

# Transient Macroscopic Chemistry in the DSMC Method

M.J. Goldsworthy, M.N Macrossan and M.Abdel-Jawad

*Centre for Hypersonics, The University of Queensland, Brisbane, Australia 4072*

**Abstract.** In the Direct Simulation Monte Carlo method, a combination of statistical and deterministic procedures applied to a finite number of ‘simulator’ particles are used to model rarefied gas-kinetic processes. Traditionally, chemical reactions are modelled using information from specific colliding particle pairs. In the Macroscopic Chemistry Method (MCM), the reactions are decoupled from the specific particle pairs selected for collisions. Information from all of the particles within a cell is used to determine a reaction rate coefficient for that cell. MCM has previously been applied to steady flow DSMC simulations. Here we show how MCM can be used to model chemical kinetics in DSMC simulations of unsteady flow. Results are compared with a collision-based chemistry procedure for two binary reactions in a 1-D unsteady shock-expansion tube simulation and during the unsteady development of 2-D flow through a cavity. For the shock tube simulation, close agreement is demonstrated between the two methods for instantaneous, ensemble-averaged profiles of temperature and species mole fractions. For the cavity flow, a high degree of thermal non-equilibrium is present and non-equilibrium reaction rate correction factors are employed in MCM. Very close agreement is demonstrated for ensemble-averaged mole fraction contours predicted by the particle and macroscopic methods at three different flow-times. A comparison of the accumulated number of net reactions per cell shows that both methods compute identical numbers of reaction events. For the 2-D flow, MCM required similar CPU and memory resources to the particle chemistry method. The Macroscopic Chemistry Method is applicable to any general DSMC code using any viscosity or non-reacting collision models and any non-reacting energy exchange models. MCM can be used to implement any reaction rate formulations, whether these be from experimental or theoretical studies.

**Keywords:** Rarefied Gas Dynamics, DSMC, MCM, chemical kinetics, transient, unsteady, macroscopic chemistry.

**PACS:** 47.40.Ki, 47.45.-n, 47.60.Dx, 82.20.Pm, 82.20.Wt

## INTRODUCTION

The Direct Simulation Monte Carlo (DSMC) method [1] is used to model rarefied flows with Knudsen numbers typically above 0.001. Simulator particles transport mass, momentum, energy and species identity between different regions within the flow-field. These simulator particles are moved in free-flight over a single computational time-step and undergo collisions at the end of each time-step. Energy exchange in collisions is computed using statistic procedures which, when accumulated over a large number of simulator particles, lead to the expected relaxation rates.

Chemical reactions are usually implemented in DSMC by calculating reaction probabilities for colliding particle pairs. However, it can be difficult to implement reaction rate data derived from experimental or theoretical studies since this data is often supplied in a temperature dependent form which is not used directly by particle-based chemistry methods. The reaction rates which will be produced by a particle-based chemistry model are constrained by the collision rates set by the collision cross-section, and hence the desired reaction rate coefficient as a function of temperature may not be realized. These difficulties may be overcome if chemical reactions are decoupled from the non-reacting collision procedures. A decoupled chemistry procedure known as the Macroscopic Chemistry Method (MCM) was proposed by Lilley and Macrossan [2] and refined by Goldsworthy et al. [3] [4]. In this method, chemical reactions are computed by solving the chemical kinetic equations at the end of each time-step, using information obtained from all the simulator particles in a cell, not just those that are selected for collisions.

Important insight may be gained into the fluid dynamics of a particular problem by observing the transient fluid motion. In some cases, the flow-field is inherently unsteady and transient simulations are necessary. Here we demonstrate a procedure for implementing MCM for unsteady flows. We test this procedure by calculating the

reactions for a ‘model gas’ for which there are two species. Species  $A$  may be converted to species  $B$ , or  $B$  into  $A$ , through the reactions



Here  $M$  is the collision partner. The  $A \rightarrow B$  reaction is endothermic, with heat of reaction  $-E_a$  ( $\equiv -\kappa\theta_a$ ) where  $\kappa$  is Boltzmann’s constant. Except for their chemical potential energy, species  $A$  and  $B$  molecules are assumed to be identical in all other respects. We compare the results with those from a particle-based chemistry procedure appropriate to this model gas.

