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Stochastic approach to chemical kinetics in ultrafine aerosols

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Abstract

We consider chemical reactions taking place in aerosol droplets when the mean number of reactant molecules present is less than unity. Situations of this kind are possible for ultrafine droplets in an atmosphere containing trace amounts of gas phase reactants. We describe an analytic description of such ‘stochastic’ chemistry, and compare the results with the predictions of traditional chemical kinetics. We establish criteria to indicate when the traditional approach can overpredict a reaction rate considerably. We determine that it is rare for such conditions to occur in the atmosphere.

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1. Introduction

Aerosols play a key role in the chemical evolution of their environment (Seinfeld & Pandis, 1998). For example, water droplets in the atmosphere provide tiny ‘reaction vessels’ within which aqueous phase chemistry can take place. Similarly, solid particles provide surfaces on which heterogeneous reactions can occur. These processes can be modelled by the usual rate equations of chemical kinetics, and complex schemes have been developed for atmospheric processes. But consider the following point. The number of molecules N of a trace atmospheric gas dissolved in a droplet will depend on its partial pressure p , the size of the droplet V and the Henry’s Law constant k_H according to

$$N = N_A 10^3 k_H p V, \quad (1)$$

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where N_A is Avogadro's number, p is in atm, V is in m^3 and k_H is in units of M atm^{-1} . Taking ozone as an example, present in the lower atmosphere typically at a concentration of 10 ppb ($p \approx 10^{-8}$ atm), with $k_H = 1.1 \times 10^{-2}$ in the quoted units for dissolution in water, we find that $N = 0.28$ for a droplet of radius 1 μm . It would appear that any aqueous phase ozone chemistry taking place in droplets of this size is operating in a regime where the (mean) reactant population is less than unity. Now, the standard treatment of chemical kinetics is designed for reaction vessels containing moles of reactants, and the reaction rate is taken to be proportional to the product of mean reactant concentrations. But for small mean populations this assumption is surely wrong: fluctuations in population are very strong and to calculate the reaction rate we should surely consider the mean of the product of concentrations rather than the product of the means. Is the standard treatment of aerosol chemistry suspect?

This is the matter we wish to address in this paper. Several papers have appeared recently addressing the very same question in the field of astrochemistry (Green et al., 2001; Biham, Furman, Pirronello, & Vidali, 2001; Stantcheva, Shematovich, & Herbst, 2002). These authors consider the simple reaction $\text{H} + \text{H} \rightarrow \text{H}_2$, which is an important reaction in the evolution of the cosmic chemical environment. Although the gas phase reaction is inefficient under interstellar conditions (Gould & Salpeter, 1963), heterogeneous reactions can occur quite efficiently on the surfaces of dust grains. The recent studies have shown that the mean population of atomic hydrogen on each particle can be very much less than unity, and that traditional heterogeneous chemical kinetics significantly overpredicts the molecular hydrogen production rate (Green et al., 2001; Biham et al., 2001). Are any atmospheric reactions in the same category?

We outline the stochastic chemistry approach in the next section and as an example, describe an analytic solution. We compare the results of this analysis with the results of traditional chemical kinetics. We provide rough criteria allowing the use of standard rate equations to describe heterogeneous chemistry in the atmosphere. We find that low mean populations of reactants are not the only factors in determining whether a different description is necessary: the relative timescale for aqueous phase reactions is important too. We describe numerical methods and consider various possible applications. Finally, we summarise our conclusions.

2. The stochastic limit

The need for a stochastic approach to chemical kinetics in the presence of strong population fluctuations has long been recognised and has been addressed in different ways. Gillespie (1976, 1977) developed numerical methods for simulating the time evolution of stochastic chemical systems involving several coupled reactions. A stochastic master equation approach was applied to the chemistry occurring in micelles by Hatlee and Kozak (1980, 1981a, b), and the presence of small mean populations of reactants in atmospheric aerosol particles has recently been noted (Mozurkewich, 1997).

In the astrochemical literature attempts have been made (Caselli, Hasegawa, & Herbst, 1998; Shalabiea, Caselli, & Herbst, 1998; Ruffle & Herbst, 2000) to address this problem by modifying the classical chemical rate equations in such a way as to match the results of Monte Carlo simulations (Charnley, 1998). However these approaches are rather empirical. A more fundamental approach is to develop the kinetics of the *probability distributions* for the number of adsorbed molecules on the

particle. This is what we call the ‘stochastic chemistry’ approach. We need to determine how these distributions, rather than the mean populations, evolve in time. The evolution of mean populations is a characteristic of traditional chemical kinetics, which we shall term the ‘classical’ approach.

To illustrate this, consider an analytical solution to a problem in stochastic chemistry, suggested by one of us (Lushnikov, 1999), and derived independently by Green et al. (2001). The problem is a simple reaction involving two molecules of one type of reactant A forming a product C.

2.1. Reaction $A + A \rightarrow C$

2.1.1. Stochastic approach

Let $W(N, t)$ be the probability of finding exactly N molecules of A dissolved in the droplet. We can then write down a so-called master equation governing the time evolution of $W(N, t)$:

$$\begin{aligned} \frac{dW(N, t)}{dt} = & j_A [W(N-1, t) - W(N, t)] \\ & + \frac{\kappa}{V} [(N+2)(N+1)W(N+2, t) - N(N-1)W(N, t)] \\ & + \lambda_A [(N+1)W(N+1, t) - NW(N, t)]. \end{aligned} \quad (2)$$

The first two terms in squared brackets describe changes in population due to the absorption of a molecule from outside the droplet. The term $j_A W(N-1, t)$ represents the increase of the probability of finding N dissolved molecules through the attachment of molecules at a rate j_A to a droplet containing $N-1$ molecules, which is to be found with probability $W(N-1, t)$. The term $j_A W(N, t)$ describes the decrease in probability of finding N molecules in the droplet, through a similar attachment process to a droplet already containing N molecules.

The second group of terms corresponds to population changes due to a binary reaction taking place with a rate constant κ . V is the volume of the droplet. The probability of finding $N+2$ molecules is $W(N+2, t)$, and the probability of finding N molecules increases at a collision rate $2\kappa/V$ multiplied by the number of pairs of A molecules that can be found amongst the $N+2$ molecules, namely $(N+2)(N+1)/2$. The third group describes the changes in population due to the evaporation of a molecule from the droplet, occurring at a rate λ_A . Factors of N , etc., appear where necessary to give the correct coefficients. The initial and normalisation conditions completely define the solution to Eq. (2).

