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# Incorporating Condensation into the Markov-MC Model

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In this chapter, the differential equations governing the growth of particles by condensation in the continuum regime (CR) and free molecular regime (FMR) are presented. Then, the methodology used to couple the solutions of the condensation equations with the Markov-MC simulation of the coagulation equation is described. This approach exploits the advantage of the Markov-MC method in allowing a cross-linking of deterministic and probabilistic models. In the present case, coagulation, which is modeled from a probabilistic approach, is combined with condensation, which is modeled deterministically. Since the two processes occur simultaneously, they are coupled through time. The coupling is carried out by using the time step for coagulation as the delta time for condensation. Thus, during every coagulating time step, the extent of growth by condensation of each particle in the aerosol is evaluated, and the particle size distribution is updated according to the new sizes of the particles. The results presented here initially focus on situations where only condensation is important, and later on, situations in which both processes, coagulation and condensation, occur simultaneously.

## 1. Condensation

When a droplet is embedded in a sufficiently supersaturated environment, the droplet grows by condensation of vapor on its surface. Diffusion theory and the kinetic theory are respectively used to calculate the rate of condensation in the CR and FMR. The expressions are known as the *growth laws* [50] and are presented in Table 1. The rate of growth is controlled by the rate of arrival of vapor molecules at the droplet surface. It is proportional to the vapor concentration difference that exists between the surface of the particle and far away from the particle. The exponential term in the growth laws describes the vapor phase concentration at the surface of the particle.

$$P = P_s \exp\left(\frac{2\sigma M}{\rho R T r}\right) \quad (1)$$

Equation (1) is well known as the Kelvin equation. It is a relationship that expresses the vapor pressure over a curved interface in terms of the saturation pressure  $P_s$ , which is the vapor pressure of the same substance over a flat surface. The vapor pressure of a liquid is determined by the energy necessary to detach a molecule from the surface by overcoming the attractive force exerted by its neighbors. When a curved interface exists, as in a small droplet, there are fewer molecules immediately adjacent to a molecule on the surface than when the surface is flat. Consequently, it requires less energy for molecules on the surface of a small drop to escape and the vapor pressure over a curved interface is greater than that over a plane surface. [64] The Kelvin effect is significant for particles smaller than  $0.1 \mu\text{m}$  in diameter.

There is a critical particle size  $r^*$  where the concentration gradient becomes zero and thus the growth laws predict no net rate of condensation. Under this condition, the system is in a metastable condition, where the rate of evaporation equals the rate of condensation. The growth laws show that all smaller particles ( $r < r^*$ ) evaporate while all the larger ones ( $r > r^*$ ) grow by condensation. The growth laws are obtained assuming that the condensation rate is sufficiently slow for the latent heat of condensation to be dissipated without changing the droplet temperature. Appendix A develops a heat transfer model to evaluate the accuracy of this assumption, and Chapter 6 presents the implications on the condensation rate when the increase in the droplet temperature is not negligible. Here the discussion is limited to situations where the assumption is reasonable. The growth laws can be expressed in terms of nondimensional variables  $\eta$ ,  $S$ , and  $\tau$  as shown in Table 1 by using  $\eta = r/r^*$ ,  $S = P/P_s$  and  $\tau = t/\tau_{\text{cond}}$ , where  $r^*$  is critical particle size for the onset of condensation;  $P$  is the vapor pressure of the condensable phase;  $P_s$  its saturation pressure; and  $\tau_{\text{cond}}$  the characteristic time for condensation. Physically,  $3\tau_{\text{cond}}$  is the time required to double the volume of a particle of size  $r^*$  by condensation. Expressions for  $\tau_{\text{cond}}$  are also presented in Table 1.

	Free Molecular Regime	Continuum Regime
Rate of growth	$\frac{d_r}{dt} = \frac{1}{\rho \sqrt{2\pi RT/M}} \left( P - P_s^* \text{Exp}\left(\frac{2\sigma v_m}{rKT}\right) \right)$	$\frac{d_r}{dt} = \frac{1}{r} \frac{DM}{RT} \left( P - P_s^* \text{Exp}\left(\frac{2\sigma v_m}{rKT}\right) \right)$
Nondimensional form	$\frac{d_\eta}{d\tau} = \frac{1}{\text{Ln}(S)} \left( 1 - S^{\frac{1}{\eta}-1} \right)$	$\frac{d_\eta}{d\tau} = \frac{1}{\text{Ln}(S)} \frac{1}{\eta} \left( 1 - S^{\frac{1}{\eta}-1} \right)$
Characteristic time for condensation	$\tau_{\text{cond}} = \frac{\rho r^* \sqrt{2\pi RT/M}}{P_s S \text{Ln}(S)}$	$\tau_{\text{cond}} = \frac{\rho RT r^{*2}}{DM P_s S \text{Ln}(S)}$
Solution for $\eta \rightarrow 1$	$\eta = 1 + (\eta_0 - 1) S^{\frac{t}{\tau_{\text{cond}}}}$	$(\eta - \eta_0) + \text{Ln}\left( \left  \frac{\eta - 1}{\eta_0 - 1} \right  \right) = \frac{t}{\tau_{\text{cond}}}$
Solution for $\eta \rightarrow \infty$	$\eta - \eta_0 = \frac{S - 1}{S \text{Ln}(S)} \frac{t}{\tau_{\text{cond}}}$	$\eta^2 - \eta_0^2 = 2^* \frac{S - 1}{S \text{Ln}(S)} \frac{t}{\tau_{\text{cond}}}$

