Collocation Methods for the Boltzmann Equation; Hot Atom Relaxation and Ion Transport in Gases

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Abstract. We present a preliminary investigation of the use of a B-spline basis for solving the Boltzmann equation with the intent of extending the methodology to treat the mobility of tracer ions moving in electric fields with arbitrary temporal and spatial dependence. The current study examines a simplified one-dimensional model using the smooth hard sphere Wigner Wilkins kernel and cubic B-splines. Eigenvalues of the collision operator are compared with accurate known values. The method produces reasonable results. However, the accuracy of the distribution function is expected to be more than enough to predict low order moments, as would be needed to study ion mobility.

Introduction

In this study, tracer particles in an inert gas start from a non-equilibrium, perturbed state and the approach to a steady state is observed. This allows us to observe the time dependence of the system. Our mathematical approach uses a cubic B-spline basis to expand the distribution function. The Boltzmann equation has been solved using numerous approaches[1–3] and the one presented here is not novel. However, the ultimate goal is to treat tracer ions in electric fields with arbitrary temporal and spatial dependence. In general, this requires solving the Boltzmann equation with full spatial and velocity dependence, which for structureless tracer particles requires a six-dimensional equation with time dependence in addition. For this reason, we seek a numerical approach that is easy to generalize to higher dimension, does not rely upon mathematical properties of the collision operator for specific models[4, 5], and is computationally efficient. In higher dimension, evaluating the integrals in the collision term can consume computational resources if not performed efficiently. Since we ultimately wish to calculate low order moments of velocity in treating the ion mobility problem, a numerical method should produce distribution functions with accuracy sufficient for this purpose. Since these moments involve integrals, we expect only modest accuracy is required for the distribution functions.

B-splines[6–9] offer several intriguing advantages for a numerical method. They are non-zero only over a finite, well-defined domain which depends upon the order of the polynomials used in the basis. This means any integral involving B-spline functions necessarily is restricted to a small local domain. Such quantities are easy to evaluate with a modest number of points using an efficient quadrature scheme. When extending such an approach to higher dimensions using a product basis of B-spline functions, higher dimensional integrals reduce to integrals only over a highly localized region about a point. This reduces by orders of magnitude the effort in evaluating these integrals, and also allows one to tailor integration routines to the behaviour of the integrand in that region of space. For example, the cusp in the collision integral can cause difficulty for bases that extend over the entire space since every integration necessarily must deal with it. With a B-spline product basis, only a small fraction of the basis functions will involve integrals near the cusp, and these can be performed with numerical methods tailored to deal with this feature. Those basis functions located away from the cusp will be part of integrals with smooth integrands that are straightforward to integrate numerically. A B-spline basis also allows some flexibility in choosing boundary conditions for the distribution function.

Of course, there are some disadvantages using B-spline bases. The basis functions are not orthogonal and this complicates the methodology somewhat. As well, because they are composed of piecewise polynomial functions, the basis functions are smooth and continuous only up to a finite number of derivatives, and this limits the ultimate accuracy of the representation. Finally, spectral convergence is not expected for B-spline bases.

Clearly, B-spline bases offer advantages and disadvantages. The key question that must be answered is whether a B-spline basis can produce distribution functions of sufficient accuracy to evaluate low-order moments accurately while at the same time delivering the numerical efficiencies that allow extension to higher dimensional problems. The current study is the first step on the path to answering this question.

Model

The model in this study is an ensemble of tracer particles of mass m_1, dilutely dispersed in inert bath gas particles of mass m_2. The collision cross section for tracer-bath collisions is approximated with a hard sphere cross section [1–3]. The number of bath particles is assumed to be far greater than that of the tracer particles, allowing us to ignore any collisions between two tracer particles. Only collisions between the bath and tracer particles are included. Our starting equation is the Boltzmann equation with the Wigner-Wilkins form of the collision kernel [10, 11], that is