This scheme replaces the much simpler equation of classical chemical kinetics:

$$\frac{d\bar{N}}{dt} = j_A - \frac{2\kappa}{V} \bar{N}^2 - \lambda_A \bar{N}, \quad (3)$$

where \bar{N} is the average number of A-molecules in the droplet. The terms on the right-hand side correspond, respectively, to deposition, reaction and evaporation. This equation can in fact be derived from Eq. (2), by multiplying both sides by N , summing over N , and regarding \bar{N} as large. The left-hand side becomes $d\bar{N}/dt$. The first term on the right-hand side of Eq. (2) leads to $j_A \sum_{N=1}^{\infty} NW(N-1, t) = j_A(\bar{N} + 1)$, and the second becomes $-j_A \sum_{N=0}^{\infty} NW(N, t) = -j_A \bar{N}$. The terms proportional to κ yield $(\kappa/V)((N-2)N(N-1) - N^2(N-1))$, and the evaporation terms give

$\lambda_A(\overline{(N-1)N} - \overline{N^2})$. Altogether, the exact equation for the evolution of the mean population is

$$\frac{d\bar{N}}{dt} = j_A - \frac{2\kappa}{V}\overline{N(N-1)} - \lambda_A\bar{N} \quad (4)$$

and for large \bar{N} we can replace $\overline{N(N-1)}$ by \bar{N}^2 , thus recovering Eq. (3). The associated equation for the change in concentration of C-molecules may be shown to be $d[C]/dt = \kappa[A]^2$: the canonical expression for first-order chemical kinetics (the square brackets denoting concentrations), and in effect a defining equation for the reaction coefficient κ . Clearly, the details of the population distribution, apart from its mean, are lost by such a procedure.

In order to solve the master equation (2) let us introduce a so-called generating function (van Kampen, 1981):

$$F(z) = \sum_{N=0}^{\infty} z^N W(N). \quad (5)$$

It can be shown that in the steady state (when $dW/dt = 0$), the master equation reduces to the following ordinary differential equation for $F(z)$:

$$\frac{\kappa}{V}(z+1)\frac{d^2F}{dz^2} + \lambda_A\frac{dF}{dz} - j_AF = 0. \quad (6)$$

This can be demonstrated by substituting expressions for $F(z)$ and its derivatives into Eq. (6) and expanding the summations explicitly, giving an infinite series with ascending powers of z . We focus on some particular value of N , collect terms in z^N from the series and equate them to zero, as required by Eq. (6). This gives

$$0 = \frac{\kappa}{V}[(N+1)NW(N+1) + (N+2)(N+1)W(N+2)] + \lambda_A(N+1)W(N+1) - j_AW(N). \quad (7)$$

Performing a similar procedure for terms in z^{N-1} gives

$$0 = \frac{\kappa}{V}[N(N-1)W(N) + (N+1)NW(N+1)] + \lambda_ANW(N) - j_AW(N-1) \quad (8)$$

and by subtracting Eq. (8) from Eq. (7), the steady-state version of the master equation (2) is recovered. Solving the ordinary differential equation (6), is equivalent to solving the original master equation, but the problem is simplified considerably. This is the purpose of introducing the generating function.

Let us now define two parameters X and ν as

$$X = j_A/\lambda_A \quad (9)$$

and

$$\nu = \frac{V\lambda_A}{\kappa} - 1. \quad (10)$$

X is the ratio of the rates of molecular absorption and desorption. It is therefore related to the gas-particle equilibrium constant, or equivalently the Henry's Law constant k_H . ν is related to the absorbed phase branching ratio: the rate of loss of A-molecules by desorption (λ_A) divided by the rate of loss by reaction (κ/V). Since all the individual parameters contributing to the definitions

of X and ν are always positive, $0 \leq X \leq \infty$ and $-1 \leq \nu \leq \infty$. When the gas-phase concentration of molecules and the particle size are both small, both X and ν will lie at the lower end of the allowed ranges. It is also useful to define another parameter $\zeta = 2\sqrt{X(\nu + 1)(1 + z)}$.

The solution of Eq. (6) may now be obtained through use of the following approach (Gradshteyn & Ryzhik, 1994; Lushnikov, 1999; Green et al., 2001). We start with a trial solution of the form:

$$F(z) = F_0(1 + z)^{-\nu/2}\phi(\zeta), \tag{11}$$

where F_0 is a constant and ϕ is some function of ζ . Inserting this expression into Eq. (6) produces the following differential equation for ϕ :

$$\zeta^2 \frac{d^2\phi}{d\zeta^2} + \zeta \frac{d\phi}{d\zeta} - (\zeta^2 + \nu^2)\phi = 0. \tag{12}$$

The solutions to Eq. (12) are the modified Bessel functions $I_\nu(\zeta)$ and $K_\nu(\zeta)$ (Abramowitz & Stegun, 1972). The general solution may therefore be expressed as

$$F(z) = A(1 + z)^{-\nu/2}I_\nu(\zeta) + B(1 + z)^{-\nu/2}K_\nu(\zeta), \tag{13}$$

where A and B are constants. However, the K_ν term is discarded for reasons described in the Appendix A. The constant A can then be evaluated by noting that $F(1) = \sum W(N) = 1$ by normalisation of $W(N)$. This implies that

$$A = 2^{\nu/2}(I_\nu(2\sqrt{2X(\nu + 1)}))^{-1} \tag{14}$$

which leads to the solution

$$F(z) = \left(\frac{1 + z}{2}\right)^{-\nu/2} \frac{I_\nu(2\sqrt{X(\nu + 1)(1 + z)})}{I_\nu(2\sqrt{2X(\nu + 1)})}. \tag{15}$$

To recap, we have solved a differential equation which is equivalent to a complicated master equation for a set of processes in population dynamics. The solution to the differential equation is the so-called generating function $F(z)$, and it takes the form of a modified Bessel function. This is a complicated mathematical expression, but it can be evaluated readily enough, and we can analyse it in various ways, to be explored in the next section. But what can it tell us about the statistical problem that we started with?

