ON THE NUMERICAL SOLUTION OF STURM-LIOUVILLE EQUATIONS IN THE THEORY OF MOLECULAR DIFFUSION

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ABSTRACT

The Sturm-Liouville equation from Budo's Theory of diffusion in the presence of potential wells is solved numerically for the normalised complex polarisability across the complete range of well depth \( (V_0/kT) \) from zero to effectively infinite. For \( V_0/kT = 0 \) and \( V_0/kT = \infty \) a Debye process is recovered, in excellent agreement with available analytical limits. At intermediate \( V_0/kT \) the original Debye process for \( V_0/kT \) (free diffusion) is supplemented by a further loss process on the high frequency side. The numerical method used allow us to investigate the origin of this process in terms of the eigenvalues and eigenfunctions of the original Sturm-Liouville equation.

INTRODUCTION

Recently, the Budo theory \([1,2]\) of interacting dipoles on a diffusing molecule has been considered again by W.T. Coffey and co-workers \([3]\) in the context of the theory of the itinerant oscillator \([4,5]\). This analysis leads to an interesting numerical problem \([6]\) involving the Sturm-Liouville equation:

\[
2\zeta'' + (\lambda + \phi'(\theta) - \phi^2(\theta))\zeta = 0 \tag{1}
\]

\[
\phi(\theta) = \frac{V}{2kT} \quad \text{;} \quad V = -\mu_1\mu_2 \cos \theta
\]

Equation (1) is insoluble analytically, except in well-defined limits and the purpose of this paper is to provide the numerical solution for the complete...
range of potential energy $V_0$, the well-depth parameter. In eqn (1), $Z_\lambda$ are eigenfunctions and $\lambda$ eigenvalues of the Sturm-Liouville equation. The differentiation in eqn. (1) is with respect to the variable $\theta$. $\mu_1$ and $\mu_2$ are the two interacting dipole moments. Results are given in terms of the complex polarisability in the range $V_0 = 0$ (free diffusion) to $V_0 + \infty$, where the dipole-dipole interaction is so strong that the two diffusing dipoles are locked.

COMPUTATION

The Sturm-Liouville equation (1) was solved with a numerical method developed by Hargrave and Pryce [7,8] and implemented [3,6] in earlier work on the original Budo model. The numerical algorithm provides eigenvalues and eigenfunctions of any self-adjoint Sturm-Liouville system using a shooting method. The numerical method is found by shooting forward from a point $x = a$ and backward from a point $x = b$ to a matching point $x = c$. A relative scaling method is used to improve the numerical behaviour. The eigenvalues are computed with an absolute error (recorded after the symbol ± in the tables of this paper). The true uncertainty in the eigenvalues is rarely more than twice, or less than a tenth, of this estimation.

The eigenfunction for a given eigenvalue is computed with a Prufer transform, upon which the numerical method is based. The method is now available as the Numerical Algorithms Group routine D02KEF and is described in detail in their literature [9]. This routine outputs eigenfunctions at unequally spaced mesh points $\theta$. Further analysis to provide normalised complex polarisability curves involves several numerical integrations over the eigenvalues as described in the literature [3]. For the problem posed by Budo, this requires seven separate numerical integrations for each eigenfunction with the specialised Numerical Algorithm Group routine D01CAF, and therefore careful control of uncertainty. The end result of these integrations are the weighting factors recorded in the tables below. Where the weighting factors become very small, the mesh $Z(\theta)$ is no longer fine enough for satisfactory error control of the numerical integrations, and this is marked with an asterisk in the tables.

BOUNDARY VALUES

It is essential to define the boundary values correctly for a physically meaningful outcome of our Sturm-Liouville problem. It is not always obvious what these boundary values are, and the following method has been adopted for
their definition.

i) It has been assumed that the eigenfunction \(Z(\theta)\) vanishes at the boundary points \(\theta = \theta_1\) and \(\theta = \theta_2\).

ii) These boundary points have been chosen in such a way that when the potential term in the Sturm-Liouville equation vanishes, i.e. when the equation reduces to:

\[
Z''_\lambda + \lambda Z_\lambda = 0
\]

the eigenvalues \(\lambda\) are integers. The integral eigenvalues of eqn. (2) follow the series 1, 4, 9, 16, .... as shown in the tables. In order to satisfy this condition, the boundary conditions for the Budo problem (eqn. (1)) must be:

\[
Z_\lambda(-\pi/2) = Z_\lambda(\pi/2) = 0
\]

By carefully controlling the absolute error in the eigenvalues and relative error in the various numerical integrations of the eigenfunctions, it is possible to produce a solution in terms of complex polarisability accurate to \(\pm 0.1\%\) or better. Therefore, the solution of any Fokker-Planck [4,5] or Chandrasekhar [6] diffusion equation reduces to a Sturm-Liouville equation and therefore to an eigenvalue problem.

