Becker-Döring rate equations for heterogeneous nucleation, with direct vapour deposition and surface diffusion mechanisms

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Abstract

We develop a set of microscopic rate equations describing the growth and decay of molecular clusters adsorbed onto a seed particle. Such Becker-Döring equations are fundamental to descriptions of homogeneous nucleation, but do not appear to have been developed for the rather more complicated case of heterogeneous nucleation. We show that the familiar Fletcher theory of heterogeneous nucleation emerges from such a Becker-Döring description, but only if the concentration of adsorbed single molecules on the surface is estimated in a rather rudimentary manner. For small seed particles, this approach fails and one needs a proper Becker-Döring approach to provide a better estimate. The change in predicted nucleation rate can be several orders of magnitude for nanometre-size seed particles. We go on to include into the Becker-Döring treatment the processes of growth and decay of clusters by monomer surface diffusion on the seed. We use recent high quality experimental data to show that the latter process can make only a small contribution to the nucleation current for nanoparticle seeds. We also use the data to demonstrate that the traditional Fletcher theory fails to account for critical sizes and nucleation currents correctly, and that a modification to the implied underlying cluster properties is necessary.

Keywords: heterogeneous nucleation, Becker-Döring equations, Fletcher theory

1 Introduction

The theory of heterogeneous nucleation of droplets on suspended seed particles has for many years been neglected in favour of the 'simpler' process, that of homogeneous nucleation in the absence of seeds. One reason is the complication of including a third phase into the system, and the crucial surface properties of the seed particle might be difficult to characterise. A second reason is the absence, until recently, of high quality experimental data for the heterogeneous process. A third reason might be a natural reluctance to address the more complex heterogeneous nucleation problem before a complete understanding of the homogeneous process is achieved. These reasons perhaps explain why it is hard to find treatments in the literature that go beyond the very rudimentary Fletcher theory of heterogeneous nucleation (and its derivatives). These treatments follow the classical theory of homogeneous nucleation in ignoring the microscopic nature of the seed and the droplet, instead employing ideas based on continuum physics, scaled down to the nanometre size range. The model is based on an estimate of the probability of a thermodynamic fluctuation that would generate a new particle by taking the system over a thermodynamic barrier.

But even though it has been neglected as research problem, heterogeneous nucleation is a much more typical process in the Earth's atmosphere than homogeneous nucleation. The latter process, where seeds are not present, requires vapour pressures that are several times higher than

the saturated vapour pressure in order to drive the formation of new droplets. Such conditions of high supersaturation are not normally found in the atmosphere, and virtually never for water, the most common condensable vapour. Instead, water condensation typically takes place on aerosol particles of previously nucleated or mechanically generated organic or inorganic materials. Such a nucleation mechanism requires a vapour pressure only slightly higher than saturation. Indeed the character of the process as a nucleation phenomenon, in which a thermodynamic barrier is overcome by thermal fluctuation, is often not apparent and the process is sometimes referred to as *activation* at a supersaturation threshold, and considered to be deterministic. Atmospheric clouds, both liquid and ice in phase, typically form by a process of heterogeneous nucleation on such seeds.

The aim of this paper is twofold. The first is to establish a set of equations describing cluster population dynamics analogous to the familiar Becker-Döring equations of homogeneous nucleation. These equations describe the addition and loss of monomers from clusters as a series of binary reactions. It comes as a surprise to us to find no reference in the literature to such a model. The outcome differs from the usual equations through the need to determine the monomer concentration adsorbed on the surface at fixed vapour supersaturation. The Becker-Döring equations for heterogeneous nucleation are non-linear and one cannot impose a linear approximation that simplifies the treatment of homogeneous nucleation. However, writing them down is straightforward, and so is their numerical solution. Having established their structure then allows further development.

The second aim of this paper is to develop equations that include both the direct vapour molecule attachment to an adsorbed cluster, and the attachment of a molecule previously adsorbed on the surface. Again, both mechanisms are well-known in principle, and have been alluded to within the Fletcher theory (Vehkamäki, 2006), but we have not found in previous studies a microscopic description based on appropriate Becker-Döring equations.

The models developed in this paper are only a limited advance beyond the simplified Fletcher theory. We can easily write down Becker-Döring equations, but the rate coefficients are unknown in general. We therefore choose to employ the capillarity approximation and the same geometric assumptions inherent in Fletcher theory. This is done largely to investigate how well the Becker-Döring equations perform as a microscopic equivalent of the Fletcher theory. But we find two major drawbacks to Fletcher theory: first, that it rests on an assumed adsorbed monomer concentration that seriously underestimates the correct concentration for small seed particles, and secondly that it cannot incorporate surface diffusion in a reasonable way. Noting the first of these drawbacks is perhaps the central point made in this article.

The organisation of this paper is as follows. We first of all review Fletcher theory, and then an equivalent Becker-Döring kinetic treatment, but including only gain and loss of molecules direct from the vapour phase. We expose the central point that the usual Becker-Döring approach employs an assumed monomer concentration, which could be much too high. A comparison between so-called *kinetic* and a *dynamical* treatments of the equations demonstrates the difference. We employ the models to describe recent heterogeneous nucleation experiments of n-propanol on nanometre size tungsten oxide seed particles. We show that whilst the Fletcher theory does reasonably well in explaining the onset saturations, the predicted critical sizes (in number of molecules), corresponding to the size of cluster that is equally likely to grow or to decay, are very poorly accounted for, as are the nucleation rates. We therefore modify the capillarity approximation to produce a model that is slightly more successful in accounting for the data, and note that more detailed microscopic information is needed. Finally, we incorporate the surface diffusion mechanism and show how the dynamical model predictions are affected by this inclusion. For the experimental data under consideration, it turns out that the surface diffusion process does not make a large contribution to the nucleation current, largely because the seeds are so small and there is little room on the surface for more than one adsorbed cluster or monomer.

