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Quasi-Random Monte Carlo Integration for Computing Dissociation Rates

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We describe our work towards implementing quasi-random Monte Carlo integration techniques for computing dissociation rates in chemical kinetics. Preliminary results indicated a significant advantage with quasi-random Monte Carlo methods, which yield accurate results at a reduced computational cost as compared to standard pseudo-random monte carlo. The internal energy relaxation processes of vibrational energy transfer, dissociation and recombination were modeled using state-to-state kinetics of diatomic nitrogen. Computational results for this test case indicate that (i) the quasi-random method converges to the same solution as the standard technique and (ii) the variability in the results are correspondingly reduced. Provided that the underlying theory is correct, the new method is an advantageous alternative to pseudo-random Monte Carlo integration. The state-specific rates can be incorporated into a solution of the master kinetic equations coupled to the fluid dynamic equations to describe the thermo-chemical non-equilibrium phenomenon in high temperature hypersonic flowfields.

Introduction

Shock waves in high speed flow of air present considerable difficulties for accurate numerical simulation of the flow around aerospace vehicles. The shock wave redistributes the high kinetic energy of the oncoming flow into various internal energy modes with varying time scales, leading to significant chemical and thermal non-equilibrium in the stagnation region of the vehicle. In the gas kinetic description, intermolecular collisions change the translational, rotational, vibrational, and electronic energies of the collision partners.[1] Thermal dissociation for these high temperature flows is a common occurrence, which needs to be modeled accurately to predict aerodynamic and heat loads experienced by the vehicle. The statistical aspect in the modeling of the dissociation process is the subject of the present study.

Generally, in modern hypersonic codes, the rate-controlling temperature to determine the non-equilibrium rates for dissociation is taken to be the geometric mean of the equilibrated translational-rotational temperature and the single vibrational temperature of the diatomic molecule. This empirical model known as the Park model[2] is widely used in hypersonic codes today due to its simplicity. However, the Park model lacks a physical basis and has been shown to be inaccurate for a wide range of temperatures.[3] The state kinetic modeling approach advanced by Billing[4,5] using the semiclassical theory to calculate transition rates for atom-diatom and diatom-diatom collisions was extended by Macheret and Adamovich[6] to develop a theory of dissociation of diatomic molecules based on the anharmonicity-corrected and energy-symmetrized forced harmonic oscillator (FHO) quantum scaling[7] in conjunction with free-rotation or impulsive energy-transfer models. The model predicts state specific dissociation rates by accounting for molecular rotation and three-dimensional collisions and has the advantage of being computationally tractable without any adjustable parameters. However, in the modeling of state kinetic dissociation, the evaluation of the multi-dimensional integrals in the dissociation cross section model for atom-molecule and molecule-molecule collisions is currently done using Monte Carlo methods and its use in today's hypersonic codes is not fully realized due to the extremely high computational requirements.

In the work of Billing and subsequent work of Macheret and Adamovich[6] the multi-dimensional Monte Carlo integration was implemented by repeated sub routine calls to a pseudo random number generator[8] by using a different seed each time. In their method, each subroutine call returns a random value for use as a given parameter of the phase space and also returns a random seed for the random generation of the next parameter. In this way

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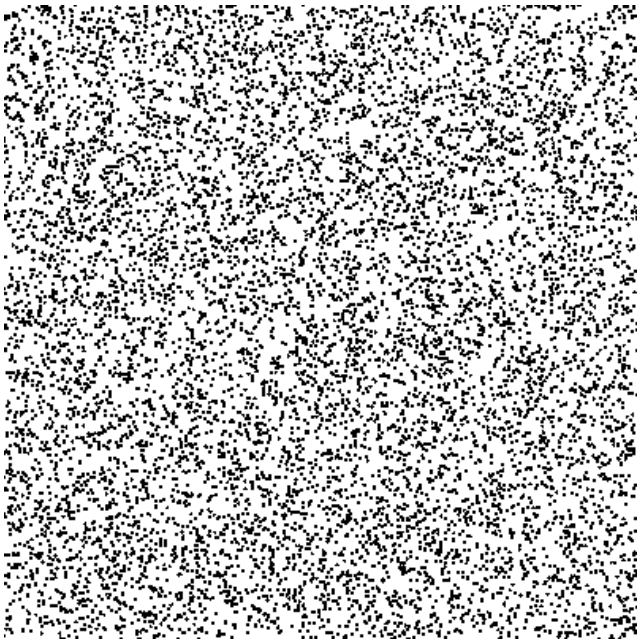
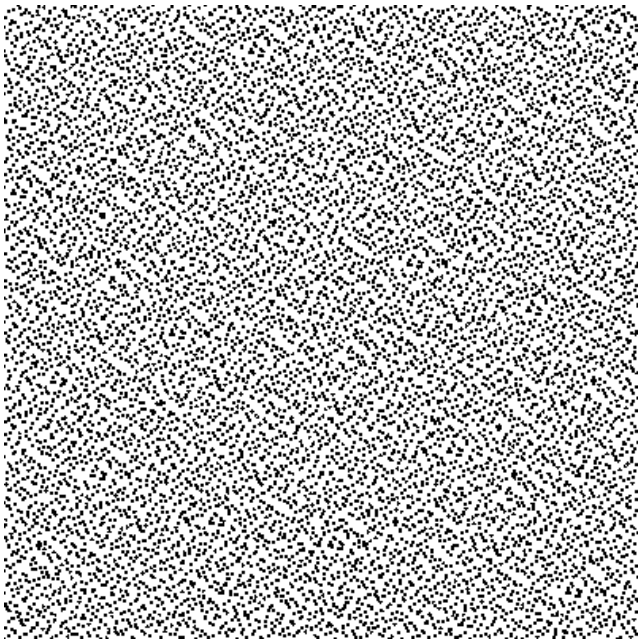