The numerical solutions were found for this work using the CDC 7600 computer of U.M.R.C.C. via remote link to the Bangor (U.N.C.W.) computer laboratory. Depending on the value of parameter such as \(V_0/kT\), a complete polarisability curve (a sum of up to fifteen integrated eigenfunctions - 105 numerical integrations and 15 separate iterative solutions of the Sturm-Liouville equation) could be generated in about eleven decimal seconds of 7600 CPU time.

DISCUSSION OF TABULATED EIGENVALUES AND WEIGHTING FACTORS

Budo Model of Interacting Dipoles in a Diffusing Molecule [1,2]

The eigenvalues \(\lambda_0, \lambda_1, \ldots, \lambda_n\) as functions of the interaction energy \(V_0/kT\) are tabulated in table (1), together with the relaxation times \(\tau_0\) defined by eqn. (1) for \(\zeta_1/\zeta = 0.5\) and \(2\zeta_1/kT = 10^{-8}\) sec, where \(\zeta_1\) and \(\zeta\) are friction coefficients [1,2] on the dipole group and whole molecule respectively. In the limit \(V_0/kT = 0\) the eigenvalues are described by the quadratic series \((n+1)^2\), \(n = 0, 1, 2, \ldots\). As \(V_0/kT\) increases, the zeroth
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$y(-\pi/2) = y(\pi/2) = 0$

$\zeta_1/\zeta = 0.5; \quad 2\zeta_1/kT = 10^{-8} \text{ sec}$
TABLE 2

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The Weighting Factors and Estimated Uncertainties (After seven numerical integrations) Inc Eqn

$\nu_1 = \nu_2 = 1.0$

B.C.'s $-\pi/2$ to $\pi/2$

Note that $I_\lambda = 0; \quad \lambda = 2n + 1$

* Mesh-nets not fine enough for accurate integration. $I_\lambda$ very small
order eigenvalue \( \lambda_0 = 0 \) but all the others increase. The effect of this behaviour on the relaxation times \( \tau_n \) is summarised in table (1). (The times are defined by repeated numerical integration as described [3] in the literature). The relaxation time \( \tau_0 \) gradually increases as a function of \( \text{Vo/kT} \) but all the others (i.e. \( n = 1,2,\ldots \)) decrease. As \( \text{Vo} \rightarrow \infty \), therefore there remains a single, finite relaxation time \( \tau_0 \) only; i.e. the complex polarisability curve becomes once more Debye type [3,4] because the two dipoles are locked together and diffuse as a single entity. This is in agreement with theoretical predictions, because the Sturm-Liouville equation (1) reduces to an analytically soluble Hermite equation [5] in the limit \( \text{Vo/kT} \rightarrow \infty \).

Table (2) records the weighting factors \( I_\lambda \) built up by seven numerical integrations from the eigenvalues of eqn. (1). These integrals are fully described in the literature [3,6]. In the limit \( \text{Vo/kT} \rightarrow 0.0 \) only the first factor, \( I_0 \), is significant, because the dipoles in this limit diffuse independently according to Debye's equation [4]. For all \( \text{Vo/kT} \) the odd weighting factors (i.e. for \( n = 1,3,5,\ldots \)) vanish and we may restrict the problem to the case \( n = 0,2,4,6,\ldots \). The factor \( I_2 \) rises to about 30% of \( I_0 \) at intermediate values of \( \text{Vo/kT} \), but thereafter \( I_{n+2}/I_n \rightarrow 0 \) as \( \text{Vo/kT} \rightarrow \infty \).

The complex polarisability from the Budo equation [1,2] is, finally, a sum over the even weighting factors and correlation times and the imaginary part, \( \alpha''(\omega) \), is illustrated in fig. (1) normalised by \( \bar{I}_\lambda \).

