The effect of surface tension (Kelvin effect) on the equilibrium radius of a hygroscopic aqueous aerosol particle

Ernie R. Lewis

Atmospheric Sciences Division, Brookhaven National Laboratory, Upton, NY 11973-5000, USA

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Abstract

The effect of surface tension (the Kelvin effect) on the equilibrium radius of an aqueous solution drop at fractional relative humidity \( h \) less than unity is analyzed mathematically. Expressions for the lowest-order corrections to the equilibrium radius and radius ratio (relative to the volume-equivalent dry radius \( r_{\text{dry}} \)) due to the Kelvin effect are presented and compared with data for solution drops of ammonium sulfate and sodium chloride. To lowest order the decrease in equilibrium radius resulting from the Kelvin effect is independent of the amount of solute in the drop and is approximated to good accuracy by \( \Delta r / r_{\text{dry}} = - (h/3) / (1 - h) \), with only weak dependences on solute and temperature. The importance of the Kelvin effect on drop radius is further quantified in several ways. The value of the volume-equivalent dry radius below which the Kelvin effect results in more than a 5% decrease in the equilibrium radius of a solution drop at given \( h \) is approximately \( r_{\text{dry,5\%}} / nm = 8h / (1 - h)^{2/3} \). The decrease in the hygroscopic growth factor \( g \) of an aqueous solution drop between a low relative humidity and \( h = 0.9 \) resulting from the Kelvin effect is given approximately by \( \Delta g \approx -(3 nm) / r_{\text{dry}} \), again with only weak dependences on solute and temperature. These approximations compare well with measurements of growth factors of ammonium sulfate solution drops for dry radius as low as 10 nm. These findings, all of which are presented for fractional relative humidity as the independent variable, allow the magnitude of the Kelvin effect and its consequences on the properties of an aqueous solution drop to be readily assessed.

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Keywords: Kelvin effect; Surface tension; Hygroscopicity; Relative humidity; Growth factor

1. Introduction

The vapor pressure of water in equilibrium with an aqueous solution drop at a given temperature depends only on the solute and its concentration and on the size of the drop (Köhler, 1936; Wright, 1936). This size dependence, which is due to the surface tension of the solution–air interface, is known as the Kelvin effect (Thomson, 1871). For an aqueous solution drop with given concentration, the equilibrium fractional relative humidity \( h \), which is equal to the equilibrium water vapor pressure divided by the saturation water vapor pressure, increases with decreasing drop radius; conversely, the equilibrium radius of a solution drop \( r \) at a given relative humidity is less than what it would be if surface tension had no effect. The Kelvin effect is of central importance to cloud drop activation, and as the equilibrium radius is a key
**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_w$</td>
<td>water activity</td>
</tr>
<tr>
<td>$c$</td>
<td>constant in power law</td>
</tr>
<tr>
<td>$C$</td>
<td>constant in expression of Fitzgerald (1975)</td>
</tr>
<tr>
<td>$f$</td>
<td>resonant frequency of shape oscillation of drop</td>
</tr>
<tr>
<td>$g$</td>
<td>hygroscopic growth factor</td>
</tr>
<tr>
<td>$\Delta g$</td>
<td>change in hygroscopic growth factor due to Kelvin effect</td>
</tr>
<tr>
<td>$h$</td>
<td>fractional relative humidity ($\equiv$ RH/100%)</td>
</tr>
<tr>
<td>$h_e$</td>
<td>value of $h$ at which efflorescence (crystallization) occurs</td>
</tr>
<tr>
<td>$h_{5%}$</td>
<td>value of $h$ at which Kelvin effect results in 5% decrease in radius</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>increase in fractional relative humidity due to Kelvin effect</td>
</tr>
<tr>
<td>$j$</td>
<td>mode number of drop oscillation</td>
</tr>
<tr>
<td>$M_w$</td>
<td>molar mass of water (0.018 kg mol$^{-1}$)</td>
</tr>
<tr>
<td>$m_{dry}$</td>
<td>dry mass of (anhydrous) solute</td>
</tr>
<tr>
<td>$n$</td>
<td>exponent in power law</td>
</tr>
<tr>
<td>$q$</td>
<td>charge on a suspended drop</td>
</tr>
<tr>
<td>RH</td>
<td>percent relative humidity</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant (8.3 J K$^{-1}$ mol$^{-1}$)</td>
</tr>
<tr>
<td>$r$</td>
<td>equilibrium drop radius</td>
</tr>
<tr>
<td>$\Delta r$</td>
<td>change in equilibrium radius due to Kelvin effect</td>
</tr>
<tr>
<td>$r_{dry}$</td>
<td>volume-equivalent dry radius</td>
</tr>
<tr>
<td>$r_{dry,5%}$</td>
<td>value of $r_{dry}$ at which Kelvin effect results in 5% decrease in radius</td>
</tr>
<tr>
<td>$r_\sigma$</td>
<td>characteristic length scale for Kelvin effect</td>
</tr>
<tr>
<td>$r_{\sigma,0}$</td>
<td>value of $r_\sigma$ evaluated for pure water ($\approx$ 1.1 nm)</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$\bar{v}_w$</td>
<td>partial molal volume of water in solution</td>
</tr>
<tr>
<td>$\bar{v}_{w,0}$</td>
<td>partial molal volume of pure water ($\approx 1.8 \times 10^5$ m$^3$ mol$^{-1}$)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>function of relative humidity in expression of Fitzgerald (1975)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>function of relative humidity in expression of Fitzgerald (1975)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>dielectric constant of solution</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>electric constant (permittivity of free space, $\approx 8.85 \times 10^{12}$ F m$^{-1}$)</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>function of relative humidity in expression of Fitzgerald (1975)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density of solution</td>
</tr>
<tr>
<td>$\rho_{dry}$</td>
<td>density of (anhydrous) solute</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>density of pure water ($\approx 1.0 \times 10^3$ kg m$^{-3}$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>surface tension of solution-air interface</td>
</tr>
<tr>
<td>$\Delta \sigma$</td>
<td>change in surface tension from that of pure water due to solute</td>
</tr>
<tr>
<td>$\sigma_w$</td>
<td>surface tension of pure water-air interface ($\approx 7.4 \times 10^{-2}$ J m$^{-2}$)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>characteristic time for rate of exponential decay of drop oscillation</td>
</tr>
<tr>
<td>$v$</td>
<td>kinematic viscosity of solution</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>radius ratio relative to volume-equivalent dry radius ($\equiv r/r_{dry}$)</td>
</tr>
<tr>
<td>$\Delta \zeta$</td>
<td>change in radius ratio due to Kelvin effect</td>
</tr>
<tr>
<td>$\zeta_\sigma$</td>
<td>ratio of characteristic length scale for Kelvin effect to $r_{dry}$ ($\equiv r_\sigma/r_{dry}$)</td>
</tr>
</tbody>
</table>