a) Pseudo–Random number generators tend to clump the points (not optimal).



b) Quasi–Random (LDS) produce a more uniform distribution (better).

Figure 1 Comparison of sequences with 10,000 points. The clumping effect leads to fluctuations and slow convergence when used in applications that simulate physical processes.

an eight or more dimensional parameter phase space point is created. The process is continued to generate the next phase space point. This was done so as to achieve as much randomness as possible for avoiding any hidden intrinsic correlations in the phase space. The state kinetic dissociation rates obtained in this manner and the state kinetic vibrational rates were implemented for the first time in the work of Josyula, et al.[9] for computing a Mach 19 thermochemical non-equilibrium flow of nitrogen gas around a hemisphere cylinder of radius 0.1524 m. In the current study, however, we focus our attention on the evaluation of the multi-dimensional integrals to compute the dissociation cross sections by replacing subroutine calls to a pseudo random number generator by calls to an eight dimensional *low discrepancy sequence* generator.[10] A brief description of the random sampling and integration procedure follows along with current results that we hope to explore further. The methodology is quite general and applicable to any problem requiring random sampling techniques.

Pseudo-Random Sampling and Integration

Pseudo-random numbers are numbers that are generated by a pseudo-random number generator (PRNG) which are widely available in modern compiled and scripting-based programming languages. A PRNG is an algorithm that generates a sequence of numbers, the elements of which are *approximately* independent of each other. Pseudo-random numbers have been a critical part of modern computing, from cryptography to the Monte Carlo method for simulating physical systems. If f is a function on the hypercube $[0,1]^n$, and $\{x_1, \ldots, x_N\}$ are random numbers from $[0,1]^n$, we have Monte Carlo integration given by

$$\lim_{N\to\infty} \frac{1}{N} \sum_{i=1}^{N} f(x_i) = \int_{[0,1]^n} f(x)\, dx \tag{1}$$

with probability one; however convergence can be slow. An improvement over pseudo-random sequences for the purpose of numeric integration is given by *quasi-random* sequences which we summarize next.

Low Discrepancy Sequences

Intuitively, a *low discrepancy sequence* (LDS) is a sequence of N points $x_i \in [0,1]^n$ which is more *uniform* than any pseudo-randomly generated sequence. Pseudo-random numbers have a tendency to cluster and mathematical methods have been developed to avoid such clustering. Figures () and () illustrate this effect by comparing a sequence of $10,000$ pseudo random numbers in $[0,1] \times [0,1]$ with $10,000$ low discrepancy points from the same space. Formal details are given by Niederreiter[10] and the references given there.

LDSs are also called quasi-random sequences in the literature. Because LDSs fill in the hypercube more uniformly than pseudo-random sequences, it is reasonable to expect that if $z_1, \ldots, z_N \in [0,1]^n$ is an LDS, then the approximation

$$\int_{[0,1]^n} f(z)dz \approx \frac{1}{N}\sum_{i=1}^{N} f(z_i) \tag{2}$$

should be better than the Monte Carlo approximation above. In fact, it has been proven ([10, Theorem 2.9, p. 18]) that

$$\lim_{N\to\infty} \frac{1}{N}\sum_{i=1}^{N} f(z_i) = \int_{[0,1]^n} f(z)\, dz \tag{3}$$

(recall that (1) is true only with probability one). Furthermore, the convergence rate of (3) is much better than that of (1) and quasi random sequences are used extensively these days for high dimensional integration.[10,11]

The van der Corput Sequence

Perhaps the oldest LDS is the Van der Corput sequence dating back to 1935 [10, p. 25]. The definition is recalled here. Given a non-negative integer n, consider the base two expansion

$$\sum_{r=0}^{h_n} a_r(n)2^r. \tag{4}$$

The van der Corput sequence is given by

$$\Phi_2(n) = \sum_{j=0}^{h_n} a_j(n)2^{-j-1}. \tag{5}$$

For example, base two, we have

$$0 \to 0,\ 1 \to 1,\ 2 \to 10,\ 3 \to 11,\ 4 \to 100,\ 5 \to 101,\ 6 \to 110\ldots \tag{6}$$

so the first six elements of the van der Corput sequence are

$$0,\ \tfrac{1}{2},\ \tfrac{1}{4},\ \tfrac{3}{4},\ \tfrac{1}{8},\ \tfrac{5}{8}, \ldots \tag{7}$$