Figure 1: Illustration of a cluster with radius r_i on the surface of a spherically symmetric seed particle with radius R_{seed} and contact angle θ according to Fletcher theory.

2 Heterogeneous nucleation theory – direct vapour deposition mechanism

2.1 Fletcher theory

In classical heterogeneous nucleation theory a critical cluster is imagined to form by thermal fluctuation on a pre-existing surface (Fletcher, 1958). The seed particle is assumed to be spherical and the critical cluster is assumed to be a cap-shaped part of a sphere – see Figure 1. The radius of the critical cluster is equal to that of a homogeneous critical cluster under the same conditions (Vehkamäki, 2006). In the Fletcher theory, the free energy of formation of a critical cluster is used to determine the probability of a thermal fluctuation that would lead to nucleation, and a model for this will be reviewed in the next section. A key area of uncertainty, however, is the proportionality factor that converts this probability into a rate per unit time. This can be provided by the Becker-Döring approach.

There are several drawbacks to this model, among them the assumed constant contact angle, that is the angle between the tangents to the solid surface (seed particle) and the liquid surface (cluster), and the assumed constant surface tensions between the contact interfaces. The physical properties of a microscopic entity are taken to be the same as for a bulk liquid (the capillarity approximation). The assumption of a continuum model of the geometry is a poor approximation especially for small cluster sizes, and should be revised. Nevertheless, we can use it to explore the kinetics of heterogeneous nucleation through establishing the equivalent Becker-Döring rate equations (Becker & Döring, 1935) and (Volmer, 1939).

2.2 Becker-Döring theory with direct vapour deposition mechanism

In Becker-Döring theory for heterogeneous nucleation (Vehkamäki, 2006) we can distinguish between two different growth and decay processes. In the direct vapour deposition model gas molecules can attach themselves to an existing cluster on the surface of the seed particle and can be evaporated from the cluster back into the gas phase. In the surface diffusion model clusters grow when monomers that are adsorbed onto the surface of the seed diffuse over the particle surface and eventually collide with the cluster. In the same fashion, monomers can be released from clusters to diffuse on the surface of the seed. The concentrations of clusters of a given size are

assumed to evolve according to these processes of gain and loss of monomers from the cluster as chemical reactions without memory. In the first part of this paper we concentrate on the direct vapour deposition mechansim. The corresponding Becker-Döring rate equations for the mean concentrations $C_i(t)$ [m^{-2}] of clusters of order i for the direct vapour deposition mechanism read

$$\frac{d}{dt}C_1(t) = j - \lambda C_1(t) + \gamma_2^{dv} C_2(t) - \beta_1^{dv} C_1(t),$$

$$\frac{d}{dt}C_i(t) = \beta_{i-1}^{dv} C_{i-1}(t) - \gamma_i^{dv} C_i(t) - \beta_i^{dv} C_i(t) + \gamma_{i+1}^{dv} C_{i+1}(t), \tag{1}$$

where $\gamma_{i_{\max}+1}^{dv} = 0$ and the index $i \in [2,...,i_{\max}]$. The maximum size of clusters, $i_{\max}$, and hence the maximum number of equations, has to be chosen to be large enough to exceed the order of the critical cluster i^* comfortably. Since growth is more probable than decay for clusters above the critical size, the choice of a cluster sink boundary condition at $i_{\max} \gg i^*$ is physically acceptable. Superscripts "dv" indicate processes taking place according to the direct vapour deposition mechanism.

The particular form of the rate coefficients we use stems from Fletcher theory. The rate coefficient j is called the *source rate* and gives the monomer flux per unit area and per unit time. It takes the form

$$j = \frac{pS}{\sqrt{2\pi mkT}} \quad [\text{s}^{-1}\text{m}^{-2}], \tag{2}$$

where p is the pressure (Nm^{-2}), $S > 1$ stands for the vapour phase saturation ratio (dimensionless) defined as the vapour pressure divided by the saturated vapour pressure, m is the molecular mass of a gas molecule (kg), k the Boltzmann constant (m^{2}kgs^{-2}K^{-1}) and T the temperature (K). The evaporation rate λ characterises the process of evaporation of molecules from the seed surface back into the vapour phase and is given by

$$\lambda = \nu \exp\left(-\frac{L}{kT}\right) \quad [\text{s}^{-1}], \tag{3}$$

where ν is the adsorbed monomer vibration frequency (s^{-1}) and L the latent heat of evaporation per monomer (J). The symbol β_i^{dv} denotes the growth rate by the direct vapour deposition mechanism (s^{-1}) for a cluster of size i, and the symbol γ_{i+1}^{dv} the decay rate by emission of a monomer direct to the vapour (s^{-1}) for a cluster of size $i + 1$. It holds that

$$\beta_i^{dv} < \gamma_i^{dv} \text{ for } i < i^*, \tag{4}$$

$$\beta_i^{dv} \geq \gamma_i^{dv} \text{ for } i \geq i^*, \tag{5}$$

which can be interpreted in the following way: up until the critical cluster size i^* is reached the probability per unit time of a cluster to decay is greater than the probability to grow. After the critical cluster size is reached it is more probable for a cluster to grow.