$$\frac{\partial f}{\partial t} = C[f] \,, \tag{1}$$

where $C[f]$ is the collision integral defined by

$$C[f] = \int_0^\infty K(x,y)f(x,t)dx - \nu(y)f(y,t) \,, \tag{2}$$

in which the kernel is given by

$$K(x,y) = \frac{1}{2}AQ^2 \left(\frac{\pi}{x}\right)^{\frac{1}{2}} \left\{ \Phi(Qy^{\frac{1}{2}} + Rx^{\frac{1}{2}}) + e^{x-y}\Phi(Ry^{\frac{1}{2}} + Qx^{\frac{1}{2}}) \right. \tag{3}$$
$$\left. \pm \left[\Phi(Qy^{\frac{1}{2}} - Rx^{\frac{1}{2}}) + e^{x-y}\Phi(Ry^{\frac{1}{2}} - Qx^{\frac{1}{2}}) \right] \right\} \,,$$

where '+' is used when $x > y$ and the '-' is used when $x < y$. The collision frequency ν is defined as[11]

$$\nu(y) = A\gamma^{-\frac{1}{2}} \left\{ \left[2(\gamma y)^{\frac{1}{2}} + (\gamma y)^{-\frac{1}{2}} \right] \frac{\sqrt{\pi}}{2}\Phi(\sqrt{\gamma y}) + e^{-\gamma y} \right\} \,, \tag{4}$$

with $\Phi(z) = \frac{2}{\sqrt{\pi}}\int_0^t \exp^{-z} dz$ the error function. The factor, A, is given by

$$A = N\pi\sigma^2 \left(\frac{kT}{2m_1}\right)^{\frac{1}{2}} \,, \tag{5}$$

in which N is number density of the bath, k is the Boltzmann constant, T is the bath temperature, and Q and R are defined as

$$Q = \frac{1}{2}\left(\gamma^{-\frac{1}{2}} + \gamma^{\frac{1}{2}}\right); \quad R = \frac{1}{2}\left(\gamma^{-\frac{1}{2}} - \gamma^{\frac{1}{2}}\right) \,, \tag{6}$$

with the mass ratio $\gamma = m_2/m_1$. With the definitions of Q and R above, a few relations are derived that proved useful in simplifying algebraic expressions. These are

$$Q^2 + R^2 = 1 \,, \tag{7}$$
$$Q - R = \sqrt{\gamma} \,, \tag{8}$$
$$Q + R = \frac{1}{\sqrt{\gamma}} \,. \tag{9}$$

To make the numerical approach better behaved the distribution function is written in the form

$$f(y,t) = \frac{2\sqrt{y}}{\sqrt{\pi}}e^{-y}g(y,t) \,, \tag{10}$$

in which $g(y,t)$ is the unknown distribution function we want to evaluate. Substituting Eq. (10) into Eqs. (1) and (2) gives

$$\frac{\partial g(y,t)}{\partial t} = \int_0^\infty \tilde{K}(x,y)g(x,t)dx - \nu(y)g(y,t), \tag{11}$$

in which the new form of the kernel can be rearranged to give

$$
\int_0^\infty \tilde{K}(x,y)g(x,t)dx \;=\; \frac{AQ^2}{2}\frac{\sqrt{\pi}}{\sqrt{y}}e^y \left\{ \int_0^y e^{-x}g(x,t)\left[\Phi(Qy^{\frac{1}{2}}+Rx^{\frac{1}{2}})-\Phi(Qy^{\frac{1}{2}}-Rx^{\frac{1}{2}})\right]dx \right. \tag{12}
$$

$$
+ \int_y^\infty e^{-x}g(x,t)\left[\Phi(Qy^{\frac{1}{2}}+Rx^{\frac{1}{2}})+\Phi(Qy^{\frac{1}{2}}-Rx^{\frac{1}{2}})\right]dx
$$

$$
+ e^{-y}\int_0^y g(x,t)\left[\Phi(Ry^{\frac{1}{2}}+Qx^{\frac{1}{2}})+\Phi(Qx^{\frac{1}{2}}-Ry^{\frac{1}{2}})\right]dx
$$

$$
\left. + e^{-y}\int_y^\infty g(x,t)\left[\Phi(Ry^{\frac{1}{2}}+Qx^{\frac{1}{2}})+\Phi(Ry^{\frac{1}{2}}-Qx^{\frac{1}{2}})\right]dx \right\} .
$$

