

Universal Approximation Formulas of Curvature Correction and Equilibrium Sizes of Hygroscopic Particles

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ABSTRACT

Theoretical analysis shows that when water activity is larger than its threshold value and the dry radius of a particle is larger than $0.005 \mu\text{m}$, the deviation of curvature correction from unity can be accurately represented by the product of two terms, with one term strongly depending upon water activity and the other depending upon dry radius. Moreover, experimental data show that the water-activity-dependent term can be approximated by linear and one-third power functions of water activity. According to the approximation made to curvature correction, water activity is solved as analytical functions of relative humidity (RH). The analytically solved water activity is then used to compute particle equilibrium sizes using a known (observed) relationship between water activity and water uptake by unit mass of dry material. The accuracy of equilibrium sizes calculated with this method is checked with seven typical classes of aerosols. Results show that when $\text{RH} \leq 99.99\%$, the equilibrium radius computed with this method is accurate to within 3% (6%) if the dry radius of a particle is larger (smaller) than $0.02 \mu\text{m}$ and that when $\text{RH} > 99.99\%$, equilibrium sizes can be estimated with an accuracy higher than 84%. Analytical approximation formulas are also derived for calculating critical equilibrium radii and critical supersaturation. The maximum relative errors of these formulas range from 3% to 15%.

1. Introduction

Equilibrium sizes of hygroscopic particles have been extensively studied by a number of investigators (e.g., Orr et al. 1958; Fletcher 1962; Mason 1971; Junge and McLaren 1971; Winkler 1973; Fitzgerald 1975; Hänel 1976; Pruppacher and Klett 1978; Hänel and Lehman 1981; Tang 1980; d'Almeida et al. 1991; Tang and Munkelwitz 1994). The Köhler equation (Pruppacher and Klett 1978) associates the equilibrium radius of a particle with its dry radius, chemical composition, and ambient relative humidity (RH). Because the Köhler equation is a nonlinear equation, iterative methods were used to obtain an accurate solution of equilibrium radius. Computation of equilibrium radius by iterative methods is very time consuming when a large number of such computations are involved, as, for example, in certain studies associated with fog formation, cloud nucleation processes, and remote sensing applications.

To facilitate the computation of the equilibrium size of a hydrophilic particle, Kasten (1969) proposed a simple radius–RH formula for quantitative prediction of visibility, but the formula can only be applied to the cases in which $\text{RH} \leq 95\%$ and dry radii are larger than

$0.1 \mu\text{m}$. Fitzgerald (1975) developed approximation formulas that express the equilibrium radius as an explicit function of relative humidity and dry radius. These formulas are accurate to within 5% for RH between 81% and 99.5% if a particle has a dry radius in the range of $0.05\text{--}3.0 \mu\text{m}$ and is composed greater than 60%, by mass, of any one of the common electrolytes. Hänel (1976) also proposed an explicit formula [Eq. (6.2) in his paper] to calculate the equilibrium radius of a particle. For maritime and urban aerosols, the approximation formula is accurate to within 3% if RH is in the range of 70%–99% and the dry radius is greater than $0.04 \mu\text{m}$. Obviously, the applicable ranges of the above-mentioned methods do not cover the entire ranges of RH and particle sizes of atmospheric interest (e.g., Feingold and Grund 1994).

The purpose of this paper is to present approximation formulas for computing equilibrium sizes of hygroscopic particles in wide ranges of RH and dry radii. Specifically, this paper demonstrates how to approximate curvature correction in the Köhler equation as a function of water activity. The paper is organized as follows. In section 2, the Hänel (1976) model is briefly described. Based on this model, in section 3 a universal approximation form of curvature correction is derived theoretically and verified with observed data. According to the universal properties of curvature correction, approximation formulas for water activity are proposed in section 4 and tested with observed data. In section 5 we investigate

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the critical phenomenon, and a summary and conclusions are presented in section 6.

2. The Hänel model

The Köhler equation (see, e.g., Pruppacher and Klett 1978) is the basis for calculating the equilibrium radius of a hygroscopic particle. However, it is not valid when a particle is not fully covered by a liquid layer, which happens when water activity (denoted as a_w) is smaller than a threshold water activity (denoted as a_{wt}). In order to compute the equilibrium radius of a wet particle in the entire range of water activity from 0 to 1, the Hänel (1976) model is used as a framework in the present paper.

The Hänel model associates the equilibrium radius of a wet particle with relative humidity (denoted as f) by the following equations:

$$r = r_0 \left(1 + \frac{\rho_0}{\rho_w} W \right)^{1/3}, \quad (1)$$

$$f = a_w \delta, \quad (2)$$

$$a_w = \exp \left(- \frac{\eta}{W} \right), \quad (3)$$

$$\delta = \begin{cases} 1, & 0 \leq a_w \leq a_{wt}/\delta_t, & (4a) \\ \frac{\delta_t a_w}{a_{wt}}, & a_{wt}/\delta_t < a_w < a_{wt}, & (4b) \\ \exp \left(\frac{2\sigma}{\rho_w R_w T r} \right), & a_{wt} \leq a_w \leq 1, & (4c) \end{cases}$$

