociated from the grain.

In previous papers (Paper IV; Gauger et al. 1990; Dominik et al. 1993) an explicit distinction was made between homogeneous processes, where the reacting molecule is the i-mer itself, and heteromolecular processes, because in the latter process the dissociation of an i-mer requires the reaction with a molecule, whereas in the homogeneous case the i-mer is spontaneously emitted from the grain, with no reaction partner involved. For the following considerations, we drop this explicit distinction, which is mainly done in order to keep a clear notation in simplified terms. However, the difference between the processes should be kept in mind.

The current treatment of nucleation phenomena is limited by these assumptions regarding the considered microscopic processes changing the cluster size. It can be characterized as hetero-/homomolecular homogeneous nucleation in a diluted vapor. Nucleation processes, where, for example, 3- or many-body reactions are involved, are beyond the scope of this paper, but more general nucleation schemes can be developed along the line of arguments presented in this paper.

2.1. Master equation

Following Paper IV the master equation for the actual particle density $f(N,t)$ of particles with size N can be written as

$$\frac{\mathrm{d}f(N,t)}{\mathrm{d}t} = \sum_{i=1}^{I} J_i^{\mathrm{c}}(N,t) - \sum_{i=1}^{I} J_i^{\mathrm{c}}(N+i,t) \tag{1}$$

where I denotes the maximum i-mer contained in the molecules contributing to the growth of the particle, and $J_i^{\mathrm{c}}(N,t)$ is the effective transition rate for the transition from dust particles of size $N-i$ to particles of size N and vice versa, due to all chemical reactions associating or dissociating an i-mer of the condensing species. This effective transition rate is given by

$$J_i^{\mathrm{c}}(N,t) = \sum_{m_i=1}^{M_i} \left\{ \frac{f(N-i,t)}{\tau_{\mathrm{gr}}(m_i,N-i,t)} - \frac{f(N,t)}{\tau_{\mathrm{ev}}(m_i,N,t)} \right\} \tag{2}$$

where m_i labels the M_i chemical reactions in which an i-mer is associated. Of course one of these M_i reactions describes the homogeneous nucleation process. $\tau_{\mathrm{gr}}(m_i,N-i,t)$ is the actual growth time scale of the growth reaction m_i for a cluster of size $N-i$, and $\tau_{\mathrm{ev}}(m_i,N,t)$ is the actual evaporation time scale of the corresponding reverse reaction.

2.2. The growth and evaporation time scales

The growth time scales can be derived directly from the consideration of the microscopic processes based on gaskinetic theory. Since the gas density in the dust forming regions of astrophysical objects is usually quite low, only two-body reactions have to be taken into account, and the mean free path of the molecules is much larger than the dimension of the dust particles. Then, the growth time scale can be written as

[1] The development can be generalized by inclusion of shape parameters.

$$\tau_{\rm gr}^{-1}(m_i, N-i, t) \;=\; A(N-i)\;\alpha(m_i, N-i)\;\cdot \\ v_{\rm rel}(n_{\rm f}(m_i), N-i)\;n_{\rm f}(m_i, t) \qquad (3)$$

Here $n_{\rm f}(m_i, t)$ denotes the particle density of the molecule of the growth (or forward) reaction m_i, $\alpha(m_i, N-i)$ is the reaction efficiency, $v_{\rm rel}(n_{\rm f}(m_i), N-i)$ is the average relative velocity between the molecule and the cluster[2], and $A(N-i)$ is a suitably defined reaction surface of the cluster of size $N-i$. In the case of heteromolecular processes the evaporation time scale of the reverse reaction corresponding to m_i can be written formally in the same way

$$\tau_{\rm ev}^{-1}(m_i, N, t) \;=\; A(N)\;\beta(m_i, N)\;\cdot \\ v_{\rm rel}(n_{\rm r}(m_i), N)\;n_{\rm r}(m_i, t) \qquad (4)$$

where $n_{\rm r}(m_i, t)$ is the particle density of the molecule in this reverse reaction and $\beta(m_i, N)$ is the respective reaction efficiency. If the reaction efficiencies were all known, the growth and evaporation time scales could be calculated directly from these equations. However, the growth efficiencies are often uncertain, and the evaporation coefficients $\beta(m_i, N)$ are mostly unknown.

For homogeneous nucleation, the evaporation process, the 'spontaneous emission' of the growth molecule or a part of it, occurs without a reaction partner from the gas phase. In this case it is in principle possible to derive the evaporation time scale from first principles, and a number of approaches have been developed recently (cf. Oxtoby 1992). However, the uncertainties inherent in these theories are still quite large. Therefore, one has to rely on equilibrium thermodynamics for the determination of the evaporation time scales for both homogeneous and heteromolecular processes.

In local thermodynamic equilibrium between the gas phase and clusters, the **principle of detailed balance** holds for the single microscopic growth processes and their respective reverse reactions. This fact can be used to express the evaporation time scale $\tau_{\rm ev}(m_i, N, t)$ of the reverse reaction in terms of the growth time scale $\tau_{\rm gr}(m_i, N-i, t)$ of the corresponding growth reaction. However, the reference equilibrium situation has to be defined carefully.

2.3. Definition of the reference equilibrium state

Conventional nucleation theory considers an artificial thermodynamic equilibrium state of clusters in a **supersaturated** vapor, which can be maintained only hypothetically by constraining the size distribution of clusters to be in equilibrium with a supersaturated vapor, but cannot be attained in reality, since the supersaturated vapor is not in phase equilibrium and therefore unstable (Katz & Wiedersich 1977; Katz & Donohue 1979). Sometimes the 'existence' of this unattainable constrained distribution is justified in principle by a Maxwell demon, who breaks up all clusters beyond a certain size and returns the particles as monomers to the system, which are then available to form clusters, again. Unfortunately, the reference to such an artificial constrained state obscures the contributions coming from kinetic theory and thermodynamic arguments, especially in situations where chemical and thermal non-equilibrium have to be taken into account.

As Katz & Wiedersich (1977) have shown it is not necessary to refer to this artificial state of constrained equilibrium in order to obtain the evaporation time scales. Following their arguments we consider the state of clusters (or N-mers) in a **saturated** vapor, which is characterized by phase equilibrium between the monomers and the bulk solid phase, i.e. $\mathcal{S}_1 = 1$, where $\mathcal{S}_1$ denotes the supersaturation ratio of the monomers. It is shown in Appendix A, that in this situation the supersaturation ratio of an N-mer with respect to the bulk solid phase is given by $\mathcal{S}_N = (\mathcal{S}_1)^N$, if the temperatures of all components are equal, i.e. the gas and the clusters are in thermal equilibrium, and if the gas phase is in chemical equilibrium. Therefore, the N-mers are in chemical equilibrium with the monomers, and in a saturated vapor with $\mathcal{S}_1 = 1$ they are also in phase equilibrium with the bulk solid phase. Consequently, the N-mers must be in phase equilibrium with the monomers as well. The latter conclusion remains valid, even if we now assume, that there is no bulk solid phase present. Thus, the principle of detailed balance holds for N-mers of all sizes in the so defined equilibrium state.

To summarize, the equilibrium state is characterized by the phase equilibrium between monomers as well as N-mers and the bulk solid, by simultaneous chemical equilibrium in the gas phase, and by thermal equilibrium, with equal temperatures of the solid, the clusters and the gas, i.e. it is a state of local thermodynamic equilibrium (LTE-state).

2.4. Application of the detailed balance

Since the values of all quantities in the LTE-state are determined, once the mass density, the abundances of the elements, and the equilibrium temperature are chosen, these quantities relate the LTE-state to the actual situation in the gas where condensation takes place. Obviously, the values of the mass density and elemental abundances are fixed by the values in the actual situation. Because we want to express $\tau_{\rm ev}$ in terms of $\tau_{\rm gr}$ for the clusters of size N, the equilibrium temperature is given by the internal temperature $T_{\rm d}(N)$ of the N-clusters. This means, that if the temperature of the clusters in the actual situation depends on their size, one has to refer to a different LTE-state for each cluster size, which is determined by the respective cluster temperature.