**Table 1.** Expressions for the rate of particle growth.

Assuming constant vapor concentration and temperature, the nondimensional versions of the growth laws were numerically integrated for several values of  $S$ . The results are presented in

Figure 1. Figure 1a shows the evolution of particle size in the FMR and Figure 1b for the CR. Three characteristic regions can be distinguished in each figure. For small sizes,  $\eta \rightarrow 1$ , the Kelvin effect is important and particle growth is slow. For large sizes,  $\eta \rightarrow \infty$ , the Kelvin effect is negligible and particles grow linearly with time in the FMR (Figure 1a) or as the square root of time in the CR (Figure 1b). In between these two extremes, there is a transition region.

Analytical solutions can be obtained in each of the two extreme cases. Table I presents these solutions. For the case of  $\eta \rightarrow \infty$ , the rate of growth equation becomes linear and then it can be directly integrated. For the case of  $\eta \rightarrow 1$ , the solution is obtained by expanding the exponential term of the growth equation in a Taylor series around  $\eta = 1$ , as follows:

$$1 - S^{\frac{1}{\eta}-1} = \ln(S) * (\eta - 1) + \text{HOT} \quad (2)$$

Then, after neglecting higher-order terms (HOT), the equation is reduced to a linear ODE that can be integrated analytically. The expressions obtained are shown in Table I. The generalized condensation solutions were obtained assuming that the droplet is embedded in an infinite medium such that the concentration of the condensable material remains constant during the entire process. The assumption is relaxed by dividing the total elapsed time for condensation into several time steps ( $\delta t_{\text{cond}}$ ) such that  $\delta t_{\text{cond}} \ll \tau_{\text{cond}}$  and by updating the vapor phase concentration at every time step, i.e., by reducing the mass in vapor phase of the condensable material by the amount of mass condensed during each time step.

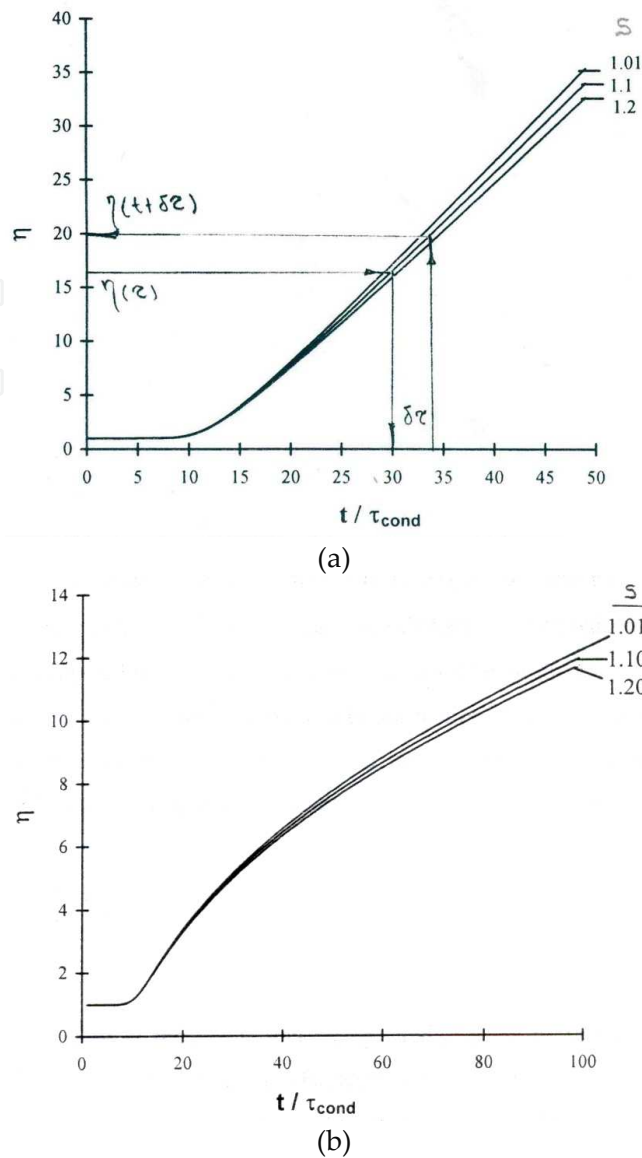
## 2. Coupling the condensation solution to the Markov-MC simulation of coagulation

The following discussion applies to two-component aerosols composed of a fully condensed material (solid or liquid) and a condensable material. Thus, condensation of only one of the components needs to be considered. Situations where the two components are condensable phases, or where there are more than two components, can be handled by a direct extension of this method but they will not be considered in this work.