The Kelvin effect can also play an important role in other atmospheric processes.

This paper examines the Kelvin effect, the quantities upon which it depends, and its effect on drop radius and growth factor. The relation between $h$ and $r$ is presented in dimensionless form using the volume-equivalent dry radius $r_{dry}$ and a characteristic length scale for the Kelvin effect $r_\sigma$. A simple expression is derived for the decrease in the
equilibrium radius of a solution drop due to the Kelvin effect, with dependences on surface tension and particle size explicitly shown, and estimates are presented for the magnitude of this effect in various situations. Examples are presented for solution drops of ammonium sulfate, \((\text{NH}_4)_2\text{SO}_4\) (based on water activities reported by Clegg, Ho, Chan, & Brimblecombe, 1995, and densities reported by Tang & Munkelwitz, 1994) and sodium chloride, NaCl (based on water activities reported by Clegg, Brimblecombe, Liang, & Chan, 1997, and densities reported by Tang, 1996), two common constituents of atmospheric aerosol particles. Pertinent properties of solution drops of these substances have been studied by numerous investigators and are quite well characterized, and the humidity dependence of the radius of drops of many other inorganic salts of atmospheric importance (and sulfuric acid) is very similar or intermediate to those of these two substances over a wide range of relative humidity (see for instance Fig. 4 of Tang, 1996); thus the behavior of these two substances provides an indication of the range of behavior that can be expected for other inorganic salts.

2. Theory

The equilibrium fractional relative humidity \(h\) above an aqueous solution drop with radius \(r\) is related to the water activity \(a_w\) in the drop by

\[
h = a_w \exp\left(\frac{2\overline{v}_w \sigma}{RT r}\right),
\]

(Tang, 1976), where \(a_w, \overline{v}_w\), and \(\sigma\) depend on the solute and its concentration. This equation could be used to calculate the Kelvin effect on the radius, but such a procedure would require iteration and would likely yield no insight into the dependence of this effect on drop size or surface tension. An alternative method which allows simple expressions to be obtained for the Kelvin effect in various situations and explicitly shows these dependencies is to express all pertinent quantities in dimensionless form using the volume-equivalent dry radius \(r_{\text{dry}}\) defined as

\[
r_{\text{dry}} \equiv \frac{3m_{\text{dry}}}{(4\pi \rho_{\text{dry}})^{1/3}},
\]

where \(m_{\text{dry}}\) is the mass of solute contained in the particle. The quantity \(r_{\text{dry}}\) is not necessarily equal to the physical radius of a dried particle, as such a particle may not be spherical, may contain some residual water, or may have a density different from that of the bulk solute (because of voids, for instance). Nevertheless, \(r_{\text{dry}}\), together with specification of \(\rho_{\text{dry}}\), provides an unambiguous measure of the mass of solute contained in the particle. The quantity \(r_{\sigma}\) depends on the solute and its concentration, and weakly on temperature, typically decreasing by less than 1% \(\circ\)C.

In terms of the equilibrium radius ratio \(\xi \equiv r/r_{\text{dry}}\), which for a given solute unambiguously specifies the concentration, and the dimensionless group \(\xi_{\sigma} \equiv r_{\sigma}/r_{\text{dry}}\), Eq. (1) can be written as

\[
h(\xi, \xi_{\sigma}) = a_w(\overline{\xi}) \exp\left(\frac{\xi_{\sigma}(\overline{\xi})}{\xi}\right),
\]

where the dependences of \(a_w\) and \(\xi_{\sigma}\) on \(\xi\) are explicitly shown. Expressing the relationship between \(h\) and \(\xi\) in terms of \(\xi_{\sigma}\) permits the role of the Kelvin effect and its dependence on surface tension and particle size to be explicitly determined. Any expression relating only \(h\) and \(\xi\) cannot include the effect of surface tension or particle size, and hence must apply only to the bulk solution. Conversely, any expression for the radius ratio that contains a dependence on \(r_{\text{dry}}\) necessarily implies that this dependence describes the Kelvin effect.

