Thermodynamics and kinetics of atmospheric aerosol particle formation and growth

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In this tutorial review we summarize the standard approaches to describe aerosol formation from atmospheric vapours and subsequent growth – with a particular emphasis on the interplay between equilibrium thermodynamics and non-equilibrium transport. We review the use of thermodynamics in describing phase equilibria and formation of aerosol particles from supersaturated vapour *via* nucleation. We also discuss the kinetics of cluster formation and transport phenomena, which are used to describe dynamic mass transport between the gaseous and condensed phases in a non-equilibrium system. Finally, we put these theories into the context of atmospheric observations of aerosol formation and growth.

1 Introduction

The air we breathe is a multi-phase system: in addition to the 10^{19} gas molecules, each cubic centimetre of atmospheric air contains typically thousands of liquid or solid particles. These aerosol particles are important players in the atmosphere. They impact the Earth's radiative budget by directly scattering sunlight and acting as condensation nuclei (CCN) for cloud droplets.[1] Aerosol particles are one of the main factors defining air quality, reducing visibility and causing thousands of premature deaths yearly.[2] When deposited, these particles stain and damage buildings and landmarks. The industrial applications involving aerosol particles include dosing of medicine through inhalation, coatings and various other nanotechnology applications. To improve our understanding on the effects of aerosol particles, the processes governing their sources and behaviour need to be understood.

Some ambient aerosol particles have entered the atmosphere in the condensed phase. Examples of such primary particles include *e.g.* dust, sea salt or pollen. During the past 20 years scientists have uncovered, however, that a major fraction of aerosol particles has been formed in the atmosphere through condensation of atmospheric vapours.[3] These particles are called secondary particles, and are the focus of this article.

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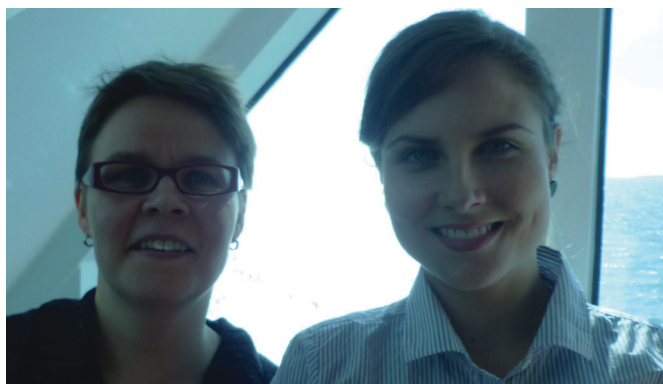
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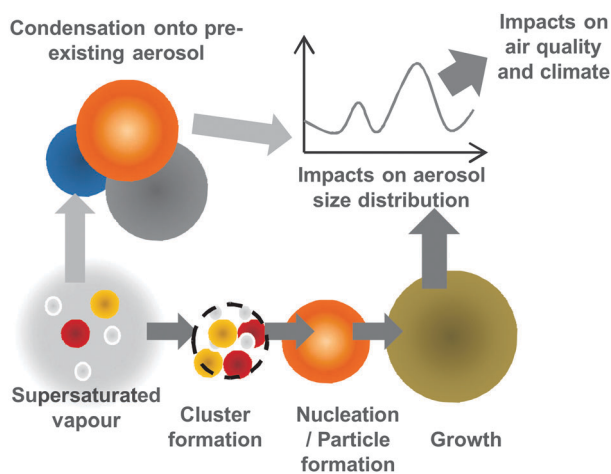
Fig. 1 Gas-to-particle conversion processes and the impacts of particle formation and growth from atmospheric vapours.

We know that vapour is turned into liquid or solid when particles are formed (Fig. 1), but in most cases the exact nature of the formation process is not known. Small stable clusters can be formed by a series of essentially irreversible chemical reactions, in which case the process is kinetically controlled: whenever suitable molecules collide, particle embryos are formed and they practically never break up – or to be more exact, the time scales of their evaporation are much longer than the rate at which new molecules collide with the cluster. On the other hand, the formation mechanism can involve competition between growth and decay of the smallest clusters, typical of any first order phase transition.

Aerosol formation processes, once understood, need to be represented with enough accuracy in atmospheric models, as the climate and air quality effects of condensable vapours can vary significantly depending on where in the aerosol size distribution they end up.

In this article we summarize the models used for phase transitions and molecular transport in systems where new aerosol particles are formed by nucleation and condensation of vapours. These models are not restricted to atmospheric applications, but are more general descriptions of the aerosol system. Also in the atmosphere, the compounds involved in particle formation vary with location, altitude and season. In this tutorial we use sulphuric acid, water and base compounds as examples since they are known to be key players in the first steps of atmospheric aerosol formation and growth in many locations in the atmospheric boundary layer (approximately the first 1 km of atmosphere above the ground).

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2 Equilibrium vapour and saturation ratio

We will consider a two-phase system consisting of a liquid and a vapour phase. It should, however, be borne in mind that the treatment of a vapour–solid system is analogous. Vapour is defined as a gas that can condense at the studied temperature, and the terms gas and vapour are often used interchangeably. Sometimes however the term gas is used to distinguish the inert gas (for example air under atmospheric conditions) from the condensable gas called vapour (for example water under atmospheric conditions). Another useful concept is fluid, in this context a common term for gas and liquid phases.

In the atmosphere, the air as an inert carrier gas is taking care of the temperature control: there are approximately 10^{19} cm^{-3} air molecules in the atmospheric boundary layer, while the concentration of water, the most abundant condensable vapour, is 10^{17} molecules cm^{-3}, and other condensable trace gases, such as ammonia, sulphuric acid or amines, less than 10^{10} molecules cm^{-3}. Between subsequent collisions of two condensable molecules, there are thus very many collisions with inert air molecules. When colliding with atmospheric particles, the inert molecules do not stick to the particle surface, but transfer energy. Helium or nitrogen is often used to serve the same role in laboratory experiments of particle formation.

When vapour and liquid phases coexist, the vapour molecules constantly collide with the liquid surface and become part of the liquid. At the same time there is a chance that molecules in the liquid escape from the liquid and become part of the vapour. At equilibrium these two processes balance, and the partial pressure of the condensable vapour i in this case is called the saturation vapour pressure $p_{i,\text{sat}}$. Saturation vapour pressure increases strongly with temperature T, and depends on the types of molecules i.

Saturation ratio S_i is the actual vapour pressure of i, p_i, divided by its equilibrium vapour pressure. In this article we restrict the use of the term 'saturation vapour pressure' to pure one component vapours and liquids, and flat vapour–liquid interfaces. In multicomponent mixtures and for curved vapour–liquid surfaces the equilibrium pressure is here called the equilibrium vapour pressure $p_{i,\text{eq}}$, but in the literature both equilibrium vapour pressure and saturation vapour pressure are varyingly used for all the cases. Moreover, saturation or equilibrium vapour pressure is often shortened to 'vapour pressure', which is unfortunately easily confused with the actual vapour pressure.

In a multicomponent case there are two factors deflecting the equilibrium vapour pressure from the pure liquid saturation vapour pressure. The first reason is statistics: if the mole fraction of molecules of type i in the liquid is x_i, in an ideal mixture where the interactions between different molecules are identical, the equilibrium pressure of component i is $p_{i,\text{eq}}(x_i) = x_i p_{i,\text{sat}}$. Second, if there are differences in the strength of bonding between different molecules to each other, this is taken into account using activity coefficients Γ_i in calculating the equilibrium pressure $p_{i,\text{eq}} = \Gamma_i(x_i,T)x_i p_{i,\text{sat}}(T)$. If different molecules are more attracted to each other than similar molecules, $\Gamma_i < 1$, and if less, $\Gamma_i > 1$. The product $\Gamma_i x_i$ is called the liquid phase activity. Each component i in a mixture has a separate saturation ratio $S_i = p_i/p_{i,\text{eq}}(x_i)$, which depends on the actual vapour pressure of component i, the composition of the liquid as well as temperature.

Gas phase activity is defined as the liquid-composition-independent fraction $p_i/p_{i,\text{sat}}$, where the actual vapour pressure is compared to the saturation vapour pressure of the pure liquid.

The gas phase activity of water expressed as a percentage is called relative humidity (RH). We return to the effect of surface curvature on equilibrium vapour pressure in Section 4.1.

If chemical reactions are taking place in the particle phase, this is reflected in the equilibrium vapour pressures. For example, the equilibrium vapour pressure of both ammonia and sulphuric acid is greatly reduced due to ammonium sulphate or bisulphate formation in the liquid or solid phases. Both ammonia and sulphuric acid can be undersaturated with respect to pure liquids ($p_i/p_{i,\text{sat}} < 1$), but supersaturated with respect to the ammonium(bi)sulphate ($S_i = p_i/p_{i,\text{eq}}(x_i) > 1$).

