

A Comparison of Collision Energy-based and Temperature-based Procedures in DSMC

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The molecules in an intermolecular collision are unaware of the macroscopic temperature and whether or not the gas is in a state of equilibrium.

All DSMC procedures should be based on collision quantities.

This generally involves the introduction of a “collision temperature” that is based on the relative translational energy and the internal energies.

The collision temperature is not uniquely defined and the procedures are phenomenological, but they must satisfy physical constraints such as equipartition and the establishment of an equilibrium state.

The quantum vibrational procedures and the chemical reactions related to the vibrational modes had, until 2005 proved to be intractable.

The solution was to quantize the “collision temperature” based on the relative translational energy and the vibrational energy of one molecule

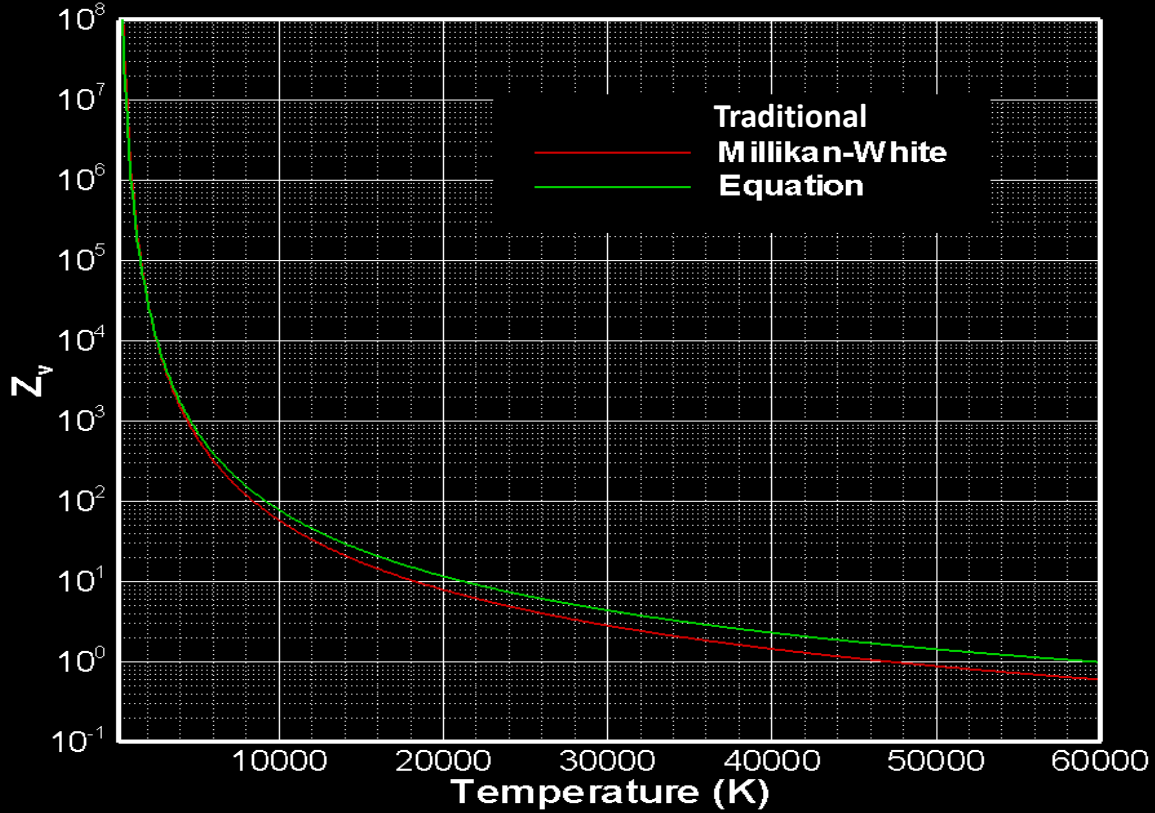
$$T_{coll} = i_{max} \theta_v / (7/2 - \omega), \text{ where } i_{max} = \text{Int} \left[E_c / (k\theta_v) \right]$$

Set Z_v to unity at Θ_d and define it by its value Z_{ref} at a reference temperature. The Millikan-White formulation then becomes :-