The value of \(h\) for a drop with given solute mass (characterized by \(\xi_{\sigma}\)) can be readily obtained from Eq. (2) as a function of solute concentration (characterized by \(\xi\)). However, in many situations it is desirable to determine \(\xi\) for a given \(h\), as the relative humidity is often externally imposed and hence is the controlling variable. For the situation \(\xi_{\sigma} = 0\), which refers to bulk solution drops (i.e., drops so large that the Kelvin effect can be neglected), the fractional relative humidity is equal to the water activity, \(h(\xi, 0) = a_w(\overline{\xi})\), and a relation of the form \(a_w = a_w(\overline{\xi})\) can (at least in principle) be inverted to yield \(\xi = \xi(a_w) = \xi(h, 0)\). For situations in which the Kelvin effect cannot be neglected it is necessary to invert Eq. (2) to yield an expression for \(\xi\) as a function of \(h\) and \(\xi_{\sigma}\), \(\xi = \xi(h, \xi_{\sigma})\), the Kelvin effect being manifested in the dependence on \(\xi_{\sigma}\). As the quantity \(\xi(h, \xi_{\sigma})\) can also be written as \(\xi(he^{-(\xi_{\sigma}/h)}, 0)\), determination of such an expression for \(\xi\) as a function of \(h\) and \(\xi_{\sigma}\) is not in general possible (as \(\xi_{\sigma}\) also depends on \(\xi\)), but an approximation can be obtained which yields the lowest-order correction to the radius ratio, \(\Delta \xi(h, \xi_{\sigma}) \equiv \xi(h, \xi_{\sigma}) - \xi(h, 0)\), and allows determination of the range of conditions for which this approximation exhibits a specified accuracy.
3. Lowest-order corrections to radius and radius ratio due to Kelvin effect

3.1. Derivation

The amount by which the equilibrium fractional relative humidity of a drop of given solute and concentration, \( h(\zeta, \zeta_\sigma) \), is larger than the water activity due to the Kelvin effect, \( \Delta h(\zeta, \zeta_\sigma) \equiv h(\zeta, \zeta_\sigma) - a_w(\zeta) \), can be determined by using Eq. (2) to express \( a_w(\zeta) \) as \( h(\zeta, \zeta_\sigma) \exp(-\zeta_\sigma/\zeta) \), yielding

\[
\Delta h(\zeta, \zeta_\sigma) = h(\zeta, \zeta_\sigma)[1 - e^{-\zeta_\sigma/\zeta}].
\]  
(3)

Expansion of the term in brackets yields

\[
1 - e^{-\zeta_\sigma/\zeta} = \frac{\zeta_\sigma}{\zeta} - \frac{1}{2} \left( \frac{\zeta_\sigma}{\zeta} \right)^2 + \cdots;
\]

when only the first term is kept this expression is accurate to within \( \sim 10\% \) for \( r > 5 \text{ nm} \). Substitution of this expression into Eq. (3) and retention of only the lowest-order term in \( \zeta_\sigma \) yields

\[
\Delta h(\zeta, \zeta_\sigma) = h(\zeta, \zeta_\sigma) \frac{\zeta_\sigma}{\zeta}.
\]  
(4)

As for a given solute \( \zeta \) is determined by \( h \) and \( \zeta_\sigma \), this expression yields the lowest-order correction to the equilibrium relative humidity due to the Kelvin effect for a solution drop with given \( r_{\text{dry}} \) at given \( h \).

The equilibrium radius ratio of a solution drop can be represented by \( \zeta(h, \zeta_\sigma) \), or equivalently, by \( \zeta(a_w, 0) \equiv \zeta(h, c(\zeta_\sigma/\zeta)) \), allowing the change in radius ratio due to the Kelvin effect, \( \Delta \zeta(h, \zeta_\sigma) \equiv \zeta(h, \zeta_\sigma) - \zeta(h, 0) \), to be obtained as

\[
\Delta \zeta(h, \zeta_\sigma) \equiv \zeta(h, c(\zeta_\sigma/\zeta)) - \zeta(h, 0) = \frac{d \zeta(h, 0)}{dh} [h(c^{-\zeta_\sigma/\zeta} - 1)] + \cdots.
\]  
(5)

The term in brackets, equal to the negative of \( \Delta h \) given by Eq. (4), can be expanded to yield the lowest-order (in \( \zeta_\sigma \)) correction to the radius ratio due to the Kelvin effect:

\[
\Delta \zeta(h, \zeta_\sigma) = -\zeta_\sigma \frac{h}{\zeta(h, 0)} \frac{d \zeta(h, 0)}{dh}.
\]  
(6)

where \( \zeta(h, 0) \) and \( d \zeta(h, 0)/dh \) refer to these quantities evaluated for the bulk solution. Similarly, the lowest-order correction to the radius due to the Kelvin effect is given by

\[
\Delta r(h, \zeta_\sigma) = -r_\sigma \frac{h}{\zeta(h, 0)} \frac{d \zeta(h, 0)}{dh}.
\]  
(7)

As \( \zeta \) is an increasing function of \( h \), these corrections are negative, implying that the radius and radius ratio calculated from bulk solution properties will be overestimated. For a given solute the quantities \( \zeta(h, 0) \) and \( d \zeta(h, 0)/dh \), and \( r_\sigma \), depend only on \( h \) (and weakly on temperature). Thus to lowest order the decrease in the radius resulting from the Kelvin effect for a given solute depends only on the relative humidity and is independent of \( r_{\text{dry}} \).