Let us denote all quantities referring to the LTE-state with an '$\circ$', which indicates also the explicit or implicit dependence on the equilibrium temperature $\overset{\circ}{T} = T_{\rm d}(N)$. As stated in the previous section the condition of detailed balance holds for each

[2] In this paper we only consider the relative velocity due to the thermal motion of the gas, but neglect any systematic motion (drift) of the grains relative to the gas. The effects of drift are discussed in a recent paper by Krüger & Sedlmayr (1997).

microscopic process and thus, the effective transition rate of the chemical reaction m_i (cf. Eq. (2)) equals zero for all cluster sizes, which leads to the following equation for the N-cluster:

$$\frac{\overset{\circ}{f}\,(N-i)}{\overset{\circ}{\tau}_{\rm gr}\,(m_i,N-i)} = \frac{\overset{\circ}{f}\,(N)}{\overset{\circ}{\tau}_{\rm ev}\,(m_i,N)}\ . \tag{5}$$

$\overset{\circ}{f}\,(N-i)$, $\overset{\circ}{f}\,(N)$, $\overset{\circ}{n}_{\rm f}\,(m_i)$, and $\overset{\circ}{n}_{\rm r}\,(m_i)$ are the *equilibrium* particle densities of the $N-i$ clusters, of the N-mers, and of the molecules involved in the growth reaction and its corresponding reverse reaction. These equilibrium particle densities can be determined from the law of mass action

$$\left(\frac{\overset{\circ}{f}\,(N-i)\ \ \overset{\circ}{n}_{\rm f}\,(m_i)}{\overset{\circ}{f}\,(N)\ \ \overset{\circ}{n}_{\rm r}\,(m_i)}\right) = \exp\left(\frac{\Delta_{\rm r}\overset{\ominus}{G}(m_i,N,T_{\rm d}(N))}{R\,T_{\rm d}(N)}\right) \tag{6}$$

The Gibbs energy of the reaction $\Delta_{\rm r}\overset{\ominus}{G}(m_i,N,T_{\rm d}(N))$ is given by the standard molar Gibbs free energy of formation of all reaction participants at the temperature $T_{\rm d}(N)$

$$\begin{aligned}&\Delta_{\rm r}\overset{\ominus}{G}(m_i,N,T_{\rm d}(N)) = \\ &\quad\Delta_{\rm f}\overset{\ominus}{G}(N,T_{\rm d}(N)) - \Delta_{\rm f}\overset{\ominus}{G}(N-i,T_{\rm d}(N)) + \\ &\quad\Delta_{\rm f}\overset{\ominus}{G}(n_{\rm r}(m_i),T_{\rm d}(N)) - \Delta_{\rm f}\overset{\ominus}{G}(n_{\rm f}(m_i),T_{\rm d}(N))\end{aligned} \tag{7}$$

With Eqs. (5) and (6) Eq. (4) can be written as

$$\begin{aligned}\tau_{\rm ev}^{-1}(m_i,N,t) = \tau_{\rm gr}^{-1}(m_i,N-i,t)\,\alpha_*(m_i,N)\,v_{\rm rel}^*(m_i,N)\,\cdot \\ \frac{n_{\rm r}(m_i,t)}{n_{\rm f}(m_i,t)}\exp\left(\frac{\Delta_{\rm r}\overset{\ominus}{G}(m_i,N,T_{\rm d}(N))}{R\,T_{\rm d}(N)}\right)\end{aligned} \tag{8}$$

which clearly demonstrates, that the decisive quantity to express $\tau_{\rm ev}$ in terms of $\tau_{\rm gr}$ is not the equilibrium cluster distribution $\overset{\circ}{f}\,(N)$, but rather the standard molar Gibbs free energies of formation $\Delta_{\rm f}\overset{\ominus}{G}$ of the reaction participants.

The non-TE effects caused by deviations from a TE-population of states of the reacting molecules in the forward and reverse reactions are comprised by the quantity

$$\alpha_*(m_i,N) = \left(\frac{\overset{\circ}{\alpha}\,(m_i,N-i)}{\alpha(m_i,N-i)}\right)\Bigg/\left(\frac{\overset{\circ}{\beta}\,(m_i,N,i)}{\beta(m_i,N,i)}\right) \tag{9}$$

with $\overset{\circ}{\alpha}\,(m_i)$ and $\overset{\circ}{\beta}\,(m_i)$ denoting the reaction efficiencies averaged over all possible quantum states of the reacting particles with respect to a TE-population of states at the temperature $T_{\rm d}(N)$ (see Paper IV, for more details). The dimensionless quantity

$$\begin{aligned}v_{\rm rel}^*(m_i,N)\ =\ &\left(\frac{\overset{\circ}{v}_{\rm rel}\,(n_{\rm f}(m_i),N-i)}{v_{\rm rel}(n_{\rm f}(m_i),N-i)}\right)\Bigg/ \\ &\left(\frac{\overset{\circ}{v}_{\rm rel}\,(n_{\rm r}(m_i),N)}{v_{\rm rel}(n_{\rm r}(m_i),N)}\right)\end{aligned} \tag{10}$$

describes the deviations caused by different relative velocities in the actual situation and in the LTE-state. We consider only relative velocities $v_{\rm rel}$ due to the thermal motion of the gas, which are proportional to the square root of the temperature of the gas divided by the reduced mass of the cluster and molecule. Therefore, the relative velocities in Eq. (10) cancel pairwise and $v_{\rm rel}^*$ equals one in the case of heteromolecular processes. For homogeneous nucleation, where no reaction partner is needed for the reverse reaction, the remaining ratio $v_{\rm rel}^* = (\overset{\circ}{v}_{\rm rel}\,(n_{\rm f}(m_i),N-i)/v_{\rm rel}(n_{\rm f}(m_i),N-i))$ results in a factor of $(T_{\rm d}(N)/T_{\rm g})^{1/2}$ appearing in Eq. (8).

If we keep the equilibrium particle densities instead of replacing them via $\Delta_{\rm r}\overset{\ominus}{G}(m_i,N,T_{\rm d}(N))$ an alternative form of Eq. (8) is obtained

$$\begin{aligned}\tau_{\rm ev}^{-1}(m_i,N,t) = \tau_{\rm gr}^{-1}(m_i,N-i,t)\,\alpha_*(m_i,N)\,v_{\rm rel}^*(m_i,N)\,\cdot \\ \frac{1}{S^i(T_{\rm d}(N))}\,\frac{1}{b_{\rm g}(m_i,T_{\rm d}(N))}\,\frac{\overset{\circ}{f}\,(N-i)}{\overset{\circ}{f}\,(N)}\end{aligned} \tag{11}$$

where $S(T_{\rm d}(N))$ is the supersaturation ratio, defined as the ratio of the actual partial pressure of the monomers to the vapor saturation pressure above the flat surface of the solid with the temperature $T_{\rm d}(N)$

$$S = \frac{p(1,t)}{p_{\rm sat}(T_{\rm d}(N))} \tag{12}$$

and $b_{\rm g}(m_i,T_{\rm d}(N))$ denotes a generalized departure coefficient with respect to the reaction m_i, which is derived in Appendix B. It comprises the effects of thermal non-equilibrium between N-clusters and the gas and the departures of the particle densities of the monomers and of the molecules of the growth and the reverse reaction m_i due to chemical non-equilibrium in the gas phase (see also Gauger et al. 1990).