**DISCUSSION**

It is clear from fig. (1) that as \( \text{Vo/kT} \) increases, a secondary loss process appears on the high frequency side of the \( \text{Vo/kT} = 0 \) curve. This loss process (or complex polarisability curve) is due to the fact that the diffusion of the two dipoles \( \mu_1 \) and \( \mu_2 \) is no longer independent. In the original model considered by Budo, the two dipoles \( \mu_1 \) and \( \mu_2 \) are those of two groups attached to the same diffusing molecule. (Experimentally [10], the process of internal rotation (e.g. of a \( \text{CH}_3 \)O-group) could produce loss curves such as those in fig. (1)). However, it is interesting to note that the potential energy \( \text{Vo} \) may originate in the interaction of two dipoles on independently diffusing molecules; the director potential of a nematicogenic environment [11], from the equations governing the interaction between rotation and translation [12], and so on. The numerical methods developed to solve eqn. (1) therefore have a wide range of applicability. The general analytical form of the overall polarisability curve is (s is the Laplace variable:}
\[ \alpha''(\omega) / \alpha'(0) \]

Fig. 1. Curves of normalised complex polarisability $\alpha''(\omega)/\alpha'(0)$ vs. $\log_{10}(\omega)$ from the Budo theory behind eqn. (1). Each curve is marked with $V_0/kT$.

\[
\begin{align*}
   \sum_\Lambda \left[ \int_0^{2\pi} \int_0^{2\pi} \cos^2 \theta \cos \theta \right] W(\theta) e^{-W(\theta)/2kT} Z_\Lambda(\theta) Z_\Lambda(\theta) d\theta d\theta \\
   = \int_0^{2\pi} W(\theta) Z_\Lambda^2(\theta) d\theta \left( s + \frac{\lambda kT}{z} \right)
\end{align*}
\]

where \[ W(\theta) = \exp \left[ -\frac{V_D}{kT} (1 - \cos \theta) \right] \]

i.e. there is a distribution of relaxation times as in fig. (1).

Analytical checks on the accuracy of the numerical results of fig. (1) can be made as follows. The analytical difference between the relaxation times in the limit $V_0 \to 0$ ($\tau_{\text{free}}$) and $V_0 \to \infty$ ($\tau_{\text{hind}}$) is given by [5]:

\[
A = \frac{1}{\pi} \int_0^{\pi} \frac{e^{-\lambda s} \cos \theta}{1 + \frac{V_D}{kT} (1 - \cos \theta)} d\theta
\]
\[ \frac{1}{\tau_{\text{free}}} - \frac{1}{\tau_{\text{hind}}} = \frac{kT}{2 \zeta_1} \]  

(5)

and the ratio by [5]:

\[ \frac{\tau_{\text{hind}}}{\tau_{\text{free}}} = \frac{\omega_{\text{max}}}{\omega_{\text{min}}} = \frac{2(1 + \zeta_1/\zeta)}{(1 + 2\zeta_1/\zeta)} \]  

(6)

The parameters used in fig. (1) were \( \mu_1 = \mu_2 = 1.0 \), \( \zeta_1/\zeta = 0.5 \); \( 2\zeta_1/kT = 10^{-8} \) and produce the analytical result:

\[ \log_{10}(\omega_{\text{free}}) - \log_{10}(\omega_{\text{hind}}) = 0.176 \]

from eqn. (6).

From fig. (1), however, for \( V_0/kT = 0 \), \( \log_{10}(\omega_{\text{free}}) = 8.48 \); for \( V_0/kT = 20.0 \), \( \log_{10}(\omega_{\text{hind}}) = 8.31 \), i.e. a difference of 0.17(0), which is already in satisfactory agreement with the limiting \( (V_0/kT - \infty) \) analytical value of 0.176. This is an important verification that numerical errors have been kept well within the bounds of acceptability, bearing in mind that each loss curve of fig. (1) requires up to 15 separate numerical solutions of the Sturm-Liouville equation and therefore up to 105 numerical integrations over unequally spaced mesh-points, with subsequent accumulation of numerical uncertainty.