In the evaluation of the collision kernel (Eq. (12)), the $\sqrt{y}$ term in the denominator of the factor multiplying the four integrals causes numerical difficulty at $y=0$. To overcome this problem, we evaluated the collision kernel in Eq. (12) analytically at this point by expanding the error function in a Taylor series about $y=0$ to give

$$
\Phi(Qy^{\frac{1}{2}}\pm Rx^{\frac{1}{2}}) \simeq \pm\Phi(Rx^{\frac{1}{2}}) + \frac{2}{\sqrt{\pi}}e^{-R^2x}Qy^{\frac{1}{2}} . \tag{13}
$$

Substituting Eq. (13) into Eq. (12) and taking the limit as y approaches zero gives

$$
\lim_{y\to 0}\int_0^\infty \tilde{K}(x,y)f(y,t)dy = \frac{2A}{\sqrt{\gamma}}Q^2\int_0^\infty e^{-Q^2x}g(x,t)dx. \tag{14}
$$

The expression for the collision frequency, $\nu(y)$ in the same limit is

$$
\lim_{y\to 0}\nu(y) = \frac{2A}{\sqrt{\gamma}} . \tag{15}
$$

Method

Our unknown distribution function is expanded in terms of cubic B-splines as

$$
g(y,t)\doteq \sum_{i=-3}^{n-1} c_i(t)B_i^3(y) , \tag{16}
$$

where $c_i(t)$ are time-dependent coefficients, and $B_i^3(y)$ are cubic B-spline functions. B-splines (*basis splines*) [6–9], are constructed using polynomials of a given degree and smoothness. Cubic B-splines are facile to work with since they are defined over an interval of four points only. Outside this range the cubic B-spline is zero. For our case we have used third order cubic B-spline functions on a uniform grid that starts from $y_0=0$ and extends to a finite value of $y_n=S$. The points on the grid are uniformly spaced with the interval between each point being Δ. The cubic B-spline, $B_i^3(w)$ ($w=\frac{y}{\Delta}-i$), is defined as

$$
B_i^3(w) = \frac{1}{6}\begin{cases} w^3, & 0\le w<1 \\ w^3-4(w-1)^3, & 1\le w<2 \\ (4-w)^3-4(3-w)^3, & 2\le w<3 \\ (4-w)^3, & 3\le w\le 4 \\ 0, & \text{otherwise} \end{cases} . \tag{17}
$$

The index i is the left most point of the curve, thus for $i=0$, $B_0^3(y)$ starts at 0 and extends to $y=y_4=4\Delta$. An example of a cubic B-spline is given in Fig. (1). Note that $B_i^3(y)$ for all $i\ge n$ extend past the defined grid so will not contribute to g. At the same time, the extension of the function $B_i^3(y)$ over an interval of four points shows that the point $y=y_0$ will have contributions from $B_{-3}^3(y), B_{-2}^3(y)$, and $B_{-1}^3(y)$. This makes
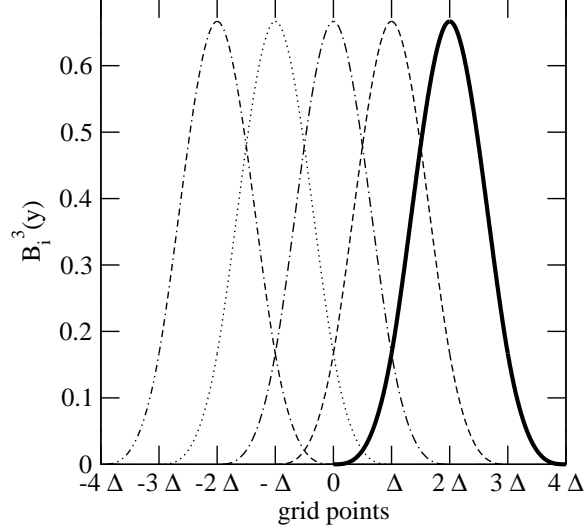
FIG. 1: Cubic B-spline functions, $B_i^3(y)$, for $i = -4, -3, -2, -1, 0$ defined on a grid of y values

the index i in Eq. (16) run from $i = -3$ to $i = n - 1$ to include the contributions from the cubic B-splines that are actually off the defined y grid. Substituting Eq. (16) into Eqs. (11) and (12) gives

$$\sum_{i=-3}^{n-1} \frac{d}{dt} c_i(t) B_i^3(y) = \sum_{i=-3}^{n-1} c_i(t) \left[\int_0^S \tilde{K}(x,y) B_i^3(x) dx - \nu(y) B_i^3(y) \right] . \tag{18}$$