The generating function $F(z)$ is very useful since differentiating it generates moments of the probability distribution, and hence the solution to the steady-state population dynamics. The mean population of A-molecules in the particle is related to the derivative of $F(z)$ at $z = 1$:

$$\bar{N} = \sum_{N=0}^{\infty} NW(N) = \left. \frac{dF}{dz} \right|_{z=1}. \tag{16}$$

We therefore write $F(z) = A(1 + z)^{-\nu/2}I_\nu(\zeta)$ and differentiate to give

$$\frac{dF}{dz} = -A \frac{\nu}{2} (1 + z)^{-\nu/2-1} I_\nu(\zeta) + A(1 + z)^{-\nu/2} \frac{dI_\nu}{d\zeta} \frac{d\zeta}{dz}. \tag{17}$$

Using standard mathematical identities involving Bessel functions (Abramowitz & Stegun, 1972) such as

$$\frac{dI_\nu(r)}{dr} = \frac{1}{2}[I_{\nu-1}(r) + I_{\nu+1}(r)] \quad \text{and} \quad I_{\nu-1}(r) - I_{\nu+1}(r) = \frac{2\nu}{r} I_\nu(r), \quad (18)$$

we obtain

$$\begin{aligned} \frac{dF}{dz} &= -A \frac{\nu}{2} (1+z)^{-\nu/2-1} I_\nu(\zeta) + A(1+z)^{-\nu/2} \left(I_{\nu+1}(\zeta) + \frac{\nu}{\zeta} I_\nu(\zeta) \right) \frac{1}{2} C(1+z)^{-1/2} \\ &= A \frac{C}{2} (1+z)^{-(\nu+1)/2} I_{\nu+1}(\zeta), \end{aligned} \quad (19)$$

where $C = 2\sqrt{X(\nu+1)}$. Evaluating this derivative at $z = 1$, and using Eq. (14) leads to the final result

$$\bar{N}_{\text{stochastic}} = \sqrt{\frac{X(\nu+1)}{2}} \frac{I_{\nu+1}(2\sqrt{2X(\nu+1)})}{I_\nu(2\sqrt{2X(\nu+1)})}. \quad (20)$$

The suffix denotes that this is the solution to the stochastic kinetics problem. The mean number of A-molecules in the droplet is therefore given by a ratio of modified Bessel functions. We can proceed further. The average production rate of C-molecules is also related to moments of the probability distribution:

$$j_C^{\text{stochastic}} = \frac{\kappa}{V} \sum_{N=0}^{\infty} N(N-1)W(N). \quad (21)$$

This is a sum of terms each of which is a product of a collision rate $2\kappa/V$ and the number of pairs available for a group of N molecules, multiplied by the probability that N molecules were actually present in the drop. However, the right-hand side of Eq. (21) is also equal to the second derivative of $F(z)$ at $z = 1$, i.e. $(\kappa/V) d^2F/dz^2|_{z=1}$, and we can evaluate this by differentiating Eq. (19) and using the identities (18) again. After some straightforward algebra, we get the result

$$j_C^{\text{stochastic}} = \frac{j_A}{2} \frac{I_{\nu+2}(2\sqrt{2X(\nu+1)})}{I_\nu(2\sqrt{2X(\nu+1)})}. \quad (22)$$

Expressions (20) and (22) for the mean A-population and the mean C production rate, characterise the solution to the stochastic problem. In the next section, we compare these results with the predictions of traditional chemical rate theory.

2.1.2. Comparison with classical approach

In order to extend our understanding of the stochastic results given in Eqs. (20) and (22), it is useful to contrast them with the corresponding results of traditional, or classical chemical kinetics. To obtain the classical mean population of A-molecules in a steady state, we set $d\bar{N}/dt = 0$ in Eq. (3). This leaves a simple quadratic equation in \bar{N} , the appropriate solution to which is

$$\bar{N}_{\text{classical}} = \frac{-\lambda_A + (\lambda_A^2 + 8(\kappa/V)j_A)^{1/2}}{4\kappa/V} \quad (23)$$

which in terms of the dimensionless X and ν variables is

$$N_{\text{classical}} = \left[\left(\frac{\nu + 1}{4} \right)^2 + \left(\frac{X(\nu + 1)}{2} \right) \right]^{1/2} - \left(\frac{\nu + 1}{4} \right). \tag{24}$$

Similarly, the classical expression for the C production rate is simply

$$j_C^{\text{classical}} = \frac{\kappa}{V} \bar{N}_{\text{classical}}^2. \tag{25}$$

The stochastic results should agree with classical theory in certain limits. For example, when $X \rightarrow \infty$ for fixed ν (j_A becoming very large for fixed λ_A and κ) the mean population becomes large as a consequence of the greater absorption rate. This is clearly a regime where the stochastic and classical treatments should coincide. Correspondingly, Eq. (20) becomes, in this limit:

$$\bar{N}_{\text{stochastic}} \approx \left(\frac{X(\nu + 1)}{2} \right)^{1/2} - \frac{2\nu + 1}{8} + \dots \tag{26}$$

having used the standard result (Abramowitz & Stegun, 1972):

$$I_n(x) \rightarrow \frac{e^{-x}}{\sqrt{2\pi x}} \left[1 - \frac{4n^2 - 1}{8x} + \dots \text{higher order terms in } \frac{1}{x} \right] \quad \text{as } x \rightarrow \infty. \tag{27}$$

Expanding Eq. (24) in $1/X$ gives

$$\bar{N}_{\text{classical}} \approx \left(\frac{X(\nu + 1)}{2} \right)^{1/2} - \frac{2\nu + 2}{8} + \dots \tag{28}$$

and so the leading terms in the classical and stochastic expressions for \bar{N} agree as $X \rightarrow \infty$.

Secondly, the limit $\nu \rightarrow \infty$ at fixed X corresponds to a vanishing reaction rate κ . The C molecule production rate should fall to zero in both treatments, and for reasons discussed at the end of Section 2.1.3, the two treatments should give the same rate as the limit is approached. We can check this here by algebraic manipulation of the Bessel functions in the stochastic solutions. Using the result $I_\nu(r) \sim (2\pi\nu)^{-1/2} (r/(2\nu))^\nu$ for large ν (Abramowitz & Stegun, 1972) we can show that $N_{\text{stochastic}} \rightarrow X$, in agreement with the classical result (24) in this limit.