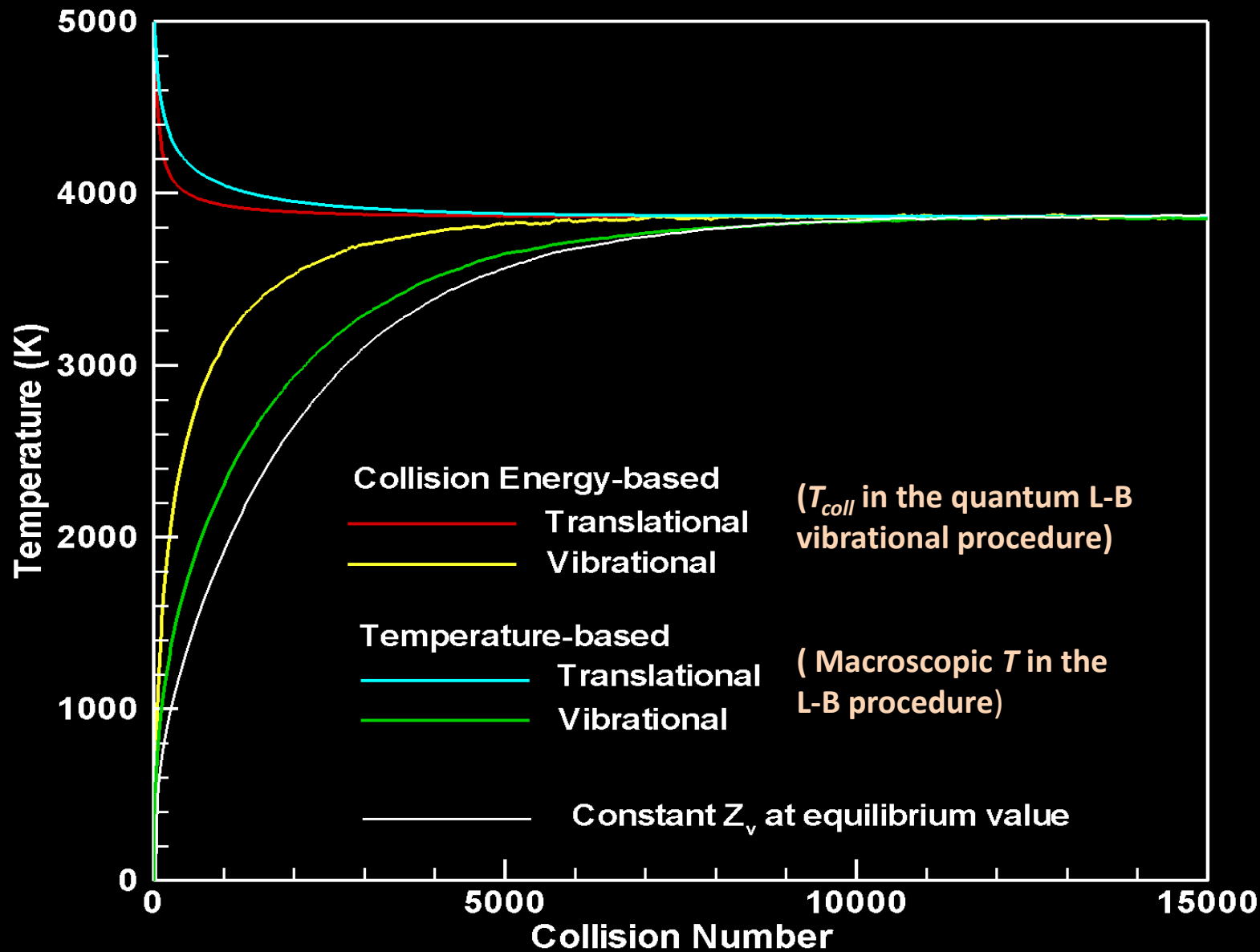
$$Z_v = \left(\frac{\theta_d}{T} \right)^\omega \left[Z_{ref} \left(\frac{\theta_d}{T_{ref}} \right)^{-\omega} \right] \left[\left(\frac{\theta_d}{T} \right)^{1/3} - 1 \right] / \left[\left(\frac{\theta_d}{T_{ref}} \right)^{1/3} - 1 \right]$$

*Plot is for oxygen with
 $Z_{ref} = 17,900$ at
 $T_{ref} = \Theta_v = 2,256$ K
 $\Theta_d = 59,500$ K*

Traditional Z_v data has unphysical values less than unity at Θ_d . Setting $Z_d=1$ is physically justifiable and is preferable to the semi-empirical “Park correction factor” that is employed in continuum CFD.



Oxygen with $Z_{ref} = 17,900$ at the characteristic vibrational temperature.