Note that this construction can be extended to base b for any positive integer b; given

$$n = \sum_{r=0}^{h_n} a_r(n)b^r \tag{8}$$

set

$$\Phi_b(n) = \sum_{j=0}^{h_n} a_j(n)b^{-j-1}. \tag{9}$$

The Halton Sequence

In dimension n, the Halton sequence is given by

$$H(i) = (\Phi_{p_1}(i), \ldots, \Phi_{p_N}(i)) \tag{10}$$

where $p_1 = 2, p_2 = 3, \ldots, p_N$ are the first N prime numbers. There are variations of these sequences that introduce a certain randomness and are called 'scrambled Halton sequences'.[12,13] Scrambled sequences can have better convergence properties than the ordinary Halton sequence. Many other types of pseudo-random sequences exist. In fact, it each dimension, there are an infinite variety of such sequences. One of these called the Soboĺ sequence is implemented in Press, et. al.[14]

Quality

Here is an example for comparing the quality of a pseudo-random to a quasi-random sequence. We compare the pseudo-random samples to Halton samples. Consider the function

$$f(x, y, z, t) = e^{-\frac{1}{2}(x^2+y^2+z^2+t^2)} \tag{11}$$

over the region $R = [0, 1] \times [0, 1] \times [0, \pi] \times [0, \pi]$. For a sample $\{\mathbf{x_1}, \ldots, \mathbf{x_N}\} \subseteq R$, we have the approximation

$$\int_0^1 \int_0^1 \int_0^\pi \int_0^\pi f(x, y, z, t) \mathrm{dx}\, \mathrm{dy}\, \mathrm{dz}\, \mathrm{dt} \approx \frac{1}{N} \sum_{i=1}^{N} f(\mathbf{x_i}). \tag{12}$$

The exact answer up to five significant figures is 0.29157. Here are the computational results:

```
100 pts      rand:integral = 0.299398      Halton:integral = 0.291991
5000 pts     rand:integral = 0.293671      Halton:integral = 0.291731
10000 pts    rand:integral = 0.290769      Halton:integral = 0.291526
```

It is noteworthy that while the MC method is converging, it is doing so more slowly than the QMC: At 5,000 points the fractional error with pseudo-random Monte Carlo (rand) equals 0.3%. For the same cost, the error with the Halton sequence is an order of magnitude less at 0.01% Also, the QMC method has better accuracy earlier on than the MC method. This means that one can get better answers with fewer points using the QMC method.

Without defining them precisely, we will use some other types of LDSs in this Section, viz. the Faure sequence,[11] the Ramshaw sequence,[15] and the Soboĺ sequence[14] to make the point that not all LDSs are exactly alike. Consider the integral of the polynomial function

$$f(x) = 5(x_1 + x_2 - x_3 + x_7 + x_8)^2 - (x_3 + x_5 + x_7 + x_8)^2 + 2x_5^2 + 4(x_1 - x_2 - x_4 - x_6)^2 \tag{13}$$

over the eight dimensional hypercube $[0, 1]^8$. The exact answer equals 15.0. Table 1 presents the results of Monte Carlo integration using a sample of 5,000 points in $[0, 1]^8$. Choosing a particular sequence (out of the infinitely many) to use for a particular problem is clearly an issue. The situation is even richer as will be pointed out in the next Section.

Table 1 Computation of eight dimensional integral using various low-discrepancy sequences.

Sequence	Approximation	Percent Accuracy
Faure	15.077851	99.4836731
Halton	14.963398	99.7559866
Ramshaw	14.996384	99.9758933
Soboĺ	15.001989	99.9867417

Scrambling

It was noticed early on[16] that correlations existed between the dimensions in Halton sequences that affected the quality of that sequence. One way to break these correlations and improve the uniformity of the sequence is to permute the digits in each dimension. This process is known as *scrambling* in the literature and much has been written about it.[12, 13, 16–18] Scrambling brings probability theory into the picture for the first time because the permutations should be chosen *at random*. The space of possible scramblings is generally quite large. Using one popular scrambling scheme, there are more than a half a million scramblings of a given sequence in dimension eight. Scrambling can have a very positive effect on the quality of a sequence, as shown in the results summarized in Table 2 and compared to those given in Table 1. The sequences listed were randomly scrambled. The "in-house" sequence was a "generalized Niederreiter sequence" in dimension eight that is one of the many optimized sequences available from an ANSI C library implemented in the work by Lambe.[19]

Dissociation Rate Calculations for Colliding Molecules

The state specific dissociation rates from the semiclassical theory of dissociation developed by Macheret and Adamovich[6] gives:

$$k_{diss}(v, T) = \left(\frac{8kT}{\pi m}\right)^{0.5} \int_0^\infty \sigma_{diss}(v, U, T) \exp\left(-\frac{U}{T}\right) d\left(\frac{U}{T}\right) \tag{14}$$

Table 2 Eight dimensional integration using selected low-discrepancy sequences, with "scrambling".