The radius r_i of a cluster of size i is derived from the assumption that the volume of the cap-shaped liquid phase V_{cap} is equal to the total volume of all molecules in the cluster combined,

$$V_{\text{cap}} := \frac{\pi}{3}r_i^3 (2 - 3\cos\Psi(r_i, R_{\text{seed}}, \theta) + \cos^3\Psi(r_i, R_{\text{seed}}, \theta))$$

$$- \frac{\pi}{3}R_{\text{seed}}^3 (2 - 3\cos\Phi(r_i, R_{\text{seed}}, \theta) + \cos^3\Phi(r_i, R_{\text{seed}}, \theta)) = iv, \tag{6}$$

where v is the volume of a molecule in the liquid phase (m^3), i is the number of molecules in the cluster, θ is the contact angle, that is the angle between the tangent of the seed surface and the tangent of the surface of the condensing liquid, and R_{seed} is the radius of the seed (m). The two cosines are defined as

$$\cos\Psi(r_i, R_{\text{seed}}, \theta) := \frac{R_{\text{seed}}\cos\theta - r_i}{\sqrt{r_i^2 + R_{\text{seed}}^2 - 2r_i R_{\text{seed}}\cos\theta}},$$

$$\cos\Phi(r_i, R_{\text{seed}}, \theta) := \frac{R_{\text{seed}} - r_i\cos\theta}{\sqrt{r_i^2 + R_{\text{seed}}^2 - 2r_i R_{\text{seed}}\cos\theta}}. \tag{7}$$

There is, of course, an error that arises from the *packaging problem*, namely the over-estimation of the volume of the cluster, but in Fletcher theory this is neglected.

We calculate the growth rate in the direct vapour approach in the following way

$$\beta_i^{dv} = j A_i^{(v,l)} \quad [\text{s}^{-1}],\tag{8}$$

where the cap area at the vapour-liquid interface is given by

$$A_i^{(v,l)} = 2\pi r_i^2 \big(1 - \cos\Psi(r_i, R_{\text{seed}}, \theta)\big) \quad [\text{m}^2].\tag{9}$$

The loss rate in the direct vapour deposition approach is determined via the expression

$$\gamma_{i+1}^{dv} = \left[\beta_i^{dv}\exp\left(\frac{\Delta G_{i+1} - \Delta G_i}{kT}\right)\right]\Bigg|_{S=1} \quad [\text{s}^{-1}],\tag{10}$$

where the formation free energy of a cluster of size i takes the form

$$\Delta G_i = \sigma(A_i^{(v,l)} - A_i^{(l,s)}\cos\theta) - ikT\ln S \quad [\text{Nm}],\tag{11}$$

with the cap area at the liquid-solid interface given by

$$A_i^{(l,s)} = 2\pi R_{\text{seed}}^2 \big(1 - \cos\Phi(r_i, R_{\text{seed}}, \theta)\big) \quad [\text{m}^2],\tag{12}$$

and where σ is the surface tension of the vapour-liquid interface (Nm^{-1}). We base equation (11) on a requirement of detailed balance in the saturated equilibrium between vapour and liquid phase, that is when the saturation ratio is taken to be equal to one.

3   Review of Experimental data

We will illustrate our theoretical investigations by comparing the calculations in the Fletcher and Becker-Döring frameworks with experimental data obtained by Winkler et al (2008). In that particular experiment, organic vapour, namely n-propanol, was condensed on molecular ions as well as on charged and uncharged inorganic nanoparticles, namely tungsten oxide particles. The activation of the pre-existing seed particles was triggered by heterogeneous nucleation. Vapour supersaturation was achieved by adiabatic expansion in a thermostated expansion chamber of a Size Analyzing Nuclei Counter (SANC). Droplet growth was observed by the Contact Angle Mie Scattering detection method (CAMS).

For each vapour saturation ratio S the fraction of activated particles relative to the total number concentration was determined, and used to create a nucleation-activation probability curve depending on the vapour supersaturation ratio for seed diameters ranging from 0.9 nm to 4 nm. The smaller the size of the seed the higher was the vapour supersaturation needed for the activation of the particles. Each nucleation-activation probability curve can be used to extract the corresponding onset saturation ratio, which is the vapour saturation ratio where 50% of particles of a specific size are activated. Accordingly, one can plot the onset saturation ratio as a function of the seed particle mobility diameter and compare the experimental data to the theoretical prediction within the Fletcher framework.

We will concentrate on the data representing the neutral tungsten oxide seed particles. In Table 1 we give the values of the parameters used in the calculations according to the experimental set-up. The small contact angle indicates that the seed particle was totally wettable to the vapour phase – see Figure 2. It has been claimed (Winkler et al, 2008) that Fletcher theory predicts the observed onset activations for neutral particles exceedingly well – see Table 2. We would like to reconsider this statement by giving attention to the nucleation current, that is the rate at which critical clusters are formed on the surface of the seed particles.