It is assumed that a particle in the two-component aerosol can be described by its size ( $r$ ) and mass fraction ( $y$ ) of the condensable material present in the particle. Size and composition of a particle are given by:

$$r = \left( \frac{3}{4\pi} \sum \frac{m_k}{\rho_k} \right)^{1/3} \quad (3)$$

$$y = \frac{m_2}{\sum m_k} \quad (4)$$



**Figure 1.** Numerical solution of the particle growth laws in the (a) FMR and (b) CR. Use of the universal solutions to evaluate particle growth due condensation for an arbitrary initial particle size, during a given nondimensional time  $\delta\tau$  and saturation ratio  $S$ .

where  $m_k$  and  $\rho_k$  are the mass and density of species  $k$  in the particle. We will let  $k = 1$  represent the fully condensed material and  $k = 2$  represent the condensable material.

The particle size range ( $R_1$ - $R_m$ ) is divided into  $m$  sections, and the particle composition range ( $Y_1 = 0$  -  $Y_p = 1$ ) into  $p$  sections. A particle within a section ( $i, j$ ) has a size  $r$  such that  $R_i < r < R_{i+1}$  and composition  $y$  such as  $Y_j < y < Y_{j+1}$ . It is assumed that all particles within a section ( $i, j$ ) have the same size and composition, and equal to the temporal values of the mass weighted mean size ( $r$ ) and mean composition ( $y$ ) of the particles within the section. Thus, these mean values can vary within their respective ranges in the section. The mean values  $r$  and  $y$  are computed from Equations (3) and (4), respectively, by using  $m_k$  as the mean mass of species  $k$  in the particle and according to:

$$m_k = \frac{M_{ijk}}{n_{ij}} \quad (5)$$

where  $M_{ijk}$  is the total mass of specie  $k$  in section  $(i, j)$ , and  $n_{ij}$  is the number of particles in section  $(i, j)$ . This methodology has three important characteristics:

1. The particles within a size-section have different sizes and different compositions. Only particles within a size-composition-section have same size and composition.
2. Mass is conserved since size and composition within a section are allowed to assume their instantaneous mean values.
3. There is no restriction about the structure of the particles. In Chapter 6, as a special case, it will be assumed that the particles consist of a solid core with a spherical coating.

Since coagulation and condensation processes occur at the same time, the Markov-MC simulation of the coagulation equation and the deterministic solution of the condensation equation must be coupled through time. This suggests the use of the following type of algorithm:

1. Perform a Markov-MC coagulating step as described in Chapter 4
2. Compute the time step for coagulation  $\delta t_{\text{coll}}$  from Equation (4 from Chapter 4) and use this time step as the elapsed time for condensation  $\delta t_{\text{cond}}$
3. For each particle in the aerosol
  - Compute the growth during  $\delta t_{\text{cond}}$
  - Update the particle size distribution by moving the particle to the appropriate section according to its size and composition
4. Update vapor concentration to account for the condensed mass

Thus, this technique requires the evaluation of the particle growth equation for all particles in the aerosol with size greater than  $r^*$  for each coagulating time step. Consequently, a direct numerical integration of the growth laws for the specific conditions of each particle would be computationally prohibitive. Instead, the nondimensional version of the particle growth laws can be solved for a range of values of  $S$ , as described in the former section. These solutions can then be stored in tables or can be represented by curve-fits for the different solutions. Thus, during the actual run, the direct numerical evaluation of the integral expression is replaced by a table-lookup process or an evaluation of the curve-fitting expression. Evaluation of particle growth for an arbitrary initial particle size  $\eta_0$ , nondimensional time step  $\delta\tau$ , and vapor concentration  $S$  using the generalized solution, through either table searching or evaluation of curve-fitted expressions, can be obtained by:

$$\delta\eta = \int_{\tau_0}^{\tau_0+\delta\tau} \frac{d\eta}{dt} dt = \int_0^{\tau_0+\delta\tau} \frac{d\eta}{dt} dt - \int_0^{\tau_0} \frac{d\eta}{dt} dt \quad (6)$$

$$\delta\eta = \eta_{0-\tau_0+\delta\tau} - \eta_{0-\tau_0} \quad (7)$$

where  $\eta_{0-\tau}$  is the tabulated universal value for growth due to condensation during  $\tau$  nondimensional times. The process is illustrated in Figure 1.

### 3. Results

A two-component aerosol will behave quite differently when the characteristic time for coagulation is greater than or less than the characteristic time for condensation. Thus, we define  $J$  as:

$$J = \frac{\tau_{coll}}{\tau_{cond}} \quad (8)$$

Expressions for  $J$  in the CR and FMR are presented in Table 2.  $J$  is a function of temperature and is proportional to  $S^* \text{Ln}^\alpha(S)/N$  in both regimes.