Another check is possible - on the normalised amplitude of the two loss curves of fig. (1). The analytical results [5] provide:

\[ \tau_{\text{hind}} = \left[ \frac{kT}{2 \zeta_1} \left( 1 + \frac{\zeta_1}{\zeta} \right) \right]^{-1} \]  

(7)

\[ \tau_{\text{free}} = \left[ \frac{kT}{\zeta_1} \left( 1 + \frac{\zeta_1}{\zeta} \right) \right]^{-1} \]  

(8)

The normalised maximum amplitude of the curve \( \alpha''(\omega)/\alpha'(0) \) of fig. (1) is given by:

\[ \frac{\alpha''(\omega)}{\alpha'(0)} = \sum_{\lambda} \frac{I_{\lambda} \omega_{\lambda}^{w_{\lambda}}}{1 + \omega^2 \tau_{\lambda}^2} / \sum_{\lambda} I_{\lambda} \]  

(9)
\begin{table}
\begin{center}
\begin{tabular}{cccccccc}
\hline \hline $\gamma \frac{\sqrt{D}}{E}$ & \multicolumn{4}{c}{0.01} & \multicolumn{4}{c}{0.10} \\
$\lambda \frac{k}{N}$ & 1.000 & 1.002 & 1.165 & 4.335 & 9.451 & 19.508 & 49.547 \\
& $\pm 8.1 \times 10^{-5}$ & $\pm 6.3 \times 10^{-5}$ & $\pm 7.5 \times 10^{-5}$ & $\pm 2.7 \times 10^{-4}$ & $\pm 7.3 \times 10^{-4}$ & $\pm 0.0018$ & $\pm 0.0031$ \\
\hline 1 & 4.000 & 4.001 & 4.134 & 7.663 & 17.637 & 37.866 & 97.951 \\
& $\pm 2.5 \times 10^{-4}$ & $\pm 0.00026$ & $\pm 2.6 \times 10^{-4}$ & $\pm 4.8 \times 10^{-4}$ & $\pm 0.0011$ & $\pm 0.0018$ & $\pm 0.0062$ \\
& $\pm 5.6 \times 10^{-4}$ & $\pm 5.6 \times 10^{-4}$ & $\pm 7.7 \times 10^{-4}$ & $\pm 0.0015$ & $\pm 0.0048$ & $\pm 0.0048$ & $\pm 0.011$ \\
\hline 3 & 16.000 & 16.001 & 16.127 & 19.250 & 30.067 & 70.813 & 191.631 \\
& $\pm 0.0010$ & $\pm 0.001$ & $\pm 0.001$ & $\pm 0.0012$ & $\pm 0.0019$ & $\pm 0.0049$ & $\pm 0.0083$ \\
\hline 4 & 25.000 & 25.001 & 25.127 & 28.205 & 38.431 & 84.840 & 236.871 \\
& $\pm 0.0016$ & $\pm 0.0016$ & $\pm 0.0016$ & $\pm 0.0018$ & $\pm 0.0024$ & $\pm 0.0053$ & $\pm 0.017$ \\
\hline 5 & 36.000 & 36.001 & 36.127 & 39.180 & 49.134 & 96.410 & 280.689 \\
& $\pm 0.0023$ & $\pm 0.0023$ & $\pm 0.0023$ & $\pm 0.0024$ & $\pm 0.0031$ & $\pm 0.0060$ & $\pm 0.015$ \\
\hline 6 & 49.002 & 49.002 & 49.127 & 52.166 & 61.962 & 106.630 & 323.501 \\
& $\pm 0.0031$ & $\pm 0.0031$ & $\pm 0.0031$ & $\pm 0.0033$ & $\pm 0.0039$ & $\pm 0.0067$ & $\pm 0.022$ \\
\hline 7 & 64.003 & 64.004 & 64.126 & 67.158 & 76.853 & 119.426 & 346.686 \\
& $\pm 0.0040$ & $\pm 0.002$ & $\pm 0.004$ & $\pm 0.0042$ & $\pm 0.0048$ & $\pm 0.0075$ & $\pm 0.014$ \\
\hline 8 & 81.001 & 81.002 & 81.124 & 84.152 & 93.779 & 135.157 & 404.662 \\
& $\pm 0.0051$ & $\pm 0.0051$ & $\pm 0.0051$ & $\pm 0.0053$ & $\pm 0.0059$ & $\pm 0.0084$ & $\pm 0.003$ \\
\hline 9 & 100.005 & 100.008 & 100.123 & 103.149 & 112.727 & 153.318 & 442.986 \\
& $\pm 0.0063$ & $\pm 0.0063$ & $\pm 0.0063$ & $\pm 0.0086$ & $\pm 0.0070$ & $\pm 0.0096$ & $\pm 0.024$ \\
\hline 10 & 121.003 & 121.002 & 121.123 & 124.142 & 133.687 & 173.720 & 479.765 \\
& $\pm 0.0076$ & $\pm 0.0076$ & $\pm 0.0076$ & $\pm 0.0078$ & $\pm 0.0084$ & $\pm 0.011$ & $\pm 0.038$ \\
\hline 11 & 144.000 & 144.001 & 144.122 & 147.140 & 156.659 & 196.277 & 514.592 \\
& $\pm 0.009$ & $\pm 0.009$ & $\pm 0.009$ & $\pm 0.0092$ & $\pm 0.0098$ & $\pm 0.012$ & $\pm 0.033$ \\
\hline 12 & 169.000 & 169.001 & 169.133 & 172.139 & 181.637 & 220.934 & 547.380 \\
& $\pm 0.011$ & $\pm 0.011$ & $\pm 0.011$ & $\pm 0.011$ & $\pm 0.011$ & $\pm 0.014$ & $\pm 0.047$ \\
\hline 13 & 195.998 & 196.000 & 196.136 & 199.110 & 208.619 & 247.664 & 577.569 \\
& $\pm 0.012$ & $\pm 0.012$ & $\pm 0.012$ & $\pm 0.012$ & $\pm 0.013$ & $\pm 0.015$ & $\pm 0.036$ \\
\hline 14 & 225.001 & 225.00 & 225.128 & 228.111 & 237.598 & 276.447 & 604.325 \\
& $\pm 0.014$ & $\pm 0.014$ & $\pm 0.014$ & $\pm 0.014$ & $\pm 0.015$ & $\pm 0.017$ & $\pm 0.052$ \\
\hline 15 & 255.999 & 255.998 & 256.121 & 259.148 & 268.598 & 307.270 & 626.913 \\
& $\pm 0.016$ & $\pm 0.016$ & $\pm 0.016$ & $\pm 0.016$ & $\pm 0.017$ & $\pm 0.019$ & $\pm 0.039$ \\
\hline
\end{tabular}
\end{center}
\end{table}