Sequence	Approximation	Percent Accuracy
Scrambled Halton I	14.980985	99.8732
Scrambled Halton II	15.006920	99.9539
In-house scrambled I	14.996392	99.9390
In-house scrambled II	15.005093	99.9661
In-house scrambled III	14.998921	99.9928
In-house scrambled IV	15.000980	99.9935

where, the expression for the dissociation cross-section assuming free-rotation approximation of diatom-atom collision:

$$\sigma_{diss}(i,E,T) \approx \pi R_m^2 \left(\frac{E}{T}\right)^2 \frac{1}{\pi^2} \int_0^1 dy \int_0^1 d\epsilon \int_0^\pi d\vartheta \int_0^\pi d\varphi \sum_f P_{if}(E,\epsilon,\vartheta,\varphi,y) \tag{15}$$

and for the diatom-diatom collision is:

$$\sigma_{diss}(i,E,T) \approx \left(\frac{E}{T}\right)^3 \frac{R_m^2}{\pi^3} \int_0^1 dy \int_0^1 d\epsilon_1 \int_0^1 d\epsilon_2 \int_0^\pi d\vartheta_1 \int_0^\pi d\vartheta_2 \int_0^\pi d\varphi_1 \int_0^\pi d\varphi_2 \sum_f P_{if}(E,\epsilon_1,\epsilon_2,\vartheta_1,\vartheta_2,\varphi_1,\varphi_2,y) \tag{16}$$

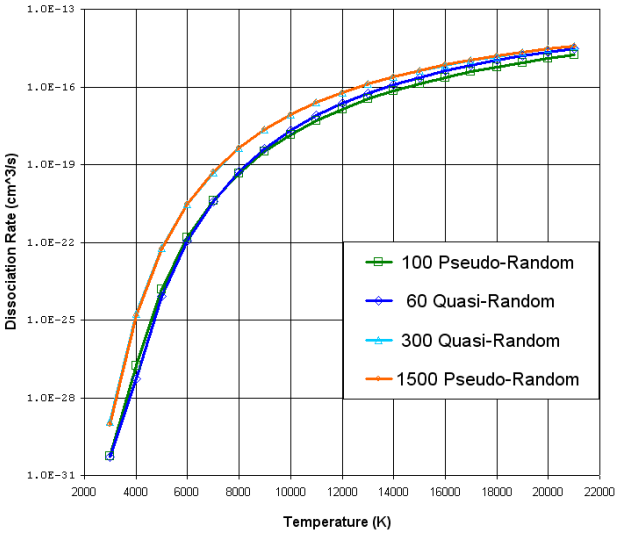
In the expression above, ϵ, ϑ, and φ are the fractional rotational energy, rotational angle, and angular momentum vector, respectively, E is the total collision energy, U is the potential energy for the 3D molecule-molecule collisions, P_{if} is the probability of the transition process, y is a function of the impact parameter, R_m is the hard sphere diameter, and i is the index of the initial vibrational quantum level, and v is the index of the quantum level. The above equations were derived (See Refs. [4–6,]) by evaluating the probabilities of vibrational transitions including dissociation, an energy transferred to a classical initially non-vibrating oscillator was calculated. To accomplish this, a potential energy surface was determined and then classical equations of motion were integrated for the system. A Monte Carlo integration was performed to solve Eqns. 15 and 16, details of which are in given in Refs.[4,5]

In their work, Macheret and Admovich,[6] obtained the cross sections at 60 values of total collision energy in a given range. For each collision energy, a specified number of phase space points were used to evaluate the multidimensional integral. These phase points are obtained with a pseudo-random algorithm and it has been mentioned by Macheret and Adamovich that about 1000 phase space points are sufficient for 10–20% accuracy in computing the cross-sections. The dissociation flux is further averaged over a Maxwellian energy distribution to obtain the vibrational state-specific dissociation rate coefficient. This integral is evaluated numerically with the procedure introduced by Billing.[4,5] The accuracy and speed of these computations, however, is not acceptable for direct coupling with non-equilibrium calculations. For this work, the dissociation rates were obtained using the code developed by Billing and modified by Macheret and Adamovich.[6] A table of values for the dissociation rates can then be generated and an interpolation procedure used to obtain dissociation rates at a given temperature.