$$\sigma = \sigma_{w0} - a(T - T_0) + \frac{bc}{W}, \quad (5)$$

where r_0 is the dry radius of the particle; ρ_w and ρ_0 are, respectively, the densities of water and dry material of the particle; W is the water uptake of a unit mass of dry material; η is the exponential mass increase coefficient; δ is the curvature correction; δ_t is the threshold value of δ ; R_w is the specific gas constant of water ($\approx 4.6151 \times 10^6 \text{ erg g}^{-1} \text{ K}^{-1}$); σ is the surface tension of the particle; σ_{w0} ($\approx 75.6 \text{ dyn cm}^{-1}$) is the surface tension of pure water at standard temperature T_0 ; a is a constant ($\approx 0.153 \text{ dyn cm}^{-1}$); b is a constant depending on the chemical properties of water-soluble substance; and ϵ is the mass fraction of soluble material in the dry particle. The combination of (2) and (4c) is the Köhler equation.

Equations (1)–(5) are not a closed system; an additional equation (or relationship) connecting the unknown variables (r , W , a_w , η , δ , and σ) is needed for the determination of r . As shown by Hänel (1976) and Hänel and Lehman (1981), measurements can be made to give a relationship between a_w and W or between a_w

and η through tables or analytical formulas. Therefore, if one can obtain a_w as a function of f from (1)–(5), then from the known a_w – W relationship one can obtain W and calculate the equilibrium radius according to (1). This paper assumes that the a_w – W relationship (or equivalently, the a_w – η relationship) is known and focuses on how to solve a_w as a function of f .

For the trivial case $f \leq a_{wt}\delta_t$, one can obtain an analytical solution of a_w as a function of f . But for the case $f \geq a_{wt}\delta_t$, to our knowledge a_w cannot be solved as an analytical function of f , due to the nonlinearity of (1)–(3), (4c), and (5). However, from (2) one can find that if curvature correction δ is a simple function of water activity, for example, δ is a linear or quadratic function of a_w , then from (2) a_w can be solved as an analytical function of f . To examine whether δ can be approximated by simple functions of a_w , curvature correction is investigated in the next section.

3. Universal approximation form of curvature correction

In this section, a universal approximation form of curvature correction is derived and verified with seven representative aerosol samples measured by Hänel and Lehman (1981). Curvature correction is approximated as a simple function of water activity.

a. Universal approximation form of curvature correction

In the following, curvature correction is studied for the case $a_w \geq a_{wt}$. Substituting r in (4c) with (1) yields

$$\delta = (e^R)^{1/r_0}, \quad (6)$$

where

$$R = \frac{2\sigma}{\rho_w R_w T} \left(1 + \frac{\rho_0}{\rho_w} W \right)^{-1/3}. \quad (7)$$

In (7), R is only a function of W that uniquely depends on water activity (a_w), and therefore R solely depends on water activity, not on the dry radius. Because R decreases as W (or a_w) increases, from (4) and (6) one can deduce that the threshold curvature correction of a particle is also the maximum curvature correction of the particle. In Hänel (1976), threshold water activity is assumed to be the value of a_w when $W = W_t \equiv \rho_w/\rho_0$, and therefore from (1) and (4) one has

$$r_t = 2^{1/3} r_0, \quad (8)$$

$$\delta_t = \exp \left(\frac{2\sigma}{\rho_w R_w T r_t} \right), \quad (9)$$

where r_t and δ_t represent, respectively, the threshold radius and the threshold curvature correction.

For particles of meteorological interest, curvature correction usually varies between 1 and 1.3. It is the deviation of curvature correction from unity that makes

TABLE 1. The characterization and physicochemical properties of aerosol samples measured by Hänel and Lehman (1981).

Sample	Type of aerosol	ρ_0 (g cm ⁻³)	b (dyn cm ⁻¹)	ϵ	Main water-soluble substances (composition in mass fraction)
1	Desert, normal condition	2.59	17.3	0.31	0.55 Na ₂ SO ₄ + 0.45 NaNO ₃
2	Desert, sand storm	2.72	15.6	0.39	0.59 Na ₂ SO ₄ + 0.41 NH ₄ NO ₃
3	Industrial	1.87	13.2	0.38	0.76 NaNO ₃ + 0.24 H ₂ SO ₄
4	Maritime	1.93	27.8	0.89	SS*
6	Background**	3.32	20.5	0.60	0.43 NH ₄ NO ₃ + 0.57 SS
8	Background**	1.92	13.1	0.40	0.57 (NH ₄) ₂ SO ₄ + 0.23 NH ₄ NO ₃ + 0.20 H ₂ SO ₄
10	Background**	1.93	24.6	0.56	0.19 NH ₄ NO ₃ + 0.81 SS

* SS—Sea salt.