3. The stationary nucleation rate for chemical and thermal non-equilibrium

3.1. A general expression for the stationary nucleation rate

For typical conditions in circumstellar dust shells two regions in particle size space can be distinguished with respect to the growth of the solid particles.

In the submacroscopic region cluster properties relevant to growth depend strongly on the cluster size, but whenever the growth processes are sufficiently fast, the 'flow' of clusters up to larger sizes can be considered to be a stationary process. In the macroscopic region those properties become independent of size, but due to the larger size of the dust particles stationarity will break down and grain growth has to be treated as a time dependent process.

This division into two size regimes can be illustrated by an estimate for the time a particle needs to grow up to a certain (macroscopic) size N. Neglecting the destructive processes and approximating the reaction rates of the growth processes by

the collisional rates the growth time $t_{\rm gr}$ is very roughly given by $t_{\rm gr}(N) \propto N^{1/3}$ which for large particle sizes exceeds e.g. the hydrodynamic time scale. A more thorough discussion and quantitative estimates of $t_{\rm gr}(N)$ for typical conditions in circumstellar dust shells of Red Giants are given in Paper IV. Comparison with the characteristic time scales for changes in the outflow shows, that depending on the reaction efficiencies stationarity may hold up to quite large N, of the order of 10^6, for C-rich AGB stars and somewhat smaller, but still large sizes for cool, oxygen-rich late-type stars (M-stars), except at the lowest observed mass loss rates, where the stationarity concept fails. From these conditions we conclude, that nucleation is a stationary process in circumstellar shells, where effective dust formation takes place. Otherwise the nucleation process has to be treated as a time dependent problem as described by the master equation (Eqs. (1) and (2)).

If the growth time $t_{\rm gr}(N_l)$ to macroscopic particles of sizes $N \geq N_l$, where the particles already show properties of the bulk solid, is small compared to the time scales for changes in the environment, the time it takes to establish a stationary flow of clusters up to N_l in cluster size space can be neglected. The stationary flow implies that the particle densities of the clusters do not change in time, i.e. $f(N,t) = \hat{f}(N)$, and this steady state distribution of cluster densities is build up almost instantaneously under the momentarily prevailing conditions.

Let us introduce the current density $\mathbf{J}^{\rm c}(N,t)$ of clusters flowing upwards in cluster size space at size N, given by

$$\mathbf{J}^{\rm c}(N,t) = \sum_{i=1}^{I} \sum_{k=0}^{i-1} J_i^{\rm c}(N+k,t) \tag{13}$$

which can be also interpreted as the rate of formation of clusters of size N. Since the $\hat{f}(N)$ are constant in time one obtains from Eq. (1) with $\mathbf{J}^{\rm c}(N,t)$ the condition of the effective transition rates

$$0 = \mathbf{J}^{\rm c}(N,t) - \mathbf{J}^{\rm c}(N+1,t) \tag{14}$$

Thus, stationarity implies that the current densities in size space are equal to one another at time t, and therefore equal to a size independent rate of cluster formation or *stationary nucleation rate*:

$$\mathbf{J}_*^{\rm c}(t) = \mathbf{J}^{\rm c}(N,t) \qquad N = I+1,\ I+2\ ... \tag{15}$$

As discussed already in Paper IV, this equation yields, in principle, an infinite system of linear equations for $\mathbf{J}_*^{\rm c}$ and the steady state particle densities of the clusters $\hat{f}(N)$. However, the destructive processes have to become negligible for sufficiently large particle sizes, since otherwise the dust particles would evaporate on average. Therefore, a truncation of the system is possible at a cluster size $\hat{N}$ chosen suitably large, but smaller than N_l, and the solution of the truncated system is independent of this special choice (see Appendix A of Paper IV for a rigorous proof).

Inserting the definitions of the effective transition rates (Eq. (2)) and the current densities (Eq. (13)) into Eq. (15), one obtains

$$\mathbf{J}_*^{\rm c}(t) = \sum_{i=-I}^{I-1} C_i(N+i,t)\ \hat{f}(N+i) \qquad N = I+1,\ ...\ , \hat{N} \tag{16}$$

(cf. Paper IV), where the coefficients are given by

$$C_i(N+i,t) = \sum_{j=|i|}^{I} \sum_{m_j=1}^{M_j} \tau_{\rm gr}^{-1}(m_j, N+i, t) \tag{17}$$

for $i = -I,\ ...\ , -1$, and by

$$C_i(N+i,t) = -\sum_{j=i+1}^{I} \sum_{m_j=1}^{M_j} \tau_{\rm ev}^{-1}(m_j, N+i, t) \tag{18}$$

for $i = 0,\ ...\ , I-1$. Since the latter coefficients vanish for $N = \hat{N}$, the system consists of as many equations as unknowns and can be solved, at least numerically, provided the necessary input data, such as the size dependent reaction efficiencies, are known.

In the most general cases, when several cluster sizes are connected by several equally important growth species only a numerical solution is possible. However, often the nucleation process is dominated by one or few molecules, for example acetylene in the formation of soot from flames (Frenklach & Wang 1994). Then an analytic expression for $\mathbf{J}_*^{\rm c}$ can be obtained, as demonstrated in Sect. 3.2.

For $N = I+1, ..., 2I$ the particle densities of the i-mers appear in the set of Eqs. (15). The usual assumption introduced at this point in classical nucleation theory (e.g. Abraham 1974) is to assume that the particle densities of the i-mers are also determined by stationarity, and that they approach the equilibrium densities of the i-mers in the artificial constrained equilibrium with the supersaturated vapor.

However, this is not appropriate if nucleation takes place in an environment where processes are present which drive the system away from equilibrium. This is the case in stellar outflows, where the particle densities of the molecules may deviate substantially from the equilibrium densities due to the presence of a velocity field or of a sufficiently strong UV radiation field (cf. Beck et al. 1992). At the same time the temperature of the clusters can be different from the gas temperature and may depend on the cluster size, if for example $T_{\rm d}(N)$ is determined by the radiation field rather than by collisions with the surrounding gas (e.g. for PAH's, see Cherchneff et al. 1991).

Once condensation is possible in such a non-equilibrium situation, the reaction chain for nucleation has to start at the i-mers with their actual particle densities as they are determined by the gas phase chemistry, and the steady state distribution of the cluster densities has to adjust accordingly.

3.2. Analytic approximation of the nucleation rate for the case of a single dominating growth species

In the following, we consider a situation where nucleation proceeds by reactions with one molecule only, which associates or dissociates an I-mer.

In this case, each growth process increases the size of the cluster by $\Delta N = I$, and it is obvious, that I separate reaction chains will develop, because the first reaction step is the reaction of the molecule containing an I-mer with other molecules containing k-mers, where k can take on the values $k = 1, 2, ..., I$. The first reaction chain starts with the addition of an I-mer to the monomer and proceeds via the sizes $N = 1 + I, 1 + 2I, ...$, the second chain starts with the dimer and proceeds via $N = 2 + I, 2 + 2I, ...$, and so forth. Since the total rate of particle formation is simply given by the sum over all reaction chains, we derive the stationary nucleation rate for one chain as an example.

It is convenient for the following derivation to express the cluster size N in terms of I, which yields:

$$N = k + \nu I \qquad \text{with} \quad \nu = 1, 2, ... \tag{19}$$

where k numbers the I separate reactions chains.