Values of \( -\Delta r \) given by Eq. (7) evaluated for bulk solution drops of ammonium sulfate and sodium chloride are shown in Fig. 1, as are the actual values of \( -\Delta r \) calculated from Eq. (1) for drops of these substances with \( r_{\text{dry}} = 10 \) and \( 25 \text{ nm} \) (the dependence of \( r_\sigma \) on solute concentration is explicitly taken into account as discussed in Appendix A). The behavior is similar between the two substances, indicating that the decrease in drop radius due to the Kelvin effect is nearly independent of solute. The magnitude of \( -\Delta r \) given by Eq. (7) provides an upper bound for the actual decrease in radius due to the Kelvin effect, being greater by an amount that increases with decreasing \( r_{\text{dry}} \) as higher-order terms become more important.

Similar conclusions can be reached from Fig. 2, which shows radius ratios for bulk solution drops of ammonium sulfate, for ammonium sulfate solution drops with \( r_{\text{dry}} \) values of 5, 10, and \( 25 \text{ nm} \) calculated from Eq. (1), and for ammonium sulfate solution drops of these sizes calculated using Eq. (6) as the lowest-order corrections from the bulk solution. At low \( h \) the radius ratio for drops of each of these sizes is near the bulk value, and the decrease due to the
Kelvin effect is accurately approximated by the lowest-order correction. With increasing $h$, the radius ratio become increasingly less than the bulk value as the Kelvin effect becomes larger, and the decrease in the radius ratio due to the Kelvin effect is overestimated by the lowest-order correction by an amount that increases with decreasing $r_{dry}$. With further increase in $h$, the radius ratio calculated using only the lowest-order correction from the bulk value reaches a maximum at a value of $h$ that increases with increasing $r_{dry}$. In these situations the lowest-order correction to the radius ratio is a substantial fraction of the radius ratio itself and higher-order terms are required for accurate results. However, inclusion of these terms is neither feasible nor useful, and an alternative approach is required (Lewis, 2006).

### 3.2. Kelvin correction for a power law dependence of radius ratio on $1 - h$

Calculation of the lowest-order Kelvin correction to the radius requires knowledge of $\xi(h, 0)$, the dependence of $\xi$ on $h$ for bulk solution drops. For many inorganic substances $\xi(h, 0)$ can be accurately approximated over wide ranges.
of relative humidity by a two-parameter power law in \(1 - h\)

\[
\xi(h, 0) = \frac{c}{(1 - h)^n},
\]  

(8)

where the values of \(c\) and \(n\) depend on the solute and on the range of relative humidity; \(c\) is typically near unity and \(n\) is typically in the range 0.20–0.33, taking values near 1/3 for \(h\) near unity, consistent with vapor-pressure lowering given by Raoult’s Law (Lewis & Randall, 1961). Approximations for radius ratios of this form are presented in Fig. 3 for ammonium sulfate and sodium chloride solutions in two ranges of fractional relative humidity, \(h_e < h < 0.90\) (where \(h_e\) is the efflorescence, or crystallization, relative humidity, below which solution drops do not exist), and 0.90 < \(h\) < 0.995 (the upper limit of measurements); the corresponding values of \(c\) and \(n\) and the accuracies of these expressions are presented in Table 1. For the lower relative humidity range the uncertainty in the measurements themselves is \(\sim 1\%\). For the higher relative humidity range much of the error in this parameterization results from the strong departure from ideality due to the electrolytic nature of the ionic solutions; greater accuracy would require a much more complicated expression (Lewis, 2006).

Table 1

<table>
<thead>
<tr>
<th>Solute</th>
<th>(h) range</th>
<th>(n)</th>
<th>(c)</th>
<th>Accuracy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((NH_4)_2SO_4)</td>
<td>0.37–0.90</td>
<td>0.22</td>
<td>1.05</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.90–0.995</td>
<td>1/3</td>
<td>0.81</td>
<td>3</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.45–0.90</td>
<td>0.265</td>
<td>1.31</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.90–0.995</td>
<td>1/3</td>
<td>1.09</td>
<td>3</td>
</tr>
</tbody>
</table>

Fig. 3. Radius ratio (relative to volume-equivalent dry radius), \(\xi \equiv r/r_{dry}\), of bulk solution drops of ammonium sulfate, \((NH_4)_2SO_4\), and sodium chloride, NaCl, at 25 °C. Also shown are power law approximations given by Eq. (8) as a function of fractional relative humidity \(h\) (upper panel) with coefficients chosen to provide good fits in two ranges of \(h\). Lower panel shows fractional error in the fits.
Evaluation of Eqs. (6) and (7) for the relation given by Eq. (8) yields

\[ \Delta \zeta = -\zeta \frac{n h}{1 - h^2}. \]  

(9)

and

\[ \Delta r = -r_\sigma \frac{n h}{1 - h^2}. \]  