*The nominal Z_{ref} must be significantly increased when the L-B distribution is based on T_{coll} !
 Z_{ref} should ideally be based on a DSMC simulation (with T_{coll}) of the original experiment !*

Dissociation must be part of the quantum vibration model and it occurs when :-

$$i_{max} > \Theta_d / \Theta_v$$

This is applied before the L-B distribution and dissociation occurs whenever it is energetically possible because there is effectively an infinite number of levels beyond the dissociation limit.

The DSMC procedure is so simple that the dissociation rate coefficient can be written for an equilibrium VHS simple harmonic gas as :-

$$k_f(T) = \frac{2\sigma_{ref}}{\varepsilon\sqrt{\pi}} \left(\frac{T}{T_{ref}}\right)^{1-\omega} \left(\frac{2kT_{ref}}{m_r}\right)^{1/2} \times \sum_{i=0}^{i_d} \left\{ Q \left[\left(\frac{5}{2} - \omega\right), \left(\frac{\Theta_d - i\Theta_v}{T}\right) \right] \exp\left(-\frac{i\Theta_v}{T}\right) / z_v(T) \right\}.$$

$Q(a, x) = \Gamma(a, x) / \Gamma(a)$ is a form of the incomplete Gamma function.

$z_v(T) = \{1 - \exp(-\Theta_v/T)\}^{-1}$ is the vibrational partition function.

i_d is the vibrational level immediately below the dissociation limit.

σ and m_r are the collision pair cross-section and reduced mass.

ε is the symmetry factor (1 for unlike and 2 for like molecules)*

Traditional DSMC chemistry procedures convert the macroscopic temperature T dependent and experimentally based rate coefficients to reactive cross-sections as $f(E_c)$, not $f(T)$!

The new procedure takes advantage of the ability of DSMC to directly model discrete quantum effects and event-driven processes!

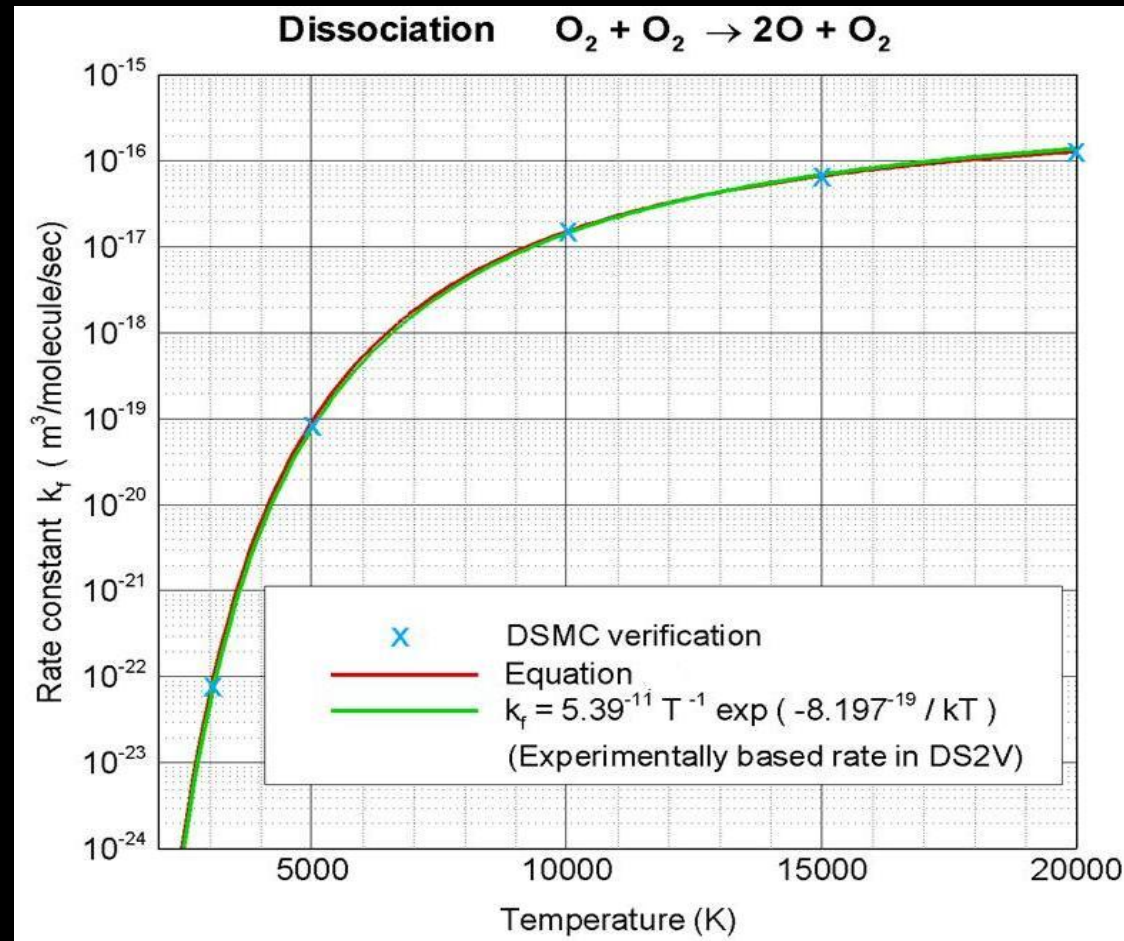
The analytical result for $k_f(T)$ is not needed for the DSMC procedure, but it is useful for comparisons with the experimentally based rates.