A limit where correspondence between the classical and stochastic approaches is not expected is $\nu \rightarrow -1$ for fixed X . A useful comparison can be made in this limit with an approach by Mozurkewich (1997). This arises when κ/V is very much greater than λ_A , corresponding to virtually instantaneous reaction between the A-molecules. In this case $N_{\text{stochastic}}$ may be rewritten using the general series representation (Abramowitz & Stegun, 1972):

$$I_\nu(r) = \left(\frac{r}{2} \right)^\nu \sum_{k=0}^{\infty} \frac{(r^2/4)^k}{k! \Gamma(\nu + k + 1)} \tag{29}$$

which after some algebra leads to the result

$$\bar{N}_{\text{stochastic}} = \frac{X}{1 + 2X} \left[1 + \frac{2X(1 - X)}{(\nu + 2)} \varepsilon + O(\varepsilon^2) \right]. \tag{30}$$

where $\varepsilon = \nu + 1$. If ε is very small ($\nu \rightarrow -1$), the factor in squared brackets can be replaced by unity. If we now consider large X , then $\bar{N} \sim 0.5$. This is in agreement with the result obtained

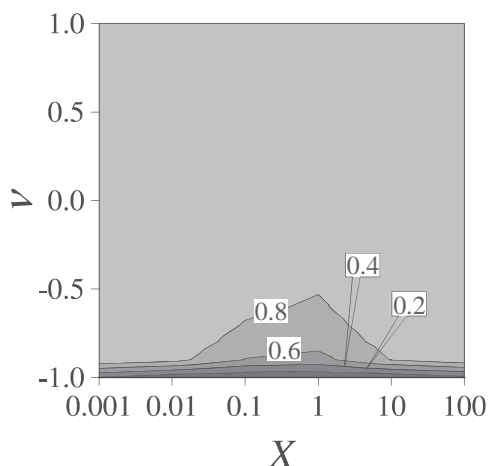


Fig. 1. Contour plot of the ratio $\bar{N}_{\text{classical}}/\bar{N}_{\text{stochastic}}$ as a function of X and ν . The values quoted in white boxes refer to the boundaries between the different shaded regions. The ratio is zero at $\nu = -1$ for all X since $\bar{N}_{\text{classical}}$ falls to zero. The stochastic model yields similar results to the classical rate equations in the limits $X \rightarrow 0$, $X \rightarrow \infty$ or $\nu \rightarrow \infty$.

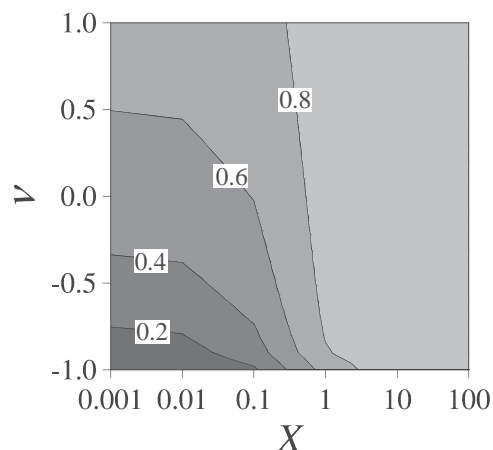


Fig. 2. Contour plot of the ratio $j_{\text{C}}^{\text{stochastic}}/j_{\text{C}}^{\text{classical}}$ as a function of X and ν .

by Mozurkewich (1997) who considered a system where desorption processes were absent: in our terms $\lambda_{\text{A}} = 0$ so $\nu = -1$ and $X = \infty$. Our analysis therefore includes Mozurkevich's problem as a special case.

It is useful to be able to compare Eqs. (20) and (24) pictorially as well as mathematically. Fig. 1 is a contour plot of the ratio $\bar{N}_{\text{classical}}/\bar{N}_{\text{stochastic}}$ as a function of X and ν . Where the ratio is close to unity, the two approaches correspond; where this is not the case, then the stochastic methods are necessary to get the right answers. The comparison is extended in Fig. 2 by plotting the ratio $j_{\text{C}}^{\text{stochastic}}/j_{\text{C}}^{\text{classical}}$ over a range of X and ν . Fig. 3 illustrates some cuts through this plot at fixed values of X . The difference between the approaches, as regards the production rate of C-molecules, is greatest when both X and ν are less than unity. This is the key conclusion to be drawn from the present mathematical analysis. In these circumstances, the stochastic treatment gives a lower C-production rate and a higher mean A-population than the classical treatment. The plots in Figs. 1 and 2 therefore give us a rough idea of the range of applicability of traditional, classical chemical kinetics.

2.1.3. Applications

Figs. 1 and 2 tell us when a classical treatment of the reaction $\text{A} + \text{A} \rightarrow \text{C}$ will fail. For practical use, however, we need to express the mathematical variables X and ν in terms of experimental parameters such as the Henry's Law constant k_{H} , the reaction rate κ and the radius r of the aerosol droplet. The X variable is the easier of the two: in the absence of reaction, $X = j_{\text{A}}/\lambda_{\text{A}}$ is just equal to \bar{N} , and using Eq. (1) we can write $X = N_{\text{A}}10^3 k_{\text{H}} p_{\text{T}} r^3$, leading to the required condition:

$$X = 2.5 \times 10^9 k_{\text{H}} f p_{\text{T}} r^3 < 1, \quad (31)$$

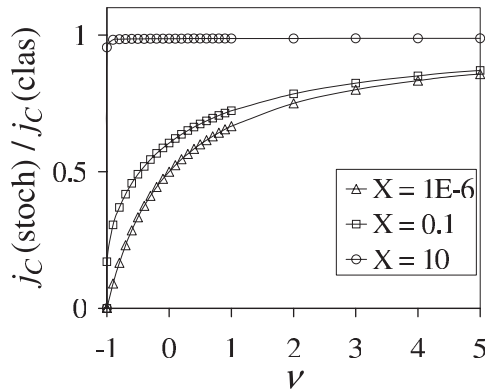


Fig. 3. Some cuts through Fig. 2: C-molecule production rate according to the stochastic model divided by the prediction of the classical rate equations, as a function of the parameter ν . The difference between the two models emerges when X and ν are small.

where k_H is in Matm^{-1} , f is the gas phase volume fraction of A-molecules, p_T is the total pressure in atmospheres, and r is the droplet radius in μm . As we saw in the Section 1, this condition is often satisfied in typical atmospheric conditions.