For a moment let us consider, for simplicity, a one-component case. When $S < 1$, the vapour is undersaturated and liquid evaporates until the equilibrium vapour pressure is reached, or the liquid runs out. When $S > 1$, the vapour is supersaturated, and condenses provided there is already a planar liquid surface present. If such a liquid does not exist, the vapour faces a dilemma: a state that minimizes free energy, a combination of energy and entropy (see Section 3), is the bulk liquid rather than supersaturated gas. However, to form a liquid, the interface between the liquid and gas must be created, which costs free energy. At a molecular level, the reason for the excess surface energy is that the molecules on the gas–liquid interface lack bonding partners – since the gas is much sparser than the liquid. Although the surface molecules pack closer to find the energetically optimal arrangement, their average energy is higher than that of the molecules in the bulk liquid.

The stochastic, kinetic process through which the supersaturated vapour forms clusters that overcome this energy barrier and turn into the first microscopic droplets of liquid is called nucleation. The exact distinction between the terms 'cluster' and 'particle' or 'droplet' is hazy. The principle however is that as soon as the molecular clusters have grown to sizes clearly larger than single molecules, and are much more likely to grow than decay, we call them particles or droplets. Often we call them 'stable particles', although they are not in thermodynamic equilibrium, since they are constantly growing, but they are stable in the sense that they stay as particles and do not vanish into the thin air, quite literally.

3   Thermodynamic equilibrium and free energies

Thermodynamics studies equilibrium based on the second law of thermodynamics which can be formulated as: 'in an isolated system, entropy increases in all spontaneous processes'. Thus, in an isolated system equilibrium is the state at which entropy $\mathscr{S}$ (here we have to use a calligraphic font not to confuse entropy with saturation ratio S) has reached a maximum. The second law of thermodynamics thus also defines the direction of all spontaneous changes (or equivalently the direction of time) in an isolated system – it tells where a given system is heading to.

Unfortunately the second law of thermodynamics does not say directly anything about systems exchanging energy E of some form with their environment, for example a heat bath keeping the temperature T constant or a pressure regulator keeping the total pressure p of the system constant. The solution for finding the equilibrium in such a case is to treat the combination of the system and the environment as an isolated system, and apply the second law for this combined system.

Provided that the environment is much larger than the actual system, maximizing the entropy of the combined system is equivalent to minimizing the free energy of the actual system.[4]

The nature of the free energy in question depends on the type of contact between the system and the environment. In the case of a contact that keeps pressure and temperature constant, the choice is the Gibbs free energy G. This is the historically standard choice in the theory of formation of a molecular cluster from vapour. If there is such a vast amount of gas in the system (whose volume is V) that the formation of molecular clusters or liquid droplets does not significantly alter the composition or the pressure of the gas phase, both the Helmholtz free energy change $\Delta F = \Delta E - T\Delta\mathscr{S}$ (T kept constant *via* contact with the environment) and the grand potential change $\Delta\Omega = \Delta E - T\Delta\mathscr{S} - \sum_i\mu_i n_i$ (T and chemical potentials μ_i in the gas phase kept constant by contact with the environment, where n_i are the numbers of molecules of different compounds i) are numerically equal to the Gibbs free energy change $\Delta G = \Delta E + p\Delta V - T\Delta\mathscr{S}$ in the cluster formation process. We use the changes in free energies rather than their absolute values, since this simplifies the formulae considerably. Free energies are auxiliary concepts, created to circumvent the problem of non-isolated systems. Their zero level is a matter of choice, but the differences in free energies contain meaningful physics or chemistry.

4   Liquid drop model as a mind-map

We can build a qualitative mind map of the cluster formation process by describing the clusters as if they were liquid droplets with bulk liquid density and surface tension. The gas phase can be simply treated as an ideal mixture of ideal gases. The resulting theory is the classical nucleation theory (CNT). Although clearly a crude approximation for the small clusters, the theory is very useful as a conceptual map of the landscape of cluster formation. Refinements based on more accurate theories (see Section 7.8) can be placed on this map to see their significance and relations to each other.

In the case of CNT, the (Gibbs) free-energy change in the formation of a droplet with, say, n_1 molecules of type 1, n_2 molecules of type 2, and fixed gas phase saturation ratios S_1 and S_2 is

$$\Delta G(n_1,n_2) = -n_1 kT\ln S_1 - n_2 kT\ln S_2 + A\sigma$$
$$+ \text{ surface excess terms}, \quad (1)$$

where A is the surface area of the droplet and σ is the surface tension and k is the Boltzmann constant. The first two terms represent the lowering of free energy when the molecules go from supersaturated vapour to liquid, and the third term is the energy cost of the surface formation. In a one-component system there is only one $-nkT\ln S$ term, but since some of our key examples involve two components, we show the two-component version here. Thermodynamic consistency requires eqn (1) to have extra terms related to the number of molecules on the surface layer of the cluster. The details of these small terms are beyond the scope of this article, and they vanish for the equilibrium clusters.[5]

4.1 Equilibrium conditions for a liquid drop

Whether maximizing the entropy of the system or minimizing any of the free energies or their changes in the cluster formation, the search for mechanical equilibrium conditions for a spherical liquid droplet with radius r_p results in the Laplace equation

$$p_l - p_g = \frac{2\sigma}{r_p}. \qquad (2)$$

Eqn (2) indicates that at equilibrium the liquid phase pressure p_l at the phase interface is larger than that of the gas, p_g, due to a force caused by the droplet surface tension σ directed towards the centre of the droplet. Consequently the equilibrium vapour pressure over a curved droplet surface $p_{i,\text{eq}}$ is higher than that over a planar surface, $p_{i,\text{flat}}$:

$$p_{i,\text{eq}} = p_{i,\text{flat}} \exp\left(\frac{2\sigma v_{i,l}}{r_p kT}\right) = \Gamma_i x_i p_{i,\text{sat}} \exp\left(\frac{2\sigma v_{i,l}}{r_p kT}\right), \qquad (3)$$

where $v_{i,l}$ is the partial molecular volume of component i in the liquid. At a molecular level a simplistic explanation for the increase in the equilibrium pressure is that on a convex surface droplet surface molecules, or at least their 'outer ends', are further away from each other than on a planar surface. Thus, their mutual interactions are weaker, and it is easier for the molecules to escape from the liquid to the gas. Eqn (3) can be rearranged to give the equilibrium radius r_p of a classical droplet in a supersaturated vapour

$$r_p = \frac{2\sigma v_{i,l}}{kT \ln S_i}. \qquad (4)$$

In a multicomponent system the radius of the equilibrium cluster along with its composition can be found from the set of eqn (4).

5 Kinetics of cluster formation: the birth–death equation

Aerosol particle formation from vapour is always essentially a kinetic cluster formation process. Clusters of a certain size are formed by collisions of two smaller clusters as well as the evaporation of larger clusters, and their size changes when they collide with other clusters or evaporate. The time evolution of the concentration, c_n, of clusters of size n (here, for simplicity, in a one-component system) is governed by the birth–death equations

$$\begin{aligned} \frac{dc_n}{dt} = {}& \sum_{n' < n} \frac{1}{2} \beta_{n'(n-n')} c_{n'} c_{(n-n')} + \sum_{n'} \gamma_{(n+n') \to n} c_{(n+n')} \\ & - \sum_{n'} \beta_{n,n'} c_n c_{n'} - \sum_{n' < n} \frac{1}{2} \gamma_{n \to n'} c_n, \end{aligned} \qquad (5)$$

where $\beta_{n,n'}$ is the collision coefficient between the n-mer and the n'-mer, and $\gamma_{n \to n'}$ is the rate coefficient for evaporation of n-mer decays producing a n'-mer (and a $(n-n')$-mer). In the case of particle formation from supersaturated vapour, the system is clearly not in equilibrium since detectable changes in the state of the system occur: clusters and more particles are formed.

The gross transport rate of the vapour molecules to the clusters can be calculated from kinetic gas theory, and it depends on the vapour concentration and temperature. While dynamic models for evaporation exist (see Section 8), in practical applications it is assumed that evaporation depends only on the cluster properties, not the surrounding vapour (apart from its temperature which is often assumed to set the cluster temperature). Thus the evaporation coefficients of clusters in equilibrium vapour can also be used for the supersaturated vapour. When the cluster with n molecules is in equilibrium with the vapour, the evaporation rate must be the same as the rate of the reverse collision process. This principle is called the detailed balance, and the cluster size distribution in the equilibrium vapour follows the exponential law $c_n^{\text{eq}} = c_{n,\text{ref}}^{\text{eq}} \exp(-\Delta G^{\text{eq}}(n)/kT)$ resulting in

$$\begin{aligned} \gamma_{n \to n'} &= \beta_{n-n',n'}^{\text{eq}} \frac{c_{n-n'}^{\text{eq}} c_{n'}^{\text{eq}}}{c_n^{\text{eq}}} \\ &= \beta_{n \to n'}^{\text{eq}} c_{\text{ref}}^{\text{eq}} \exp\left(\frac{\Delta G^{\text{eq}}(n) - \Delta G^{\text{eq}}(n - n') - \Delta G^{\text{eq}}(n')}{kT}\right). \end{aligned} \qquad (6)$$

This result essentially reduces the calculation of the evaporation rates to the calculation of formation free energies $\Delta G^{\text{eq}}(n)$ of different clusters. Here $c_{\text{ref}}^{\text{eq}}$ is the concentration cluster of reference size (often single molecules, that is monomers), in the equilibrium vapour for which the free energies have been calculated. The same principle holds for the further growth or evaporation of the clusters and particles: the forward condensation rate of vapour molecules onto the particle surface can be described by gas kinetic or diffusion theory, whereas equilibrium thermodynamics are needed to calculate the evaporation rate from the condensed phase. Unlike most theoretical approaches, Schenter et al. (1999)[6] applied eqn (6) the other way around: they used variational transition state theory to calculate the evaporation rates, and obtained the collisions rates from the detailed balance.