Free Molecular Regime	Continuum Regime
$J = \frac{1}{16\sigma} \sqrt{\frac{KT}{3\pi\sigma}} \frac{P_s SL}{N} n^{\frac{5}{2}}(S)$	$J = \frac{3\mu D}{16\sigma^2 v_m} \frac{P_s SL}{N} n^3(S)$

**Table 2.** Expression for  $J$ , the ratio of the characteristic time for coagulation and the characteristic time for condensation.

The condition  $J \rightarrow \infty$  designates situations where only condensation is important and  $J \rightarrow 0$  designates situation where only coagulation occurs. The following sections describe the results obtained for  $J \rightarrow \infty$ ,  $J \rightarrow 0$  and  $J \sim 1$ .

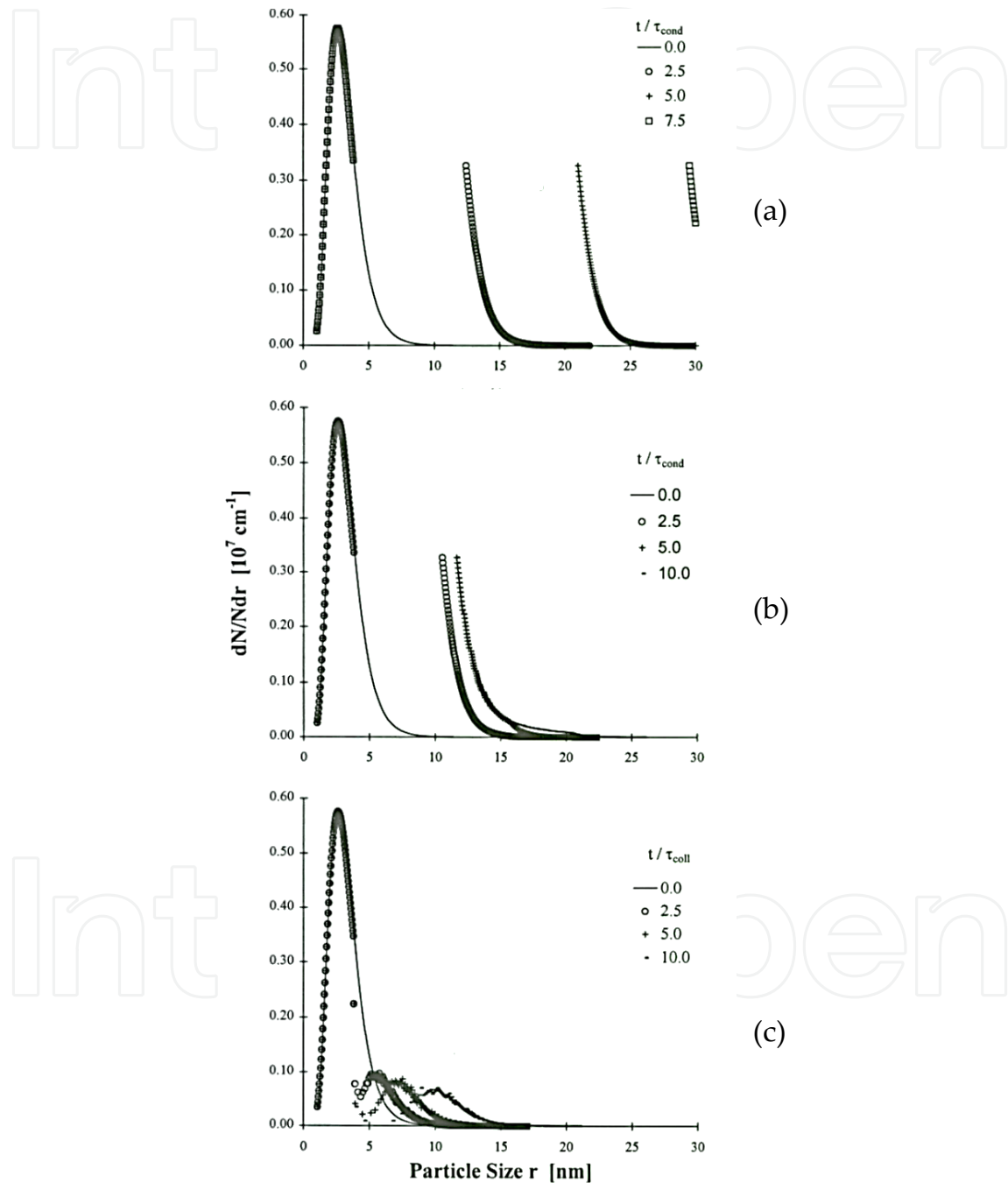
#### 3.1. Results for $J \rightarrow \infty$

The performance of the Markov-MC method for simulating an aerosol subject to condensation but not coagulation was evaluated. A lognormal distributed aerosol with parameters  $r_m = 3.0$  nm,  $N = 10$  [18] particles/m<sup>3</sup>, and  $\sigma_g = 1.45$  was taken as the initial particle size distribution.