The condition $\nu < 1$ can also be recast. If we use $\lambda_A = j_A/X$, together with $j_A = 4\pi r^2 p / (2\pi mkT)^{1/2}$, where p is the vapour pressure and m the molecular mass of species A, together with Eq. (1), then the condition becomes

$$\frac{\nu + 1}{2} = 10^{17} \frac{r^2}{\kappa k_H n^{1/2}} \left(\frac{273}{T} \right)^{1/2} < 1, \tag{32}$$

where κ is in $\text{M}^{-1} \text{s}^{-1}$, n is the mass of an A-molecule in proton masses, T is the temperature in K, k_H is in Matm^{-1} and r is in μm . This condition may be fulfilled either through having a large k_H (or equivalently a small evaporation rate λ_A), a large reaction rate κ , or a small droplet radius r .

Now let us insert some example physical parameters. Seinfeld and Pandis (1998) provide a convenient compilation of aqueous phase chemical reactions, and a few can be found taking the form $A + A \rightarrow C$. The hydroperoxyl radical HO_2 dissolves in water with a Henry's Law constant of $k_H = 2 \times 10^3 \text{ Matm}^{-1}$ at 298 K and then dissociates into $\text{H}^+ + \text{O}_2^-$, with a dissociation constant $K_e = 3.5 \times 10^{-5} \text{ M}$. There are three reactions which can then take place. The first of these involves the combination of two dissolved HO_2 radicals to form hydrogen peroxide H_2O_2 :



for which the rate constant is $\kappa_1 = 8.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (Bielski, Cabelli, & Arudi, 1985). The second reaction involves a dissolved HO_2 and a superoxide anion:



where the rate constant is $\kappa_2 = 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Bielski et al., 1985). Finally, it is possible for two superoxide anions to combine:



but the reaction rate is so low ($\kappa_3 < 0.3 \text{ M}^{-1} \text{ s}^{-1}$) that we shall ignore this process here.

It is possible to regard all three reactions (even reaction 2) as members of the class $A + A \rightarrow C$. How can this be justified? We first of all note that the dissolved hydroperoxyl radicals are in equilibrium with superoxide anions: $\text{HO}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^-$. On the microscopic scale a particular O_2^- can capture a proton and later on lose it again as it moves through the droplet. This happens rapidly on the timescale of encounters with another superoxide ion, since protons are much more numerous in the droplet. We therefore regard the dissolved hydroperoxyl radical as species A, whether or not it has lost a proton to become a superoxide ion. When this species A encounters a potential reaction partner (O_2^- or HO_2), the probability $p(\text{HO}_2)$ that it will be in its HO_2 state can be computed from the dissociation constant K_e , defined by $K_e = [\text{O}_2^-][\text{H}^+]/[\text{HO}_2]$, that is

$$p(\text{HO}_2) = \frac{[\text{HO}_2]}{[\text{HO}_2] + [\text{O}_2^-]} = \left(1 + \frac{K_e}{[\text{H}^+]}\right)^{-1}. \quad (36)$$

Similarly, we can determine the probability that the reaction partner is O_2^- or HO_2 . From this point of view, reaction 1 above is of the class $A + A \rightarrow C$ with rate constant $\kappa'_1 = \kappa_1 p(\text{HO}_2)p(\text{HO}_2)$. Similarly, reaction 2 is an $A + A \rightarrow C$ reaction with rate coefficient given by $\kappa'_2 = \kappa_2 p(\text{HO}_2)p(\text{O}_2^-)$, with

$$p(\text{O}_2^-) = \frac{[\text{O}_2^-]}{[\text{HO}_2] + [\text{O}_2^-]} = 1 - p(\text{HO}_2). \quad (37)$$

In this way, the correlations in population of the reactants HO_2 and O_2^- in reaction 2 are brought out, and the effects on the chemical kinetics can be examined.

At pH=6, for example, $[\text{H}^+] = 10^{-6}$ and $p(\text{HO}_2) = 1/36$. Most of the dissolved HO_2 is then present as O_2^- . The rates of the two reactions are then $\kappa'_1 = 7.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $\kappa'_2 = 2.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Reaction 2 dominates under these conditions, and will continue to do so for higher pH. For more acidic conditions, on the other hand, $p(\text{O}_2^-)$ falls and κ'_2 becomes smaller than κ'_1 , and for these conditions, reaction 1 dominates.

For both reactions, we need to determine the effective Henry's Law constant k'_H for species A. Since $[\text{A}] = [\text{HO}_2] + [\text{O}_2^-]$ we deduce that

$$k'_H = k_H \left(1 + \frac{K_e}{[\text{H}^+]}\right) \quad (38)$$

which at pH = 6 yields $k'_H = 36k_H = 7.2 \times 10^4 \text{ M atm}^{-1}$ at 298 K.

Focussing on conditions at pH = 6, and with the parameters k'_H and κ'_2 specified above, together with $f = 40$ ppt, $p_T = 1$ atm, $n = 33$ and $r = 0.1 \mu\text{m}$, the left-hand side of Eq. (31) (corresponding to X) is equal to 7.2. This criterion is therefore not quite satisfied for these conditions; it would require a reduction in particle radius to 50 nm to fulfil this criterion.

More critically, putting the parameters into Eq. (32), we find that $(v + 1)/2$ is around 857, a value far greater than unity. The second criterion for the failure of a classical treatment, Eq. (32), is satisfied only when we reduce the droplet radius to about 3.5 nm. For such small droplets curvature effects are likely to appear (probably increasing the evaporation rate λ_A), so there is no guarantee that the Henry's Law constant remains the same. In any case, chemistry on such tiny droplets is unlikely to be important in the atmosphere, and we can conclude that it is appropriate to treat these reactions according to classical kinetics.

A second example is the self-reaction of NO_2 in water, giving nitrate and nitrite ions (Seinfeld & Pandis, 1998). The relevant data are $k_{\text{H}} = 1.0 \times 10^{-2} \text{ M atm}^{-1}$ and $\kappa = 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, so for $r = 0.1 \mu\text{m}$, $p_{\text{T}} = 1 \text{ atm}$, $n = 46$ and $f = 1 \text{ ppb}$, we have $X = 2.5 \times 10^{-5}$. For the second criterion, however, we have $(v + 1)/2 = 1.5 \times 10^8$. This exceeds the threshold by many orders of magnitude and the reaction definitely does not need a stochastic treatment. This is in spite of the fact that the mean population of dissolved NO_2 is less than unity in this example.

It is the second failure criterion (32) which is clearly harder to fulfil. The crucial qualifying conditions are a high reactant solubility (or Henry's Law constant) and a rapid reaction rate, together with a small droplet radius. The application of these methods to $\text{H} + \text{H} \rightarrow \text{H}_2$ on the surface of interstellar dust particles (Green et al., 2001; Biham et al., 2001) is more relevant because atomic hydrogen sticks strongly to the cold surface (effectively the Henry's Law constant is high and v is small) while the gas phase density is tiny, so that the value of X remains very small.