** Also combined with particles from surrounding industrial zones and local sources.

the difference for different RH and particle size. To distinctly describe the deviation of δ from unity, we define a scaled deviation of curvature correction from unity, N_δ , as

$$N_\delta = \frac{\delta - 1}{\delta_t - 1}. \quad (10)$$

Expanding (10) into Taylor series of R/r_0 and R_t/r_0 and neglecting terms higher than third order give

$$N_\delta \approx \frac{R}{R_t} \left(1 + \frac{1}{2} \frac{R}{r_0} \right) \left(1 + \frac{1}{2} \frac{R_t}{r_0} \right)^{-1}, \quad (11)$$

where R_t is the value of R at threshold water activity, $R_t = R(a_{wt})$. Note that $R \leq R_t$, and therefore if $R_t/r_0 \leq 1$, then (11) can be further approximated as

$$N_\delta \approx \frac{R}{R_t}. \quad (12)$$

Since R only depends on a_w and R_t exclusively on a_{wt} , N_δ in (12) is only a function of a_w and independent of dry radius. The meaning of (12) is that for any particle with dry radius far larger than R_t , the scaled deviation of curvature correction from unity N_δ follows the same universal form (12) that depends only on water activity.

To check the accuracy of (12), it is sufficient to examine the difference (denoted as DV) between (11) and (12). Subtracting (12) from (11) gives

$$DV = \frac{R}{R_t} \frac{R - R_t}{2r_0 + R_t}. \quad (13)$$

It can be shown that the maximum absolute value of DV (denoted as DV_{max}) occurs at $R = R_{\max} = 0.5R_t$ and $N_\delta \approx 0.5$. Therefore, using $\delta_t = \exp(R_t/r_0)$, one can obtain

$$DV_{\max} = \frac{\ln \delta_t}{8 + 4 \ln \delta_t}. \quad (14)$$

Equation (14) indicates that the maximum difference between (11) and (12) is proportional to $\ln \delta_t$. From (4c), (5), and (14), one can estimate that for r_0

$= 0.005 \mu\text{m}$, $\delta_t \approx 1.3$ and $DV_{\max} = 0.029$; and that for $r_0 = 0.1 \mu\text{m}$, $\delta_t \approx 1.01$ and $DV_{\max} = 0.0012$. Note that at $R = R_{\max}$, $N_\delta \approx 0.5$. Therefore, at $R = R_{\max}$, the relative error in N_δ estimated by (12) is about 6% for $r_0 = 0.005 \mu\text{m}$ and 0.2% for $r_0 = 0.1 \mu\text{m}$. Thus, one can conclude that the universal approximation formula (12) is very accurate for $r_0 \geq 0.005 \mu\text{m}$.

b. N_δ - a_w relationship from experimental data

To see whether the above theoretical analysis is correct and how curvature correction changes with water activity, seven typical tropospheric aerosol samples measured by Hänel and Lehman (1981) were used to examine the N_δ - a_w relationship. The characterization and physicochemical properties of aerosol samples are listed in Table 1. As can be seen in Table 1, the aerosol samples are composed of a diversity of water-soluble substances, so these samples provide a wide scope for one to investigate the characteristics of the N_δ - a_w relationship.

In the original data of Hänel and Lehman (1981), the water uptake W of a unit mass of dry aerosol is listed separately for RH increasing and RH decreasing cases to account for the RH hysteresis effect (e.g., Orr et al. 1958; Hänel 1976). In this paper, this hysteresis effect is not considered. For a given water activity, W used in this paper is the average of W for the cases of increasing and decreasing relative humidity.

Figure 1 shows how N_δ changes with a_w for particles having different sizes in sample 10. In Fig. 1, N_δ reaches a maximum value of 1 at threshold water activity, in the section where $a_w < a_{wt}$ the curves for different particles separate remarkably, and while in the section where $a_w \geq a_{wt}$, the difference in N_δ of different particles is very small. The maximum difference between N_δ for $r_0 = 0.005 \mu\text{m}$ and that for $r_0 = 0.1 \mu\text{m}$ is about 0.035, and appears in the region of $N_\delta \approx 0.5$. This is consistent with previous analysis.

Figure 2 displays the N_δ - a_w relationship for particles in sample 3. It can be seen in Fig. 2 that the curves for different particles change with a_w in a way much like that in Fig. 1, although the chemical composition and origins of the two samples are very different.

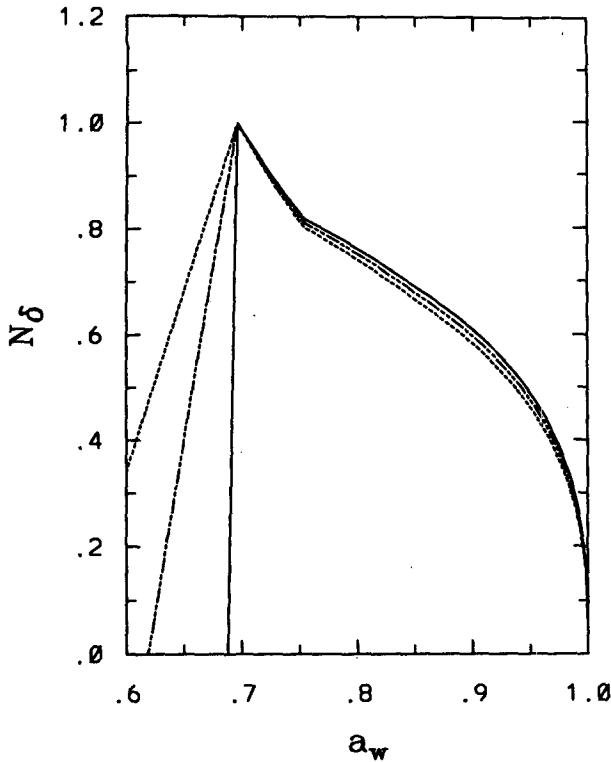


FIG. 1. Scaled deviation of curvature correction from unity (N_δ) versus water activity (a_w) for particles having different dry radii (r_0) in sample 10. Solid line— $r_0 = 0.1 \mu\text{m}$, dash-dotted line— $r_0 = 0.01 \mu\text{m}$, dotted line— $r_0 = 0.005 \mu\text{m}$.