## PROCEDURE FOR UNSTEADY FLOWS

The DSMC method is appropriate for a dilute gas assumption in which three body collisions are ignored. For a general reaction  $A+B \rightarrow \text{products}$ , the rate of reactant depletion can be expressed as

$$\Delta \dot{N}_A = k_f N_A N_B / V. \quad (2)$$

Here  $N_A$  is the number of species  $A$  particles in a region of volume  $V$  and  $k_f$  is the reaction rate coefficient for the forward reaction. In MCM, the change in the number of a given species  $A$  over a computational time-step is calculated from an expression similar to Eq. (2) and the numbers of each species are then adjusted to account for this. For steady flows, time-averaged number densities and temperatures are employed in Eq. (2) throughout the simulation, and this leads to the correct reaction rate in the limit of a large sample. For unsteady flows, time-averaged values cannot be employed and direct use of Eq. (2) would lead to incorrect ensemble-averaged reaction rates since  $\overline{NN} \neq \bar{N}\bar{N}$ .

In DSMC collision procedures, the number of collisions involving  $A$  and  $B$  particles in a computational time-step depends on the same term  $N_A N_B / V$  as in Eq. (2). Bird [5] has proposed a modification of the method by which the simulator collision rate is set. In place of  $\bar{N}\bar{N} / V$ , he uses  $N(N-1) / V$ , where  $N$  is the instantaneous number of particles in a cell, and  $\bar{N} / V$  is the time-averaged ‘best estimate’ of the local flow number density. He shows that if the fluctuations in  $N$  are distributed according to a Poisson distribution, then  $\overline{N(N-1)} = \bar{N}\bar{N}$  and the correct collision rate is obtained. In unsteady simulations, for which the time-averaged number density is not available, we use the new procedure to set the collision rate and we model instantaneous chemical rates in a similar way.

The net change in the number of species  $A$ , over a time-step  $\Delta t$ , due to the reaction  $A + M \rightarrow B + M$  where  $M = A, B$  is computed using

$$\Delta N_A = \frac{1}{2} \left[ -k_{f_{M=A}} N_A (N_A - 1) + k_{b_{M=B}} N_B (N_B - 1) + 2(-k_{f_{M=B}} + k_{b_{M=A}}) N_A N_B \right] W \Delta t / V. \quad (3)$$

In this expression the term  $N_i(N_i - 1)$  is evaluated only for  $N_i \geq 1$ .  $W$  is the number of real particles represented by each DSMC simulator particle. Since  $\Delta t$  is necessarily smaller than the mean collision time,  $\Delta N_A$  is usually a fractional number. Thus, the value of  $\Delta N_A$  is compared to a random fraction; a reaction is processed if the random number is larger than  $\Delta N_A$ . In the case where  $\Delta N_A > 1$ ,  $\lfloor \Delta N_A \rfloor$  (the integer part of  $\Delta N_A$ ) reactions are processed and if the remaining fraction is greater than a random number, one more reaction is processed. This procedure ensures that there is no delay in processing reactions and that the correct number of reactions is modelled in the limit of a large ensemble-average. When the reaction rate coefficient is given as a function of temperature, MCM uses the total energy of the simulator particles in the cell to estimate the temperature. Here we use the variance of the sample population to evaluate the kinetic temperature. For a multi-species gas, the overall kinetic temperature is given by

$$T = \frac{2m_s}{3\kappa} \left[ \frac{1}{N} \sum_s N_s \langle E_s \rangle \right], \text{ where } \langle E_s \rangle = \frac{m_s}{2N_s^2} \sum_{i=x,y,z} \left[ N_s \sum v_i^2 - \left( \sum v_i \right)^2 \right]. \quad (4)$$

Here  $\langle E_s \rangle$  is the mean translational energy of species  $s$ ,  $m_s$  is the mass of one particle and  $N_s$  is the number of species  $s$  in the cell. When a reaction occurs, reactant particles selected at random from the cell are converted into product species particles while ensuring that the total mass, momentum and kinetic energy of the products is the same as that for the reactants. The total net change in chemical energy due to all reactions in a cell is removed from the thermal energy of all particles in the cell; thus the mean particle velocity must be calculated in each cell at each time-step. The details of these procedures are given by Lilley and Macrossan [2]. The calculation of the cell mean velocity and cell kinetic temperature requires little computational expense. The macroscopic chemistry procedure may be added to a DSMC code by implementing a separate chemistry step after the calculation of collisions.