The system of equations resulting from Eqs. (16)-(18) for the reaction chain k can be solved analytically by the procedure of Becker & Döring (1935). Thereby the algebraic equations for each $N = k + \nu I$ are solved by a simple elimination procedure, i.e. by inserting the expression for the steady state density $\hat{f}(N' - I)$ resulting from the equation for $N = N'$ into the equation for $N = N' - I$, which finally yields one equation for the stationary nucleation rate $J^{\rm c}_{*,k}(t)$ for the kth chain:

$$J^{\rm c}_{*,k}(t) \left(1 + \sum_{\nu=1}^{\hat{\nu}-1} \prod_{\mu=1}^{\nu} \frac{\tau_{\rm gr}(m_I, k+\mu I, t)}{\tau_{\rm ev}(m_I, k+\mu I, t)} \right) = \tag{20}$$

$$\frac{f(k,t)}{\tau_{\rm gr}(m_I, k, t)} - \frac{\hat{f}(k+\hat{\nu} I)}{\tau_{\rm ev}(m_I, k+\hat{\nu} I, t)} \prod_{\nu=1}^{\hat{\nu}-1} \frac{\tau_{\rm gr}(m_I, k+\nu I, t)}{\tau_{\rm ev}(m_I, k+\nu I, t)}$$

Here $f(k,t)$ is the *actual* particle density of the k-mer at which the chain starts. As explained in the previous section, this particle density can be different from the equilibrium density in the state of LTE between the cluster and the gas.

Since the destructive processes can be neglected for $N \geq \hat{N} = k + \hat{\nu} I$ the second term on the r.h.s. vanishes and we obtain a direct expression for the nucleation rate $J^{\rm c}_{*,k}(t)$ in terms of the growth and evaporation time scales

$$J^{\rm c}_{*,k}(t) =$$

$$\frac{f(k,t)}{\tau_{\rm gr}(m_I, k, t)} \left(1 + \sum_{\nu=1}^{\hat{\nu}-1} \prod_{\mu=1}^{\nu} \frac{\tau_{\rm gr}(m_I, k+\mu I, t)}{\tau_{\rm ev}(m_I, k+\mu I, t)} \right)^{-1} \tag{21}$$

As discussed in Sect. 2.2 the evaporation time scales $\tau_{\rm ev}$ are mostly unknown, but they can be expressed in terms of the growth time scales $\tau_{\rm gr}$ and equilibrium quantities referring to the LTE-state defined in Sect. 2.3. Inserting Eq. (8) for the evaporation time scale into Eq. (21) results in

$$J^{c\,-1}_{*,k}(t) = \frac{\tau_{\rm gr}(m_I, k, t)}{f(k,t)} \cdot$$

$$\left[1 + \sum_{\nu=1}^{\hat{\nu}-1} \frac{\tau_{\rm gr}(m_I, k+\nu I, t)}{\tau_{\rm gr}(m_I, k, t)} \left(\frac{n_{\rm r}(m_I, t)}{n_{\rm f}(m_I, t)} \right)^{\nu} \cdot \right.$$

$$\prod_{\mu=1}^{\nu} \alpha_*(m_I, k+\mu I)\, v^*_{\rm rel}(m_I, k+\mu I) \cdot$$

$$\left. \exp\left(\frac{\Delta_{\rm r}\overset{\ominus}{G}(m_I, k+\mu I, T_{\rm d}(k+\mu I))}{R\, T_{\rm d}(k+\mu I)} \right) \right] \tag{22}$$

Consequently, the task of predicting the rate of nucleation has been reduced to two simpler problems (see also e.g. Katz & Donohue 1979):

i) the determination of the growth time scale $\tau_{\rm gr}$ from chemical kinetic theory or rate measurements, and
ii) the determination of the thermodynamic properties of the N-clusters and their reaction partners, as comprised in the $\Delta_{\rm f}\overset{\ominus}{G}$'s, from equilibrium thermodynamics.

If these quantities are known the summation in Eq. (22) can be evaluated numerically rather easily, especially because apart from the actual particle densities of the reaction partners $(n_{\rm f}(m_I, t), n_{\rm r}(m_I, t))$ only the actual particle density $f(k,t)$ of the k-mer, at which the reaction chain starts, appears in the stationary nucleation rate. Unfortunately, in practice the necessary thermodynamic data, especially the size dependent Gibbs free energy of formation of the clusters, is lacking for many cases. Furthermore, often even the sequences of chemical reactions in the nucleation processes are not known definitely, for example for the condensates in circumstellar dust shells of oxygen-rich, late-type stars. In such cases one has to fall back upon the concepts of conventional nucleation theory in order to obtain the equilibrium distribution of clusters.

The expression (11) can be used alternatively to express $\tau_{\rm ev}$ in terms of $\tau_{\rm gr}$ and the equilibrium particle densities. Then, Eq. (22) reads

$$J^{c\,-1}_{*,k}(t) = \frac{\tau_{\rm gr}(m_I, k, t)}{f(k,t)} \left[1 + \right.$$

$$\sum_{\nu=1}^{\hat{\nu}-1} \frac{\tau_{\rm gr}(m_I, k+\nu I, t)}{\tau_{\rm gr}(m_I, k, t)} \prod_{\mu=1}^{\nu} \frac{\overset{\circ}{f}(k+(\mu-1)I)}{\overset{\circ}{f}(k+\mu I)} \cdot$$

$$\left. \prod_{\mu=1}^{\nu} \frac{\alpha_*(m_I, k+\mu I)\, v^*_{\rm rel}(m_I, k+\mu I)}{S^I(T_{\rm d}(k+\mu I))\, b_{\rm g}(m_I, T_{\rm d}(k+\mu I))} \right] \tag{23}$$

This equation as well as Eq. (22) cannot be simplified more, because in general the equilibrium quantities in the products

on the r.h.s. refer to different LTE-states, which are characterized by the cluster temperature corresponding to the respective cluster size (cf. Sect. 2.4). To proceed further we introduce the assumption that the temperature of the clusters does not depend on their size, i.e. $T_{\rm d}(N) = T_{\rm d}$, which means, that the equilibrium quantities refer to a single LTE-state with the temperature $T_{\rm d}$.

Since only relative velocities due to the thermal motion of the gas are considered, we have $v^*_{\rm rel} = 1$ for heteromolecular processes, and $v^*_{\rm rel} = (T_{\rm d}/T_{\rm g})^{1/2}$ for homogeneous processes (see Sect. 2.4). If we moreover assume, that $\alpha_*(m_I, N) = \alpha_*(m_I)$, independent of N, Eq. (23) reduces to

$$J^{c\ -1}_{*,k}(t) = \frac{1}{S^k(T_{\rm d})\, b_{\rm g}(k, T_{\rm d})} \cdot \sum_{\nu=0}^{\hat{\nu}-1} \frac{\tau_{\rm gr}(m_I, k+\nu I, t)}{\overset{\circ}{f}\,(k+\nu I, T_{\rm d})} \left(\frac{\alpha_*(m_I)\, v^*_{\rm rel}(m_I)}{S^I(T_{\rm d})\, b_{\rm g}(m_I, T_{\rm d})} \right)^{\nu} \tag{24}$$

where $b_{\rm g}(k, T_{\rm d})$ denotes the generalized departure coefficient for the k-mer (see Appendix B). In the following we will drop the dependence of the equilibrium quantities on the temperature $T_{\rm d}$ of the LTE-state (shown here for clarity), in most arguments.