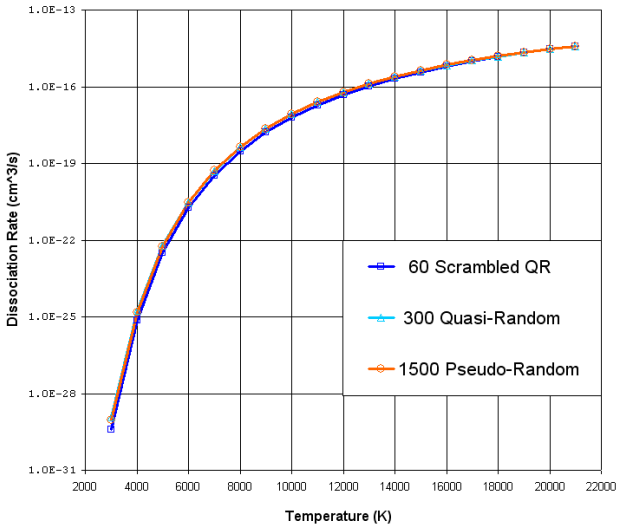
In the work presented here, we developed a procedure for replacing the pseudo-random multidimensional integral evaluation with a more effective procedure based on low discrepancy sequences (as described above). In our preliminary results, we demonstrate that the new methodology improves both the quality and computation cost required to obtain the dissociation rates. If a significant gain in efficiency can be guaranteed, it may be possible to couple the computation of dissociation rates directly with the numerical flow simulation.

Results for State-Specific Dissociation Rates

To explore the potential benefits of using quasi-random numbers in realistic applications, we implemented a procedure for obtaining the dissociation rates for state-to-state chemical kinetics. As we mentioned, the computer program uses a Monte Carlo method with subroutine calls to exactly eight independent pseudo-random numbers in a main loop. To see if the results could be improved using a quasi-random sequence in dimension eight, we replaced calls to the pseudo-random numbers. The sequence used was generated by a program written in ANSI C and used to generate files with $100, 500, \ldots, 10000$ (by increments of 500) pseudo-random points in $[0,1]^8$. By calculating the norm of the difference between an output file and its successor, we found that convergence sets in at about 1500 points for the state-specific dissociation rate for the oxygen-argon collision model. We also



a) Standard (state-of-the-art) Monte-Carlo Method applied to calculation $O_2 - Ar$ dissociation rates requires 1500 sample points to converge.



b) The Quasi-Random method requires only 300 points to show equivalent convergence.

Figure 2 Comparison of standard MC method and quasi-random MC. The custom Quasi-Monte-Carlo Method (60 scrambled QR) gives the same result as the converged solution (1500 Pseudo-random) with only 60 points. For comparison, the 300-point quasi-random calculation is also included. The results give confidence that low-discrepancy sequences can be applied in practical problems with success.

generated scrambled Halton sequences (using the first eight primes) of length 60 and 300. The results are given in Figure (2(a)). We found that 300 scrambled Halton points gave an answer as good as 1500 pseudo-random points. The graph of the 1500 point result overlays that of the 300 point result in Figure (2(a)). The results give confidence that low-discrepancy sequences can be applied in practical problems with success.

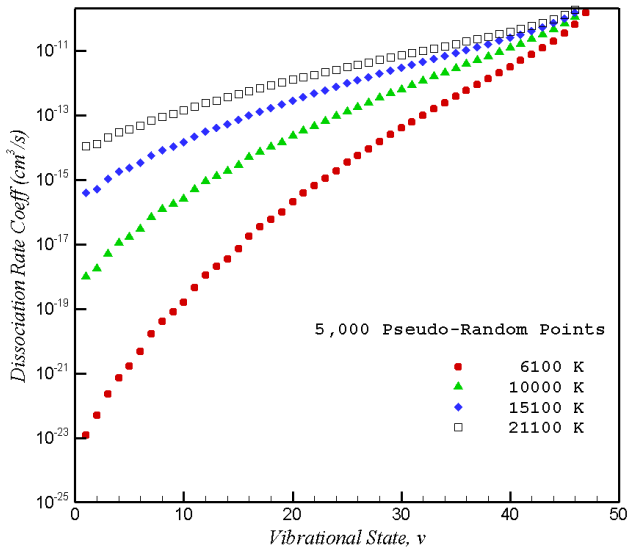
Figure (2(b)) shows the effect of an optimized eight-dimensional LDS obtained using methods developed in.[19] The method implements one of Niederreiter's algorithms[10] over the field[20] with eight elements. The sequence was optimally scrambled. It was found that a sample of only 60 points of this LDS were compared well with the previous sample of 1500 pseudo random points. It is remarkable that a properly chosen LDS can lead to such savings. Numerical calculations using the data confirm these graphical results. Theses results give confidence that low-discrepancy sequences can be applied in practical problems with success; other applications are quite wide-ranging, given the pervasive use of Monte-Carlo methods.