This proposed reconsideration is driven by the observation that standard Fletcher theory leads to disparities between the value of the critical cluster size obtained from theoretical considerations compared to an experimental estimation. The First Heterogeneous Nucleation Theorem (Vehkamäki et al, 2007) together with the nucleation-activation probability curve provides the

constants	$R^*_{\text{seed}} = 1$ nm	$R^*_{\text{seed}} = 2$ nm
θ^* [rad]	5.24e-3	
p^* [Pa]	535.96	
$S\mid^*_{P=0.5}$ [1]	2.62	1.67
m^* [kg]	1e-25	
T^* [K]	275	
$\nu^\dagger$ [s^{-1}]	8.85e11	
L^* [J]	8.29e-20	
$\delta^\dagger$ [m]	1e-10	
$E^\dagger$ [J]	8.29e-21	
σ^* [Nm^{-1}]	0.025	
j^* [s^{-1}m^{-2}]	2.87e25	1.83e25
λ^* [s^{-1}]	290.57	
k [JK^{-1}]	1.38e-23	

Table 1: List of values for physical parameters as implied by the experimental set-up (indicated with *) (Winkler et al, 2008) and theoretical estimates (indicated with †) (Määttänen et al, 2007) and (Seki & Hasegawa, 1983).

means to determine the number of molecules in the critical cluster. Since the First Heterogeneous Nucleation Theorem is derived from general statistical mechanical considerations this calculation is independent of the model used to describe the cluster. However, one has to be careful concerning the monodispersity of the particles. The number of molecules in the critical cluster as obtained in this fashion will be referred to as the *experimental critical cluster size*. In the particular study the experimental critical cluster size i^*_{exp} was between twenty and twenty-five – see Winkler et al (2008). Yet, if one calculates the critical cluster size as predicted by Fletcher theory one finds higher values than the experimental data imply – see Table 2. This disparity is explored in the next section.

4 The heterogeneous nucleation current for the direct vapour deposition mechanism

We want to compare experimental data for the nucleation current with a Fletcher theory of heterogeneous nucleation driven by the direct vapour deposition mechanism, and with the equivalent Becker-Döring model.

4.1 Experimental nucleation current

The *experimental nucleation current* (Lazaridis et al, 1992), expressed per unit seed particle surface area and unit time, is given by

$$J_{\text{exp}} = -\frac{\ln(1-P)}{4\pi R^2_{\text{seed}} t_{\text{exp}}} \qquad [\text{m}^{-2}\text{s}^{-1}], \tag{13}$$

where R_{seed} is the radius of the seed particle, t_{exp} the activation time and P is the nucleation probability over that time interval. We employ an activation time of $t_{\text{exp}} = 1$ ms (Winkler, 2008). We take $P = 1/2$ and consider J_{exp} to be characterised by the supersaturation S_{exp} corresponding to this condition.

4.2 Fletcher nucleation current

The nucleation current as given in Fletcher theory (Fletcher, 1958) reads

$$J_{\text{Fletcher}} = K^* \exp\left(-\frac{\triangle G^*}{kT}\right), \tag{14}$$

where the symbol $\triangle G^*$ denotes the formation free energy of the critical cluster. The factor K^* is a kinetic prefactor and is given by

$$K^* = Z^* \beta_{dv}^* C_{\text{ads}}, \tag{15}$$

where Z^* is the Zeldovich factor for heterogeneous nucleation processes:

$$Z^* := Z_{\text{hom}}^* f(r_{\text{Fletcher}}^*, R_{\text{seed}}, \theta),$$

$$Z_{\text{hom}}^* := \frac{v\sqrt{\sigma}}{2\pi r_{\text{Fletcher}}^{*2} \sqrt{kT}},$$

$$f(r_{\text{Fletcher}}^*, R_{\text{seed}}, \theta) := \sqrt{4}\left(2 + \frac{(1 - X\cos\theta)(2 - 4X\cos\theta - (\cos^2\theta - 3)X^2))}{(1 - 2X\cos\theta + X^2)^{\frac{3}{2}}}\right)^{-\frac{1}{2}} \tag{16}$$

with $X := R_{\text{seed}}/r_{\text{Fletcher}}^*$. The Fletcher critical cluster radius is given by

$$r_{\text{Fletcher}}^* := \frac{2v\sigma}{kT \ln S}. \tag{17}$$

The growth rate of the critical cluster β_{dv}^* in Fletcher theory is

$$\beta_{dv}^* = j2\pi r_{\text{Fletcher}}^{*2}(1 - \cos\Psi(r_{\text{Fletcher}}^*, R_{\text{seed}}, \theta)). \tag{18}$$

The concentration of the adsorbed monomers is estimated via

$$C_{\text{ads}} = \frac{j}{\lambda}. \tag{19}$$

Note that

$$r_{\text{Fletcher}}^* = r_{i_{\text{Fletcher}}^*}, \tag{20}$$

where r_i is determined from equation (6) and the heterogeneous critical cluster size in Fletcher theory i_{Fletcher}^* is inserted according to

$$i_{\text{Fletcher}}^* = i_{\text{Fletcher;hom}}^* g(r_{\text{Fletcher}}^*, R_{\text{seed}}, \theta),$$

$$i_{\text{Fletcher;hom}}^* := \frac{4\pi r_{\text{Fletcher}}^{*3}}{3v},$$

$$g(r_{\text{Fletcher}}^*, R_{\text{seed}}, \theta) :=$$
$$\frac{1}{4}\left(2 + 3\frac{1 - X\cos\theta}{\sqrt{1 + X^2 - 2X\cos\theta}} - \left(\frac{1 - X\cos\theta}{\sqrt{1 + X^2 - 2X\cos\theta}}\right)^3\right)$$
$$-\frac{1}{4}\left(X^3\left(2 - 3\frac{X - \cos\theta}{\sqrt{1 + X^2 - 2X\cos\theta}} + \left(\frac{X - \cos\theta}{\sqrt{1 + X^2 - 2X\cos\theta}}\right)^3\right)\right). \tag{21}$$