In order to determine the coefficients $c_i(t)$, $n + 3$ conditions are required. Equation (18) must hold at the grid points $y = y_j$; $j = 0, \ldots, n$. This provides $n + 1$ constraints for $c_i(t)$. However, 2 additional conditions are required and to determine these we force the derivatives of g, that is

$$\frac{\partial^2}{\partial y \partial t} g(y,t) = \sum_{i=-3}^{n-1} \frac{d}{dt} c_i(t) \frac{d}{dy} B_i^3(y) , \tag{19}$$

to be zero at the grid boundaries $y = \{y_0, y_n\}$. We have explicitly chosen these boundary conditions but the procedure for choosing the constraints is a very general one and can include other types of constraints. With the constraints imposed, Eq. (18) can be expressed in matrix notation as

$$\frac{d\mathbf{c}}{dt} = \mathbf{L}\mathbf{c}, \tag{20}$$

where

$$\mathbf{L} = \tilde{\mathbf{B}}^{-1} \left(\tilde{\mathbf{K}} - \nu \mathbf{B} \right) , \tag{21}$$

and the matrices $\tilde{\mathbf{B}}$, $\mathbf{B}$, and $\boldsymbol{\nu}$ have the form

$$
\tilde{\mathbf{B}} = \frac{1}{6}
\begin{pmatrix}
-\frac{3}{\Delta} & 0 & \frac{3}{\Delta} & 0 & \ldots & 0 & 0 \\
1 & 4 & 1 & 0 & \ldots & 0 & 0 \\
0 & 1 & 4 & 1 & \ldots & 0 & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
0 & 0 & \ldots & 1 & 4 & 1 & 0 \\
0 & 0 & \ldots & 0 & 1 & 4 & 1 \\
0 & 0 & \ldots & 0 & -\frac{3}{\Delta} & 0 & \frac{3}{\Delta}
\end{pmatrix}
, \;
\boldsymbol{\nu} =
\begin{pmatrix}
0 & 0 & \ldots & 0 & 0 \\
0 & \nu_0 & 0 & 0 & 0 \\
0 & 0 & \nu_1 & 0 & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots \\
0 & 0 & 0 & \nu_n & 0 \\
0 & 0 & \ldots & 0 & 0
\end{pmatrix}
,
$$

$$
\mathbf{B} = \frac{1}{6}
\begin{pmatrix}
0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
1 & 4 & 1 & 0 & \ldots & 0 & 0 \\
0 & 1 & 4 & 1 & 0 & \ldots & 0 \\
0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
0 & 0 & \ldots & 0 & 1 & 4 & 1 \\
0 & 0 & 0 & \ldots & 0 & 0 & 0
\end{pmatrix} .
\tag{22}
$$

and for the matrix $\tilde{\mathbf{K}}$ the first and last rows are zero, and the remaining elements are given by

$$
\tilde{\mathbf{K}}_{ji} = \int_0^S \tilde{K}(x, y_j) B_i^3(x) dx .
\tag{23}
$$

This integral is evaluated using a Gauss-Legendre quadrature scheme. In principle, if S were infinitely large then $\nu_j = \nu(y_j)$. Since S is finite, $\tilde{\mathbf{K}}\mathbf{c}$ does not equal precisely $\boldsymbol{\nu}\mathbf{B}\mathbf{c}$ at equilibrium. To remedy this, the values of $\boldsymbol{\nu}$ are adjusted to correct for this discrepancy by setting $\nu_j = \sum_i \tilde{K}_{ji}$.