Condensation was assumed to occur in the FMR and a vapor with  $S = 1.2$  and  $r_o^* = 3.9$  nm was considered.

Figure 2 shows the results obtained with a)  $S = \text{constant}$  and no Kelvin effect, b) vapor phase mass depletion and no Kelvin effect, and c) vapor phase mass depletion and Kelvin effect. Since  $r^*$  is the critical size above which condensation occurs, there is a discontinuity in the particle size distribution at  $r = r_o^*$ . When the Kelvin effect is neglected and the concentration of the vapor remains constant, the tail of the particle distribution above  $r^*$  is observed to steadily increase, appearing as equally spaced parallel curves (Figure 2a). This result is

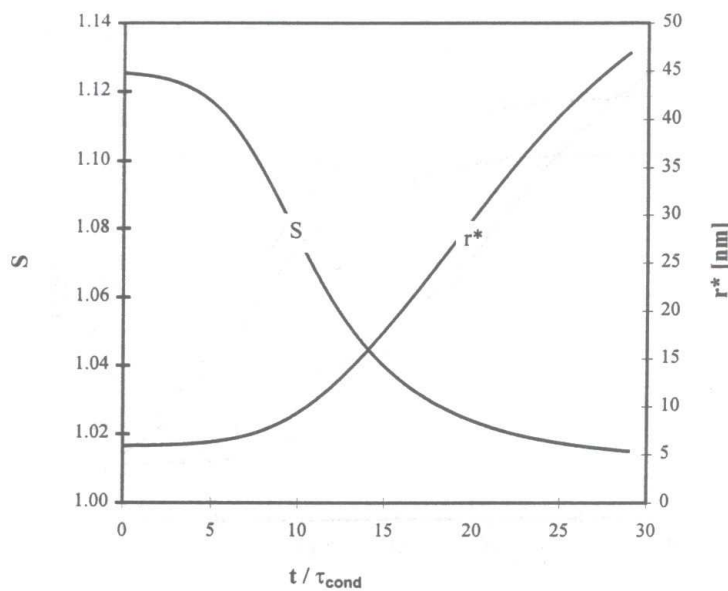
expected because particle growth is independent of size in the FMR when the Kelvin effect is negligible. Figure 2a also shows that the Markov-MC method is able to handle discontinuities in size distribution and does not suffer from numerical dispersion or diffusion as is the case with the sectional method. [60]



**Figure 2.** Evolution of an aerosol in the FMR when only condensation is important for the case of (a)  $S = \text{constant}$  and no Kelvin effect, (b) vapor phase mass depletion and no Kelvin effect, and (c) vapor phase mass depletion and Kelvin effect. The initial conditions is a lognormal distributed aerosol with parameters  $r_m = 3.0$  nm,  $N = 10$  [18] particles/ $\text{m}^3$ , and  $\sigma_g = 1.45$  and a vapor with  $S = 1.2$  and  $r_o^* = 3.9$  nm. The solid line is the initial particle size distribution.

Figure 2b shows the corresponding evolution when the mass of the condensable vapor is depleted as condensation occurs. Two additional effects are observed. First, as condensation takes place, the rate of growth slows down and then, the distributions are no longer equispaced in time. Second, as condensation proceeds,  $S$  decreases,  $r^*$  becomes larger (Figure 3), and then the growth of the particles with sizes  $r_0^* < r < r^*$  diminishes and the particle size is frozen.

For the same conditions but including the Kelvin effect, Figure 2c shows the slow growth of particles with sizes close to  $r^*$ . The evolution of the aerosol can be described as the superposition of the lognormal distribution tail over the exponential variation with size of the Kelvin effect, which leads to bimodal distributions. Due to the Kelvin effect, small particles ( $r \cong r^*$ ) grow slowly and larger particles grow faster, in an exponential relation with size. Therefore, the concentration of particles widens more strongly at the smaller sizes, and thus the particle size distribution (particle concentration per unit size) diminishes more strongly at smaller sizes. Furthermore, when the particles reach size  $r > \sim 5r^*$ , the Kelvin effect becomes negligible and particles grow at the same rate. Thus, the spreading effect stops first for the larger particles. The net effect is the formation of the bimodal distribution.