The birth–death eqn (5) describes the cluster concentrations at one point of space, or in a volume cell, where there are no spatial differences in vapour and cluster concentrations. If, and when, there are differences in concentrations between different locations in space, the transport of molecules is described using transport equations.

6 On molecular transport phenomena

Deviations from thermodynamic equilibrium induce momentum, heat and mass transfer, whose direction is defined by the second law of thermodynamics. If the system is isolated and left untouched for a long enough time, these transport phenomena will bring the system to thermodynamic equilibrium where no changes occur and nothing is flowing. In this article we will focus on the molecular scale transport processes linked to aerosol particle formation and growth under typical atmospheric conditions. In addition to the molecular scale phenomena, heat or mass can be transported through the macroscopic flow of the fluid. This is called convective transport,[7] and will not be discussed in detail here.

Molecular level transport occurs via molecular movement and collisions. If the system is large enough (contains enough molecules), the net transport can be formulated through the bulk (average) properties of the system – rather than treating each molecule separately. In this case the flux densities I of the transported variables (momentum, mass or heat) as a function of

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the position $\bar{r}$ and time t are proportional to the gradient ∇N (also called the driving force of the transport), and the transport coefficient C:

$$\bar{I}(\bar{r},t) \propto -C(\bar{r},t)\nabla N(\bar{r},t). \qquad (7)$$

For molecular momentum transport, C is the viscosity (internal friction in fluids, in N s m^{-2}) and N the velocity (m s^{-1}), while for energy or mass transport C is the thermal conductivity (in J s^{-1} m^{-1} K^{-1}) or diffusivity (in m^2 s^{-1}), and N the temperature (in K) or molecular concentration (in m^{-3}), respectively. Estimates for the transport coefficients can be calculated for ideal equilibrium vapour using the kinetic gas theory, but in practical applications empirical studies are often used to infer these coefficients.

Besides being driven by the gradient in the quantity itself, the transport is affected by gradients in other variables as well. As an example, in addition to being governed by a concentration gradient (ordinary diffusion) molecular mass transport is affected also by temperature (thermal diffusion) and pressure (pressure diffusion) gradients. When considering mass or heat transport to aerosol particles under typical atmospheric conditions, however, these effects are of minor importance as compared with the primary driving force of concentration inhomogeneities.[8] The transport equations describe the dynamic behaviour of the system, whereas in thermodynamics all changes are infinitesimally slow.

For the formation and growth of liquid or solid particles in a gas mixture at atmospheric (constant) pressure, the relevant forms of molecular transport are usually mass and heat transport: to condense or nucleate, supersaturated vapour needs to diffuse into an existing liquid surface or find a cluster of molecules to join. The phase transition, on the other hand, can cause temperature gradients due to the latent heat released or absorbed upon the transition.

The appropriate theory for treating mass or heat transport to/from liquid droplets in a gas mixture depends on the dimensions of the particle as compared with the gas phase density. If the particle surface is large and vapour density is high enough, the particle exhibits a large number of collisions with gas phase molecules and macroscopic theories describing the behaviour of the bulk gas can be used. If, on the other hand, the particle dimensions are small and the density of vapour molecules is low, the collisions between the particles and the gas phase molecules are scarcer and need to be accounted for on a molecular basis. The non-dimensional Knudsen number Kn = λ/r_p, where λ is the mean free path of the gas and r_p the droplet radius, is commonly used to describe this division. If Kn $\ll$ 1 the droplet is said to be in the continuum regime, and macroscopic laws like Fick's law of diffusion or Fourier's law of thermal conduction can be applied (see eqn (7)). In the kinetic regime Kn $\gg$ 1, and kinetic gas theory is used to calculate the collisions and the resulting heat or matter exchange between the particles and the gas phase molecules. The Kn range between the two limiting cases is called the transition regime, where the two theories are typically combined semi-empirically. We will return to the transport phenomena when studying the growth of droplets by condensation in Section 8.

7 Particle formation

7.1 Nucleation, barrier vs. barrierless processes

The shape of the cluster formation free energy curve, $\Delta G(n)$ of eqn (1), plotted against the cluster size n (see Fig. 2) depends on the nature of the system and on the vapour concentration compared to the equilibrium concentration. For a simple one component system like water (black lines), vapour concentration below the saturation level results in curves that tend monotonously upward for all sizes (dashed line). Vapour is the stable phase, and liquid does not form.

With a supersaturated vapour there is a critical size corresponding to a maximum in the free energy curve after which the curve tends downward (solid line). In this case the vapour is a metastable phase, and formation of the stable liquid phase is hindered by a free energy barrier. The barrier arises from the different radius (or molecular number) dependencies of the $nkT\ln S$ term, and the surface term in the cluster formation free energy: the former is proportional to the volume of the cluster, that is, r_p^3 or n, and thus increases faster with the cluster size than the latter, which is proportional to the surface area, that is, r_p^2 or $n^{2/3}$.

When the vapour concentration is far above saturation, the curve tends downwards for all sizes (dotted line in Fig. 2), corresponding to a barrierless process. The vapour phase is now completely unstable, and the liquid phase is the only stable phase. In a barrierless process, two similar or different molecules meet and form a dimer, a two-molecule cluster which is stable in the sense that it evaporates back to monomers at a lower rate rather than colliding with (and sticking to) a third molecule of the vapour. The dimer, and all subsequent cluster sizes, will grow without energy penalty by condensation as soon as further suitable molecules collide with the cluster,
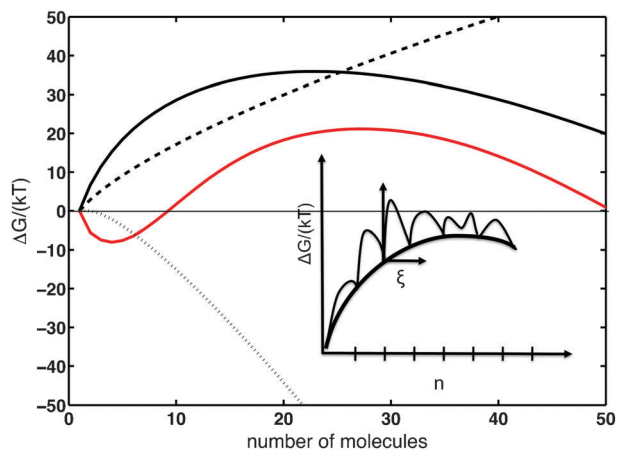

Fig. 2 Free energy as a function of cluster size in different cases: nucleation without stable pre-critical clusters (black solid line), nucleation with stable pre-critical clusters represented by a minimum (red solid line), infinite barrier of undersaturated vapour (black dashed line), barrierless kinetically controlled processes (black dotted line). Inset: schematic representation of the reaction barriers (thinner lines forming spike-like structures) and their relation to the free energy barriers. The horizontal axis related to each of the reaction barriers is not the number of molecules n, but an orthogonal axis ξ describing for example the geometric arrangement of the molecules.

and reach sizes at which they can be considered as liquid droplets. The formation of clusters is thus governed by kinetic collisions, with dimer formation being the 'critical' step – the critical cluster size n_{crit} is thus nominally 1 and the cluster formation rate depends on the second power of vapour concentration. Barrierless cluster formation reduces to a kinetic condensation process, depending directly on the difference between the ambient vapour pressure (the forward condensation rate) and the equilibrium vapour pressure defined above the cluster (the evaporation rate) (see Section 8).

When two molecules, or a molecule and a cluster, meet, they may have to overcome a different kind of barrier before they form a cluster. For simplicity, we call this type of barrier a reaction barrier. The reason for this barrier can be structural and/or energetic. The atoms in the cluster have to substantially rearrange themselves before they form a favourable cluster configuration. The colliding parties may also have too much excess energy for stable cluster formation, and other molecules colliding with the cluster are needed to carry this energy away. These processes give rise to effects called mass or energy non-accommodation, which are theoretically described by the mass and thermal accommodation coefficients α_m and α_T. Both coefficients are assumed to be unity in eqn (5) and (6) and thus not explicitly visible in the formulae. The inset of Fig. 2 illustrates the relationship between the reaction barriers and the free energy barriers.