Mathematical analysis can illustrate further the importance of the second criterion. For extremely small values of κ , the population of A-molecules dissolved in a droplet is given approximately by a Poisson distribution (this can be seen by noting that $F(z)$ satisfies $dF/dz = j_{\text{A}}F/\lambda_{\text{A}}$ in this limit, giving the solution $F(z) = \exp((z - 1)j_{\text{A}}/\lambda_{\text{A}})$ and hence $W(N) = (N!)^{-1}a^N \exp(-a)$ where $a = j_{\text{A}}/\lambda_{\text{A}}$: a Poisson distribution). Treating the reaction process as a small perturbation, we can evaluate its rate using Eq. (21). We then find it to be equal to $(\kappa/V)(j_{\text{A}}/\lambda_{\text{A}})^2$, precisely the classical rate in Eq. (25) with the mean population given by the classical rate Eq. (3) solved in the limit $\kappa = 0$. The correspondence is expected on the basis of the mathematical analysis given in Section 2.1.2. The additional point to be made here is that unless the Poisson distribution is disturbed by a significant reaction rate (reducing the relative values of $W(2)$, $W(3)$, etc., compared with $W(1)$) then the classical treatment is appropriate, even though the mean population could be very small.

2.2. Reaction $\text{A} + \text{B} \rightarrow \text{C}$

2.2.1. Stochastic and classical approaches compared

The $\text{A} + \text{A} \rightarrow \text{C}$ case is typical of chemical reactions. We should now consider the situation where molecules of two different chemical species A and B deposit onto the droplet, and react in solution to form the product C. Most heterogeneous atmospheric reactions are of this sort. We need to consider the probability $W(N_{\text{A}}, N_{\text{B}}; t)$ of finding N_{A} A-molecules and N_{B} B-molecules in the droplet. We shall now have two different source rates, j_{A} and j_{B} , and evaporation rates λ_{A} and λ_{B} . The master equation for the process can be written

$$\begin{aligned} \frac{dW(N_{\text{A}}, N_{\text{B}}; t)}{dt} = & j_{\text{A}}[W(N_{\text{A}} - 1, N_{\text{B}}; t) - W(N_{\text{A}}, N_{\text{B}}; t)] \\ & + j_{\text{B}}[W(N_{\text{A}}, N_{\text{B}} - 1; t) - W(N_{\text{A}}, N_{\text{B}}; t)] \\ & + \frac{\kappa}{V} [(N_{\text{A}} + 1)(N_{\text{B}} + 1)W(N_{\text{A}} + 1, N_{\text{B}} + 1; t) - N_{\text{A}}N_{\text{B}}W(N_{\text{A}}, N_{\text{B}}; t)] \\ & + \lambda_{\text{A}}[(N_{\text{A}} + 1)W(N_{\text{A}} + 1, N_{\text{B}}; t) - N_{\text{A}}W(N_{\text{A}}, N_{\text{B}}; t)] \\ & + \lambda_{\text{B}}[(N_{\text{B}} + 1)W(N_{\text{A}}, N_{\text{B}} + 1; t) - N_{\text{B}}W(N_{\text{A}}, N_{\text{B}}; t)]. \end{aligned} \quad (39)$$

This equation is constructed using the same kind of arguments as used in the derivation of Eq. (2). In order to simplify the problem, we once again introduce a generating function

$$F(x, y; t) = \sum_{\substack{N_A=0 \\ N_B=0}}^{\infty} W(N_A, N_B; t) x^{N_A} y^{N_B} \quad (40)$$

and by similar arguments to those used in Section 2.1.1, the master Eq. (39) reduces to a second-order time-dependent partial differential equation:

$$\frac{\partial F}{\partial t} = \left(j_A(x-1) + j_B(y-1) - \lambda_A(x-1) \frac{\partial}{\partial x} - \lambda_B(y-1) \frac{\partial}{\partial y} - \frac{\kappa}{V}(xy-1) \frac{\partial^2}{\partial x \partial y} \right) F. \quad (41)$$

The average numbers of molecules A and B are related to derivatives of this generating function:

$$\begin{aligned} \bar{N}_A &= \sum_{\substack{N_A=0 \\ N_B=0}}^{\infty} N_A W(N_A, N_B; t) = \left. \frac{\partial F}{\partial x} \right|_{x=y=1}, \\ \bar{N}_B &= \sum_{\substack{N_A=0 \\ N_B=0}}^{\infty} N_B W(N_A, N_B; t) = \left. \frac{\partial F}{\partial y} \right|_{x=y=1}. \end{aligned} \quad (42)$$

This can all be contrasted with the classical rate equations for the steady-state populations of the two species:

$$\begin{aligned} 0 &= j_A - \frac{\kappa}{V} \bar{N}_A \bar{N}_B - \lambda_A \bar{N}_A, \\ 0 &= j_B - \frac{\kappa}{V} \bar{N}_A \bar{N}_B - \lambda_B \bar{N}_B \end{aligned} \quad (43)$$

which may be shown to be consistent with Eq. (39) in the steady state and in the large population limit (by multiplying Eq. (39) by N_A or N_B and summing, as before).

Unfortunately, we have not found general analytical solutions to Eq. (41). However, if we ignore the last term in Eq. (41) (i.e. neglect the reaction rate) then the distributions of A- and B-molecules become uncoupled, the generating function $F(x, y)$ factors into separate x - and y -dependent parts, and according to the analysis at the end of the last section, the solution is

$$F(x, y) = \exp((x-1)j_A/\lambda_A) \exp((y-1)j_B/\lambda_B). \quad (44)$$

We shall use this generating function to provide a starting point for the computations described in Section 2.2.3.

2.2.2. Evolution of the probability distribution

The most straightforward numerical treatment of this problem is to evolve the probabilities $W(N_A, N_B; t)$ in time according to Eq. (39) until a steady state has been reached.

This approach was employed by Green et al. (2001) and Biham et al. (2001). It is easy to implement, but involves lengthy computations since there are so many equations involved.

We cannot evolve all the probability elements $W(N_A, N_B; t)$, where $0 \leq N_A \leq \infty$ and $0 \leq N_B \leq \infty$. We therefore set an upper limit on the number of A and B molecules that the droplet can possess

at a given time, namely introduce limits N_A^{\max} and N_B^{\max} . The elements of W labelled by N_A^{\max} and N_B^{\max} must be sufficiently small to ensure the representation of the system is adequate: this restricts the mean populations to rather low values.