The equilibrium state to which the $\overset{\circ}{f}\,(N)$ refer, is the case of LTE between clusters and the gas, i.e. the vapor is saturated. In this state the equilibrium distribution $\overset{\circ}{f}\,(N)$ decreases monotonically with N (e.g. McDonald 1962). However, from a comparison with the results of standard nucleation theory for nucleation at thermal and chemical equilibrium (but no phase equilibrium) it is obvious, that $\overset{\circ}{f}\,(N)$ divided by the second term in Eq. (24) must have a minimum, which again defines critical cluster size N_*. Assuming this ratio to change smoothly with the cluster size around the critical cluster, and since the main contribution to the sum comes from this region, the summation in Eq. (24) can be replaced by an integration w.r.t. the cluster size. With a transformation from the size variable ν back to $N = k + \nu I$ one obtains

$$J^{c\ -1}_{*,k}(t) = \frac{1}{I\, S^k(T_{\rm d})\, b_{\rm g}(k)} \left(\frac{S^I(T_{\rm d})\, b_{\rm g}(m_I)}{\alpha_*(m_I)\, v^*_{\rm rel}(m_I)} \right)^{k/I} \cdot \int_k^{\hat{N}-I} \frac{\tau_{\rm gr}(m_I, N, t)}{\overset{\circ}{f}\,(N)} \exp\left\{ -\frac{N}{I} \ln\left(\frac{S^I(T_{\rm d})\, b_{\rm g}(m_I)}{\alpha_*(m_I)\, v^*_{\rm rel}(m_I)} \right) \right\} {\rm d}N \tag{25}$$

For an equilibrium state the particle densities of the clusters are given by a Boltzmann-like distribution in size space

$$\overset{\circ}{f}\,(N) = \overset{\circ}{f}\,(1)\ \exp\left\{ -\frac{\triangle G(N)}{R\, T_{\rm d}} \right\} \tag{26}$$

(Abraham 1974), where $\overset{\circ}{f}\,(1)$ is the equilibrium density of the monomer. Since we refer to the LTE-state of clusters in a saturated vapor, $\overset{\circ}{f}\,(1)$ is equal to the particle density corresponding to the vapor saturation pressure $p_{\rm sat}(T_{\rm d})$ (see Appendix A). Thus, $\overset{\circ}{f}\,(1)$ is not an undetermined quantity, which can be set equal to $f(1, t)$, as it is done in classical nucleation theory (Girshick & Chiu 1990). $\triangle G(N)$ denotes the free energy change associated with the formation of a cluster of size N from the saturated vapor, and it is related to the standard molar Gibbs free energy of formation of the N-cluster $\Delta_{\rm f}\overset{\ominus}{G}\,(N)$ by

$$\triangle G(N) = \Delta_{\rm f}\overset{\ominus}{G}\,(N) + R\, T_{\rm d}\ \ln\left(\frac{p_{\rm sat}(T_{\rm d})}{\overset{\ominus}{p}} \right) - N \Delta_{\rm f}\overset{\ominus}{G}_1(s) \tag{27}$$

where $\Delta_{\rm f}\overset{\ominus}{G}_1(s)$ is the standard molar Gibbs free energy of formation of the solid phase and $\overset{\ominus}{p}$ denotes the pressure of the standard state (see Appendix A). Some approximations for this free energy change, which are based on the concepts of classical nucleation theory are discussed in Sect. 3.3.

Inserting Eq. (26) into Eq. (25) and combining the two exponential functions into one yields

$$\exp(\mathcal{A}(N)) = \exp\left\{ \frac{\triangle G(N)}{R\, T_{\rm d}} - \frac{N}{I} \ln\left(\frac{S^I(T_{\rm d})\, b_{\rm g}(m_I)}{\alpha_*(m_I) v^*_{\rm rel}(m_I)} \right) \right\} \tag{28}$$

We now approximate the argument of the exponential function $\mathcal{A}(N)$, which has a maximum at N_*, by its truncated Taylor expansion around N_*

$$\mathcal{A}(N) \approx \frac{\triangle G(N_*)}{R\, T_{\rm d}} - \frac{N_*}{I} \ln\left(\frac{S^I(T_{\rm d})\, b_{\rm g}(m_I)}{\alpha_*(m_I)\, v^*_{\rm rel}(m_I)} \right) + \frac{(N-N_*)^2}{2R\, T_{\rm d}} \left(\frac{\partial^2 \triangle G}{\partial N^2} \right)_{N_*} \tag{29}$$

Since the growth time scale depends only weakly on the size, $\tau_{\rm gr}$ can be replaced by its value at N_*, to obtain after some algebra

$$J^{c\ -1}_{*,k}(t) = \frac{1}{I\, S^k(T_{\rm d})\, b_{\rm g}(k)} \left(\frac{S^I(T_{\rm d})\, b_{\rm g}(m_I)}{\alpha_*(m_I)\, v^*_{\rm rel}(m_I)} \right)^{(k-N_*)/I} \cdot \frac{\tau_{\rm gr}(m_I, N_*, t)}{\overset{\circ}{f}\,(N_*)} \cdot \int_{-(N_*-k)}^{\hat{N}-N_*-I} \exp\left\{ \frac{1}{2R\, T_{\rm d}} \left(\frac{\partial^2 \triangle G}{\partial N^2} \right)_{N_*} x^2 \right\} {\rm d}x \tag{30}$$

If most of the contribution comes from the region around N_*, the value of the integral will change insignificantly, if we replace the lower limit by $-\infty$ and the upper limit by ∞. The solution of the resulting integral is given by

$$\int_{-\infty}^{\infty} \exp\{-a x^2\}\ {\rm d}x = \sqrt{\frac{\pi}{a}} \tag{31}$$

The r.h.s. of this equation (31) is the inverse of the well known Zeldovich factor, which is defined by

$$Z(N_*) = \left(\frac{1}{2\pi R\, T_\mathrm{d}} \left| \frac{\partial^2 \triangle G}{\partial N^2} \right|_{N_*} \right)^{1/2} \tag{32}$$

With these rather mathematic approximations we finally obtain the following expression for the stationary nucleation rate:

$$\begin{aligned} J^\mathrm{c}_{*,k}(t) \;=\; & I\, \frac{\overset{\circ}{f}\,(N_*)}{\tau_\mathrm{gr}(m_I, N_*, t)}\, Z(N_*) \;\cdot \\ & S^k(T_\mathrm{d})\, b_\mathrm{g}(k) \;\cdot \\ & \exp\left\{ \frac{(N_* - k)}{I} \ln\left(\frac{S^I(T_\mathrm{d})\, b_\mathrm{g}(m_I)}{\alpha_*(m_I)\, v^*_\mathrm{rel}(m_I)} \right) \right\} \end{aligned} \tag{33}$$

The factor in the first line of Eq. (33) resembles the usual expression for the nucleation rate, which describes nucleation in the classical case of thermal equilibrium between clusters and gas and chemical equilibrium in the gas phase, but no phase equilibrium between clusters and the gas (e.g. Eq. (2.17) in Paper I; Eq. (8) in Feder et al. (1966)).

The departure coefficient $b_\mathrm{g}(k)$ corresponding to the actual particle density of the k-mer $f(k,t)$, which appears in Eq. (33), reflects the difference to the classical approach. In our treatment the reaction chain starts at the k-mer, with its particle density, as it is determined by the gas phase chemistry, which can deviate significantly from the particle density in chemical equilibrium, as defined in Sect. 2.3. The exponential function represents a correction of the 'classical' bulk term, which accounts for the effects of deviations from thermal equilibrium and chemical equilibrium.

Finally, the total nucleation rate for addition or dissociation of an I-mer at time t is given by the sum over all reaction chains of the dominant nucleation reaction m_I, i.e.

$$\mathbf{J}^\mathrm{c}_*(t) = \sum_{k=1}^{I} J^\mathrm{c}_{*,k}(t) \tag{34}$$

3.3. Some remarks on the Gibbs free energy change $\Delta G(N)$ and the equilibrium cluster size distribution

In this section we compare different approximations for $\Delta G(N)$, which are based on the concepts of the classical theory, and discuss their effects on the analytic expression for J^c_*.

In Sect. 3.2 we introduced with Eq. (26) the following expression for the equilibrium size distribution of clusters

$$\overset{\circ}{f}\,(N) = \overset{\circ}{f}\,(1) \exp\left\{ -\frac{\triangle G(N)}{R\,T} \right\}$$

where $\triangle G(N)$ is the Gibbs free energy change associated with the formation of the N-cluster from the vapor, and $\overset{\circ}{f}\,(1)$ is the equilibrium particle density of the monomer. Obviously, the value of $\overset{\circ}{f}\,(1)$ as well as the form of $\triangle G(N)$ depend on the definition of the reference equilibrium state.