Nucleation is by definition formation of embryos of a stable phase within a metastable mother phase, and thus corresponds to the case with a barrier in Fig. 2. In such a case, there is a critical cluster size $n_{crit} \geq 2$ above which the clusters are more likely to grow than evaporate. Clusters smaller than n_{crit} (or some of them, see the last paragraph of this section) are more likely to evaporate than grow. A rather unprobable sequence of stochastic collisions must add several more molecules to the cluster before it has nucleated, in other words reached critical size. In homogeneous nucleation only vapour is present in the initial state, and the vapour molecules form the cluster alone. In heterogeneous nucleation there is a surface onto which the clusters are formed. Fog formation onto dust particles while breathing out in cool air or onto spectacles when moving indoors from cold weather are everyday examples of heterogenous nucleation. In heterogeneous nucleation the seed surface is assumed to be insoluble in the condensing liquid. If the cluster is formed around a single ion or an electrically charged seed particle, we speak of ion-induced nucleation. If the condensing vapour consists of one type of molecules, we have one-component (unary) nucleation, if there are several types of molecules, multicomponent nucleation takes place. The two-component case is often called binary, and the three-component case ternary nucleation. One- or multicomponent nucleation can be homogeneous, heterogeneous or ion-induced, and sometimes it is difficult to draw the line: is sulphuric acid nucleating on a large organic molecule two component homogeneous nucleation or one component heterogeneous nucleation? If one and only one of the organic molecules is needed for each formed cluster, heterogeneous nucleation can be a sensible model depending on the solubility issues, but if there can be a varying number of the organic molecules in the cluster, homogenous two-component nucleation is a more correct description.

Even in a nucleating system small subcritical truly stable clusters with n_{min} molecules can exist. For example a dimer can be stable, equally likely to grow than decay, but the trimer more likely to decay, and a larger size has to be reached before growth is again more likely than decay. The stable pre-critical clusters manifest themselves as minima in the free energy curves plotted as a function of size. A well-known example is the ion induced nucleation around a small ion (Section 7.4). The appearance of the minimum means that the ion gathers a few molecules of vapour around it, but these clusters have not yet overcome the free energy barrier, and cannot grow by condensation.

7.2 Nucleation rate

In classical nucleation theory the time-independent solution of the birth–death eqn (5) is performed analytically to yield the net rate at which critical clusters are formed. In one component system this can be done explicitly, in multicomponent nucleation well justified approximations are involved. The analytical treatment is restricted to the case where monomer collisions dominate the growth of the critical clusters. The result for the critical cluster formation rate, that is the nucleation rate, is then

$$J = W_{c_1} \beta_{crit,1} Z \exp\left(\frac{-\Delta G_{crit}}{kT}\right). \qquad (8)$$

This is essentially the collision rate of monomers with concentration c_1 with the critical clusters, whose concentration in the equilibrium vapour is $W\exp(-\Delta G_{crit}/kT)$. Here W is the normalization factor for the cluster distribution and Z is the Zeldovich factor taking care of differences between the equilibrium vapour and the nucleating vapour, as well as the fact that overcritical clusters can decay back to subcritical sizes. This formula emphasises the importance of accurately predicting the critical cluster formation free energy, since the rate is dependent on its exponential. The nucleation rate (eqn (8)) does not reduce to the correct kinetic limit equation when the vapour concentration increases beyond the point where the barrier vanishes. Thus, to correctly model particle formation processes, one should first check whether the process in question is actually nucleation, and if it turns out that there is no barrier, apply much more simple kinetic equations instead of eqn (8).

7.3 Nucleation theorems

Combining the nucleation rate (eqn (8)) with the formation free energy (eqn (1)) for the critical cluster yields the nucleation theorems. These theorems can also be derived from a statistical mechanical treatment much more general than the classical nucleation theory. In the simple case represented by the black solid line in Fig. 2, the first nucleation theorem states that the rate of barrier crossing is proportional to the vapour concentration to the power $n_{crit} + \delta$, where δ is of the order of one, a term arising from the pre-exponential in the rate expression.[9] For one-component homogeneous nucleation $\delta = 1$. The second nucleation theorem connects the temperature dependence of the nucleation rate with the binding energy of the critical cluster. If stable pre-critical clusters exist these simple relationships are no more valid. In the ion-induced case, where stable pre-nucleation clusters of the same sign do not attach together

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to form clusters, the power connecting the nucleation rate and vapour concentration is $n_{crit} - n_{min} + \delta$. In a neutral case with a free energy minimum the growth of the critical cluster is dominated by collisions with the stable pre-nucleation clusters, whose concentration is much larger than that of monomers, and the nucleation theorems cannot be readily applied.[10]

7.4 Ion-induced nucleation

The formation free energy in a one-component vapour nucleating around an ion (electrical charge) is classically written as

$$\Delta G = -nkT \ln S + A\sigma + \frac{q^2}{8\pi\varepsilon_0}\left(1 - \frac{1}{\varepsilon_r}\right)\left(\frac{1}{r_p} - \frac{1}{r_{ion}}\right). \quad (9)$$

Here q is the charge of the ion, ε_0 is the permittivity of the vacuum, ε_r is the dielectric constant of the particle and r_{ion} is the radius of the ion. The first two terms give the formation free energy in the case of homogenous nucleation in the absence of the ion. At moderate saturation ratios (moderate vapour concentrations) there is first a minimum in the free-energy as a function of number of molecules in the cluster n. Fig. 3 illustrates a comparison between the standard homogenous nucleation case and a case with pre-nucleation clusters gathered around an ion for one-component water nucleation with ion radii 0.1 nm or 1 nm. For the 0.1 nm ion at low vapour concentrations, where the saturation ratio is below one, there is only the minimum in the curve, after which the formation free energy increases with size, and nucleation cannot take place. At intermediate concentrations there is a minimum followed by a maximum representing the critical size. At very high concentrations both the minimum and the maximum disappear, formation free energy decreases with size, and we are in the barrierless condensation regime. Note that if the ion is large enough (the blue curves in Fig. 3), there is no pre-critical minimum even in the ion-induced curves.

7.5 Example: two component nucleation of sulphuric acid and water

Let us study two different cases where the cluster is formed from sulphuric acid and water. First, in the two-component nucleation of water and sulphuric acid, the problem is defined
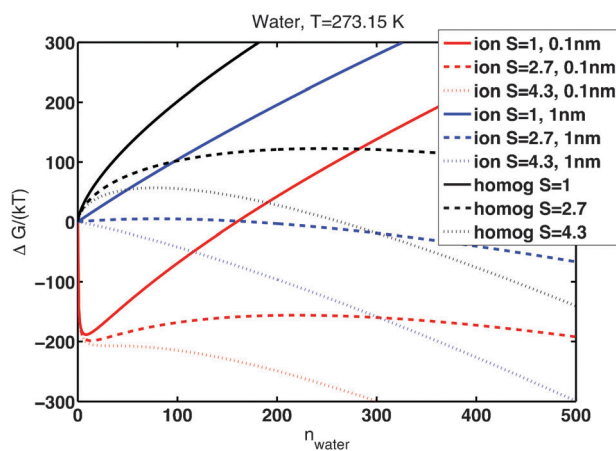

Fig. 3 The formation free energy vs. cluster size curves for ion-induced (red and blue) and homogenous (black) nucleation for water at three different relative humidities, with two ion radii (red: 0.1 nm, blue: 1 nm).
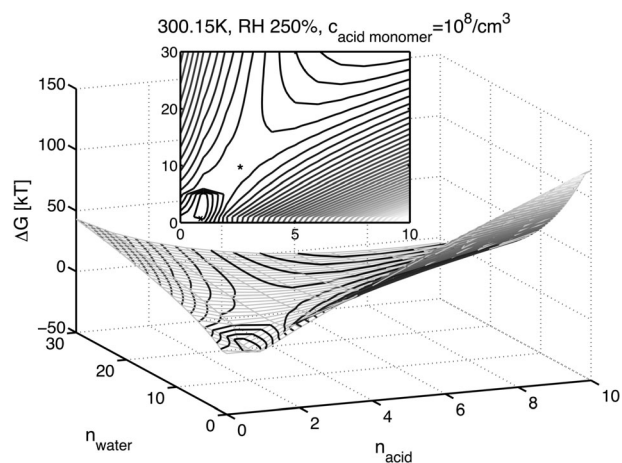

Fig. 4 The formation free energy of sulphuric acid–water clusters as a function of the number of molecules in the cluster as a three dimensional plot and contour plot (inset). In the contour plot the asterisk marks the critical cluster and the cross the stable pre-critical cluster.

as follows: temperature, relative humidity and sulphuric acid vapour concentration are known and kept constant, and we have to find the radius and composition of the cluster in equilibrium with this known vapour. We know from experiments the saturation vapour pressures of both water and sulphuric acid above their mixture, and also the liquid density and surface tension of this mixture as functions of composition and temperature. Eqn (3) can only be solved numerically, but we find two solutions for the number of sulphuric acid molecules $n_1 = n_{acid}$ and the number of water molecules $n_2 = n_{water}$ in the equilibrium cluster.

Fig. 4 shows the formation free energy surface plotted as a function of n_{acid} and n_{water}. The first solution is in typical conditions of $n_{acid} = 1$ sulphuric acid and $n_{water} = 1$–2 water molecules. This is a hydrate, a stable pre-nucleation cluster that forms even if the vapour is not supersaturated. Sulphuric acid as a strong acid wants to donate its proton(s), and when clustering with water it can satisfy this urge with water acting as a base and accepting the proton. Free sulphuric acid molecules are thus rare in humid air. This point is a minimum in all directions on the free energy surface corresponding to stable equilibrium with the vapours. The corresponding cluster is equally likely to grow and decay, and if one molecule is added or taken away, the cluster tends to return to its original size.