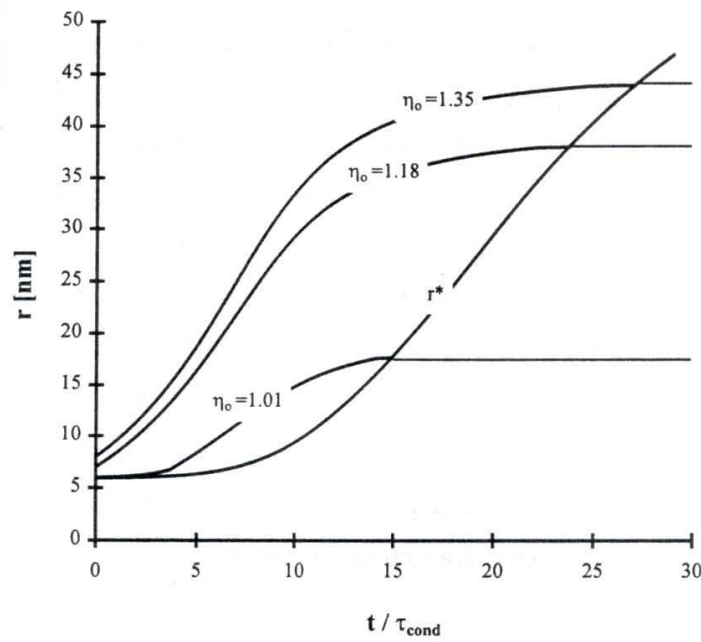


**Figure 3.** Evolution of  $S$  and  $r^*$  during condensation for the conditions for an initially lognormal distributed aerosol with parameters  $r_m = 3.0$  nm,  $N = 10$  [18] particles/ $\text{m}^3$ , and  $\sigma_g = 1.45$  and a vapor with  $S = 1.2$  and  $r_0^* = 5.9$  nm.

### 3.1.1. Evolution of a single particle

To have a better understanding of the effect of gas-phase depletion on particle size evolution, tagged particles have been observed during the condensation process. Figure 4 shows their behavior. For a particle with initial size close to  $r_0^*$ , say  $\eta = r/r_0^* = 1.01$ , the growth is strongly affected by the Kelvin effect and the particle grows very slowly. As the particle becomes larger, the Kelvin effect is less important, and the particle grows faster. As the condensable material is depleted, particle growth slows down and the particle starts to approach its asymptotic size

which is reached when the condition  $S = 1$  is reached. However, before that equilibrium condition is reached  $r^*$  can be larger than the particle size, and consequently its growth is frozen. In this model reevaporation processes have not been considered and thus the particle maintains its maximum size. The larger particles, e.g.,  $\eta_o = 1.18$  and  $\eta_o = 1.35$ , exhibit similar behavior initially. However, the cumulative influence of the Kelvin effect separates particle sizes.



**Figure 4.** Evolution of tag particles during condensation. Initially, the particle is subject to the Kelvin effect. At the end, gas-phase depletion slows down particle growth and the particle approaches asymptotically its final equilibrium size.

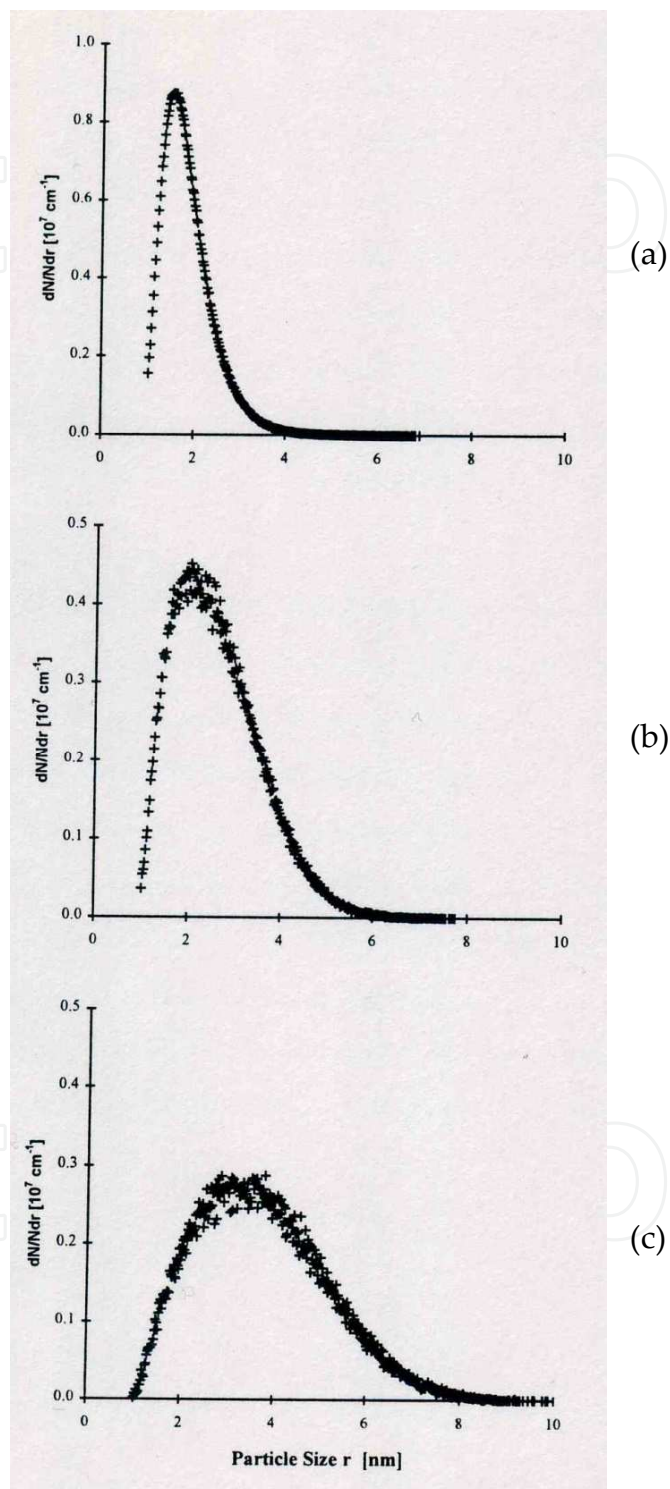
When condensation occurs in the FMR over all the particles in the aerosol, i.e., when  $r_m \gg r^*$ , the particle size distribution is not affected by condensation provided that  $S = \text{const}$ . However, when vapor-phase mass depletion is considered, the condensation process widens the particle size distribution during the final stages of the process. On the other hand, condensation in the CR is proportional to  $(1/r)$  and then condensation causes the particle size distribution to narrow.