Oxygen dissociation was chosen as the first test and, while the agreement in this case has to be regarded as fortuitous, the discrepancies are generally consistent with the uncertainties in the experimental data.

Also, the analytical result could be combined with the equilibrium constant (law of mass action) to obtain the reverse (recombination) reaction rate.

While the calculation is very complex, the probability of oxygen recombination in a three-body collision with molecules of number density n_t is well approximated by

$$P_{rec} = 5.1 (n_t / n_0) T^{-1.1}, \quad \text{where } n_0 \text{ is the standard number density.}$$



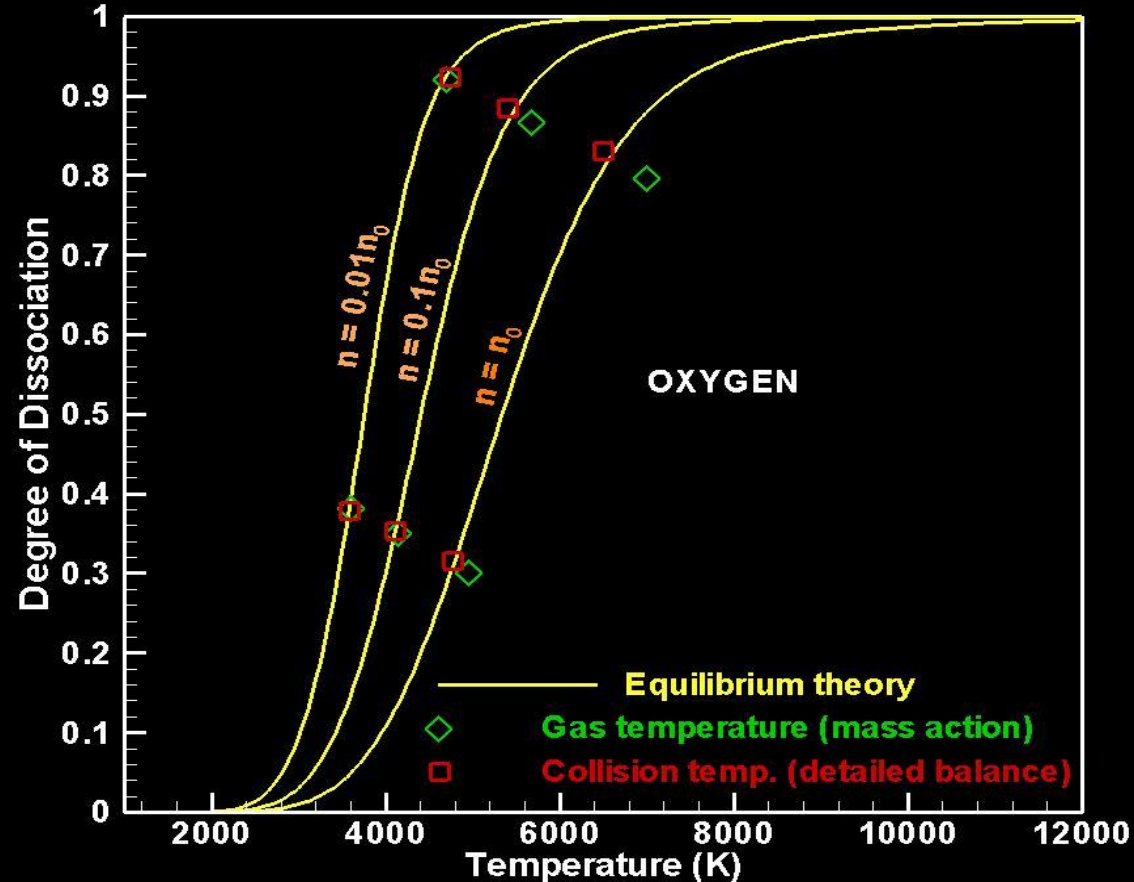
A DSMC procedure can be based on this result and it would be consistent with those in continuum CFD. However, the macroscopic temperature should be avoided and it is far preferable to use detailed balance instead of the law of mass action.