We have examined the practicality of this approach. The initial condition was chosen as $W(0, 0; t=0)=1$ with all other elements of W equal to zero, equivalent to the complete absence of molecules in the droplet to start with. The converged solution for W gives us the steady-state mean populations and the reaction rate. These calculations can be carried out. However, for conditions where the mean populations take higher values, when j_A or j_B are increased for example, larger N_A^{\max} and N_B^{\max} limits are required, and the calculations are more lengthy. For these circumstances, the following approach is more suitable.

2.2.3. Evolution of the generating function

An entirely different approach, analogous to the approach used in Section 2.1.1 to solve the $A + A \rightarrow C$ case, is to find the steady-state generating function solution to Eq. (41). We work with the function:

$$G(x, y; t) = \ln[F(x, y; t)] \quad (45)$$

which is smoother and more easy to deal with than $F(x, y)$. Eq. (41) can be re-written as

$$\begin{aligned} \frac{\partial G}{\partial t} = & j_A(x-1) + j_B(y-1) - \lambda_A(x-1) \frac{\partial G}{\partial x} - \lambda_B(y-1) \frac{\partial G}{\partial y} \\ & - \frac{\kappa}{V}(xy-1) \left\{ \frac{\partial^2 G}{\partial x \partial y} + \left(\frac{\partial G}{\partial x} \right) \left(\frac{\partial G}{\partial y} \right) \right\}. \end{aligned} \quad (46)$$

Furthermore, using the identity $\partial \ln F / \partial x = (1/F)(\partial F / \partial x)$, and using the fact that $F(1, 1; t) = 1$, we note that the mean populations may be written in terms of derivatives of G :

$$\bar{N}_A = \left. \frac{\partial F}{\partial x} \right|_{x=y=1} = F \left. \frac{\partial \ln F}{\partial x} \right|_{x=y=1} = \left. \frac{\partial G}{\partial x} \right|_{x=y=1} \quad (47)$$

and similarly $\bar{N}_B = \partial G / \partial y|_{x=y=1}$.

In order to solve Eq. (46), j_A , j_B , κ , λ_A , λ_B and V are provided as input parameters and the time-dependent problem is solved, starting from the trial solution for G given in Eq. (44), and terminating when the solution has converged to a steady state, while maintaining the boundary condition $G(x = y = 1; t) = 0$, which corresponds to the normalisation condition on $W(N_A, N_B)$. The space $0 \leq x \leq 1$, $0 \leq y \leq 1$ as well as time t are discretised and the explicit Euler method is employed to evolve the difference equations for G . We found that the successful evolution of G can be a very delicate process, particularly as the mean populations become smaller. This arises from the insufficient means by which the solution is fully determined by the boundary conditions. With sufficient attention to this point, however, computations are quite rapid.

2.2.4. Results

In the light of the conclusions reached in Section 2.1.2, we need to focus our attention on species A and B with high solubilities, trace atmospheric concentrations, and which react together rapidly in solution. Let us consider the important aqueous phase reaction $\text{HSO}_3^- + \text{OH} \rightarrow \text{SO}_3^- + \text{H}_2\text{O}$, which has reaction rate $\kappa = 4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Seinfeld & Pandis, 1998). The hydroxyl radical dissolves

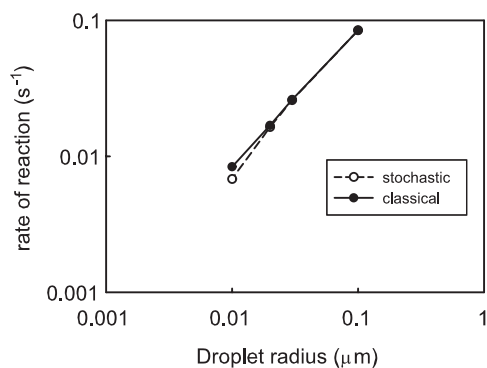


Fig. 4. Production rate of SO_3^- in reaction $\text{HSO}_3^- + \text{OH} \rightarrow \text{SO}_3^- + \text{H}_2\text{O}$, according to stochastic and classical approaches, for parameters specified in the text, and for various droplet radii. At very small droplet sizes, the difference between the stochastic and classical predictions is apparent.

from the gas phase with a Henry's Law constant of 25 M atm^{-1} , and a typical concentration in the atmosphere is 0.3 ppt (Seinfeld & Pandis, 1998). The value of X for OH when $p_T = 1 \text{ atm}$ and $r = 0.1 \mu\text{m}$ is therefore 1.9×10^{-5} , well below unity.

As for the other reactant, HSO_3^- is present in droplets through the dissolution and dissociation of gaseous SO_2 . As in our discussion of HO_2/O_2^- in Section 2.1.3, we regard reactant B as the dissolved sulphur species, whether it be the hydrate $\text{SO}_2 \cdot \text{H}_2\text{O}$, the HSO_3^- ion or even SO_3^{2-} . The equilibrium between these species is well established on the timescale of encounters between the sulphur species and the exceedingly rare OH. In fact, at pH values between 3 and 6, almost every SO_2 molecule is converted to the HSO_3^- ion under this equilibrium. As is described by Seinfeld and Pandis (1998), the effective Henry's Law constant for aqueous HSO_3^- with respect to the gas phase partial pressure of SO_2 is $k_H^{\text{SO}_2} K / [\text{H}^+]$ where $k_H^{\text{SO}_2} = 1.23 \text{ M atm}^{-1}$ is the Henry's law constant for SO_2 and $K = 1.3 \times 10^{-2} \text{ M}$ is the dissociation constant for $\text{H}_2\text{SO}_3 \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$. This gives an effective Henry's law constant for bisulphite of $1.6 \times 10^3 \text{ M atm}^{-1}$ at pH = 5. Assuming an atmospheric concentration of 1 ppb SO_2 these parameters yield $X = 4$ for HSO_3^- when $p_T = 1 \text{ atm}$ and $r = 0.1 \mu\text{m}$. Therefore, the mean populations of both reactants are small.

More critically, using the above value of κ , the parameter $(\nu + 1)/2$ given by Eq. (32) is equal to 16 for $r = 0.1 \mu\text{m}$ using the effective Henry's Law constant for HSO_3^- , rising to 2000 if the constant for OH is used. In order to detect differences between stochastic and classical kinetics, therefore, we would need to consider chemistry on droplets smaller than $0.1 \mu\text{m}$ in radius.