The literature review of Section 3.3.2 concluded that most of the problems of the numerical methods for modeling aerosols arise when coagulation and condensation occur simultaneously. The next section describes the results obtained when the Markov-MC method is used to simulate simultaneous coagulation and condensation in a single-component aerosol. Results for two-component aerosols will be presented in Chapter 6.

### 3.2. Results for $J = 0.18$

The results presented are for an atmospheric aerosol in the FMR. Initially, the particles have a lognormal distribution with  $r_m = 1.85$  nm and  $\sigma_g = 1.56$ . The vapor concentration is assumed to remain constant with parameters  $S = 1.2$  and  $r^* = 5.9$  nm. The results were obtained using a

linear grid with 1000 sections to cover the range 1–20 nm. The evolution of the aerosol is described in terms of the parameters  $r$ ,  $\tau = t/\tau_{\text{cond}}$ ,  $n/N$ , and  $J$ .



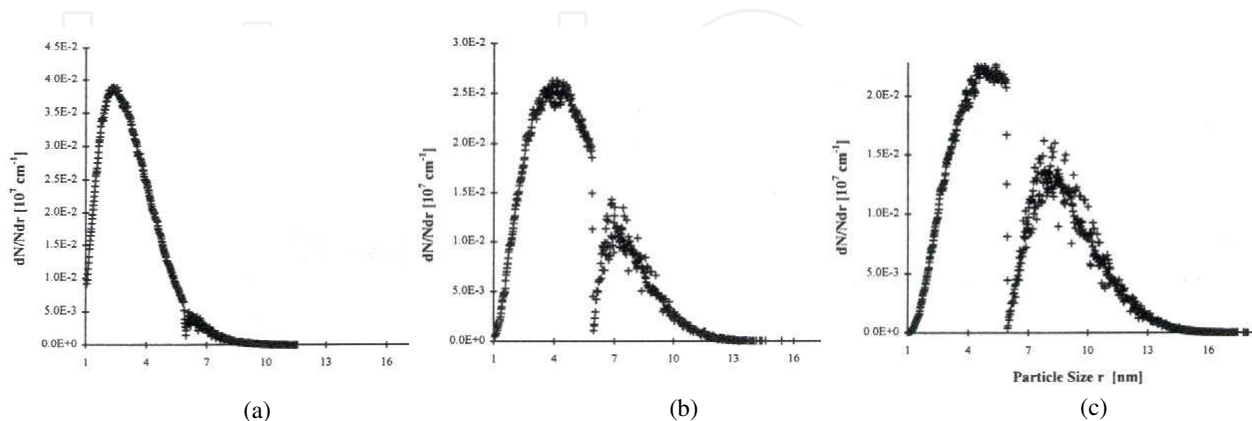
**Figure 5.** State of evolution of an atmospheric aerosol (a)  $\tau = 43$ , (b)  $\tau = 765$ , and (c)  $\tau = 2500$ . The initial condition is a lognormal distributed aerosol with parameters  $r_m = 1.85$  nm,  $N_o = 10$  [21] particles/m<sup>3</sup> and  $\sigma_g = 1.56$ ; vapor with constant concentration and parameters  $S = 1.2$  and  $r^* = 5.9$  nm.  $J = 0.18$  ( $\tau_{\text{cond}} = 7.87 \times 10^{-6}$  s).

For  $J = 0.18$ , Figure 5 shows the state of evolution of the aerosol at  $\tau = 42$ , 765, and 2500. The initial particle concentration is  $N_0 = 10$  [21] particles/ $\text{m}^3$  and the characteristic time for condensation is  $\tau_{\text{cond}} = 7.87 \times 10^{-6}$  s. Under these circumstances the rate of condensation, even though high, is small compared to the rate of coagulation ( $\tau_{\text{coll}} = 9.27 \times 10^{-7}$  s). Therefore, the effect of condensation on the particle size distribution is negligible, as shown in Figure 5. The evolution of the aerosol is similar to that discussed in Section 4.4.2 when only coagulation is important.