The second solution is the critical cluster in metastable equilibrium with the vapour, typically with $n_{acid} = 3$–5 and $n_{water} = 10$–20. The critical cluster is generally found at the saddle point of the free energy surface, in other words, it is a maximum in one direction of the surface, and a minimum in all other directions.

7.6 Example: water nucleating or condensing on a sulphuric acid seed

In this not very realistic but illustrative example we force our cluster to contain a constant number of sulphuric acid molecules which cannot evaporate, and call that the 'seed' cluster. We assume that there is no sulphuric acid in the vapour phase, but only in the cluster, and water plays the role of the condensing vapour that can join the cluster and also evaporate.
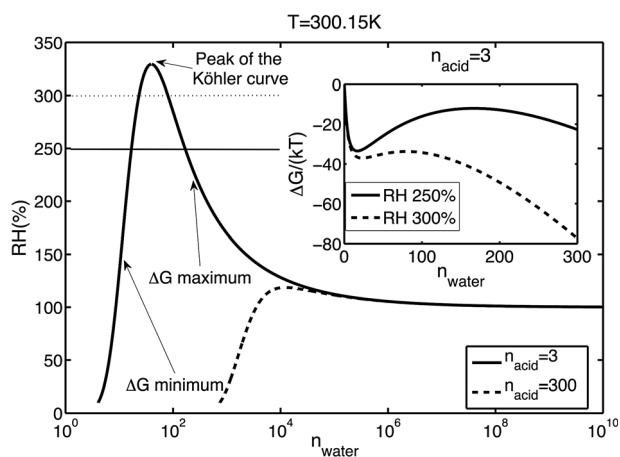
Fig. 5 Inset: the formation free energy as a function of the number of water molecules in the cluster for artificially constrained cases where each cluster has three sulphuric acid molecules. The curves representing two relative humidities are shown. Main figure: the locations of the minimum (left of the peak) and the maximum (right of the peak) in the curves shown in the inset, as a function of relative humidity. The cases for 3 and 300 sulphuric acid molecules in the cluster are shown. The curves are analogous to Köhler curves.

The relative humidity and temperature are known and kept constant. The equations to be solved are exactly the same as before, only now instead of fixing the concentration of the acid vapour, we fix the number of acid molecules in the cluster. In this case we do not have a three dimensional formation free energy surface as in Fig. 4, but a two dimensional curve shown in the inset of Fig. 5, a slice of the three dimensional surface at n_{acid} = constant. The situation differs from heterogeneous nucleation on an insoluble seed, since now the seed is soluble in the condensing liquid.

Again, at a certain range of relative humidities there are two solutions to the equilibrium problem: a minimum, corresponding to a truly stable cluster, and a maximum, corresponding to the metastable critical cluster. If we plot the size of the stable cluster (minimum) and the size of the critical cluster (maximum) at different relative humidities, we get the curves of Fig. 5. These curves are analogous to Köhler curves representing the standard theory of cloud droplet formation by condensation of water onto a soluble seed called the cloud condensation nucleus (CCN).[11] The seed in cloud formation can consist of mixtures of mainly inorganic molecules, and water is still the condensing vapour. The left-hand branch of the Köhler-curve corresponds to the minimum in the formation free energy plots in the inset of Fig. 5. The right-hand branch corresponds to the maximum, which does not exist if the relative humidity is below 100% (in this case the curve in the inset would continue forever upwards after the minimum). When the relative humidity increases, the minimum and maximum approach each other. At the relative humidity corresponding to the peak of the Köhler curve, the minimum and maximum merge, and the formation free energy curve points monotonously downward at all n, indicating that the barrier has vanished.

The traditional Köhler theory for CCN activation commonly states that the seeds do not activate for growth until the relative

humidity of the peak has been reached; the seeds gather vapour molecules around them according to the equilibrium number indicated by the minimum of the formation free energy curve, but cannot grow further. From the point of view of nucleation theory, which relies on stochastic barrier crossing, there is however a non-zero possibility that the clusters nucleate over the barrier between the minimum and the maximum (i.e. that the system is not in thermodynamic equilibrium at all times). For this example system, and the condensation of water on a typical CCN, the barrier crossing rate is practically zero until the barrier vanishes, and the simple idea that these processes only happen once the barrier has vanished matches experimental evidence.

The suggested nano-Köhler mechanism[12] considering the 'activation' of freshly nucleated sulphate clusters by organic vapours is an analogous process for formation of atmospheric nanoparticles. Sulphuric acid is then assumed to be the condensing vapour, and the seed is speculated to consist of organic molecules or organosulphates. The thermodynamic data for the relevant mixtures are not known for bulk liquid, not to speak of the small cluster size corrections, and thus free energy and Köhler curves related to these systems cannot readily be plotted. It must, however, be kept in mind that at these small cluster sizes, where the addition of a few molecules can result in a large difference in the free energy, it is possible that the process proceeds with a significant rate even before the barrier vanishes.

The Köhler-type of behaviour, where the saturation ratio of the vapour can increase without any measurable effect until a certain threshold value is reached, and then the process suddenly takes place at a large rate, prompts the use of the term 'activation'. Nucleation processes exhibit a similar behaviour: the nucleation rate as a function of vapour concentration resembles a step function. 'Activation' has also been used to characterize all processes, where the particle formation rate depends on the first power of the concentration of some key vapour, typically sulphuric acid.[13] Observed powers close to one have been explained by the existence of pre-critical nuclei, whose concentration is independent of sulphuric acid concentration, and their 'activation' by sulphuric acid. Bearing in mind that the possible existence of stable pre-critical clusters forbids the straightforward use of the nucleation theorem, this category of formation mechanisms coined 'activation' can also be multi-component nucleation involving stable pre-critical clusters.

7.7 Assumptions of classical nucleation theory and its known problems

We have drawn the map of processes related to particle formation based on classical nucleation theory, and here we give a brief account on the validity of this simple thermodynamic theory.

In an ideal gas molecules do not interact with each other, and thus cannot form clusters. However, for the gas phase alone this is not a bad assumption, and a more complicated equation of state can be inserted to revise the theory. We also, usually justifiably, assume that the temperature is kept constant when the particle forms.

The volume of the cluster in CNT is calculated using bulk liquid density. This assumption is not as outrageous as it

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sounds from the outset, since it is connected to the cluster definition. There is no unambiguous way to say what the radius of a molecular cluster is, even if it is spherically symmetric. From the point of view of density, a cluster is a much denser region in the gas phase and when moving outwards from the centre of the cluster the density decreases gradually rather than abruptly. There is some total excess number of molecules in the cluster region compared to the situation where the same region would be filled with gas.

One way of defining the dividing surface where the cluster ends and gas phase begins is the equimolar surface: the radius of the cluster is taken to be that of a sphere which, when filled with bulk liquid, would contain the excess number of molecules. When using the equimolar surface, the radius is thus actually defined so that bulk liquid density is exactly a correct description of the cluster density. Another appealing consequence of using the equimolar surface as the cluster radius definition is that the surface tension at the equimolar surface is independent of the cluster size, *i.e.* the surface tension of a planar surface can be used also for small clusters. The density of the liquid is assumed to be much larger than the density of gas, and also usually independent of the liquid pressure, although compressibility can be taken into account if needed. The exchange of molecules between the interior and the surface layer of the cluster is justifiably assumed to be much faster than between the cluster and the gas phase.

Now there is only one big problem, and that is the measurement of surface tension. When planar surface tension is measured, it is done mechanically, and by definition the mechanic and thermodynamic surface tensions are only equal if the dividing surface is taken to be the surface of tension. In the classical liquid drop model we just have to hope that this surface is close to the equimolar surface, and if it is not, the theory can fail catastrophically producing for example negative numbers of molecules in the critical cluster. This is the case for example in a surface active water–ethanol mixture and, although to a lesser extent, from the atmospheric point of view, in a more relevant water–sulphuric acid–ammonia system.

CNT suffers from known self-consistency problems, since the formation free energy (eqn (1)) does not give zero for the monomer, as it should. This is rather easily corrected in a one-component system by subtracting the nominal non-zero monomer formation free energy from expression (1). In multicomponent systems it is more complicated to devise a thermodynamically consistent expression for the formation free energy that would give zero for all the monomers, and cluster distribution that would reduce to the one-component case when the numbers of molecules on other components are set to zero.[14] The strengths of CNT are that it requires only bulk liquid density, planar surface tension and saturation vapour pressure to be known, and it has a reasonable, although not always negligible, computational cost. Solving a set of highly non-linear eqn (4) can sometimes be surprisingly difficult. A two-component system (if not surface active) is usually doable, but a three component system poses serious numerical problems. If the listed set of data is not available, which is the case for many atmospherically relevant multicomponent mixtures, the liquid drop model is toothless. Interestingly, also the treatment of condensation growth or evaporation is considerably complicated when moving from two-component to three-component systems.