As we have pointed out in Sect. 2.3 classical nucleation theory refers to a state of **constrained** equilibrium between the clusters and the supersaturated vapor at the same supersaturation ratio S and temperature T existing in the real situation. Based on thermodynamic arguments the Gibbs free energy of formation for the N-cluster in this constrained equilibrium is derived as

$$\frac{\Delta G(N)}{RT} = -N\, \ln(S) + \theta_\infty\, N^{2/3} \quad \text{with} \quad \theta_\infty = \frac{4\pi r_0^2 \sigma}{k_B T} \tag{35}$$

(McDonald 1962), where the cluster is considered to be a spherical droplet with a hypothetical monomer radius r_0, and σ is the surface energy of the macroscopic solid, thus neglecting any dependence of the surface energy of the cluster on size. The first term gives the free energy of N monomers in the bulk solid, and the second term describes the surface free energy, i.e. the contribution from the creation of the surface of the N-cluster.

Due to the definition of the constrained equilibrium, the equilibrium particle density of the monomer in this state is equal to the monomer particle density in the actual situation, $\overset{\circ}{f}\,(1) = f(1,t)$, which yields

$$\overset{\circ}{f}\,(N) = f(1,t)\, \exp\left\{ N\, \ln(S) - \theta_\infty\, N^{2/3} \right\} \tag{36}$$

for the cluster size distribution in the constrained equilibrium state. If this is inserted into $J_*(t) = \tau_\mathrm{gr}^{-1}(1, N_*, t)\, \overset{\circ}{f}\,(N_*) Z(N_*)$ (cf. Eq. (33)) the result of classical nucleation theory (e.g. Abraham 1974) is recovered.

Despite the fact that the classical approach presupposes thermal equilibrium between the clusters and the gas, and chemical equilibrium in the gas phase, the classical expression for $\Delta G(N)$ has two additional shortcomings: the size dependence of the surface energy of the clusters is neglected, and it does not yield the the correct limit $\Delta G(N) \to 0$ for $N \to 1$, i.e. it is not consistent.

The latter problem has been pointed out by several authors and Blander & Katz (1972) formulated the following consistent modification

$$\overset{\circ}{f}\,(N) = f(1,t)\, \exp\left\{ (N-1)\, \ln(S) - \theta_\infty\, (N^{2/3} - 1) \right\} \tag{37}$$

which results in a correction of the classical rate by a factor of e^θ / S. A similar correction of the classical form of the Gibbs free energy change has been made by Draine & Salpeter (1977), who obtained in the limit of the bulk material for the surface energy

$$\overset{\circ}{f}\,(N) = f(1,t)\, \exp\left\{ (N-1)\, \ln(S) - \theta_\infty\, (N-1)^{2/3} \right\} \tag{38}$$

Although the consistency correction for $\Delta G(N)$ in Eqs. (37) and (38) seemingly is applied to both the bulk term and the surface term, in fact only the classical surface term needs to be corrected if the LTE-state of a **saturated** vapor as defined

in Sect. 2.3 is chosen as the reference equilibrium. In this state $\overset{\circ}{f}(1)$ equals the particle density corresponding to the vapor saturation pressure, and $\Delta G(N)$ consists of the surface contribution to the Gibbs free energy only.

With this reference state the bulk contribution is a natural result of the derivation of J_* from kinetic theory and thermodynamic arguments (cf. Girshick & Chiu 1990), as a closer inspection of Eq. (33) shows. For $k = I = 1$, $T_\mathrm{d} = T_\mathrm{g}$, $\alpha_*(1) = 1$, and chemical equilibrium in the gas phase, one obtains

$$J^\mathrm{c}_{*,1}(t) \;=\; \tau_\mathrm{gr}^{-1}(1, N_*, t)\, Z(N_*) \\ f(1,t)\, \exp\left\{(N_* - 1)\, \ln(S) - \frac{\Delta G(N_*)}{R T_g}\right\} \quad (39)$$

where we have inserted Eqs. (26) and (B4) for $\overset{\circ}{f}(N_*)$ and $b_\mathrm{g}(1)$, respectively, and expressed $\overset{\circ}{f}(1)$ in terms of $f(1,t)$ and S.

The modified $\Delta G(N)$ satisfy the limit $N = 1$, however, the effects of the curvature on the surface energy for small clusters are not accounted for. To consider this effect Gail et al. (1984) defined a size dependent θ_N, which leads to

$$\frac{\Delta G(N)}{RT} = \theta_\infty \frac{N-1}{(N-1)^{1/3} + N_f^{1/3}} \quad (40)$$

where N_f is a fit factor, essentially representing the particle size at which the surface energy is reduced to one half of the bulk value. Another extension of classical nucleation theory, which corrects for effects of the curvature on σ for smaller clusters, was suggested by Dillmann & Meier (1991).

To conclude this section, we give an expression for the stationary nucleation rate for those cases, where the thermodynamic data of the clusters are not known, and one has to rely on the approximations for the Gibbs free energy reviewed in this section. Inserting Eq. (40) into Eq. (33) and recasting yields

$$J^\mathrm{c}_{*,k}(t) = I\, \tau_\mathrm{gr}^{-1}(m_I, N_*, t)\, Z(N_*) f(1,t) b_\mathrm{g}(k) \frac{T_\mathrm{g}}{T_\mathrm{d}} \cdot \\ \exp\left\{(N_* - 1)\ln(S(T_\mathrm{d})) - \theta_\infty \frac{N_* - 1}{(N_* - 1)^{1/3} + N_f^{1/3}} \right. \\ \left. + \frac{(N_* - k)}{I} \ln\left(\frac{b_\mathrm{g}(m_I)}{\alpha_*(m_I)\, v^*_\mathrm{rel}(m_I)}\right)\right\} \quad (41)$$

where it should be noted, that the ratio of the temperatures always cancels with the corresponding factor in the generalized departure coefficient of the k-mer (cf. Eq. (B4)).

In conventional nucleation theory the critical cluster size N_* is determined by the minimum of the cluster size distribution $\overset{\circ}{f}(N)$ for the artificial constrained equilibrium, which is equivalent to the maximum of the corresponding $\Delta G(N)$. The size distribution in the LTE-state, in contrast, is a monotonically decreasing function of N. However, as already mentioned in Sect. 3.2, the function $\mathcal{A}(N)$ introduced in Eq. (28) still has a maximum, which defines N_*, provided nucleation is possible. The decisive quantity for nucleation to take place is the product $(S^I(T_\mathrm{d})\, b_\mathrm{g}(m_I)/\alpha_*(m_I) v^*_\mathrm{rel}(m_I))$. If its logarithm is greater than unity, $\mathcal{A}$ has a maximum and the particles can nucleate. It is important to note that the value of the supersaturation ratio S is not alone the predictor for nucleation. Only if deviations from chemical and thermodynamic equilibrium are negligible, the value of S determines the onset of nucleation.