(10)

Estimates for \( \Delta r \) can be obtained through substitution of \( r_\sigma,0(\approx 1.1 \text{ nm}) \) for \( r_\sigma \) and the choice \( n = 0.3 \) as a typical value to yield

\[ \frac{\Delta r}{\text{nm}} \approx \frac{-h/3}{1 - h}. \]  

(11)

For a given solute the quantity \( r_\sigma \) depends only on \( h \) and increases with decreasing \( h \) (increasing solute concentration); however, the decrease in the exponent \( n \) with decreasing \( h \) (Table 1) somewhat compensates for the increase in \( r_\sigma \), so that their product exhibits much less of a dependence on \( h \) than either quantity separately. The magnitude of the decrease according to this approximation, \( -\Delta r \), is also shown in Fig. 1 and is quite accurate over a wide range of \( h \) and \( r_{dry} \). As the magnitude of \( \Delta r \) increases with increasing \( h \) approximately as \((1 - h)^{-1}\) compared to the radius itself, which varies approximately as \((1 - h)^{-1/3}\), the fractional change in radius, and thus the importance of the Kelvin correction, increases with increasing relative humidity.

### 3.3. Range of validity of using only the lowest-order correction to the radius ratio

The range of validity of using only the lowest-order Kelvin correction to the radius from the bulk solution value can be determined from the relationship between \( h \) and \( r_{dry} \) for which this correction is a given fraction of the radius itself. The relationship will of course depend on the value chosen for the fraction; the (arbitrary) choice of 5% is made here. For a power-law dependence of \( \zeta \) on \( 1 - h \) given by Eq. (8), the fractional change in the radius due to the Kelvin effect can be obtained from Eq. (9) as

\[ \frac{\Delta r}{r} = \frac{\Delta \zeta}{\zeta} = -\frac{\zeta \sigma n h}{c(1 - h)^n} = -\frac{r_\sigma}{r_{dry}} \frac{n h}{c(1 - h)^{1-n}}. \]  

(12)

where \( r_\sigma \) depends on the concentration and thus on \( h \). Eq. (12) can be inverted to determine the value of \( r_{dry} \) below which the Kelvin effect makes more than a 5% decrease in the radius ratio as

\[ r_{dry,5\%} = \frac{r_\sigma}{0.05} \frac{n h}{c(1 - h)^{1-n}}. \]  

(13)

With \( r_\sigma \) taken as \( r_{\sigma,0} \) and for \( n = 1/3 \) and \( c = 0.95 \) (intermediate to the values for ammonium sulfate and sodium chloride solutions; Table 1), this becomes

\[ r_{dry,5\%} \approx \frac{8h}{(1 - h)^{2/3}}, \]  

(14)

shown in Fig. 4. Values of \( r_{dry,5\%} \) are also shown in Fig. 4 for solution drops of ammonium sulfate and sodium chloride determined from Eq. (1), evaluated as above. As \( r_{dry,5\%} \) is less than \( \sim 15 \text{ nm} \) for values of \( h \) below 0.75–0.80, in which range extrapolations are required for surface tension and thus for \( r_\sigma \) (Appendix A), the consequences of the uncertainty in these extrapolations is unimportant for a wide range of drops sizes.

An expression for the value of relative humidity \( h_{5\%} \) at a given \( r_{dry} \) above which neglect of the Kelvin effect results in more than a 5% decrease in the radius might in principle be obtained by inverting Eq. (12) or Eq. (14), but this is not in general possible. An estimate for this value (which provides a lower bound) can be obtained by taking \( h \) to be unity in the numerator of Eq. (12), yielding

\[ h_{5\%} > 1 - \left[ \frac{1}{0.05} \frac{r_\sigma}{c r_{dry}} \right]^{1/(1-n)} \]  

(15)

for \( r_\sigma \) taken as \( r_{\sigma,0} \), \( n = 1/3 \), and \( c = 0.95 \) (as above), this becomes \( h_{5\%} > 1 - [(8 \text{ nm})/r_{dry}]^{3/2} \).
These results imply that for sufficiently small solution drops \( r_{\text{dry}} < \sim 15 \text{ nm} \) the lowest-order correction to the radius is less than \( \sim 5\% \) only at low relative humidities, and therefore that under most situations in the atmosphere the Kelvin effect plays a large role in determining the sizes of such drops. Hence for such small drops application of formulations relating radius (or radius ratio) and relative humidity based on bulk solutions might result in substantial error.

3.4. Application to hygroscopic growth factor

Measurements of the hygroscopic growth factor \( g \), the ratio of the radius at relative humidity \( h_2 \) to that at \( h_1 \),

\[
g(h_1, h_2, \zeta) \equiv \frac{r(h_2, \zeta)}{r(h_1, \zeta)} = \frac{\zeta(h_2, \zeta)}{\zeta(h_1, \zeta)},
\]

have been used to infer composition of atmospheric aerosol particles, with particles consisting mostly of sodium chloride (such as sea salt aerosol particles) exhibiting larger growth factors (by \( \sim 40\% \)) than particles consisting mostly of sulfate, and particles consisting mainly of nonhygroscopic carbonaceous substances or crustal materials exhibiting growth factors near unity. For example, the values of \( \zeta(0.9, 0) \) for bulk solution drops of sodium chloride and ammonium sulfate, approximately equal to the growth factors from a low relative humidity to \( h = 0.9 \), are 2.4 and 1.7, respectively. Commonly \( g \) is examined as a function of the radius of the dried particle, measured with a tandem differential mobility analyzer (TDMA), to assess possible dependence of composition on this radius, with radii as low as 25 nm reported by McMurry and Stolzenburg (1989), by Zhang, McMurry, Hering, and Casuccio (1993), and by Svenningsson et al. (1997), 17.5 nm by Berg, Swietlicki, and Krejci (1998), and by Swietlicki et al. (2000), and 12 nm by Gasparini, Li, and Collins (2004). Thus it is necessary to examine the Kelvin effect on the growth factor \( g \) as a dependence on \( r_{\text{dry}} \).