Note that the formulation described above deviates somewhat from the conventional one. Usually when employing a basis set and obtaining a set of equations as in Eq. (18) the desired coefficients are isolated by multiplying both sides with a member of the basis and integrating over all coordinates. In this case, we could have multiplied Eq. (18) by some $B_k^3(y)$ and integrated both sides over y to produce a set of linear equations in $c_i(t)$. In our case, because the B-spline basis is not orthogonal, such a procedure does not simplify the resulting equation as much as desired because an overlap matrix still couples different $c_i(t)$. In addition, this leads to a double integral evaluation on the right hand side. Extending such a procedure to higher dimensional cases would immediately double the already numerous integrations that must be performed. For this reason, we employed the procedure above which is numerically less intensive as it involves only a one-dimensional integral, namely just the one shown in Eq. (18).

Results

There are several means by which the accuracy of the cubic B-spline expansion can be tested and we have chosen initially to examine the eigenvalues of $\mathbf{L}$ because this should be a stringent test. The collision operator has one zero eigenvalue corresponding to the equilibrium solution, as well as a series of discrete and continuous eigenvalues. When scaled by $\nu(0)$ of Eq. (15) all the discrete eigenvalues occur with magnitudes less than 1 while the continuous ones occur with magnitudes greater than 1. Converged and accurate values of the lowest discrete eigenvalues for a number of mass ratios have been reported[11–13] and we compare those with our calculated values in Table I.

The eigenvalues do not converge as quickly as a function of the number of basis functions as other methods reported in the literature[12, 13]. With a small number of B-spline basis functions the errors are only a few percent but quite a large number of basis functions are required to reduce the errors to below 1%. This convergence behaviour is not unexpected due to the nature of the B-spline basis. The absolute accuracy of the values is limited by the low order B-spline functions used (cubic in this case). However, as was pointed out in the Introduction, the goal of the method is to produce a distribution function with sufficient accuracy so that low-order moments can be accurately predicted. It is possible such a method may not produce accurate values for the discrete eigenvalues of the collision operator with only a few basis functions but still produce quite adequate moment predictions,

TABLE I: Comparison of selected discrete eigenvalues of the collision operator **L** with known values from the literature.

	n	$\|\lambda_1/\nu(0)\|$	$\|\lambda_2/\nu(0)\|$	$\|\lambda_3/\nu(0)\|$
$m=1$	10	0.7481	1.0796	
	20	0.7873	0.9820	
	50	0.8134	0.9601	1.0455
	100	0.8173	0.9677	1.0113
	150	0.8179	0.9722	1.0021
SLR[12]		0.8190	0.9795	0.9985

Currently, we are in the process of using other means for testing the accuracy of the method including comparisons of the distribution functions explicitly, as well as the ability to predict low order moments.

Acknowledgments

References

[1] Mason, E.A. and McDaniel, E.W.,Transport Properties of Ions in Gases, Wiley, New York, 1988.
[2] Chapman, S. and Cowling, T.G.,The Mathematical Theory of Non-uniform Gases: An Account of the Kinetic Theory of Viscosity, Thermal Conduction and Diffusion in Gases, Cambridge University Press, 3rd Ed., 1991.
[3] Pidduck, P.D., *Proc. London Math. Soc.* **15**, 89 (1916).
[4] Ivchenko, I.N., Loyalka, S.K., Tompson, R.V., *Ann. Nucl. Energy* **23**, 1489-1495 (1996).
[5] Siewert, C.E., *J. Quant. Spec. & Rad. Trans.* **74**, 789-796 (2002).
[6] Cheney, Kincaid, Numerical Methods and Computing, Brooks/Cole Pub Co., 3rd Ed. 1994.
[7] Bior, C.D., A Practical Guide to Splines, Springer, 1994.
[8] Prenter, P.M., Splines and Variational Methods, John Wiley & Sons, 1989.
[9] Schumaber, L.L., Spline Functions - Basic Theory, Krieger Publishing Company, 1993.
[10] Wigner, E.P., Wilkins, J.E., *U.S. Atomic Energy Commission Report* AECD 2275, 1944.
[11] Hoare, M.R. and Kaplinsky, C.H., *J.Chem. Phys.* **52**, 3336 (1970).
[12] Shizgal, B., Lindenfeld, M.J., Reeves, R., *Chem. Phys.* **56**, 249-260 (1981).
[13] Shizgal, B., Blackmore, R., *Chem. Phys.* **77**, 417-427 (1983).