From Eqs. (40) and (28) the critical cluster size is given by

$$N_* - 1 = \\ \frac{N_{*,\infty}}{8}\left(1 + \sqrt{1 + 2\left(\frac{N_\mathrm{f}}{N_{*,\infty}}\right)^{\frac{1}{3}}} - 2\left(\frac{N_\mathrm{f}}{N_{*,\infty}}\right)^{\frac{1}{3}}\right)^3 \quad (42)$$

as in Paper I (Eq. (2.15)), but with $N_{*,\infty}$ given by

$$N_{*,\infty} = \left[\frac{2}{3}\,\theta_\infty\, I \Big/ \ln\left(\frac{S^I(T_\mathrm{d})\, b_\mathrm{g}(m_I)}{\alpha_*(m_I)\, v^*_\mathrm{rel}(m_I)}\right)\right]^3 \quad (43)$$

Using Eqs. (32) and (40) the corresponding Zeldovich factor is given by

$$Z(N_*) = \left(\frac{\theta_\infty}{9\pi\,(N_* - 1)^{4/3}} \frac{\left[1 + 2\left(\frac{N_f}{N_* - 1}\right)^{1/3}\right]}{\left[1 + \left(\frac{N_f}{N_* - 1}\right)^{1/3}\right]^3}\right)^{1/2} \quad (44)$$

Thus, the corrections, which account for chemical and thermal non-equilibrium, enter into the nucleation rate explicitly by the additional factors in Eq. (41) and implicitly via the modified critical cluster size.

For the homogeneous nucleation of the monomer, i.e. $k = I = 1$, Eq. (41) reduces to

$$J^\mathrm{c}_{*,1}(t) \;=\; \tau_\mathrm{gr}^{-1}(1, N_*, t)\, Z(N_*)\, f(1,t) \cdot \\ \exp\left\{(N_* - 1)\ln\left(\frac{S(T_\mathrm{d})}{\alpha_*(1)}\sqrt{\frac{T_\mathrm{d}}{T_\mathrm{g}}}\right) \right. \\ \left. - \theta_\infty \frac{N_* - 1}{(N_* - 1)^{1/3} + N_f^{1/3}}\right\} \quad (45)$$

which shows, that in this case only departures from thermal equilibrium affect the nucleation rate, whereas no chemical departure coefficient appears in this expression. However, the actual particle density of the monomer $f(1,t)$ is given by the chemical non-equilibrium in the gas.

4. Summary

We have presented a new formulation of the nucleation process, that accounts for effects due to chemical non-equilibrium in the gas phase and thermal non-equilibrium between the gas and the clusters or dust particles. In this approach the derivation of

expressions for the nucleation rate is based on kinetic theory and, where necessary, on thermodynamic arguments, which refer to a physically realizable equilibrium state.

Following Katz & Wiedersich (1977) an unconstrained equilibrium state of clusters in a saturated vapor has been defined, which is characterized by the phase equilibrium between monomers as well as N-mers and the bulk solid, and furthermore by simultaneous chemical equilibrium in the gas phase and thermal equilibrium between the clusters and the gas. Reference to this true LTE-state allows a straightforward inclusion of thermal and chemical non-equilibrium in the formulation of the nucleation process.

Since the nucleation process can be treated as a stationary problem for typical conditions in circumstellar dust shells (cf. Paper IV), we have obtained a hierarchy of expressions for the stationary nucleation rate $J_*^{\rm c}$.

The most general expression for $J_*^{\rm c}$, which describes nucleation involving several important growth species connecting several cluster sizes, results from a system of equations, which can be evaluated at least numerically provided all the necessary input data are known.

If, however, nucleation is dominated by a single growth species, the system can be solved analytically, which yields a direct expression for the nucleation rate in terms of the growth and evaporation time scales for all cluster sizes in the stationary regime. This expression has to be used, as long as the temperature of the clusters and other quantities depend on the cluster size. If the cluster temperature is independent of size, and the size dependency of other quantities can be neglected, an approximate analytic equation for $J_*^{\rm c}$ is obtained, which essentially depends on the growth time scale and the Gibbs free energy of formation of the critical cluster in the LTE-state.

Often the latter quantity is not known for the relevant cluster sizes. In such cases one can rely on the concepts of classical nucleation theory, which approximates the Gibbs free energy in terms of the surface free energy of the bulk liquid or solid phase. The applicability of this approach to small clusters has long been a matter of debate (e.g. Donn & Nuth 1985). However, the classical approach with modifications to account for the size dependence of the surface energy can be adjusted to describe even the properties of small clusters quite well.

Nevertheless different types of laboratory experiments as, for example, measurements of absorption characteristics of the clusters, experimental investigations of the relevant elementary chemical reactions underlying the nucleation process, and experimental studies of vapor-phase nucleation of refractory materials are needed to make full use of the developed theoretical treatment.

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Appendix A: on the supersaturation ratio of N-clusters

In a saturated vapor the monomers are in phase equilibrium with the the bulk solid phase and, if the solid phase and the gas phase are also in thermal equilibrium characterized by the temperature $\overset{\circ}{T}$, the partial pressure of the monomers $\overset{\circ}{p}\,(1)$ is equal to the vapor saturation pressure above the flat surface of the solid phase $\overset{\circ}{p}_{\rm sat}\,(1)$. Then, one obtains for the supersaturation ratio of the monomers

$$\mathcal{S}_1 = \frac{\overset{\circ}{p}\,(1)}{\overset{\circ}{p}_{\rm sat}\,(1)} = 1. \tag{A1}$$

Assuming now chemical equilibrium in the gas phase the partial pressures of the N-mers can of course be expressed in terms of the partial pressures of the monomers by means of the law of mass action, which yields

$$\frac{\overset{\circ}{p}\,(N)}{\overset{\ominus}{p}} = \left(\frac{\overset{\circ}{p}\,(1)}{\overset{\ominus}{p}}\right)^N \exp\left(-\frac{\Delta_{\rm f}\overset{\ominus}{G}(N) - N\Delta_{\rm f}\overset{\ominus}{G}(1)}{R\ \overset{\circ}{T}}\right) \tag{A2}$$

where $\Delta_{\rm f}\overset{\ominus}{G}(N)$ is the standard molar Gibbs free energy of formation for the N-mer, $\Delta_{\rm f}\overset{\ominus}{G}(1)$ is the standard molar Gibbs free energy of formation for the monomer, and $\overset{\ominus}{p}$ denotes the pressure of the standard state, to which the standard Gibbs energies are referred to.

Since, the vapor saturation pressure $\overset{\circ}{p}_{\rm sat}\,(1)$ is given by

$$\frac{\overset{\circ}{p}_{\rm sat}\,(1)}{\overset{\ominus}{p}} = \exp\left(\frac{\Delta_{\rm f}\overset{\ominus}{G_1}(s) - \Delta_{\rm f}\overset{\ominus}{G}(1)}{R\ \overset{\circ}{T}}\right) \tag{A3}$$

where $\Delta_{\rm f}\overset{\ominus}{G_1}(s)$ denotes the standard molar Gibbs free energy of formation of the solid phase, and with $\overset{\circ}{p}\,(1) = \overset{\circ}{p}_{\rm sat}\,(1)$ one obtains from Eq. (A2)

$$\frac{\overset{\circ}{p}\,(N)}{\overset{\ominus}{p}} = \exp\left(\frac{N\Delta_{\rm f}\overset{\ominus}{G_1}(s) - \Delta_{\rm f}\overset{\ominus}{G}(N)}{R\ \overset{\circ}{T}}\right) \tag{A4}$$

The comparison of this equation with Eq. (A3) implies, that the r.h.s. is just the vapor saturation pressure of the N-mer above the flat surface of the solid, i.e. we have

$$\frac{\overset{\circ}{p}\,(N)}{\overset{\ominus}{p}} = \frac{\overset{\circ}{p}_{\rm sat}\,(N)}{\overset{\ominus}{p}} \tag{A5}$$

This means, that if the monomers are in phase equilibrium with the solid phase, which is also in thermal equilibrium with the gas, and if chemical equilibrium prevails in the gas phase and thus between the N-mers and the monomers, the N-mers are in phase equilibrium with the solid too.