Apart from the above-mentioned features of the N_δ - a_w relationship, there is another striking feature shared by the curves in Figs. 1 and 2. In Fig. 1, for $a_{wr} \leq a_w \leq 0.75$, N_δ of different particles decreases with a_w in an approximately linear way, and in the range $0.75 \leq a_w \leq a_{wm} = 0.96$, it also decreases quasi-linearly with a_w but with a different slope. Also, in Fig. 2, N_δ decreases approximately linearly with a_w when a_w is in the range $a_{wr} \leq a_w \leq 0.96$. The linear relationship between N_δ and a_w makes it very easy for one to get an approximate solution of a_w as a function of relative humidity by using (2).

The N_δ - a_w relationship was also investigated for other samples. Results indicate that the universal properties of N_δ - a_w curves shown in Figs. 1 and 2 still exist regardless of the different chemical compositions and origins that other samples have.

c. Approximation of curvature correction

Based on the findings in the previous subsections, N_δ is approximated with two pieces of the linear function of a_w when $a_{wr} \leq a_w \leq a_{wm} = 0.96$. Given the characteristics of N_δ - a_w curves in Figs. 1 and 2 and also for the sake of simplicity, the common point (denoted as $a_{w,j}$) of the two pieces of the linear function is defined

as the a_w at which the true N_δ has maximum deviation from the linear function $1 + [N_\delta(0.96) - 1](a_w - a_{wr})(0.96 - a_{wr})^{-1}$. Since N_δ has little dependence on r_0 , the common point for any r_0 is assumed to be the same.

For the case $a_w \geq 0.96$, from Figs. 1 and 2 one can see that N_δ decreases very rapidly with a_w when a_w is larger than about 0.96 and approaches zero when $a_w \rightarrow 1$. This indicates that N_δ can only be fit with certain fractional power functions of $(1 - a_w)$. In the following, N_δ 's properties are examined for the case $a_w \rightarrow 1$. When a_w approaches 1, the exponential mass increase coefficient in (3) approaches a constant value η_0 . Assuming η is a constant, from (1), (3), and (4c) and using $\ln a_w \rightarrow a_w - 1$, one can obtain

$$\delta = 1 + c_1(1 - a_w)^{1/3}, \tag{15}$$

$$N_\delta = \frac{c_1}{\delta_t - 1} (1 - a_w)^{1/3}, \tag{16}$$

where

$$c_1 = \frac{2[\sigma_{w0} - a(T - T_0)]}{R_w T r_0} \left(\frac{1}{\rho_w^2 \rho_0 \eta_0} \right)^{1/3}. \tag{17}$$

Equation (16) indicates that N_δ is a power function of $(1 - a_w)$ to the one-third when $a_w \rightarrow 1$. Equation (16) was tested against the seven samples listed in Table 1.

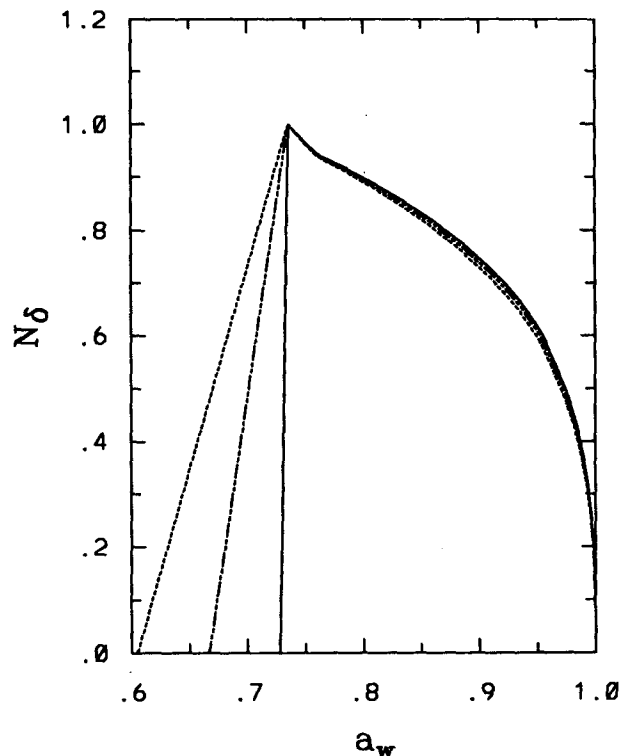


FIG. 2. As in Fig. 1 but for sample 3.