This is due to very similar reasons as with the nucleation theory: partly to computational requirements in treating ≥ 3 instead of 2 types of molecules, and partly to lack of thermodynamic data for these complex mixtures.

CNT gives a good qualitative description of particle formation in many simple and also atmospherically relevant systems, but fails in the details. The particle formation rates can be several orders of magnitudes off as compared with observations, but the dependence of formation rates on vapour concentrations is typically fairly correct. The temperature dependence, on the other hand, is almost always wrong. Nucleation theorems (see Section 7.3) imply that the critical cluster size is predicted correctly, but its formation energy is wrong. Various revised versions of the classical nucleation theory and more advanced theories relying on essentially the same principles have been developed over the past decades. A certain revised theory typically improves the agreement with experiments for a certain substance at a certain temperature, but not for other substances or even the same substance at a different temperature. Another problem is that the more advanced models like density functional theory are only applicable, with a feasible computational cost, to spherically symmetric molecules or cylindrically symmetric linear molecules, and thus cannot be directly used to understand atmospheric particle formation involving, for example, sulphuric acid and water.

7.8 Molecular modelling schemes

If we would be able to describe the individual molecular interactions accurately from first principles, we would surely be able to build a model superior to the thermodynamic description of the clusters. There are roughly two main types of molecular simulations: molecular dynamics and Monte Carlo.[15]

Molecular dynamic simulations are essentially solutions of Newton's second law $F = ma$ for a many-body system. The molecules are given initial locations and velocities, the molecular interactions give the forces acting on the molecules, and we can follow what happens to their location and speed in time: do they form clusters, do the clusters evaporate, and how long do these processes take. Temperature control must be devised somehow in the simulations if we wish to mimic constant temperature experiments. If we could also simulate the inert carrier gas molecules controlling temperature in the atmosphere or in laboratory experiments, we would have a very realistic model of the cluster formation. This is however computationally far too expensive due to a large number of gas molecules, and cheaper methods for temperature control called thermostats are usually applied. In molecular dynamics, ideally we would not need to find the formation free energy at all, but get directly values for the evaporation rates or the formation rate of critical clusters – without having to count on the predictions equilibrium thermodynamics.

The reason why molecular dynamic simulations cannot be directly applied to atmospheric particle formation is the computational cost. The interaction potentials required to describe molecules that form particles in the atmosphere are complicated and essentially require a quantum mechanical description. One realistic simulation of cluster formation in a water–sulphuric acid mixture would take of the order of 10 000 years

even if we used all the computers of the world simultaneously. Thus, computationally cheaper options are needed. Monte Carlo simulations study the averages of cluster properties relying on statistical mechanics. These studies do not involve time dependence, but replace time averages with ensemble averages. The formation free energy of a cluster of size n can be inferred by comparing a monomer with a dimer, a dimer with a trimer and so on. There are various algorithms for doing this. In the canonical or grand canonical ensembles temperature is a parameter given to the algorithm, and is by default constant. Even these studies are too expensive to use together with fully quantum mechanical interaction energies.

Molecular dynamics and Monte Carlo simulations have been successfully employed to study simple molecules like noble gases well described by classical Lennard-Jones potential. Also classical potentials for water–water interaction capture many features of water cluster formation well. Simulation results as computer experiments can be compared to classical nucleation theory or various more advanced theories applied to the same model system (for example water, using the surface tension, liquid density and saturation vapour pressure of TIP4P model water rather than those of real water). Thus, even not completely realistic simulations yield insight into the reasons why the theories behave in undesired ways.

The molecules forming particles in the atmosphere require quantum mechanical treatment, first and foremost because they undergo proton transfer reactions when forming clusters. It is precisely these proton transfer reactions that make the cluster formation favourable. The formation energy of a cluster where this acid meets a base has a large negative value, and in the product cluster the proton may have transferred to the base. The problem with classical interaction potentials is that they tend to keep molecules intact. Reactive models have been developed, but they do not, at least yet, describe atmospheric clustering in a reasonable manner. Combining quantum mechanics and molecular dynamics or Monte Carlo simulations for atmospheric clusters is constantly probed with increasing computer resources, but so far almost all the work using a set of methods that we call quantum chemistry has been finding the minimum energy configurations for certain clusters.

Quantum chemistry is a numerical solution of the Schrödinger equation for the systems consisting of many nuclei and electrons, which can take any positions with respect to each other. The methods involve an extensive set of approximations to overcome the otherwise overwhelming theoretical and numerical burden (apart from very simple cases like hydrogen and helium dimers). The level of theoretical and numerical approximations is indicated by lengthy acronyms such as B3LYP/CBSB7 or RI-CC2/aug-cc-pV(T+d)Z. When applying quantum chemistry, formation free energies are calculated using the energies of the minimum energy configuration of a certain cluster size. Of course, at a non-zero temperature an average over various configurations would be a more representative picture of the cluster. The entropy contributions are obtained by assuming the clusters to be rigid rotors and their vibration modes harmonic, with anharmonic corrections sometimes applied.

The results of quantum chemical calculations must be compared to experiments to make sure the various approximations have not

resulted in skewed physics or chemistry. The computational cost of methods that are accurate enough to describe sulphuric acid containing clusters scales as the number of electrons to the power of 7, so only the smallest clusters can be treated with quantum chemistry. Currently the limit is on the order of four sulphuric acid molecules and four base molecules (ammonia or dimethylamine, for example).

Treatment of water, which is certainly present in atmospheric clusters (due to the large concentration of water compared to other condensable vapours), is difficult and time consuming due to the relatively weak interactions and resulting large configuration space to be sampled. Very large clusters can be certainly treated with thermodynamics, so the most promising way forward is to make these ends meet and find an intermediate solution for the sizes in between. Cluster size-dependent surface tension and/or liquid density could be inserted into the classical expression of formation free energy to achieve this. The size dependence of the extent of proton transfer, however poses a problem. Classical nucleation theory assumes complete proton transfer in the case of, for example, a cluster with equally many sulphuric acid, ammonia and water molecules. This is the case in a macroscopic water solution of ammonium bisulphate, whose properties are used to describe the nanoscale clusters (see *e.g.* Wexler and Clegg *et al.*, 2002 and references therein). Quantum chemistry, however, shows that no proton transfer has occurred in a cluster with one sulphuric acid, one ammonia and one water molecule. Proton transfer depends on truly many body interactions, and in the tiniest clusters the bulk picture fails. The difference between CNT and quantum chemical models is dramatic: for the one sulphuric acid, one ammonia and one water molecule cluster CNT predicts an ammonia evaporation rate of 10^{-5} s^{-1} while quantum chemistry predicts a rate of 10^5 s^{-1}, ten orders of magnitude faster. As a general rule, the erroneous treatment of proton transfer by CNT results in significant overbinding of the smallest clusters. The extent of proton transfer does not follow the n ($r_p{}^3$) or the $n^{2/3}$ ($r_p{}^2$) dependence of the terms in the classical formation free energy (eqn (1)) and thus modifying the parameters in that equation to capture also the properties of the smallest clusters seems artificial or even futile.

8 Condensation growth of aerosol particles

Let us now consider a droplet that has just overcome the nucleation barrier (*i.e.* whose size equals the critical cluster size), immersed in a gas mixture with a condensable vapour saturation ratio $S > 1$ (this has to be the case for nucleation to happen), atmospheric pressure and temperature T. Since $S > 1$, and the condensed phase exists in the form of a critical cluster, the vapour will tend to condense and grow the particle further. The condensation growth/evaporation of the particle can be calculated with laws of mass and heat transport as discussed in Section 6.

Typical mean free paths of gases under atmospheric conditions are of the order of 10^{-8}–10^{-7} m, whereas the diameters of the freshly nucleated clusters are of the order of 10^{-9} m, so the particles start their growth in the kinetic regime (Kn $\gg$ 1). If the saturation ratio remains above unity, and no significant scavenging processes take place, the particle can reach continuum

regime sizes (Kn ≪ 1). Activated cloud droplets are, for instance, typically well above the continuum regime limit.

Somewhat different from the nucleation processes, mechanics and dynamics of condensation growth and evaporation of aerosol particles are theoretically relatively well understood.[8,16,17] If the identities and thermodynamic and kinetic properties of the condensing/evaporating vapours are known, condensation models reproduce observations of aerosol growth with extremely good accuracy – particularly in the continuum regime.[18] We also need to know what happens to the molecules after they have been transferred to the condensed phase. In the following we summarise the equations that govern the mass and heat transport to an aerosol particle[18] in the kinetic, continuum and transition regimes.