N2-N2 Dissociation and Recombination Rates

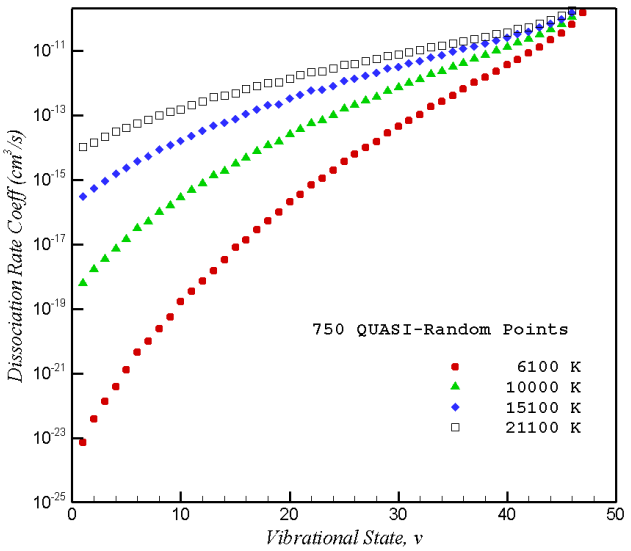
We developed the quasi-random Monte Carlo method described above further and applied it to the calculation of nitrogen dissociation and recombination process based on the semi-classical theory and statistical mechanics. The LDS method, as implemented, is purely a mathematical technique; there is no measure of "physical accuracy" other than trusting that the theory has been properly coded for numerical solution. Convergence to the theoretical integral is a proven theorem for the quasi-random Monte Carlo integration while the same holds only with probability one for pseudo-random Monte Carlo. The LDS method is "non-intrusive" in the sense that if we trust the code for computing dissociation rates to give a correct answer, then using LDS is actually better (our claim) than using pseudo-random integration.

The results show that we can achieve the same level of accuracy with fewer sample points using scrambled LDS's compared to standard MC integration. Here, by again calculating norms, we found that the Monte Carlo integration converges at around 5000 points. Given the physical theory, we claim that replacing the eight-dimensional numerical integral for $N_2 - N_2$ dissociation rates with LDS *does not* interfere with the theory. To improve, one needs to better understand the integrand itself so that the true power of variance reductions techniques could be used. Since we have done nothing with the physics, the attentive reader who is aware of how Monte Carlo integration is done, will easily recognize the power of what these results indicate and may be motivated to try it. These methods will work will proper tuning; if the physics models are trustworthy, then the answer will be better with LDS than with pseudo-random Monte Carlo.

Figure (3) shows that Quasi-Monte Carlo integration using only 750 LDS points compares well with the 5000 pseudo-random points. Numerically, the norm of the difference of the output is 0.0000000000309. We may



a) Standard Monte Carlo Method. The results shown here for the dissociation rate of nitrogen in modeling $N_2 - N_2$ collisions are assumed to be converged, using $5,000$ sample points.



b) Quasi-Random Monte Carlo Method. The results shown here for the dissociation rate of nitrogen in modeling $N_2 - N_2$ collisions are of equal quality to the converged solution, using only 750 sample points.

Figure 3 The Quasi-Random Monte Carlo method yields results that are comparable with the best (converged) results using the standard method. Here, only 750 quasi random are used to obtain accuracy comparable to that obtained with 5,000 points using pseudo-random Monte Carlo.

conclude, therefore, that if the underlying theory is correct and the integrand properly coded, the two solutions converge to essentially the same answer, to within 3.1×10^{-11} on average.

State-Specific Recombination Rates

Results of the dissociation rates for molecular nitrogen collisions are used to compute the corresponding recombination rates using statistical mechanics. The recombination rates are determined from the equilibrium constant at various translational temperatures. At equilibrium, the state populations in the vibrational quantum levels are described by a Boltzmann distribution such that

$$\frac{n[v]}{n[v-1]} = -\left(\frac{\epsilon[v] - \epsilon[v-1]}{kT}\right) \tag{17}$$

The details of the development yield a formula for the recombination coefficient

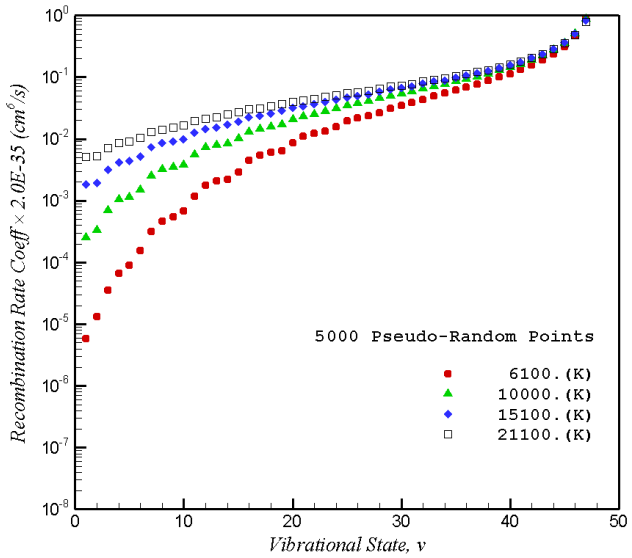
$$k_r[v,t] = k_d[v,T]\frac{2I_{AB}\lambda_\mu^3}{\beta h^2 Z_N^2}\exp\left\{\frac{D_0 - \epsilon[v]}{kT}\right\}. \tag{18}$$

where λ_μ is the thermal deBroglie wavelength, Z is the partition function, h is the Planck constant, and $\beta = 1/kT$. Details of the formula and other definitions are given by Josyula, et. al.[9] So the inaccuracies in the dissociation rates carry over, yielding very coarse recombination rates; inaccuracies in the dissociation rates are amplified in the recombination rates. To compare the best results, we used 5000 points with the pseudo-random MCM and 750 points with the quasi-random MCM and obtained the recombination rates shown in Figure (4). Figure (4(a) shows the converged result with the pseudo-random MCM. The same calculation using 750 points with the quasi-random MCM gives the (somewhat) smoother data set shown in Figure (4(b)).