It was found that (16) can underestimate N_δ by as much as about 10% at $a_w = 0.96$. This error is mainly caused by the variation of η with a_w . Hänel and Lehman (1981) pointed out that η_0 could be 17% to 55% larger than the η at $a_w = a_{wm} = 0.96$, and therefore using $\eta = \eta_0$ in (17) leads to the underestimation of N_δ .

To ensure that δ is a continuous function of a_w , c_1 is estimated directly from the δ at $a_w = 0.96$ —that is,

$$c_1 = 0.04^{-1/3}[\delta(0.96) - 1]. \quad (18)$$

Substituting c_1 in (16) with (18) gives

$$N_\delta = N_\delta(0.96) \left(\frac{1 - a_w}{0.04} \right)^{1/3}. \quad (19)$$

Equation (19) was also tested against the seven samples. In Fig. 3, N_δ calculated with (19) agrees very well with that computed with (4c) for $a_w \in (0.96, 1)$. Moreover, N_δ calculated with (19) matches very well with that obtained with (4c) even when a_w is as small as 0.8. Tests on the six other samples also demonstrate that N_δ computed with (19) can compare very well with that obtained from (4c) when $0.96 \leq a_w \leq 1$. In addition, results show that when $a_w < 0.96$, for all seven samples N_δ computed with (19) is still very close to (within 0.04) that obtained from (4c) if $W > 2W_c$.

4. Approximation formulas of water activity as functions of RH

In this section, (2) is solved with the N_δ - a_w (or δ - a_w) relationship obtained in the previous section. Approximation formulas for water activity are derived as functions of relative humidity. Accuracy of equilibrium sizes calculated with water activity given by these formulas is examined.

In this paper, the performance of the approximation formulas was investigated only for the stable subcritical case $a_w \leq a_{wc}$, where a_{wc} is the critical water activity [$df/da_w|_{a_w=a_{wc}} = 0$]. In the case where $a_w \leq a_{wc}$, a_w monotonically increases with f . For a given f , this monotonic relationship between a_w and f determines what approximation formula of δ should be used to solve (2).

a. Water activity as a function of RH

For the case $a_w \in (a_{wr}, 0.96)$, δ and N_δ can be approximated by two piecewise linear functions of a_w . Assuming

$$\delta = a_1 + b_1 a_w, \quad (20)$$

from (2) and (20) one can obtain

$$a_w = \frac{1}{2b_1} [-a_1 \pm (a_1^2 + 4b_1 f)^{1/2}]. \quad (21)$$

For the two roots in (21), one can easily determine that only one root has physical meaning.

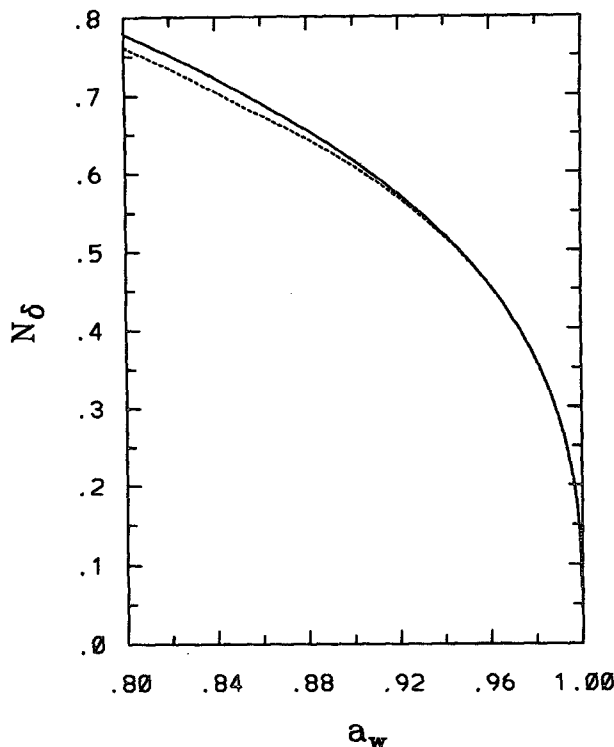


FIG. 3. Scaled deviation of curvature correction from unity (N_δ) versus water activity (a_w) for a particle with dry radius of $0.1 \mu\text{m}$ in sample 10. Solid line is calculated with Eq. (19), and dotted line is the true value calculated with Eqs. (4c) and (10).

For the case where $a_w \in (0.96, a_{wc})$, from (2) and (15) [note that c_1 is defined by (18)] one can obtain

$$(f - a_w)^3 = c_1^3 a_w^3 (1 - a_w). \quad (22)$$

Equation (22) is a fourth-order algebraic equation. Although it has analytical solutions, the roots are complicated functions of f . Since a_w is in the narrow range from 0.96 to 1, the term a_w^3 on the rhs of (22) is approximated with $0.98^3 = 0.9412$. Thus, (22) is reduced to a cubic equation. This cubic equation may have two real roots of a_w if $a_{wc} > 0.96$, with one of the roots less than a_{wc} and the other greater than a_{wc} .