Typically \( h_1 \) is chosen to be below the efflorescence relative humidity so that the particle is ostensibly dry, in which situation the lowest-order correction to the growth factor resulting from the Kelvin effect can be approximated using Eq. (16) as

\[
\Delta g(0, h, \zeta) \approx \Delta \zeta(h, \zeta) = \frac{\Delta r(h, \zeta)}{r_{\text{dry}}},
\]
where it is assumed that the dry radius measured using the TDMA (which is a mobility radius and thus requires a shape factor for nonspherical particles) is equal to the volume-equivalent radius \( r_{\text{dry}} \). The value of \( h_2 \) is typically chosen near 0.9, in which situation Eq. (11) can be used to obtain

\[
\Delta g(0, 0.9, \xi) \approx \frac{-3 \text{ nm}}{r_{\text{dry}}},
\]

with only a weak dependence on solute. For drops with \( r_{\text{dry}} = (10, 15, 25)\text{ nm} \), comparable to the smallest values of the radius for which growth factors have been measured, the lowest-order decrease due to the Kelvin effect in the hygroscopic growth factor from a low relative humidity to \( h = 0.9 \) given by Eq. (18) is \( \sim (0.3, 0.2, 0.1) \), an appreciable fraction of the growth factor itself. Hence failure to take into account the effect of particle size on the growth factor might result in misattribution of differences in growth factors to differences in composition.

3.5. Comparison with measurements of ammonium sulfate solution drops

The Kelvin effect on the equilibrium radius of an aqueous solution drop can be investigated through measurements of radii of very small drops as a function of relative humidity. Such data have been reported as growth factors \( g(0, h, \xi) \) for ammonium sulfate solution drops for various values of \( h \), measured using a TDMA by Hämeri, Väkevä, Hansson, and Laaksonen (2000) for dry radii of 4, 5, 7.5, 15, and 25 nm, and by T. Onasch (unpublished data) for dry radii of 2.4, 4.45, 10.0, 10.8, 25.15, and 27.3 nm. Some of these data are shown in Fig. 5. As noted above, the dry radii measured by a TDMA are not necessarily equal to the values of \( r_{\text{dry}} \), and thus these growth factors are not necessarily equal to radius ratios \( \xi(h, \xi) \); however, for comparison purposes the measured dry radii are assumed equal to \( r_{\text{dry}} \) values, and the growth factors are thus assumed to be equal to, and are compared with, radius ratios.

The measured growth factors of small drops are less than the growth factor of bulk solution drops by an amount that increases with decreasing \( r_{\text{dry}} \) and increasing \( h \). The decrease in the efflorescence relative humidity from the bulk value of \( \sim 0.37 \) to near \( \sim 0.30 \) is evident for drops with \( r_{\text{dry}} = 10 \) and 25 nm, and no efflorescence is apparent for drops with \( r_{\text{dry}} = 5 \) nm. The scatter within each size range of dry radius is a few percent, and for the most part the two data sets are consistent with each other, although for relative humidities less than \( \sim 0.6 \) the growth factors of Onasch for dry radii 4.5 nm are \( \sim 4-5\% \) lower than those of Hämeri et al. for dry radii 4 and 5 nm. For drops with \( r_{\text{dry}} = 10 \) and 25 nm the agreement between the theoretical prediction and the measurements is quite good for \( h \) above \( \sim 0.6 \), and within \( \sim 2\% \) at lower \( h \). For drops with \( r_{\text{dry}} = 5 \) nm the theoretical prediction yields values of the radius ratio for \( h < 0.6 \) that are greater than the measurements of Hämeri et al. by \( \sim 2\% \) and those of Onasch by \( \sim 5\% \), although at higher values of \( h \) the agreement is better.