8.1 Mass transport to a particle

When Kn ≫ 1, kinetic gas theory is used to calculate the mass transport between the gas and particulate phases. An approximate expression for the net mass flux j_i of molecules of type i (kg s^{-1}) to a particle in the kinetic regime can be formulated (e.g. Hirschfelder et al., 1964) and is often used in the form

$$j_{i,\text{kin}} = M_i \pi r_p^2 \alpha_{i,m} \langle v_i \rangle (c_{i,\infty} - c_{i,a}), \qquad (10)$$

where M_i is the molar mass of type i. $\langle v_i \rangle$ is the mean thermal speed of the particle and the vapour. The term proportional to $c_{i,\infty}$, the concentration of i far away from the droplet, describes the forward condensation rate of the vapour molecules to the particles. The term proportional to $c_{i,a}$, the concentration corresponding to the equilibrium vapour pressure of i over the particle surface, describes the evaporative flux away from the particle. $\alpha_{i,m}$ is the mass accommodation coefficient.[19] Eqn (10) is an approximation based on the kinetic collision frequency between the particle and vapour molecules, assuming that the particle is considerably larger than the vapour molecule, and thus the radius of the molecules and the average velocity of the particle can be assumed to be negligible. Eqn (10) is a special case of the birth–death eqn (5) – assuming a monodisperse particle population in the system and tracking its size as it grows or evaporates. Also, only monomers are assumed to be colliding with the particle and mass accommodation is explicitly included in eqn (10). Although kinetic mass transport is described in a non-equilibrium situation, the condensation and evaporation rates in eqn (10) assume ideal gas molecules that follow the Maxwell–Boltzmann statistics.

When Kn ≪ 1 the particle sees the surrounding vapour as a continuum, and the mass transport can be treated based on the Fick's law of diffusion (see eqn (7)). At constant total pressure, the mass flux of condensable vapour to the particle with radius r_p can be written as[8]

$$j_{i,\text{con}} = \frac{4\pi r_p M_i D_i p}{k T_\infty} \ln\left(\frac{1 - \frac{p_{i,a}}{p}}{1 - \frac{p_{i,\infty}}{p}} \right), \qquad (11)$$

where D_i is the diffusion coefficient of i in the gas mixture, p is the total pressure of the gas phase, and $p_{i,a}$ and $p_{i,\infty}$ are the partial pressures of i at the particle surface and far away from the droplet. The surface of a spherical droplet or cluster can usually be assumed to be in a local equilibrium with the vapour just adjacent to it, and $p_{i,a}$ is thus the equilibrium

vapour pressure described by eqn (3). In dilute gas mixtures (where the mole fraction of the condensing vapour is low) the logarithmic term multiplied by the total pressure can be approximated simply with the difference $p_{i,\infty} - p_{i,a}$.

For the case where Kn ≈ 1, semi-empirical approaches need to be used. Usually this is done by forcing the kinetic and continuum regime fluxes to coincide at a distance, of the order of the mean free path, away from the particle surface with a correction factor f that depends on Kn and $\alpha_{i,m}$, so that the expression for the mass flux at all Kn becomes[1,20]

$$j_i = f_{i,m}(\text{Kn}_i, \alpha_{i,m}) j_{i,\text{con}}, \qquad (12)$$

where Kn is defined for the vapour. Eqn (12) simplifies into eqn (10) and (11) in the kinetic and continuum regimes, respectively.

Eqn (10)–(12) describe the condensational mass transport to particles using gas phase transport theories. Information on the properties of the condensed phase enters these equations through the equilibrium vapour pressures and the mass accommodation coefficients. As compared with the CNT equations, for instance, eqn (8) describing the nucleation rate where S is in the exponent, the dependence of condensation growth on S is weaker – only to the power of one. Condensation is thus relatively more sensitive to the kinetic transport properties of the vapours.

As in the case of nucleation, the presence of electrical charge enhances the condensation mass flux of polar molecules onto charged aerosol particles.[21] The ion-enhancement to the atmospheric nanoparticle growth is, however, shown to be of importance only at the smallest (<3 nm) particle sizes – as the Coulomb force decreases strongly as a function of distance and thus the particle diameter – and is outside the scope of this paper.

8.2 Heat transport to a particle

The condensation onto atmospheric freshly nucleated particles is usually slow enough and the particle concentration is low enough that heat transport can be neglected in condensation growth calculations. In many laboratory applications studying condensation at low pressures, high supersaturations and/or particle concentrations, however, the heat transport needs to be accounted for.[8,11,18,22]

The heat transfer to an aerosol particle is analogous to the mass transfer equations. The heat flux Q to the particle of radius r_p at all Kn can be formulated[17,23] as

$$Q = 2\pi r_p K f_{I,T}(T_\infty - T_a) - \sum_i H_{i,g} j_i, \qquad (13)$$

where the first term corresponds to the conductive transport and the second term to the energy transported with the condensing molecules. K is the thermal conductivity of the gas mixture, T_∞ and T_a are the gas phase temperatures far away from the particle and at the particle surface, respectively, and $H_{i,g}$ is the specific enthalpy of vapour phase i. $f_{I,T}$ is the transition regime correction factor for heat transport[20] analogous to $f_{i,m}$, but Kn$_I$ is now defined with the mean free path of the inert gas I. $\alpha_{I,T}$ is the thermal accommodation coefficient of the inert gas, i.e. the probability that a molecule that hits the particle surface becomes in thermal equilibrium with it.[19]

Eqn (14) approximates thermal conductivity and the specific enthalpy of vapour with constants, but similar equations can be derived taking into account their dependence on *e.g.* temperature or gas phase composition.[17]

8.3 Example: condensation growth of water droplets

Let us now consider the condensation of water vapour onto a particle population of 10^4 particles cm^{-3} in three cases: (1) a system with constant total (atmospheric) pressure p and no heat exchange with the environment (*i.e.* an adiabatic air parcel that can change its volume); (2) a system with constant total pressure and temperature; (3) a system with constant total pressure and relative humidity – as defined using pure water at the initial temperature as the reference liquid. The initial gas phase temperature in all cases is assumed to be $T_\infty = 5$ °C, the initial particle size is a few nanometers, and the relative humidity far away from the droplet is 150%.

In case (1) the droplet will continue to grow and consequently the relative humidity will drop until all the "excess" gas has condensed, the partial pressure of the condensable vapour is the equilibrium pressure ($S = 1$ and relative humidity 100%), and there is no driving force for the mass transport of molecules from the gas to the particulate phase (blue curves in Fig. 6). Also, following the requirement of thermal equilibrium, the system temperature will be uniform. This final temperature will be a few degrees higher than the initial temperature, due to the latent heat released upon condensation (blue curves in Fig. 6B).

In case (2) (constant p, constant T_∞) the droplet will grow until the partial vapour pressure of water corresponds to the equilibrium pressure at T_∞ – yielding a slightly higher final size as compared with case (1) (red curves in Fig. 6) as the excess energy (latent heat) is constantly removed by the heat bath.

In case (3) (constant p, constant partial pressure of water vapour) the droplets will continue to grow until the latent heat production has caused the system temperature to be so high
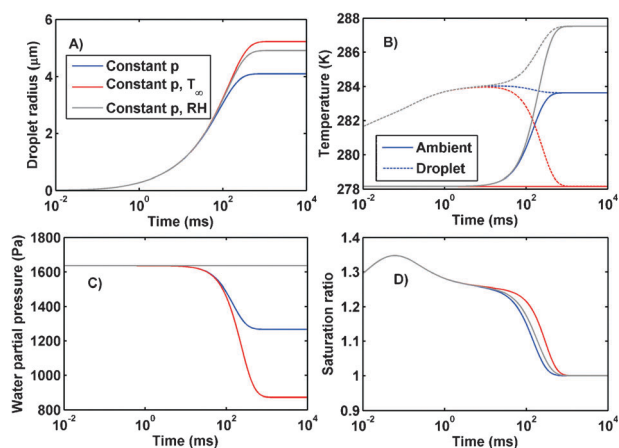
that the constant partial vapour pressure corresponds to equilibrium (gray curves in Fig. 6). In this case also the final equilibrium size of the droplet is larger than in case (1), *i.e.* relatively more molecules are in the condensed phase – because new gas phase water molecules need to be constantly fed to the system to maintain the constant relative humidity.

9 Atmospheric particle formation and growth

The formation of new small nanoparticles (<3 nm in diameter) followed by their condensation growth is observed frequently in various environments around the world.[3] Fig. 7 presents the time evolution of the atmospheric aerosol size distribution on March 25, 2003 at the SMEAR II[24] station in Finland – which is an example of a boundary layer site with frequent atmospheric aerosol formation. Intense formation of particles with diameters close to the detection limit of the DMPS (Differential Mobility Particle Sizer) instrument of 3 nm is observed during the day, and the newly formed particles grow to climatically relevant sizes with a growth rate of some nanometers per hour.[3]

Particle formation events are characterized by the formation rate of new particles, and the diameter growth rate (GR) of the newly-formed aerosol population. GR is related to the concentrations of condensable vapours through the relationship between the total mass flux j to the particle of radius r_p and diameter D_p:

$$j = \sum_i j_i = \frac{dm_p}{dt} = \rho_p \frac{dV_p}{dt} = 4\pi\rho_p r_p^2 \frac{dr_p}{dt} = \frac{1}{2}\pi\rho_p D_p^2 \mathrm{GR},$$

$$(14)$$

where ρ_p and V_p are the particle density and volume, respectively, and the summation is over all condensing species.