4.3   Becker-Döring nucleation currents

Assuming that clusters of order $i_{\max} + 1$ do not decay, an expression for the nucleation current according to the Becker-Döring equations in the steady state (Becker & Döring, 1935):

$$0 = j - \lambda C_1(t) + \gamma_2^{dv} C_2(t) - \beta_1^{dv} C_1(t),$$
$$0 = \beta_{i-1}^{dv} C_{i-1}(t) - \gamma_i^{dv} C_i(t) - \beta_i^{dv} C_i(t) + \gamma_{i+1}^{dv} C_{i+1}(t),$$

where $\gamma_{i_{\max}+1}^{dv} = 0$ and $i \in [2, ..., i_{\max}]$, is well known to be

$$J_{\text{BD,kin}}(C_1^{\text{kin}}) = \frac{\beta_1^{dv} C_1^{\text{kin}}}{1 + \sum_{i=2}^{i_{\max}} \prod_{j=2}^{i} \frac{\gamma_j^{dv}}{\beta_j^{dv}}}, \tag{22}$$

where the mean monomer concentration can again be estimated via

$$C_1^{\text{kin}} \approx \frac{j}{\lambda}. \tag{23}$$

We explicitly note that $J_{\mathrm{BD,kin}}$ is a function of a specified monomer concentration. The above expression (22) may be referred to as the *kinetic Becker-Döring nucleation current*.

The full Becker-Döring equations are in fact non-linear equations for the cluster concentrations, and the steady state solution referred to above is obtained in terms of a given monomer concentration. In a system undergoing heterogeneous nucleation, the monomers are in fact a participating species with a freely variable population. Therefore C_1^{kin} will in general differ from j/λ. To allow for this, we could solve the equations iteratively, using the steady state Becker-Döring solution, or alternatively, simply perform a numerical solution of the time-dependent non-linear differential equations, and identify a steady state solution at late times. The largest cluster size under consideration must satisfy $i_{\max} > i^*$, and one therefore has to solve $i_{\max}$ equations for the unknown i-mer concentrations $C_i(t)$. Having done this, we obtain a *dynamical Becker-Döring nucleation current*, defined in simplest form as

$$J_{\mathrm{BD,dyn}}(t_\infty) = \beta_{i_{\max}}^{dv} C_{i_{\max}}(t_\infty), \tag{24}$$

where t_∞ indicates late times corresponding to a steady state solution. Notice that the difference between $J_{\mathrm{BD,dyn}}$ and $J_{\mathrm{BD,kin}}$ corresponds to the difference between a self-consistent, and an estimated monomer concentration, respectively. One should expect, however, to find that $J_{\mathrm{BD,kin}}(C_1(t_\infty)) = J_{\mathrm{BD,dyn}}(t_\infty)$.

4.4 Comparison of models with data

The Fletcher critical size and onset supersaturation (20) are calculated for two particular seed particle sizes in Table 2 and compared with experimental data. The radius of the experimental critical cluster $r_{i_{\mathrm{exp}}^*}$ is obtained using the experimental critical cluster size i_{exp}^*. The disparity between model and experimental critical sizes is obvious, even though the onset supersaturations are in reasonable agreement.

Calculations of the nucleation current according to the Fletcher and kinetic Becker-Döring models can be found in Table 3. For a seed radius of value $R_{\mathrm{seed}} = 1$ nm we choose the largest cluster size to be $i_{\max} = 135$ and for a seed radius of value $R_{\mathrm{seed}} = 2$ nm we assume $i_{\max} = 820$. The choice of $i_{\max}$ can be regarded as relatively low given the value of the critical cluster size i_{Fletcher}^*. However, one expects the estimate of the nucleation current to decrease with increasing value of $i_{\max}$. Therefore, the calculated values of the nucleation currents as given in Table 3 can be understood as an upper limit which is already significantly below the experimental value.

We observe that the agreement between the experimental nucleation current J_{exp} and the Fletcher nucleation current J_{Fletcher} is better for a smaller seed radius than for the bigger seed particle. The Fletcher nucleation current J_{Fletcher} and the kinetic Becker-Döring nucleation rate in the steady state $J_{\mathrm{BD,kin}}(C_1^{\mathrm{kin}})$ are of the same order of magnitude. Clearly, neither is an acceptable description of the data for both seed radii. We shall now attempt to address this by modifying the capillarity approximation.

5 The heterogeneous nucleation current for the modified direct vapour deposition mechanism

In order to remove the disparity between the experimental and theoretical critical cluster size we modify parameters such that the critical cluster size as predicted by Fletcher theory, i_{Fletcher}^*, coincides with the experimental critical cluster size i_{exp}^*:

$$i_{\mathrm{Fletcher}}^* = i_{\mathrm{exp}}^* = 25. \tag{25}$$

The simplest way to arrange this is to replace the bulk surface tension between the vapour phase and the droplet with what we will call the *effective surface tension* σ_{eff} and which is given in Table 4. As a consequence of forcing $i_{\mathrm{Fletcher}}^* = i_{\mathrm{exp}}^*$ we have $r_{i_{\mathrm{exp}}^*} = r_{i_{\mathrm{Fletcher}}^*} = r_{\mathrm{Fletcher}}^*$. All other physical and experimental parameters are unchanged. We recalculate the nucleation currents for the various models used in the last subsection with the assumed value $i_{\max} = 30$ and summarise the results in Table 5. The Becker-Döring equations are evolved from zero population initial

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Figure 2: Illustration of a seed particle with radius R_{seed} totally wettable to the vapour phase, and r_i the radius of the cluster.