It is worth mentioning that formulas (21) and (22) use only three δ values at the three interpolation points of a_w (i.e., a_{wr} , a_{wj} , and $a_{wm} = 0.96$). Because (21) and (22) are in simple forms, the computation cost to calculate the equilibrium radius of a particle is very low when compared with iterative methods. When the approximation formulas are applied to a group of particles of different sizes or to a particle in a RH varying environment, (21) and (22) can further lower the computation cost when compared with iterative methods because R in (6) is independent of r_0 and RH, and therefore needs to be calculated only once at the three interpolation points of a_w .

b. Accuracy and error analysis

In order to check the accuracy of (21) and (22), highly accurate solutions of (1)–(5) are needed as reference values. To this end, an iterative method was employed to solve (1)–(5). The convergence criterion of the iterative method is that (2) is accurate within 1.0×10^{-8} at the last iteration step. Hereafter, solutions of (1)–(5) obtained with the iterative method are referred to as true values (or solutions).

To quantitatively examine the accuracy of (21) and (22), the relative error of equilibrium radius (denoted as ER) computed with water activity given by (21) and (22) is defined as follows:

$$ER = \frac{|r - \tilde{r}|}{\tilde{r}}, \quad (23)$$

where \tilde{r} represents the true value of equilibrium radius and r is the equilibrium radius calculated with water activity given by (21) or (22).

The relative error of equilibrium radius obtained from water activity given by (21) and (22) was examined for RH ranging from the threshold relative humidity $f_i = a_w \delta_i$ to the critical relative humidity f_c of a particle. Listed in Table 2 is the maximum ER in the RH range $f_i < f \leq 99.99\%$. From Table 2 one can find that the maximum ER is usually around 1%–3% when the dry radius is larger than $0.02 \mu\text{m}$ and is below 5.5% when $r_0 < 0.02 \mu\text{m}$. These results demonstrate that the approximation method developed in this paper can accurately estimate particle equilibrium sizes when relative humidity does not exceed 99.99%.

Results (not shown) also demonstrate that when relative humidity is larger than 99.99% and is close to the critical relative humidity, the relative error of equilibrium radius computed with the proposed method can be as large as 30% if $r_0 > 0.01 \mu\text{m}$. The sensitivity of equilibrium sizes to water activity can be estimated as follows. Assuming that η does not change with W , then from (1) and (3) one has

$$\frac{\Delta r}{r} = \frac{1}{3} \left(\frac{\rho_w \ln a_w}{\rho_0 \eta} - 1 \right)^{-1} \frac{\Delta a_w}{a_w \ln a_w}, \quad (24)$$

where Δa_w stands for the error in a_w and $\Delta r/r$ is the relative error of r . Equation (24) shows that the relative error of equilibrium radius becomes more and more sensitive to the error in water activity as water activity increases—that is, as RH increases. When $a_w \rightarrow 1$, $\Delta r/r$ is extremely sensitive to the error in a_w . Fortunately, the approximate N_δ – a_w relationship (19) is accurate to within 1.5% when $a_w > 0.96$.

Results also show that overall, the relative error of equilibrium radius decreases with the increase of dry radius for a fixed a_w if a_w is not very close to 1. This is because the error in a_w obtained from (21) and (22) decreases with the increase of r_0 . This conclusion can be verified through examining (2), (10), and (24) (de-

TABLE 2. The maximum relative errors (%) of equilibrium radius computed with water activity from Eqs. (21) and (22) in the relative humidity range $f_i \leq \text{RH} \leq 99.99\%$ for different aerosol samples and different ranges of dry radius r_0 .

Sample	1	2	3	4	6	8	10
$r_0 < 0.02 \mu\text{m}$	1.0	1.5	1.0	5.5	2.2	1.0	2.8
$0.02 \mu\text{m} \leq r_0 \leq 10 \mu\text{m}$	1.2	3.3	1.0	1.1	2.0	1.5	1.7

tails are omitted here). When a_w is very close to 1, although from (2) and (10) one has $\Delta a_w \rightarrow 0$, the term $\Delta a_w / \ln a_w$ in (24) may not be small, so certain errors may remain in the equilibrium radius computed with the proposed method. This kind of error occurs most distinctly in the vicinity of the critical point. It is discussed thoroughly in the next section.

5. Problems associated with the critical point

In this section, critical equilibrium radius and supersaturation are studied with the proposed δ – a_w relationship. Error analysis is performed to equilibrium sizes computed with a_w given by (22) when $100\% < \text{RH} \leq f_c$. Modified formulas are developed to reduce errors in the critical supersaturation and equilibrium radius.

a. Critical equilibrium radius and supersaturation

When ambient relative humidity is larger than 100%, particles with critical humidity less than the ambient relative humidity will be activated. To investigate the r – f relationship near the critical point, investigators (e.g., Fletcher 1962; Mason 1971; Pruppacher and Klett 1978) developed some methods to approximate the Köhler equation when $a_w \rightarrow 1$. As pointed out by Hänel (1976), for some representative salts such as NaCl and $(\text{NH}_4)_2\text{SO}_4$, previous approximation methods give equilibrium sizes remarkably larger than true values.