Fig. 6 The growth of a water droplet in the 3 different cases. Blue: total gas phase pressure is held constant, no heat exchange with the environment. Red: total gas phase pressure and temperature are held constant. Gray: total gas phase pressure and water vapour partial pressure are held constant. (A) Time evolution of droplet radius; (B) time evolution of the gas phase (solid) and particle (dashed) temperature; (C) time evolution of the water vapour partial pressure; (D) time evolution of the saturation ratio.
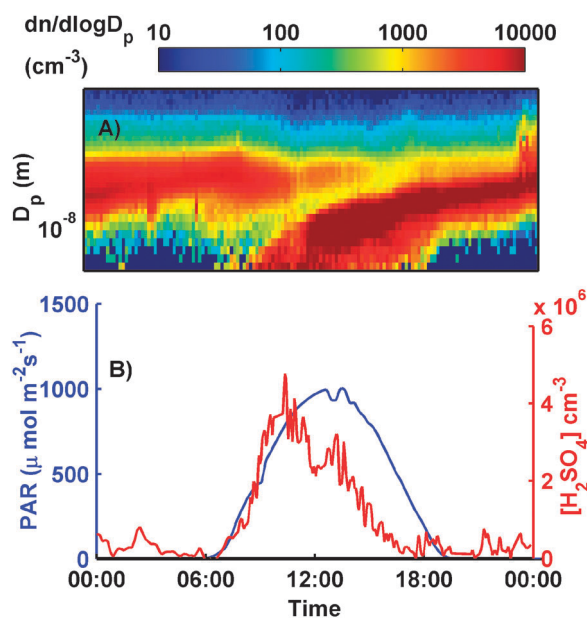

Fig. 7 Particle formation and growth event recorded with the Differential Mobility Particle Sizer (DMPS) instrument (A).[3] The time evolution of photosynthetically active radiation and sulphuric acid concentration measured with a Chemical Ionization Mass Spectrometer (CIMS) (B).[13,26]

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On the other hand, j can be expressed by the mass transfer formulae outlined in eqn (10)–(13). In the case of simple reversible condensation (where the ambient and equilibrium vapour pressures, rather than *e.g.* chemical reaction or mass transfer rates in the particles, limit the growth) the vapour pressures at the particle surface can be described with the equilibrium vapour pressures of each species i (see Section 8).

A vast number of studies investigating the particle formation mechanisms, the vapours participating in the formation and growth processes, as well as the conditions favourable to secondary aerosol formation have been published.[3,25–27] In the mesosphere (at 50–100 km height) dust is formed from meteoric ablation products,[28] and at coastal locations algae in the sea bottom exposed during low tide produce vast amounts of particles by emitting iodine compounds.[29] There is strong evidence that in many locations in the boundary layer sulphuric acid, atmospheric bases such as ammonia and amines,[27] along with organic compounds participate in particle formation.[30] Consistently, it has been observed that boundary layer particle formation is often linked to sunlight (strong photochemical activity produces condensable vapours through oxidation and boundary layer mixing is driven by the solar radiation), and low enough concentration of pre-existing aerosols. The processes limiting new particle formation can be different at different locations – although the production and presence of condensable vapours is naturally a prerequisite for particle formation and growth.

Pre-existing aerosol particles hinder particle formation from condensable vapours. If there is sufficient aerosol surface area around, the vapours will condense on the pre-existing aerosol instead of forming new small particles. This limitation follows directly from the mass flux eqn (10)–(12), and is the reason why it was earlier believed that homogenous nucleation cannot take place in the lower atmosphere. The pre-existing larger aerosol particles are also a sink for the freshly formed new nanoparticles: the main loss mechanism for these small particles is their coagulation – the more there is pre-existing surface area available for them to collide with, the shorter their average lifetime. The coagulation sink CoagS (in s^{-1}) is a measure of the loss rate of the freshly-formed particles, and is defined for particles of diameter D_p as

$$\mathrm{CoagS}(D_p) = \int_{D_p}^{D_p'} \kappa(D_p, D_p', T, \ldots)\eta(D_p')\mathrm{d}D_p', \qquad (15)$$

where η is the aerosol particle size distribution function and κ the coagulation kernel between particles with sizes D_p and D_p', essentially describing their collision rate.[1] The larger the difference between D_p and D_p', the more efficient their coagulation.

The probability of freshly formed particles to survive at climatically relevant sizes (approximately 50 nm and larger) is governed by the competition of their condensation growth and their coagulation loss rates: as the particles grow, their coagulation rate decreases. Also, the faster the particles grow, the faster they reach sizes where they can have a climatic relevance as CCN and directly scatter radiation. Fig. 8 draws
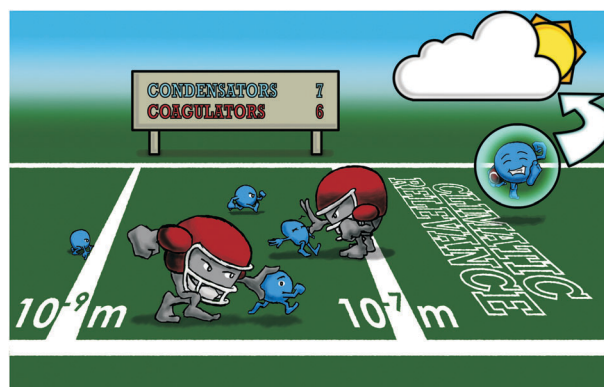

Fig. 8 The competition of condensation growth and coagulation scavenging determining the atmospheric lifetime and climatic relevance of nucleated particles. The freshly-formed nanoparticles (∼1 nm in diameter, "Condensators" in blue) need to grow by vapour uptake to CCN sizes (50–100 nm) to have climatic relevance. While growing, the small particles are prone to scavenging by coagulation with larger aerosols ("Coagulators" in red). Only a small fraction of the new particles survive this challenge. Graphic design by Dr Teemu Hynninen.

an analogy between the competition of particle growth with coagulation and a game of American football.

9.1 Atmospheric nucleation or barrierless kinetics?

Although very compelling evidence exists that the phenomenon depicted in Fig. 7 presents a secondary particle formation event, it is not clear whether the particle formation takes place through nucleation, *i.e.* a process involving an energetic barrier, or some barrierless processes such as essentially irreversible chemical reactions. Some information on this can be obtained by investigating the dependence of the particle formation rate on the saturation ratio of the condensable vapour.

Many studies indicate that the dependence of the atmospheric particle formation rate on ambient sulphuric acid concentration is of a relatively low order, the exponent typically ranging from 1 to 3.[13,31,32] Ideally, the nucleation theorems (see Section 7.3) could be used to study the implications of this dependence on the nucleation mechanism. The situation is unfortunately more complicated than this. First, the nucleation theorem fails if a local minimum free energy exists – and the fact that the chemical nature of particle forming vapours in the atmosphere is still uncertain does not make this task any easier. Second, varying temperature and vapour (other than sulphuric acid) concentrations, coagulation scavenging of the small particles, combined with the fact that most commercial instruments can detect particles only after they have grown to 3 nm, skew the analysis. However, based on what we know from Section 7, the observed relationship between atmospheric particle formation rates probably means that either (1) only 1–3 sulphuric acid molecules are present in the critical cluster or (2) the nucleation process takes place through a stable cluster state manifested by a minimum in the free energy curve for the growing clusters.

9.2 Vapour pressure driven condensation or reactive uptake of atmospheric vapours?

The dynamics of a simple reversible condensation/evaporation between a well-defined liquid and its vapours are theoretically well understood, as long as the thermodynamic and kinetic properties such as saturation vapour pressures, liquid phase activities and accommodation coefficients of the molecules are known. Unfortunately the composition of the freshly-formed particles is not fully resolved, so the identities and properties of the vapours growing the particles to climatically relevant sizes are uncertain.

Sulphuric acid is a significant player in the growth of the smallest (sub-3 nm) particles. At larger sizes, however, sulphuric acid condensation can typically explain only some percentage of the growth at the SMEAR II station and observations suggest that organic compounds are probably present already at particle sizes as small as 2 nm.[33] The important role of organics in growing the freshly-formed particles to climatically relevant sizes is also supported by the mass spectrometric analysis of the growing nucleation mode particles after they reach sizes larger than 20 nm.

Multiple observations from the SMEAR II station suggest that there is something of extremely low volatility (one-component equilibrium vapour pressure 10^{-7} Pa or less – even when accounting for the Kelvin effect described by eqn (3)) in the growing nucleation mode.[35] It is not fully understood what the origin of this material is. Potential explanations include gas phase production of low-volatility organic vapours, oligomerization in the particulate phase, or formation of organic salts through acid–base chemistry.[34]

Eqn (10)–(12) account for condensed phase properties through their dependence on the equilibrium vapour pressure. If particle-phase formation of the low-volatility compounds is fast enough (or in the case of kinetic limitations, the evaporation is slow enough), one might be able to treat the condensation onto nucleation mode particles as a one-way process which is only limited by the gas phase concentrations of the vapours (*i.e.* by setting the equilibrium vapour pressure to zero in eqn (10)–(12)) – at least up to a specific particle size. If the time scales of the chemical reactions are comparable to the time scales of the evaporation of the precursor molecules, these processes need to be explicitly implemented into the mass transfer equations.

Acknowledgements

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