	$R_{\text{seed}} = 1$ nm	$R_{\text{seed}} = 2$ nm
S_{exp}	2.62	1.67
S_{Fletcher}	2.71	1.87
i^*_{exp}	25	25
i^*_{Fletcher}	130	814
$r_{i^*_{\text{exp}}}$ [m]	1.2e-9	2.06e-9
$r_{i^*_{\text{Fletcher}}}$ [m]	1.69e-9	3.17e-9

Table 2: List of calculated quantities: the experimental onset saturation ratio S_{exp} taken from (Winkler et al., 2008), the onset saturation ratio as obtained from Fletcher theory S_{Fletcher}, the experimental critical cluster size i^*_{exp} taken from (Winkler et al, 2008), the size of the critical cluster as given by Fletcher theory i^*_{Fletcher}, the radius of a cluster evaluated for the experimental critical cluster size $r_{i^*_{\text{exp}}}$, the radius of a cluster evaluated for the size of the critical cluster as given by Fletcher theory $r_{i^*_{\text{Fletcher}}}$ (equivalent to the Fletcher radius r^*_{Fletcher}) for two particular radii of the seed particle R_{seed}.

nucleation rate [m^{-2}s^{-1}]	$R_{\text{seed}} = 1$ nm	$R_{\text{seed}} = 2$ nm
J_{exp}	5.52e19	1.38e19
J_{Fletcher}	6.32e17	3.61e-8
$J_{\text{BD,kin}}(C_1^{\text{kin}})$	2.0e18	9.05e-8

Table 3: List of the calculated nucleation currents in the various models: the experimental nucleation current J_{exp}, the Fletcher nucleation current J_{Fletcher}, the kinetic Becker-Döring nucleation rate $J_{BD,kin}(C_1^{\text{kin}})$ for two particular radii of the seed particle R_{seed}.

	$R_{\mathrm{seed}} = 1$ nm	$R_{\mathrm{seed}} = 2$ nm
σ_{exp} [Nm^{-1}]	2.51e-2	2.51e-2
σ_{eff} [Nm^{-1}]	1.79e-2	1.63e-2
$i^*_{\mathrm{exp}} = i^*_{\mathrm{Fletcher}}$	25	25
$r_{i^*_{\mathrm{exp}}} = r_{i^*_{\mathrm{Fletcher}}} = r^*_{\mathrm{Fletcher}}$ [m]	1.2e-9	2.06e-9
S_{exp}	2.62	1.67
S_{Fletcher}	1.94	1.47

Table 4: List of calculated quantities in the modified model: the experimental surface tension σ_{exp} taken from (Winkler et al., 2008), the effective surface tension σ_{eff}; the experimental critical cluster size i^*_{exp} taken from (Winkler et al., 2008), the size of the critical cluster as given by Fletcher theory i^*_{Fletcher}, the radius of a cluster evaluated for the experimental critical cluster size $r_{i^*_{\mathrm{exp}}}$, the radius of a cluster evaluated for the order of the critical cluster as given by Fletcher theory $r_{i^*_{\mathrm{Fletcher}}}$, and the Fletcher radius r^*_{Fletcher} for two particular radii of the seed particle R_{seed}; the experimental onset saturation ratio S_{exp} taken from (Winkler et al., 2008), and the onset saturation ratio as obtained from Fletcher theory S_{Fletcher},

nucleation rate [m^{-2}s^{-1}]	$R_{\mathrm{seed}} = 1$ nm	$R_{\mathrm{seed}} = 2$ nm
J_{exp}	5.52e19	1.38e19
J_{Fletcher}	1.79e29	4.81e29
$J_{\mathrm{BD,kin}}(C_1^{\mathrm{kin}})$	3.32e29	1.62e30
$J_{\mathrm{BD,dyn}}(t_\infty)$	2.87e25	1.83e25
$J_{\mathrm{BD,kin}}(C_1(t_\infty))$	2.87e25	1.83e25

Table 5: List of the calculated nucleation currents in the various modified models: the experimental nucleation current J_{exp}, the Fletcher nucleation current J_{Fletcher}, the kinetic Becker-Döring nucleation rate $J_{\mathrm{BD,kin}}(C_1^{\mathrm{kin}})$, the nucleation rate at late times as derived from the dynamical Becker-Döring rate equations $J_{\mathrm{BD,dyn}}(t_\infty)$, and the kinetic Becker-Döring nucleation current obtained with the late time mean monomer concentration as calculated from the dynamical Becker-Döring rate equations $J_{\mathrm{BD,kin}}(C_1(t_\infty))$, for two particular radii of the seed particle R_{seed}.

conditions. Now the modified Fletcher theory overpredicts the nucleation current − compare with Table 3 − yet the result for the bigger seed particle is closer to the experimental nucleation current than in the unmodified theory.

The difference in the values of $J_{BD,kin}(C_1^{\mathrm{kin}})$ − see (22) − and $J_{\mathrm{BD,dyn}}(t_\infty)$ − see (24) − as given in Table 3 arises due to the estimation of the monomer concentration by the ratio j/λ (23) in the kinetic model. This can be illustrated by considering the ratio

$$F(R_{\mathrm{seed}}) := \frac{J_{\mathrm{BD,kin}}(C_1^{\mathrm{kin}})}{J_{\mathrm{BD,kin}}(C_1(t_\infty))} = \frac{C_1^{\mathrm{kin}}}{C_1(t_\infty)}. \tag{26}$$

We have $F(R_{\mathrm{seed}} = 1 \text{ nm}) = 1.16\text{e}4$ and $F(R_{\mathrm{seed}} = 2 \text{ nm}) = 8.86\text{e}4$. If one recalculates the nucleation rate $J_{\mathrm{BD,kin}}$ taking the late time value of the mean monomer concentration $C_1(t_\infty)$ according to the solution of the dynamical Becker-Döring rate equations (1) instead of using the estimation for the mean monomer concentration in the steady state (23), one finds that

$$J_{\mathrm{BD,kin}}[C_1(t_\infty)] = J_{\mathrm{BD,dyn}}(t_\infty). \tag{27}$$

as expected. The Fletcher nucleation current J_{Fletcher} clearly overestimates the true nucleation current in the same way as the kinetic Becker-Döring nucleation rate $J_{\mathrm{BD,kin}}$, and for the same reason. Using $J_{\mathrm{BD,dyn}}$ the disparity with respect to experimental data is reduced, and a better dependence on a change in seed radius is obtained. Clearly, however, the fundamental limitations of Fletcher theory prevent a more successful representation of the data.