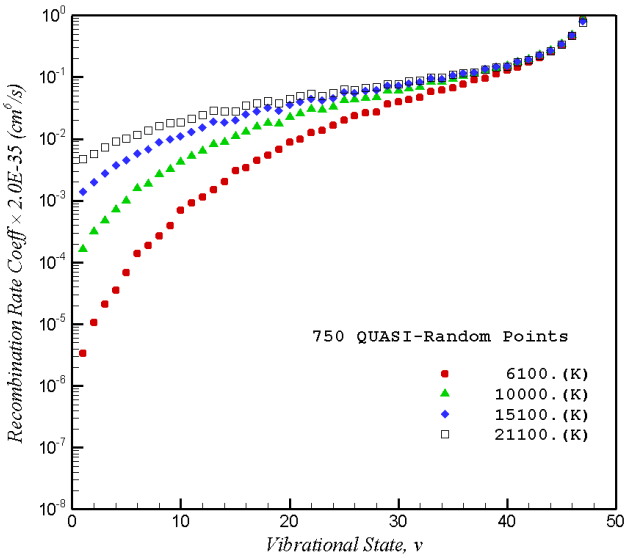
Preliminary Error Analysis

To obtain some understanding of how well the quasi-random MCM compared to the standard approach, we performed a series of calculations with the intent of measuring the differences. As a measure of convergence, we used the standard approach typically used for analyzing iterative methods. For comparing data sets, we computed

$$\|\boldsymbol{x}_1 - \boldsymbol{x}_2\| = \sqrt{\sum_k \left(x_{1,k} - x_{2,k}\right)^2} \tag{19}$$

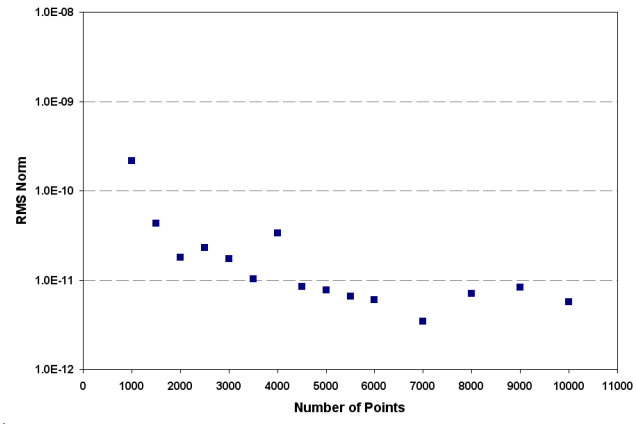


a) Recombination rates obtained with standard (pseudo-random) MCM with 5000 integration points.



b) Recombination rates obtained with 750 points using quasi-random MCM.

Figure 4 Even with 5000 sample points, the standard Monte-Carlo method gives some variability in the recombination rates. The quasi-random MCM gives an improved (smoother) set of data points.



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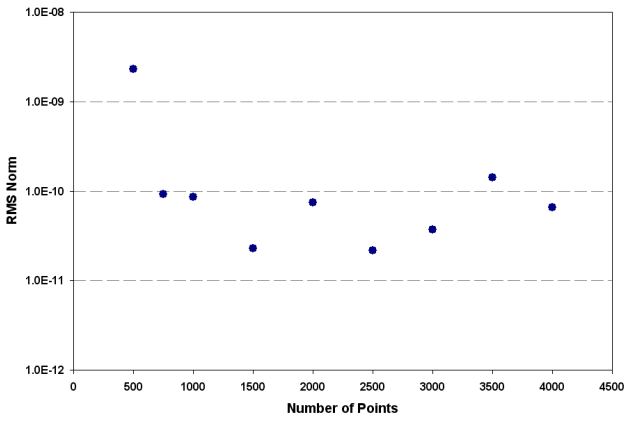


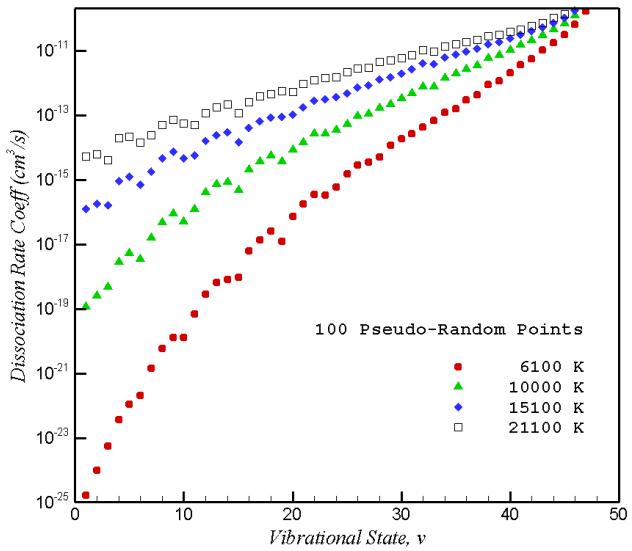
b)

Figure 5 With 5,000 sample points, the standard Monte-Carlo method is arguably converged. Comparable quality with quasi-random method is obtained with only 750 points. The RMS norm quantifies differences between data sets.