\[
\frac{d^2y}{dx^2} + \left[ \lambda - \frac{\gamma^2}{8} + \frac{\gamma}{2} \cos x + \frac{\gamma^2}{8} \cos(2x) \right] y = 0
\]

with \( y(0) = 0 \); \( y(\pi) = 0 \)
and in the limit $V_0/kT \rightarrow 0.0$, there is only one eigenvalue, equivalent to the weighting factor $I_0'$. It is then easy to see that the maximum of $a''(\omega)/a'(0)$ is 0.5, because $\omega_0 = 1$ at this frequency. The numerical result of figure (1) for $V_0/kT$ is 0.500.

Finally, in the "locked-in limit" of $V_0/kT \rightarrow \infty$, there is, theoretically, an infinite number of correlation times, each with its own weighting factor $I_\lambda'$. (This pattern begins to emerge in table (2) for $V_0/kT = 10.0$). In this case:

$$\begin{vmatrix} a''(0) \\ a'(0) \end{vmatrix}_{\text{max}} = \frac{0.5 I_0}{\sum \frac{I_\lambda}{\lambda}}$$

(10)

The intensity of the normalised complex polarisability curve therefore decreases with respect to the intensity in the limit $V_0/kT = 0$. This is again in agreement with the results from the computer (fig. (1), and tables (1) and (2)).

Another Sturm-Liouville system of importance which occurs in itinerant oscillator theory is [5]:

$$\frac{d^2y}{dx^2} + \left[ \lambda - \frac{\gamma^2}{8} + \frac{\gamma}{2} \cos x + \frac{\gamma}{8} \cos (2x) \right] y = 0$$

(11)

with boundary conditions $y(0) = 0$; $y(\pi) = 0$ and the numerical methods developed by Hargrave and Pryce [7-9] produce the eigenvalues $\lambda$ of table (3) for this system, as a function of a dipole-electric field potential ($\gamma = \mu E/kT$). It can be seen that small differences in the structure of the Sturm-Liouville equation produce quite different eigenvalue patterns (cf eqn. (1); table 1; and eqn. (11); table (3)).

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REFERENCES

9  N.A.G. Library, Routines D02KEF and D01GAF (FORTRAN).
11 ref. 4, Chapter 8, for example.