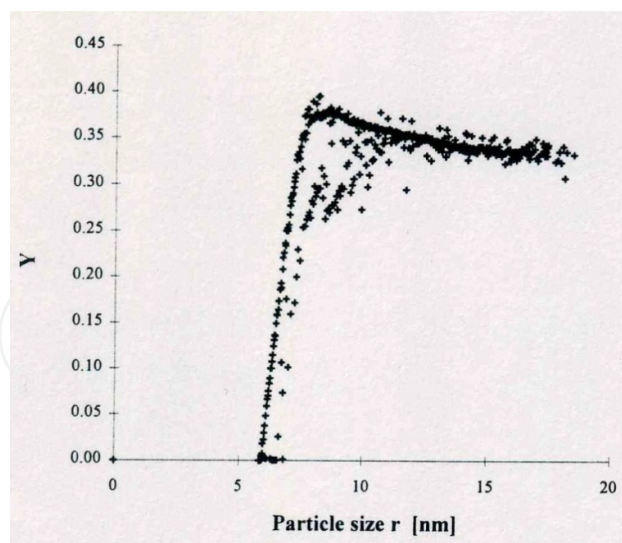
### 3.3. Results for $J = 1.18$

Keeping the same set of conditions, but decreasing  $N_0$  up to 10 [20] particles/ $\text{m}^3$  so that  $J = 1.18$ , the effect of condensation on the particle size distribution begins to be important, as shown in Figure 6. In this case, the aerosol exhibits a pseudo bimodal distribution, which can be explained as follows: The Kelvin effect dictates that particles with  $r > r^*$  grow by condensation but smaller particles will not. Then condensation results in a bulk motion of the distribution toward larger sizes for  $r > r^*$ , creating a gap in the distribution around  $r^*$ . Particle concentration does not change due to condensation but coagulation depletes the concentration of small particles and increases the concentration of the larger ones. Part of the coagulating particles partially fills the gap created by condensation. The combined effect is shown in Figure 6.

During the evolution of the aerosol, the model keeps track of the composition of the particles. For each particle, it distinguishes the mass coming from condensation from the mass coming from coagulation. For single-component aerosols, as in this case, particle composition is defined as the ratio of the mass of the particle due to condensation over the total mass of the particle. Figure 7 shows the average size-composition distribution of the aerosol at  $\tau = 3320$ . It shows that particles with  $r < r^*$  are formed through pure coagulating processes. Particles with sizes slightly larger than the critical size are affected by the Kelvin effect and thus the content of the condensed phase is small but increases with particle size. A maximum is reached and then for larger particles, the mass ratio decreases due to further coagulation with smaller particles, i.e., with particles that have not received mass through condensation.



**Figure 6.** State of evolution of an atmospheric aerosol (a)  $\tau = 630$ , (b)  $\tau = 2075$ , and (c)  $\tau = 3320$ . The initial condition is a lognormal distributed aerosol with parameters  $r_m = 1.85$  nm,  $N_0 = 10$  [20] particles/ $\text{m}^3$ , and  $\sigma_g = 1.56$ ; vapor with constant concentration and parameter  $S = 1.2$  and  $r^* = 5.9$  nm.  $J = 1.18$  ( $\tau_{\text{cond}} = 7.87 \times 10^{-6}$  s).



**Figure 7.** Particle size-composition distribution at  $\tau = 3320$  for an initially lognormal distributed atmospheric aerosol subject to condensation.

#### 4. Concluding remarks

It has been shown that the Markov-MC method is an effective approach to modeling aerosol dynamics under conditions of pure coagulation, pure condensation, and when both coagulation and condensation occur simultaneously. Because the Markov-MC method does not have restrictions in the number of sections used, the particle size distribution of aerosols can be represented with high resolution. It also can be applied to broad particle size ranges and can evaluate the evolution of aerosols over long time periods.

The method is accurate in solving the condensation equation in multicomponent aerosols because it evaluates the growth of each particle in the aerosol at the time, and in doing such evaluation it uses generic exact solutions of the condensation equation. The errors introduced come from the methodology used to store the exact solutions of the particle growth equation. However, this process can be optimized up to any degree of accuracy as desired. Furthermore, when the Kelvin effect can be neglected, analytical expressions are available and no errors are introduced during this step. This approach can be extended to include other aerosol processes such as source/removal, and chemical reactions. The assumptions made for coagulation and condensation are summarized as follows:

1. Particles are spherical and stick together upon collision
2. Rate of condensation and coagulation independent of particle composition
3. Particles within an  $(i, j)$  section have the same, but not constant, size, and composition

In the following chapter, the Markov-MC method will be applied to a two-component aerosol to study the particle encapsulation process.

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