6 Becker-Döring framework with surface diffusion and direct vapour deposition mechanisms

We continue our investigations employing the effective instead of the experimental surface tension. We extend the calculations from the consideration of the direct vapour deposition mechanism only, to the full framework, that is including surface diffusion processes as well as direct vapour deposition processes into our model. The Becker-Döring rate equations for the mean concentrations $C_i(t)$ (m^{-2}) of clusters of size i in the surface diffusion and direct vapour deposition model read

$$\frac{d}{dt}C_1(t) = j - \lambda C_1(t) + \gamma_2^{dv}C_2(t) - \beta_1^{dv}C_1(t)$$

$$- \beta_1^{sd}C_1(t) + \gamma_2^{sd}C_2(t) - \sum_{i=1}^{i_{\max}}\left(\beta_i^{sd}C_i(t) - \gamma_{i+1}^{sd}C_{i+1}(t)\right),$$

$$\frac{d}{dt}C_i(t) = \left(\beta_{i-1}^{dv} + \beta_{i-1}^{sd}\right)C_{i-1}(t) - \left(\gamma_i^{dv} + \gamma_i^{sd}\right)C_i(t)$$

$$- \left(\beta_i^{dv} + \beta_i^{sd}\right)C_i(t) + \left(\gamma_{i+1}^{dv} + \gamma_{i+1}^{sd}\right)C_{i+1}(t), \tag{28}$$

where $\gamma_{i_{\max}+1}^{dv} = \gamma_{i_{\max}+1}^{sd} \equiv 0$ and the index $i \in [2, ..., i_{\max}]$. Superscripts "dv" indicate processes taking place according to the direct vapour deposition model, superscripts "sd" denote processes in the surface diffusion model. The rate coefficients β_i^{sd} (s^{-1}) and γ_{i+1}^{sd} (s^{-1}) characterise the surface diffusion processes concerning the growth of a cluster of size i by an adsorbed monomer and the loss of a monomer from a cluster of size $i+1$. The other rate coefficients (j, λ, β_i^{dv}, γ_i^{dv}) are determined as before. The factor of two in the evolution equation for the mean monomer concentration in the surface diffusion terms $\beta_1^{sd}C_1(t)$ and $\gamma_2^{sd}C_2(t)$ arises from the fact that in the surface diffusion mechanism two adsorbed monomers have to collide in order to form a dimer. However, in the direct vapour deposition approach a molecule from the gas phase lands on top of a monomer residing on the surface of the seed, hence the coefficient of unity for the terms $\beta_1^{dv}C_1(t)$ and $\gamma_2^{dv}C_2(t)$.

The derivation of the rate coefficients in the surface diffusion model follows that of the rate coefficients in the direct vapour deposition model except that the growth rate coefficient in the surface diffusion model depends on the unknown mean adsorbed monomer concentration, namely

$$\beta_i^{sd} := \beta_i^{sd}(t) = \beta_i'^{sd}C_1(t) \quad [\mathrm{s}^{-1}], \tag{29}$$

where the constant factor $\beta_i'^{sd}$ is determined by the number of molecules in a circular region around the cluster, times the vibration frequency leading to jumps, times an exponential function containing the activation energy for surface diffusion, or more precisely,

$$\beta_i'^{sd} = 2\pi R_{\mathrm{seed}}\delta\sin\Phi(r_i, R_{\mathrm{seed}}, \theta)\nu\exp\left(-\frac{E}{kT}\right) \quad [\mathrm{m}^2\mathrm{s}^{-1}], \tag{30}$$

where δ is the average jumping distance and E the energy of the surface diffusion process (Vehkamäki, 2006). The values of the newly introduced physical parameters used in the following calculations are included in Table 1.

The decay rate in the surface diffusion approach can be obtained via

$$\gamma_{i+1}^{sd} = \left[\frac{\beta_i'^{sd}j}{\lambda}\exp\left(\frac{\Delta G_{i+1} - \Delta G_i}{kT}\right)\right]\bigg|_{S=1} \quad [\mathrm{s}^{-1}], \tag{31}$$

which is again derived from a detailed balance argument − see Figure 3.