For most hygroscopic particles, the critical water activity is larger than 0.96, and hence one can use (15) to find the critical water activity. Using (2) and (15) [note that c_1 is defined by (18)] and assuming that $df/da_w = 0$, one can obtain

$$\frac{4}{3} c_1 y^3 + y^2 - \frac{c_1}{3} = 0, \quad (25)$$

where

$$y = (1 - a_w)^{1/3}. \quad (26)$$

When $c_1 < 1.0$, a very precise solution of (25) is its second-order approximated root,

$$y_c = y_1 + \frac{1}{2} (1 + 4c_1 y_1)^{-1} \times \{-c_2 + [c_2^2 - 16(1 + 4c_1 y_1) y_1^5]^{1/2}\}, \quad (27)$$

where

$$y_1 = \left(\frac{c_1}{3}\right)^{1/2}, \quad (28)$$

$$c_2 = \frac{4}{3}c_1^2 + 2y_1. \quad (29)$$

From (2), (15), (26), and (27), one can obtain the critical supersaturation (denoted as S_c)

$$S_c \equiv f_c - 1 = -y_c^3 + c_1(1 - y_c^3)y_c \quad (30)$$

and critical water activity

$$a_{wc} = 1 - y_c^3. \quad (31)$$

As y_c is a unique function of c_1 , so in (30) and (31) the critical supersaturation and water activity are unique functions of c_1 . If a dry radius is large enough, from (18) one has $c_1 \rightarrow 0$. Thus, (30) and (31) reduce to

$$S_c \approx \frac{2}{3\sqrt{3}} c_1^{3/2} \quad \text{for } c_1 \rightarrow 0 \quad (32)$$

and

$$a_{wc} \approx 1 - \left(\frac{c_1}{3}\right)^{3/2} \quad \text{for } c_1 \rightarrow 0. \quad (33)$$

In Fig. 4, the critical supersaturation calculated with (30) compares well with its true value, especially when a dry radius is small. The relative error of S_c calculated with (30) is about 5% when $r_0 = 0.04 \mu\text{m}$, is about 10% when $r_0 = 0.13 \mu\text{m}$, and approaches a maximum value of about 15% at $r_0 = 10 \mu\text{m}$. The increase of relative error of S_c with r_0 is caused by the inaccuracy of c_1 when $a_w \rightarrow 1$. Results show that S_c computed with (32) differs by less than 1% from that computed with (30) when $r_0 > 0.05 \mu\text{m}$, so (32) can be used to estimate the error in S_c . From (32), one can deduce that the relative error of S_c is 1.5 times as large as the relative error of c_1 . For sample 8, the c_1 determined by (18) is about 12% larger than the c_1 determined by (17), which corresponds to the case of infinite dilution ($a_w = 1$). Therefore, (30) and (32) overestimate S_c by about 18% at $a_w = 1$.

From (24), (32), and (33), one can prove that the relative error of critical equilibrium radius is about one-third of the relative error of S_c . For all samples listed in Table 1, results show that if $r_0 \geq 0.01 \mu\text{m}$, S_c estimated by (32) is accurate to within 15% and the critical equilibrium radius (r_c) computed with water activity given by (33) is accurate to within 5%.

b. Errors and improvements around the critical point

As mentioned earlier, ER is very sensitive to the error in a_w when $a_w \rightarrow 1$ [see (24)]. The inaccuracy of water activity computed with (22) is partially caused

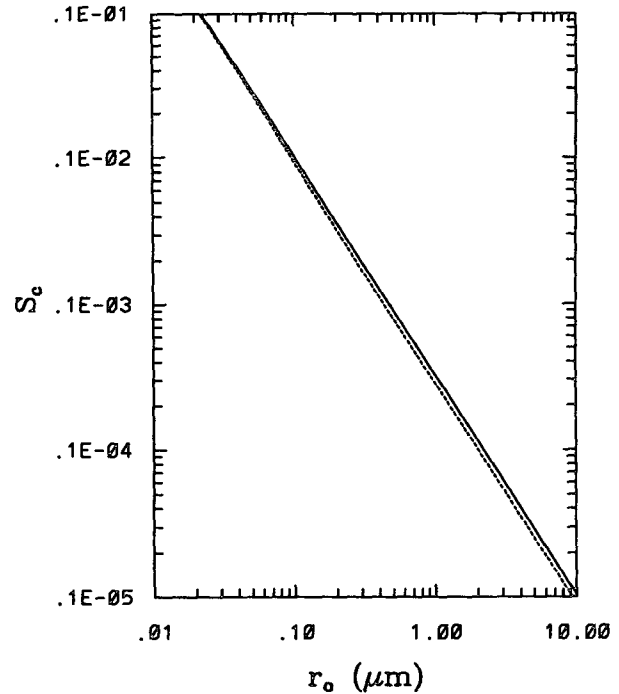


FIG. 4. Critical supersaturation S_c versus dry radius r_0 for sample 8. Solid line is computed with Eq. (30), and dotted line is the true value.

by the assumption that c_1 is independent of a_w . To more accurately estimate c_1 , based on (17), we modify (18) into

$$c_1(a_w) = c_1(0.96) \left[\frac{\eta(0.96)}{\eta(a_w)} \right]^{1/3}. \quad (34)$$

Since $\eta(a_w)$ is unknown before a_w is determined, a one-step iteration is used to estimate $\eta(a_w)$. Computations show that the error in the a_w calculated with (22) and (34) is about half of that in the a_w computed with (22) and a constant value of c_1 [see (18)].