### Chemical Rate Equations for the Model Gas

For simplicity, we make comparisons between the particle and macroscopic chemistry methods for simulations using a model gas. The model gas consists of species  $A$  and  $B$  particles with the same properties as argon; they have no rotational or vibrational energy storage modes. The variable hard sphere [1] (VHS) collision model is employed with the modified NTC collision procedure, *i.e.* with  $N(N-1)/V$  in place of  $N\bar{N}/V$ . The collision cross-section is such that the Chapman-Enskog viscosity is given by  $\mu = \mu_r (T/T_r)^\omega$ , where  $\mu_r = 2.3 \times 10^{-5}$  (kg/m/s),  $T_r = 300$  K and  $\omega = 0.72$ . The only reactions are those in Eq. (1). The reaction rates are taken to be those produced by the following particle-based chemistry model. In the particle chemistry model,  $S_f = 0.2$ ,  $S_b = 0.001$  and  $E_a/\kappa = 5000$  K. Let  $E_c$  be the centre of mass energy of the collision pair then:

- (1)  $A - A$  pairs with  $E_c > E_a$  become  $B - A$  with probability  $S_f$
- (2)  $B - B$  pairs become  $A - B$  with probability  $S_b$
- (3)  $A - B$  pairs with  $E_c > E_a$  become  $B - B$  with probability  $S_f$  and  $A - A$  with probability  $S_b$
- (4)  $A - B$  pairs with  $E_c < E_a$  become  $A - A$  with probability  $S_b$ .

In order to match the particle-based results with MCM, we require the theoretical reaction rate coefficient produced by the particle method. The corresponding forward and backward rate coefficients may be expressed as

$$k_f = Z_c F S_f \text{ and } k_b = Z_c S_b. \quad (5)$$

Here  $F$  is the fraction of VHS collision pairs with  $E_c > E_a$  and  $Z_c$  ( $m^3/s$ ) is the VHS collision constant. Under thermal equilibrium conditions  $Z_c$  and  $F$  are given by

$$Z_c = \frac{1}{f_s} \frac{15\kappa T_r}{2\mu_r (2.5 - \omega)(3.5 - \omega)} \left(\frac{T_r}{T}\right)^{\omega-1}, \quad F = \Gamma(2.5 - \omega, E_a/\kappa T), \quad (6)$$

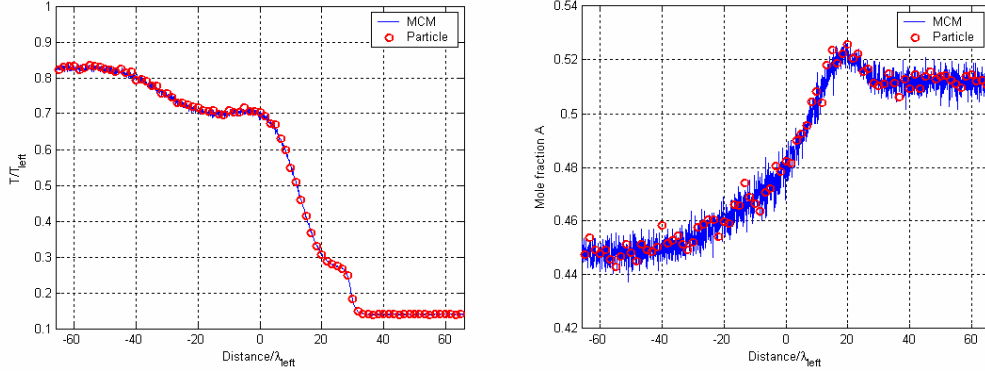
where  $f_s = 2$  for  $A - A$  and  $B - B$  collisions and  $f_s = 1$  for  $A - B$  collisions. Note that these rate coefficients are not in the simple Arrhenius form. In MCM, the thermal equilibrium reaction rates evaluated from the given rate coefficients, in this case those in Eqs. (5) and (6), are multiplied by two ‘rate correction factors’  $\psi_z$  and  $\psi_f$  as described by Goldsworthy et al. [3]; this accounts for the deviation between the actual non-equilibrium distribution function and the thermal equilibrium distribution function as derived from the cell temperature.