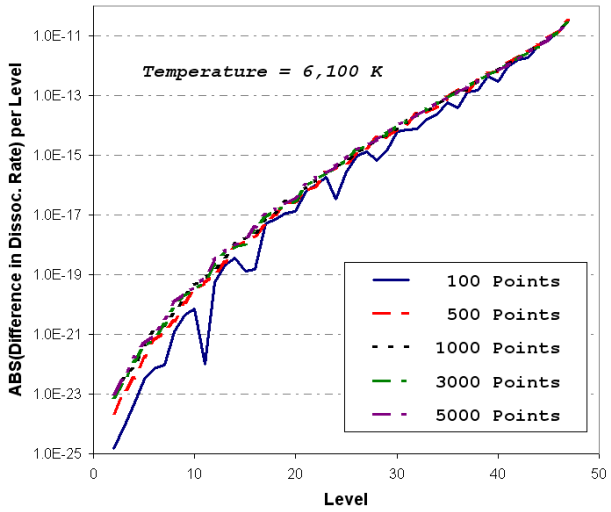
This root-mean-square (RMS) difference between data sets quantifies convergence. In Figure (5), the RMS norm between data sets shows a decreasing trend until fluctuations appear. In Figure (5(a)), the pseudo-random calculation is arguably converged at 5000 points. In Figure (5(b)), the quasi-random Monte-Carlo results are converged at about 750 points and consistently yield improvement in quality compared to the standard pseudo-random Monte Carlo. This gives a quantitative measure of convergence to complement the smoothness and unchanging state observed in the data graphically in Figure (3).

In addition to convergence, we also note that the variability in the results is reduced for the pseudo-random sequence as convergence is achieved. We use the term "variability" to measure the "wiggles" in the data and to avoid confusion with with variance as defined statistically. Variability in computed results is a well-known problem where Monte Carlo sampling is used; the effect has also been described as scatter. For the quasi-random sequence, variability in the results is consistently lower, with the corresponding smooth solution. Without a full-blown statistical analysis, an attempt was made to quantify the variability in the data. Figure (6(b)) shows the difference in dissociation rates between levels, calculated as

$$\Delta k_{diss} = |k_1 - k_2| \,. \tag{20}$$



a) The Monte-Carlo Method with 100 phase-space points for numerical integration gives results with a high degree of variability ("wiggles"). As the solution converged, the variability decreased as well and is clearly evident in Figure (3(a)).



b) A measure of the variability can be quantified by calculating the absolute value of the difference between levels. The spikes indicate sudden changes between levels and are not physically relevant.

Figure 6 Without a full-blown statistical analysis, an attempt was made to quantify the variability in the data. The figure on the right shows the difference in dissociation rates between levels. If the curve were continuous, this would equal the tangent slope. As convergence is approached, this measure of variability produces a smoother line, i.e., the "wiggles" decrease.

If the curve were continuous, this would equal the tangent slope; the spikes would indicate sudden changes between levels and are not physically relevant. As convergence is approached, this measure of variability produces a smoother line, i.e., the "wiggles" decrease. While results are shown only for temperature at $6,100K$ the same was observed for across all temperatures used in the calculations.

Conclusion

The state-specific dissociation rates coefficients of $N_2 - N_2$ collisions were based on the semiclassical theory of Macheret and Adamovich. State-specific recombination rate coefficients were obtained by detailed balance. Dissociation and recombination rate coefficients were computed using two random sampling techniques for evaluating an eight-dimensional integral. The comparison between the pseudo-random Monte-Carlo Method and the newly developed quasi-random technique for this application shows consistent improvement: We can compute accurate results with much less points. For this test case, we showed that (i) the quasi-random method converges to the same solution as the standard technique and (ii) the variability in the results are correspondingly reduced. Provided that the underlying theory is correct, the new method is an advantageous alternative to pseudo-random Monte Carlo integration. These results can be incorporated into a solution of the master kinetic equations coupled to fluid dynamic equations to perform computational simulation of high-speed non-equilibrium flow. We plan to continue to develop this methodology in this area. Furthermore we are investigating various schemes to interpolate or otherwise accurately approximate values using the data generated using state-of-the-art statistical methods. With improved optimized algorithms, it may be feasible to write a subroutine for directly calculating the dissociation rate fully coupled with the numerical flow simulation program.

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