Defining the supersaturation ratio of the N-mers by

$$\mathcal{S}_N = \frac{\overset{\circ}{p}\,(N)}{\overset{\circ}{p}_{\rm sat}\,(N)} \tag{A6}$$

this phase equilibrium results in the following relationships

$$\mathcal{S}_N = (\mathcal{S}_1)^N = 1\,. \tag{A7}$$

Appendix B: definition of the generalized departure coefficients

In Sect. 2.3 we have defined the reference LTE-state, which is introduced in order to express the usually unknown characteristic time scales of the reverse (evaporation) processes $\tau_{\rm ev}$ in terms of the corresponding characteristic time scales of the forward (growth) processes. Compared to this LTE-state the conditions in the real situation where nucleation takes place, such as the temperature of the gas or the particle densities of the growth species, are different, and the effects of these deviations can be conveniently described in terms of *generalized departure coefficients* (cf. Gauger et al. 1990).

Let us first consider the case of chemical equilibrium in the gas phase at the actual gas temperature $T_{\rm g}$. The equilibrium densities of the reacting molecules are denoted by a '˜', i.e. $\tilde{n}_{\rm f}(m_i)$ and $\tilde{n}_{\rm r}(m_i)$ are the densities of the molecules involved in the growth reaction m_i and its reverse, if chemical equilibrium was established in the gas phase at the actual mass density, elemental abundances, and gas temperature $T_{\rm g}$.

The deviations of the actual particle densities $n_{\rm f}(m_i,t)$ and $n_{\rm r}(m_i,t)$ from those in a situation of chemical equilibrium in the gas phase at $T_{\rm g}$ are given by

$$\tilde{b}_{\rm f}(m_i) = \frac{n_{\rm f}(m_i,t)}{\tilde{n}_{\rm f}(m_i)} \qquad \text{and} \qquad \tilde{b}_{\rm r}(m_i) = \frac{n_{\rm r}(m_i,t)}{\tilde{n}_{\rm r}(m_i)} \tag{B1}$$

These are the usual chemical departure coefficients describing a chemical non-equilibrium (non-CE) situation.

Let us now consider the following ratio of the actual particle densities and the particle densities $\overset{\circ}{n}_{\rm f}\,(m_i)$ and $\overset{\circ}{n}_{\rm r}\,(m_i)$ in the LTE-state with the temperature $T_{\rm d}(N)$ of the N-clusters under consideration, which enters into the relationship for $\tau_{\rm ev}^{-1}$ (Eq. (8)):

$$\frac{n_{\rm r}(m_i,t)}{n_{\rm f}(m_i,t)}\,\frac{\overset{\circ}{n}_{\rm f}\,(m_i)}{\overset{\circ}{n}_{\rm r}\,(m_i)}$$

Converting the particle densities by means of the ideal gas law into partial pressures and multiplying with ratios of one yields

$$\frac{n_{\rm r}(m_i,t)}{n_{\rm f}(m_i,t)}\,\frac{\overset{\circ}{n}_{\rm f}\,(m_i)}{\overset{\circ}{n}_{\rm r}\,(m_i)} = \left(\frac{p(1,t)}{\overset{\circ}{p}\,(1,T_{\rm d}(N))}\right)^{-i}\left(\frac{p(1,t)}{\tilde{p}(1,T_{\rm g})}\right)^{i}\cdot \tag{B2}$$

$$\frac{p_r(m_i,t)}{\tilde{p}_r(m_i,T_{\rm g})}\,\frac{\tilde{p}_f(m_i,T_{\rm g})}{p_f(m_i,t)}\,\frac{\tilde{K}_r(m_i,T_{\rm g})}{\overset{\circ}{K}_r\,(m_i,T_{\rm d}(N))}\,\frac{\overset{\circ}{K}_f\,(m_i,T_{\rm d}(N))}{\tilde{K}_f(m_i,T_{\rm g})}$$

where $p(1,t)$ is the actual partial pressure of the monomers, $\overset{\circ}{p}\,(1,T_{\rm d}(N))$ is the partial pressure of the monomers in the LTE-state, and $\tilde{p}(1,T_{\rm g})$ is the partial pressure of the monomers if chemical equilibrium at $T_{\rm g}$ was established. The $K_f(m_i,T)$ and $K_r(m_i,T)$ denote the dissociation constants for the molecule in the forward and reverse of reaction m_i at temperature T. If the monomer is given by a molecular species, $\overset{\circ}{K}_f\,(m_i,T_d(N))$ ($\tilde{K}_f(m_i,T_g)$) describes the equilibrium constant of the formation of $\overset{\circ}{n}_f\,(m_i)$ ($\tilde{n}_f(m_i)$) with respect to the monomer and not with respect to the elements this molecule is formed from. These constants enter, because in chemical equilibrium the partial pressures of the molecules can be expressed in terms of the partial pressures of the elements in atomic form, which constitute the respective molecule, and by definition the molecule of the forward reaction is build up from i monomers and the molecule of the reverse reaction.

In the LTE-state the partial pressure of the monomer is equal to the vapor saturation pressure $p_{\rm sat}(T_{\rm d}(N))$ above the flat surface of the solid at temperature $T_{\rm d}(N)$ (see Appendix A). Therefore, the first ratio on the r.h.s. can be expressed in terms of the supersaturation ratio, which has been defined by Eq. (12) in Sect. 2.4.

Now we define the generalized departure coefficient of reaction m_i by

$$b_{\rm g}(m_i,T_{\rm d}(N)) = \underbrace{\frac{1}{\tilde{b}^i(1)}\,\frac{\tilde{b}_{\rm f}(m_i)}{\tilde{b}_{\rm r}(m_i)}}_{non-CE}\cdot \tag{B3}$$

$$\underbrace{\left(\frac{\tilde{K}_{\rm f}(m_i,T_{\rm g})}{\overset{\circ}{K}_{\rm f}\,(m_i,T_{\rm d}(N))}\right)\Bigg/\left(\frac{\tilde{K}_{\rm r}(m_i,T_{\rm g})}{\overset{\circ}{K}_{\rm r}\,(m_i,T_{\rm d}(N))}\right)}_{non-TE(cluster-gas)}$$

where the remaining ratios of partial pressures have been expressed by the chemical departure coefficients. As indicated, the first two terms comprise the effects which result from the chemical non-equilibrium in the gas phase, and the last term comprises the effects due to the thermal non-equilibrium between the N-clusters and the gas.

In the case of homogeneous processes, i.e. the addition of i-mers, where no molecule is involved in the reverse reaction, the generalized departure coefficient is given by

$$b_{\rm g}(i,T_{\rm d}(N)) = \underbrace{\frac{\tilde{b}(i)}{\tilde{b}^i(1)}}_{non-CE}\;\underbrace{\frac{\tilde{K}(i,T_{\rm g})}{\overset{\circ}{K}\,(i,T_{\rm d}(N))}\,\frac{T_{\rm d}(N)}{T_{\rm g}}}_{non-TE(cluster-gas)} \tag{B4}$$

(cf. Gauger et al. 1990). Here $\tilde{b}(1)$ is the chemical b-factor for the monomer and $\tilde{b}(i)$ is the chemical b-factor for the i-mer, and $K(i,T)$ denotes the equilibrium constant of the formation of an i-mer from i monomers. Finally inserting Eq. (B3) into Eq. (B3) yields:

$$\frac{n_{\rm r}(m_i,t)}{n_{\rm f}(m_i,t)}\,\frac{\overset{\circ}{n}_{\rm f}\,(m_i)}{\overset{\circ}{n}_{\rm r}\,(m_i)} = \frac{1}{S^i(T_{\rm d}(N))\;b_{\rm g}(m_i,T_{\rm d}(N))} \tag{B5}$$

If the gas is phase is in chemical equilibrium and the temperature difference between the N-clusters and the gas vanishes, $b_{\rm g}$ is equal to one. Therefore, the generalized departure coefficient represents a correction to the supersaturation ratio which accounts for the effects of chemical and thermal non-equilibrium.

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