### Shock-Expansion Tube Simulation

We have applied the transient MCM procedures to simulations of an unsteady 1-D flow in a shock-expansion tube, filled with the model gas described above. The initial condition consists of two regions, both at rest and with temperatures  $T_{\text{left}} = 1000$  K and  $T_{\text{right}} = 100$  K. The density  $\rho$  is uniform along the tube and all cells contain equal numbers of both species. Results are normalized by a nominal mean free path  $\lambda_{\text{left}} = 2\mu/\rho\bar{c}$  where  $\bar{c} = \sqrt{8\kappa T/m}$  is a characteristic thermal speed and  $\mu$  is the gas viscosity, both evaluated for  $T = T_{\text{left}}$ . The characteristic time is  $\tau_{\text{left}} = \lambda_{\text{left}}/\bar{c}$ . Since the forward reaction rate coefficient is independent of density, the normalized results apply to any density. Instantaneous results are output at  $t = 500\tau_{\text{left}}$ . A total of 2000 computational cells ( $\Delta x = 0.066\lambda_{\text{left}}$ ) span the domain. Simulations using the particle and macroscopic chemistry methods with 50000 particles were run. For each case, results from 1000 separate simulations were combined.

Profiles of temperature  $T$  (left) and species  $A$  mole fraction  $X_A$  (right) are shown in Figure 1. MCM results are shown as solid lines; particle chemistry results are plotted every 25<sup>th</sup> cell using circles. No spatial or time-averaging is used. A shock wave has propagated towards the low temperature region a distance of approximately  $28.5\lambda_{\text{left}}$ . The shock wave spans almost  $3.5\lambda_{\text{left}}$ . An expansion wave can be seen moving through the high temperature region. Neither the shock nor the expansion wave has been reflected from the end walls at this elapsed time. Since both forward reactions are exothermic and have an activation temperature  $E_a/\kappa = 5 \times T_{\text{left}}$ , the forward reactions resulting in  $A \rightarrow B$  transitions are much faster in the higher temperature region and act to lower the temperature there. The reverse transitions  $B \rightarrow A$  are endothermic and the rate at which they occur is proportional to the collision rate. The temperature in the undisturbed region in front of the shock is slightly higher than the initial value because of these

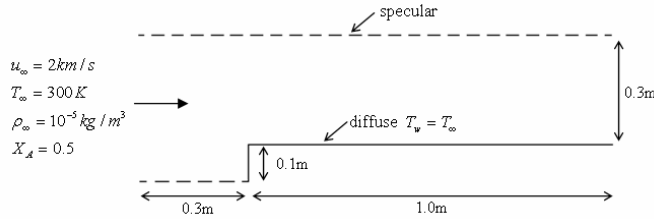
endothermic reactions. The value of  $X_A$  reaches a maximum behind the propagating shock wave where the high density and hence collision rate and relatively low temperature favour the  $B \rightarrow A$  reaction. It is apparent from these plots that a very close agreement is obtained between MCM and the particle-based method.



**FIGURE 1.** Left: Ensemble-averaged profiles of  $T/T_{\text{left}}$ . Right: Ensemble-averaged profiles of  $X_A$ . Results are shown at  $t = 500\tau_{\text{left}}$  for macroscopic and particle-based chemistry simulations. Particle results are shown for every 25<sup>th</sup> cell only.