Due to the difference of several orders of magnitude between the constant rate coefficients $\beta_i'^{sd}$ and γ_i^{sd} problems in the numerical evaluation of the evolution equations (28) arise. In order to avoid these numerical difficulties we employ an estimate of the mean monomer concentration at late times to solve the Becker-Döring rate equations (28) iteratively in the following way. The

iteration for the mean monomer concentration $C_1(t_\infty)$ at late times t_∞ is performed according to the scheme

$$[C_1^{m+1}(t_\infty)]_{in} = \left([C_1^m(t_\infty)]_{out}[C_1^m(t_\infty)]_{in} \right)^{\frac{1}{2}}, \tag{32}$$

where $[C_1^m(t_\infty)]_{in}$ is the input value and $[C_1^m(t_\infty)]_{out}$ the output value for the m-th iteration step. The above estimate for the mean monomer concentration at late times is inserted into the expression for the rate coefficients

$$\beta_i^{sd} = \beta_i^{'sd}[C_1^m(t_\infty)]_{in} \tag{33}$$

and the system of Becker-Döring rate equations (28) is solved. In the zeroth iteration step the mean monomer concentration at late times is estimated to be

$$[C_1^0(t_\infty)]_{in} = \frac{j}{\lambda}. \tag{34}$$

The iteration procedure is terminated when

$$\frac{[C_1^m(t_\infty)]_{out}}{[C_1^m(t_\infty)]_{in}} \approx 1 \tag{35}$$

and in our calculation this point is reached when $m = 4$ at which $[C_1^m(t_\infty)]_{out}/[C_1^m(t_\infty)]_{in} = 1 \pm O(1e-4)$.

The nucleation current from the full Becker-Döring rate equations for both the surface diffusion and the direct vapour deposition mechanisms can be obtained using the expression

$$J_{\text{BD,dyn}}(t_\infty) = \left(\beta_{i_{\max}}^{dv} + \beta_{i_{\max}}^{'sd} C_1(t_\infty) \right) C_{i_{\max}}(t_\infty), \tag{36}$$

with $i_{\max} > i^*$, where one has to solve $i_{\max}$ number of equations. In Table 6 we compare the dynamical Becker-Döring nucleation current as computed for the direct vapour deposition model according to equation (24) with the dynamical Becker-Döring nucleation current as computed for both mechanisms according to equation (36). One observes that the nucleation current that was calculated taking both the direct vapour deposition and the surface diffusion mechanism into account is generally an order of magnitude less than the nucleation current that results from the consideration of the direct vapour deposition mechanism only. This is a slightly unexpected result but might be rationalised by considering that the inclusion of surface diffusion allows both the additional growth, but also additional decay of adsorbed clusters. The additional decay can potentially reduce the nucleation rate since the wider kinetic scheme reduces the concentration of clusters on the surface.

It can be concluded from the relatively small change in the nucleation current that surface diffusion processes do not play an essential role, at least for the heterogeneous nucleation conditions studied in the experiments. A reason for this may be the observation that the linear dimension of a single molecule is of the same order of magnitude as the radius of the seed particle in the experiments, and that very quickly after a heterogeneous nucleus has started to grow, there is little seed surface left upon which the additional adsorbed monomers can attach and diffuse.

7 Conclusions

In this study we have developed rate equations describing the process of heterogeneous nucleation of droplets on aerosol seed particles. These take the form of the familiar Becker-Döring equations. It is recognised that these are non-linear instead of linear in the cluster populations. Nevertheless the steady state solutions to the equations can be found relatively easily. It appears to us that such a development has not been noted in the literature previously.

The approach demonstrates that the traditional Fletcher theory of heterogeneous nucleation rests on a rather rough estimate of adsorbed monomer concentration, which could be seriously

Figure 3: A schematic of nucleation kinetics according to Becker-Döring theory. Changes in mean i-mer concentrations are brought about by the growth of clusters by monomers (β_i) and by the loss of monomers from clusters (γ_i). The superscripts distinguish the direct vapour deposition model from the surface diffusion model. In addition, the mean monomer concentration is altered by an incoming flux of monomers (j) and by the loss of monomers to the gas phase (λ).

nucleation rate [m^{-2}s^{-1}]	$R_{\text{seed}} = 1$ nm	$R_{\text{seed}} = 2$ nm
$J_{\text{BD,dyn}}^{dv}(t_\infty)$	2.87e25	1.83e25
$J_{\text{BD,dyn}}^{sd,dv}((t_\infty)$	1.52e24	1.16e24

Table 6: List of the calculated nucleation currents in the modified models as derived from the dynamical Becker-Döring rate equations in the direct vapour deposition model, $J_{\text{BD,dyn}}^{dv}(t_\infty)$, and $J_{\text{BD,dyn}}^{sd,dv}(t_\infty)$ as derived from the dynamical Becker-Döring rate equations for the combined mechanism (direct vapour deposition and surface diffusion mechanism) for two particular radii of the seed particle R_{seed}.

in error for small seed particles. We have developed Becker-Döring models that demonstrate this difference. We have also used the equations to include the additional processes of cluster growth and decay through the surface diffusion mechanism, namely the addition of surface-adsorbed monomers to the cluster, and the reverse process. In usual treatments, growth by direct attachment of monomers from the vapour is normally assumed. We show that for nanometre size seed particles, direct attachment makes a dominant contribution to the current, largely because space on the seed particle for additional adsorbed monomers is rather limited. Inclusion of the surface diffusion mechanism reduces the current slightly. For larger seed particles, the inclusion of the surface diffusion mechanism should become more important.

We have studied recent experimental data and concluded that whilst the traditional Fletcher theory might account reasonably well for the onset saturations for heterogeneous nucleation, it fails in detail when considering critical sizes and nucleation currents, particularly with respect to the dependence on seed particle size. We regard Fletcher theory with great caution. We have pointed out that that amongst its many deficiencies it can suffer from an incorrect estimate of adsorbed monomer concentration. Furthermore, like other versions of the classical nucleation theory, Fletcher theory is founded upon the rather dubious capillarity approximation, as well as inappropriate geometric assumptions for *microscopic* molecular clusters. We conclude that analysis of data and estimates of atmospheric behaviour should really be conducted using a truly microscopic theory of heterogeneous nucleation.

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