As a more detailed study of the kinetics, Fig. 4 shows results for the production rate of SO_3^- as a function of droplet radius r , taking all other parameters as described above. They were generated using the numerical methods described in Sections 2.2.2 and 2.2.3. The stochastic prediction begins to fall below the classical rate for droplets below a radius of about 10 nm, as we expected on the basis of the above estimates of the X and ν parameters. Again, chemistry taking place in these tiny droplets is probably of no significance in the atmosphere, so the traditional treatment of this particular reaction process is probably adequate. Nevertheless, a regime where it is necessary to take a different view of chemical kinetics in aerosol droplets is not so far away from the conditions encountered in practice.

3. Conclusions

We have investigated a stochastic model proposed independently by Lushnikov (1999) and Green et al. (2001) to describe chemical reactions between trace atmospheric gases dissolved in ultrafine aerosol particles. Analytic solution is possible for reactions of type $A + A \rightarrow C$. For reactions of type $A + B \rightarrow C$ analytic solution is not feasible and we have solved the model numerically.

We can conclude that differences in the reaction rate for $A + A \rightarrow C$ emerge when $X < 1$ and $\nu < 1$, where X and ν are dimensionless combinations of the fundamental process parameters given in Eqs. (31) and (32). This is illustrated in Fig. 3. In order for stochastic methods to be necessary, a combination of small particle size, trace concentration of gas phase reactants in the atmosphere, good solubility of reactants, and a rapid reaction rate are needed. The stochastic model then predicts a larger mean absorbed population of reactant and a smaller rate of formation of product than the classical approach. Similar features emerge for the more complex reaction of type $A + B \rightarrow C$.

Such circumstances have been shown by Green et al. (2001) and Biham et al. (2001) to apply in the interstellar medium. We have focussed our attention on heterogeneous reactions taking place in atmospheric droplets. Although mean populations of molecules in aerosol droplets can be extremely small, the rate of binary reactions seems to be well approximated by a calculation within classical chemical kinetics, at least for the cases of atmospherically relevant heterogeneous reactions we have studied. The main result of our study is therefore to eliminate most of the concern that there might be in using classical kinetics. Nevertheless, our theoretical methods would allow one to study aerosol chemistry for the unusual, but not inconceivable, conditions where the standard kinetic treatment fails.

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Appendix A.

We explore the analytic solution for the generating function $F(z)$ in the case of reaction $A + A \rightarrow C$ and show why only the first of the two terms in Eq. (13) should be retained.

Consider the definition of $F(z)$ according to Eq. (5). The gradient of $F(z)$ at $z = -1$ is

$$\left. \frac{dF}{dz} \right|_{z=-1} = \sum_{N=0}^{\infty} N(-1)^{N-1} W(N) \leq \sum_{N=0}^{\infty} N W(N) = \bar{N} \quad (\text{A.1})$$

and also

$$\left. \frac{dF}{dz} \right|_{z=-1} \geq - \sum_{N=0}^{\infty} N W(N) = -\bar{N}. \quad (\text{A.2})$$

Hence the gradient is strictly finite at $z = -1$. Solutions for $F(z)$ must exhibit this feature.

For convenience, the full solution expressed in Eq. (13) can be written as

$$F(z) = A(1+z)^{-v/2} I_v(C(1+z)^{1/2}) + B(1+z)^{-v/2} K_v(C(1+z)^{1/2}), \quad (\text{A.3})$$

where A and B are integration constants and C is a specified combination of the parameters V , j_A and κ .

Let us first examine the I_v part of the solution and write

$$F_I(z) = (1+z)^{-v/2} I_v(C(1+z)^{1/2}), \quad (\text{A.4})$$

so using the identities (18) for the derivative of Bessel function, we obtain

$$\begin{aligned} \frac{dF_I}{dz} &= -\frac{v}{2} (1+z)^{-v/2-1} I_v(\zeta) + (1+z)^{-v/2} \left(I_{v+1}(\zeta) + \frac{v}{\zeta} I_v(\zeta) \right) \frac{1}{2} C(1+z)^{-1/2} \\ &= \frac{C}{2} (1+z)^{-(v+1)/2} I_{v+1}(\zeta), \end{aligned} \quad (\text{A.5})$$

where $\zeta = C(1+z)^{1/2}$.

Consider the behaviour of this gradient when $z \rightarrow -1$ and hence $\zeta \rightarrow 0$. For this we utilise a standard expansion of Bessel functions for very small arguments. We find that as $z \rightarrow -1$

$$\frac{dF_I}{dz} \sim \left(\frac{C}{2} \right)^{v+1} \frac{1}{\Gamma(v+2)} (1+z)^{-(v+1)/2} (1+z)^{(v+1)/2} \quad (\text{A.6})$$

which is finite, irrespective of the sign of v .

Now let us examine the K_v part of the solution in Eq. (A.3) and write

$$F_K(z) = (1+z)^{-v/2} K_v(C(1+z)^{1/2}). \quad (\text{A.7})$$

In order to evaluate the gradient of F_K we use the standard result

$$\frac{dK_p(r)}{dr} = -K_{p+1}(r) + \frac{p}{r} K_p(r) \quad (\text{A.8})$$

which leads to the relation

$$\frac{dF_K}{dz} = -\frac{C}{2} (1+z)^{-(v+1)/2} K_{v+1}(\zeta). \quad (\text{A.9})$$

To see the behaviour of dF_K/dz in the limit $z \rightarrow -1$ ($\zeta \rightarrow 0$) we observe that

$$K_p(r) \sim \frac{\Gamma(p)}{2} \frac{r^{-p}}{2} \quad \text{as } r \rightarrow 0 \quad (\text{A.10})$$

for positive p and it is also known that $K_p(r) = K_{-p}(r)$. Applying this to Eq. (A.9) we find that as $z \rightarrow -1$,

$$\frac{dF_K}{dz} = -\left(\frac{C}{2} \right)^{-v} \frac{\Gamma(v+1)}{2} (1+z)^{-(v+1)/2} (1+z)^{-(v+1)/2} \quad (\text{A.11})$$

which goes to infinity even if v is negative, remembering the fact that the value of v has a lower limit of -1 . Hence the K_v part of the solution in Eq. (13) cannot be used.

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