## Cavity Flow Simulation

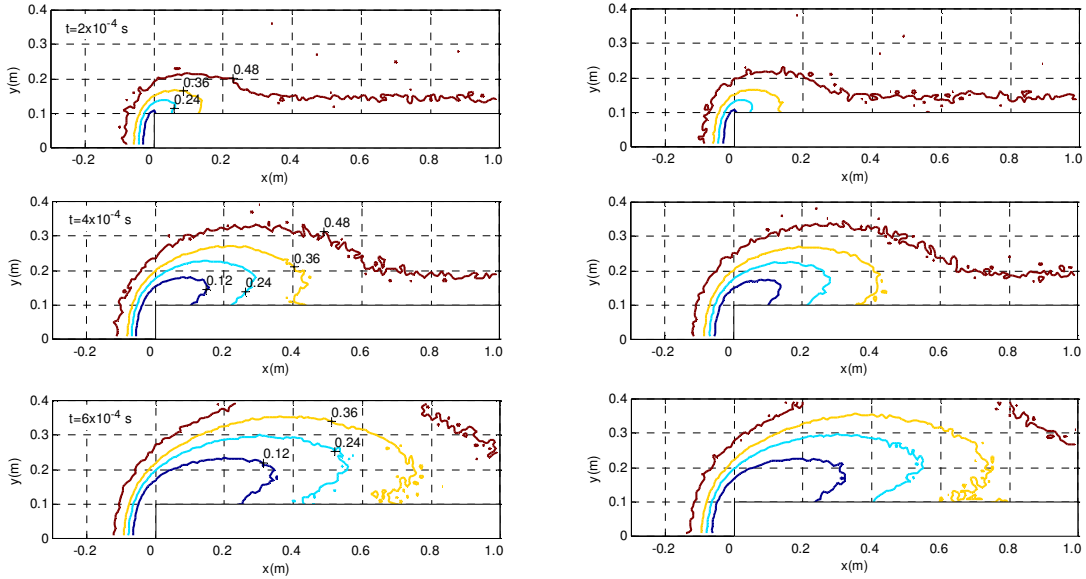
The unsteady MCM procedure has also been tested by simulating the unsteady startup phase of flow of the model gas through a two-dimensional cavity. The simulation domain and inflow conditions are shown schematically in Figure 2. The free-stream consists of 50% species A molecules with  $M_\infty = 6.2$  and  $Kn = 0.12$  (based on the step height). The free-stream (non-reacting) stagnation temperature is 7988K and the chemical activation temperature of species A is 5000K indicating that the chemical reactions should occur extremely rapidly as the free-stream flow is slowed by the step. The simulations used an unstructured adapted grid of 9460 triangular cells constructed using a Delaunay triangulation procedure [6]. A total of 5000 time-steps of size  $10^{-6}$  s were run giving a final number of 400000 particles. Results were obtained using 100 ensemble-averages and comparisons are made between the particle and macroscopic chemistry methods.



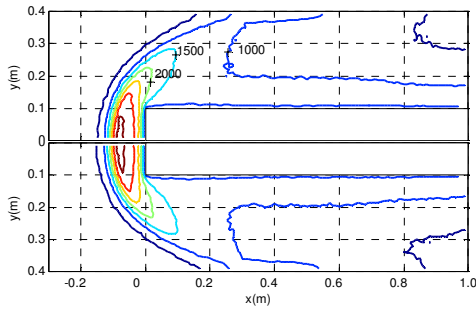
**FIGURE 2.** Schematic simulation domain and initial conditions for cavity flow simulation.

Contours of  $X_A$  are shown in Figure 3 at  $t = 2 \times 10^{-4}$ ,  $4 \times 10^{-4}$  and  $6 \times 10^{-4}$  s. The plots at  $t = 6 \times 10^{-4}$  s are close to steady-state conditions; the flow does not become choked through the cavity for this configuration. Comparison of the left (macroscopic chemistry) and right (particle chemistry) plots shows that there is very close agreement between the two models. The endothermic  $A \rightarrow B$  reaction occurs in the high-temperature, stagnation region in front of the cavity. Along the diffuse cavity surface  $X_A$  is lower since the  $B$  particles are formed in the low speed region in front of the cavity.

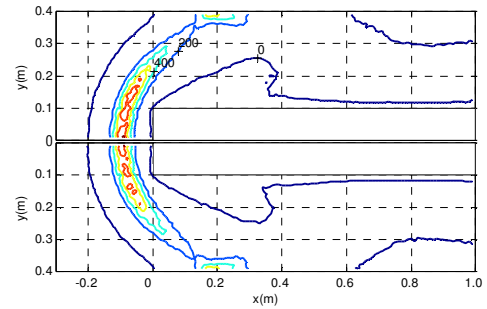
Temperature contours at  $t = 5 \times 10^{-4}$  s, shown in Figure 4, also demonstrate that there is close agreement between the methods. Contours of the accumulated number of net reactions per cell are shown in Figure 5. The ‘0’ contour corresponds to the boundary between net production and net removal of species A, hence it is sensitive to the predicted rate of chemical reactions. The two reaction rate correction factors have correctly matched the thermal non-equilibrium reaction rate predicted by the particle method.



**FIGURE 3.** Contours of  $X_A$  for macroscopic (left) and particle (right) chemistry for  $t = 2 \times 10^{-4}$ ,  $4 \times 10^{-4}$  and  $6 \times 10^{-4}$  s .