As a result, the equilibrium radii computed with a_w given by (22) and (34) have a higher accuracy. For all samples in Table 1, the relative error (ER) of equilibrium radius computed with (22) and (34) is less than 2% when $r_0 \geq 0.02 \mu\text{m}$ and $\text{RH} \leq 100\%$. For the case $100\% < \text{RH} \leq f_c$ and $r_0 \leq 10 \mu\text{m}$, results show that the maximum ER calculated with (22) and (34) ranges from 9% to 16% for the seven samples in Table 1, which is about half of that calculated with (22) and a constant value of c_1 .

Similarly, by taking c_1 as a function of a_w , the accuracy of critical equilibrium radius and supersaturation computed with the approximation method can be increased. Using (2), (15), and (34), one can modify (25) into

$$\frac{c_1}{3} \left(4 - \frac{\partial \ln \eta}{\partial \ln a_w} \right) y^3 + y^2 - \frac{c_1}{3} = 0. \quad (35)$$

Equation (35) differs from (25) only by the coefficient of the first term. Again, a one-step iteration is used to estimate c_1 and $\partial \ln \eta / \partial \ln a_w$, which is approximated with finite difference. Computation shows that for $0.01 \mu\text{m} \leq r_0 \leq 10 \mu\text{m}$ and $f_c \leq 102\%$, the critical equilibrium radius and critical supersaturation obtained from (35) are accurate within 3.3% and 5.2%, respectively. For sample 8, the maximum relative error of S_c computed with (35) is about one-third of the maximum relative error of S_c obtained from (25).

As mentioned in section 3c, the exponential mass increase coefficient (η) is 17%–55% larger at $a_w = 1$ than at $a_w = 0.96$. The above results indicate that if η changes more than 17% from $a_w = 0.96$ to $a_w = 1$, considering the change of c_1 with a_w can greatly increase the accuracy of estimated critical supersaturation and equilibrium sizes.

6. Summary and conclusions

To study the relationship between curvature correction (δ) and water activity (a_w), a scaled deviation of curvature correction from unity, N_δ , is defined as $N_\delta = (\delta - 1)(\delta_t - 1)^{-1}$, where δ_t is the threshold curvature correction at the threshold water activity (a_{wt}) (Hänel 1976). It was shown theoretically that N_δ can be very accurately represented by a universal function of water activity if the dry radius of a particle is larger than $0.005 \mu\text{m}$ and $a_w > a_{wt}$. Furthermore, through studying seven representative aerosol samples measured by Hänel and Lehman (1981), it was found that N_δ can be approximated by two piecewise linear functions of a_w when $a_{wt} < a_w < 0.96$ and by a $1/3$ power function of $(1 - a_w)$ when $a_w \geq 0.96$.

Using these simple approximation formulas of N_δ and the Köhler equation, water activity is solved as an analytical function of relative humidity, and the equilibrium size of a wet particle is analytically computed from a given relationship between water activity and water uptake by unit mass of dry material. Moreover, the approximation formulas of N_δ are used to derive analytical formulas for calculating critical supersaturation S_c and critical equilibrium radius r_c .

TABLE 3. Relative errors (%) of equilibrium radius in different ranges of RH and dry radius r_0 .

Equations for computing a_w	$f_t \leq \text{RH} \leq 99.99\%$		99.99%
	$r_0 \leq 0.02 \mu\text{m}$	$0.02 < r_0 \leq 10 \mu\text{m}$	$\leq \text{RH} \leq f_c$ $r_0 \leq 10 \mu\text{m}$
(18), (21), and (22)	≤ 5.5	≤ 3.3	≤ 30
(21), (22), and (34)	≤ 5.5	≤ 2.0	≤ 16

TABLE 4. Relative errors (%) of critical equilibrium radius r_c and critical supersaturation S_c when dry radius is less than $10 \mu\text{m}$ and $S_c \leq 2\%$.

Equations for computing a_w	Relative error of r_c	Relative error of S_c
(18) and (25)	≤ 5.0	≤ 15
(34) and (35)	≤ 3.3	≤ 5.2

The accuracy of equilibrium radius r , r_c , and S_c obtained from the above-mentioned method was checked with seven aerosol samples measured by Hänel and Lehman (1981). The relative errors of r , S_c , and r_c , along with the equations used to calculate water activity and its ranges of application, are listed in Tables 3 and 4. For formulas listed in Tables 3 and 4, (21) was derived from the linear relationship between N_δ and a_w , while (22), (25), and (35) were derived from the one-third power relationship between N_δ and a_w . In (18), the parameter c_1 was defined as a constant, whereas in (34) c_1 was treated as a function of a_w . Formulas in Table 3 are applicable to the case where RH is greater than the threshold relative humidity ($f_t = a_{wt}\delta_t$). For the case where $\text{RH} < f_t$, one can use the Hänel model [see (1)–(5)] to obtain an analytical relationship between a_w and RH. In addition, results (not shown) also demonstrate that the hysteresis effect of RH on equilibrium radius does not affect the accuracy of the approximation formulas developed in this paper.

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