The small differences between theory and measurement might be attributed to measurement uncertainty, the extrapolation required for surface tension for drops supersaturated with respect to the solute, and the assumptions that the dried particles were spherical and that the measured dry radii are equal to the stated \( r_{\text{dry}} \) values. Uncertainties in measured radii were stated by Onasch to be 1–2%, and those of Hämeri et al. were probably similar. Additionally, Hämeri et al. noted that their measured values differed somewhat from those determined from electrodynamic balance measurements, from which the vast majority of hygroscopic data in the supersaturated regime have been determined. Supersaturation of bulk ammonium sulfate solutions occurs at \( h = 0.80 \) (for which \( \xi = 1.49 \)), but the Kelvin effect increases this value to \( h = (0.95, 0.87, 0.83) \) for drops with \( r_{\text{dry}} = (5, 10, 25) \) nm; thus most of the measurements involved supersaturated drops and required large extrapolations of the surface tension (Appendix A). However, to account for the difference between the trend of the data and theory for values \( h < 0.6 \) would require that the dependence of surface tension on concentration be even greater, by more than a factor of two. Finally, overestimation of measured dry radii, resulting in underestimation of the radius ratios, could occur if the dried particles were not spherical or if they contained inclusions or any surface water. Small particles may contain some water, either as inclusions or on the surface, even when at relative humidities at which they are expected to be dry (Cziczo, Nowak, Hu, & Abbatt, 1997; Weis & Ewing, 1999; Cziczo & Abbatt, 2000). With regard to surface water uptake, the consequences would be greater for smaller particles, and only a small amount of uptake would be required to account for the differences between measurements and theory. For example, a surface monolayer of water (of thickness \( \sim 0.2 \) nm) on a dry particle with radius 5 nm results in a 4% increase in the radius—enough to account for the difference for drops of this size. When these factors are taken into consideration, it can be concluded that the agreement between theory and experiment for small drops of ammonium
sulfate is quite good and that the experiments are consistent with the expected behavior with regard to the Kelvin effect on equilibrium radius.

4. Previous parameterizations of the Kelvin effect

Several empirical expressions for the radius ratio as a function of relative humidity that contain a dependence on $r_{\text{dry}}$, and thus implicitly include the Kelvin effect, have previously been presented, although none of these has a physical basis and none contains a characteristic length scale which would allow it to be expressed in dimensionless form to explicitly indicate the dependences on surface tension and other pertinent quantities.

An expression for the radius ratio for a number of different inorganic solutes presented by Fitzgerald (1975) can be written in the form $\zeta = x r_{\text{dry}}^{\beta - 1}$, where $x = C \exp[0.066 h/(\Phi - h)]$, $C$ is a constant that depends only on the solute, $\Phi$ is a function of $h$, and $\beta = \exp[0.00077 h/(1.009 - h)]$ for all substances considered. The value of $x$ and therefore that of $C$ depend on the units of $r_{\text{dry}}$, which must be expressed in micrometers for the constants presented by Fitzgerald.

The limits of validity of this formulation were stated as $h = 0.81$–0.995 and $r_{\text{dry}} = 0.05$–3 $\mu$m, and it was further stated that the accuracy of this approximation decreases rapidly outside the limits. According to this formulation the ratio of the radii at two values of $h$ (i.e., the growth factor) depends only on $r_{\text{dry}}$ and is independent of the solute, in contrast to the known behavior of solutions of these solutes. The effect of surface tension is contained in the factor $r_{\text{dry}}^{\beta - 1}$, and as $\beta - 1$ takes its maximum value of 0.056 at $h = 0.995$, this factor, which can be written as $\exp[(\beta - 1) \ln(r_{\text{dry}}/\mu m)]$, ...
can be accurately approximated over the stated range of validity as $1 + (\beta - 1) \ln(r_{\text{dry}}/\mu\text{m})$. Thus according to this formulation the lowest-order correction to the radius due to surface tension is directly proportional to $(r_{\text{dry}})(\ln r_{\text{dry}})$, implying that for sufficiently large drops at a given $h$ this correction increases with increasing $r_{\text{dry}}$ instead of being independent of $r_{\text{dry}}$ as determined above.

The results of Fitzgerald for sea salt aerosol particles for $r_{\text{dry}}$ from 0.1 $\mu\text{m}$ to over 100 $\mu\text{m}$ were fitted by Andreas (1989, 1990) under the assumption that such particles behaved similarly to sodium chloride solution drops, yielding two expressions (depending on how Fitzgerald’s results were fitted) for the ratio of the radius of a drop at $h = 0.80$ to that at $h = 0.98$,

$$\frac{r(0.80)}{r(0.98)} = 0.5175[r(0.98)]^{-0.0244}$$

and

$$\frac{r(0.80)}{r(0.98)} = 0.4954[r(0.98)]^{0.0029},$$

where $r(0.98)$ is in micrometers. Under the assumption that sea salt aerosol particles have similar hygroscopic growth behavior to sodium chloride drops, for which $\zeta(0.98, 0) = 4.0$ and $\zeta(0.80, 0) = 2.0$, the ratio $r(0.80)/r(0.98)$ is approximated using Eq. (11) as $0.50 + (0.002\mu\text{m})/r_{\text{dry}}$, whereas the expressions presented by Andreas yield $0.50 - 0.012[\ln(r_{\text{dry}}/\mu\text{m})]$ and $0.50 + 0.0014[\ln(r_{\text{dry}}/\mu\text{m})]$ for this ratio (to lowest order). Thus according to these expressions the lowest-order correction to the radius due to the Kelvin effect does not approach zero with increasing $r_{\text{dry}}$, contrary to the results obtained above.

Another expression for the radius ratio as a function of fractional relative humidity up to and including values of $h$ equal to unity, and which thus implicitly includes the Kelvin effect, was proposed by Gerber (1985). Although this expression provides fairly accurate values for the radius ratio as $h$ approaches unity, it does not provide the correct lowest-order correction to the radius ratio at values of $h$ far from unity. This expression is discussed further in Lewis (2006).