**FIGURE 4.** Contours of temperature for macroscopic (top) and particle (bottom) chemistry at  $t = 5 \times 10^{-4}$  s .



**FIGURE 5.** Contours of accumulated number of reactions per cell for macroscopic (top) and particle (bottom) chemistry.

## DISCUSSION

We have demonstrated that the Macroscopic Chemistry Method, when applied to unsteady simulations of a model gas in hypersonic flow, leads to close agreement with a particle chemistry method. We have chosen to use a ‘model gas’ in these simulations so that the precise reaction rate employed by the particle chemistry model is known. This reaction rate yields a realistic temperature dependence similar to that given by an Arrhenius type model. In this report, we have formulated the overall reaction rate in MCM by closely matching the rates predicted by the particle chemistry method. In practice, the reaction rates in MCM would be implemented directly in an Arrhenius type form, and the two reaction rate correction factors which account for thermal non-equilibrium effects could then be added if desired. An important distinction is that we consider that the baseline reaction rates should be those derived from theoretical or experimental studies, and that any thermal non-equilibrium ‘correction’ factors should be added later, if required. This is in contrast to the particle chemistry approach in which the reaction rates are ‘predicted’ by the DSMC simulation, albeit with the aid of model constants calibrated to match external data.

For the 2-D simulations, the CPU and memory requirements were similar for both methods. For the 1-D simulation, the macroscopic method required considerably more CPU time, though in practice this would be greatly reduced when a simpler reaction rate model is used.

One further point should be mentioned. Even if real molecules behaved exactly as those of our model gas, it is possible that, because of the finite sample size in DSMC, the reaction rate per particle might be different in the simulation from that in the real gas. In MCM we could possibly account for this effect when we calculate the cell temperature by using the best estimate of the unknown ‘parent population’ variance, *i.e.*  $\sum_i (x_i - \bar{x})^2 / (N - 1)$ , rather than the finite sample variance which we did use. This measure of cell temperature did produce slightly different results, though the correct results (those obtained using a large value of  $N$ ) were found to be given by the simulation using Eq. (4).

## CONCLUSION

We have shown how the macroscopic chemistry method may be used to obtain results in agreement with a particle-based chemistry method in two unsteady simulations. In traditional DSMC, macroscopic information in the form of the number density is used to determine the simulator collision rate. The same information is needed in MCM to set the reaction rates, and we have followed Bird in replacing the time-averaged simulator number density in a cell  $\bar{N}/V$  by  $(N-1)/V$  in setting both the collision rate and the reaction rate in unsteady simulations where  $\bar{N}$  is unavailable. In the macroscopic chemistry method we also use information from the kinetic energy of all the particles in the cell (*i.e.* the kinetic temperature); similar information is obtained in the particle-based method by sampling of particle pairs for possible collisions. In addition, the reaction rate in the particle-based method depends on the non-equilibrium distribution of particle energies in collision pairs; in MCM the analogous non-equilibrium information is extracted by comparing information sampled during the collision procedure with the expected equilibrium values, and adjusting the reaction rate accordingly.

The primary advantage of the macroscopic approach is that any general reaction rate data may be used with any DSMC collision model, without the need for calibration; thus different reaction rate mechanisms involving large numbers of reactions can be quickly implemented and compared.

## REFERENCES

1. Bird, G.A, “Simulation of multi-dimensional and chemically reacting flows” in *Rarefied Gas Dynamics: Proceedings of the 11th International Symposium*, edited by R. Campargue, Vol. 1, Paris, 1979, pp. 365-388.
2. Lilley, C. R. and Macrossan, M. N., *Physics of Fluids A*, **16**, 2054-2066 (2004).
3. Goldsworthy, M., Macrossan, M. N. and Abdel-jawad. M., *Physics of Fluids*, **19**, 066101 (2007).
4. Goldsworthy, M., Macrossan, M. N. and Abdel-jawad. M., *Physics of Fluids*, **19**, 116102 (2007).
5. Bird, G.A, ‘Sophisticated DSMC’, Notes from DSMC07 meeting, Santa Fe, September 2007, available at: <http://www.gab.com.au/Resources/DSMC07notes.pdf>. (Accessed 7 Nov 2007).
6. Per-Olof Persson and Gilbert Strang, *SIAM Review*, **46**, 329-345 (2004).