5. Summary

An expression for the change in the equilibrium radius of a solution drop due to the Kelvin effect has been presented as a function of relative humidity, together with an approximation that is accurate over a wide range of relative humidities and drop sizes. The novel result was obtained that at a given relative humidity the lowest-order decrease in the equilibrium radius resulting from the Kelvin effect is independent of the mass of solute in the drop and depends only weakly on the composition of the solute. This decrease ranges from $\sim 0.35 \text{ nm}$ at 50% RH to $\sim 3 \text{ nm}$ at 90% RH and $\sim 35 \text{ nm}$ at 99% RH. Formulæ are also presented for the range of dry radii for which the Kelvin effect results in more than a given fractional decrease in radius at a given RH, and for the decrease in the hygroscopic growth factor as a function of dry radius resulting from the Kelvin effect. These results readily allow determination of the range of relative humidities and particle sizes for which the Kelvin effect is important.

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Appendix A. Surface tension of supersaturated solutions

The dependences on solute concentration of $\overline{v}_w$ and $\sigma$, and hence of $r_\sigma$, are required for evaluation of various expressions and quantities presented in this paper. These dependences are accurately known for bulk solutions that are subsaturated with respect to the solute (i.e., water activities greater than 0.80 for ammonium sulfate and 0.75 for sodium chloride), and accurate measurements have been reported for densities (from which the partial molal volumes
of water can be calculated) of supersaturated solutions of ammonium sulfate (Tang & Munkelwitz, 1994) and sodium chloride (Tang, 1996), but no measurements have been reported for surface tension in the supersaturated regime. Hence values that are used for surface tension for solutions that are supersaturated with respect to the solute are necessarily extrapolations.

One expression for the surface tension for supersaturated ammonium sulfate solutions is that proposed by Korhonen, Laaksonen, Batris, and Viisanen (1998), a seventh-order polynomial in solute mass faction based primarily on six values of $\Delta \sigma (\equiv \sigma - \sigma_w)$ for subsaturated ammonium sulfate solutions from Vol. 4 of International Critical Tables (Young & Harkins, 1928, p. 464). However, as these data could be fitted to a single-parameter expression (in molality) to within stated uncertainties (3–9%), it would appear that little justification can be made for this mode of extrapolation.

The alternative approach taken here for evaluation of the dependence on solute concentration of the surface tension and thus of values that are used for surface tension for solutions that are supersaturated with respect to the solute are necessarily extrapolations based on linear relations for subsaturated solutions.

Table 2

<table>
<thead>
<tr>
<th>Solute</th>
<th>$a_w$</th>
<th>$\sigma / \sigma_w$</th>
<th>$\tau_w / \tau_{w,0}$</th>
<th>$r_f / r_{f,0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>0.80</td>
<td>1.20</td>
<td>0.96</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>1.60$^a$</td>
<td>0.90</td>
<td>1.45$^a$</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.75</td>
<td>1.15</td>
<td>0.99</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>1.35$^a$</td>
<td>0.97</td>
<td>1.30$^a$</td>
</tr>
</tbody>
</table>

$^a$Values of the surface tension and hence $r_f$ for supersaturated solutions are extrapolations based on linear relations for subsaturated solutions.

A possible approach that could be used to determine the surface tension of supersaturated solutions and its dependence on concentration is to measure the resonant frequencies of shape oscillations of a supersaturated solution drop suspended in an electrodynamic balance. The resonant frequency of the $j$th mode of such an oscillation for an isolated drop with radius $r$, density $\rho$, surface tension $\sigma$, dielectric constant $\varepsilon$, and containing charge $q$, is given by

$$f_j \text{ Hz} = \frac{1}{2\pi} \left[ \frac{j(j-1)(j+2)}{\rho r^3} \right]^{1/2} \left[ \sigma - \frac{q^2(1 - (1/\varepsilon))}{16\pi \varepsilon_0 r^3 (j + 2)} \right]^{1/2},$$

(Lord Rayleigh, 1882). The charge on the drop, which can be obtained from characteristics of the electrodynamic balance, typically has negligible effect on the equilibrium vapor pressure of a drop, although its effect on the resonant frequency of oscillation might not be negligible. For a typical values for density $1.5 \text{ g cm}^{-3}$ and surface tension $100 \text{ g s}^{-2}$, the lowest nonzero frequency $(j = 2)$ is $\sim 10^5 \text{ Hz}$ for a drop with $r = 10 \mu$m and $\sim 3 \times 10^5 \text{ Hz}$ for a drop with $r = 5 \mu$m, if the term containing the charge can be neglected. Eq. (A.1) can be inverted to yield

$$\sigma = \frac{\pi^2 \rho r^3 f_j^2}{2} + \frac{q^2(1 - (1/\varepsilon))}{64\pi \varepsilon_0 r^3},$$

(A.2)

which allows determination of surface tension from measurement of the lowest nonzero resonant frequency together with knowledge of the radius, density, and charge (results would be insensitive to the value of $\varepsilon$ as it is typically much
greater than unity). This method might also be employed to determine the kinematic viscosity of the solution \( \nu \), as an unforced shape oscillation of mode \( j \) of a drop decays exponentially with characteristic time \( \tau_j \) given by

\[
\tau_j = \frac{r^2}{(j - 1)(2j + 1)\nu}
\]

(A.3)

(Lamb, 1932, Section 355).

References