Detailed balance can be written $P_{ij}\pi_i = P_{ji}\pi_j$, where P_{nm} is the probability of a transition from state n to state m , and π_n is the equilibrium probability of state n . This is the basis of the Larsen-Borgnakke procedure for the distribution of energy to the vibrational mode. A reverse reaction therefore occurs in a collision if a provisional L-B distribution leads to a transition that is inverse to that in the forward reaction. The probability $P_{diss}(i)$ of a collision leading to dissociation is sampled for each level i of a molecular species. For the fraction of atom-atom collisions that are regarded as three body collisions, a provisional L-B redistribution of the relative translational energy and the dissociation energy leads to vibrational level i^* in the potential molecule. The probability of recombination is then

$$P_{rec} = P_{diss}(i^*)$$

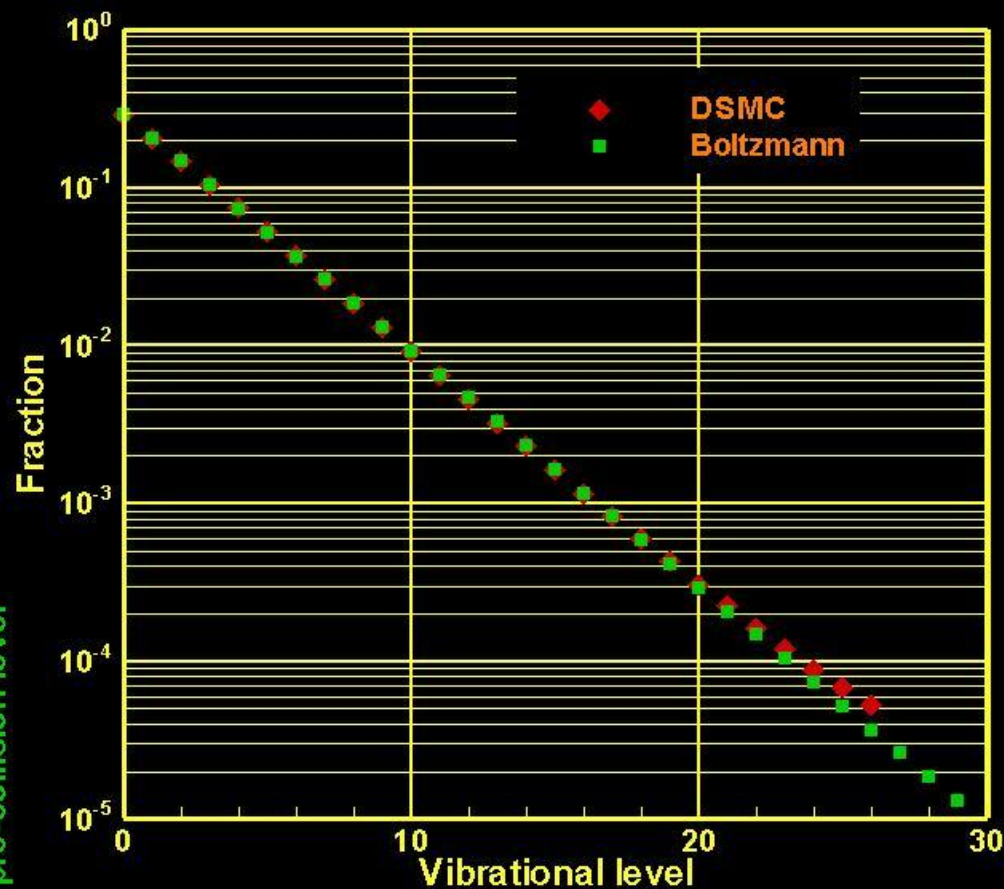
The fraction of a three-body or ternary collision cannot be precisely defined. It has been assumed here to be equal to the probability of another molecule being within a sphere with radius equal to the sum of the radii of the three colliding molecules.

The degree of dissociation from a DSMC calculation based on this detailed balance model is then in good agreement with the results from both equilibrium statistical mechanics and a calculation based on the law of mass action.



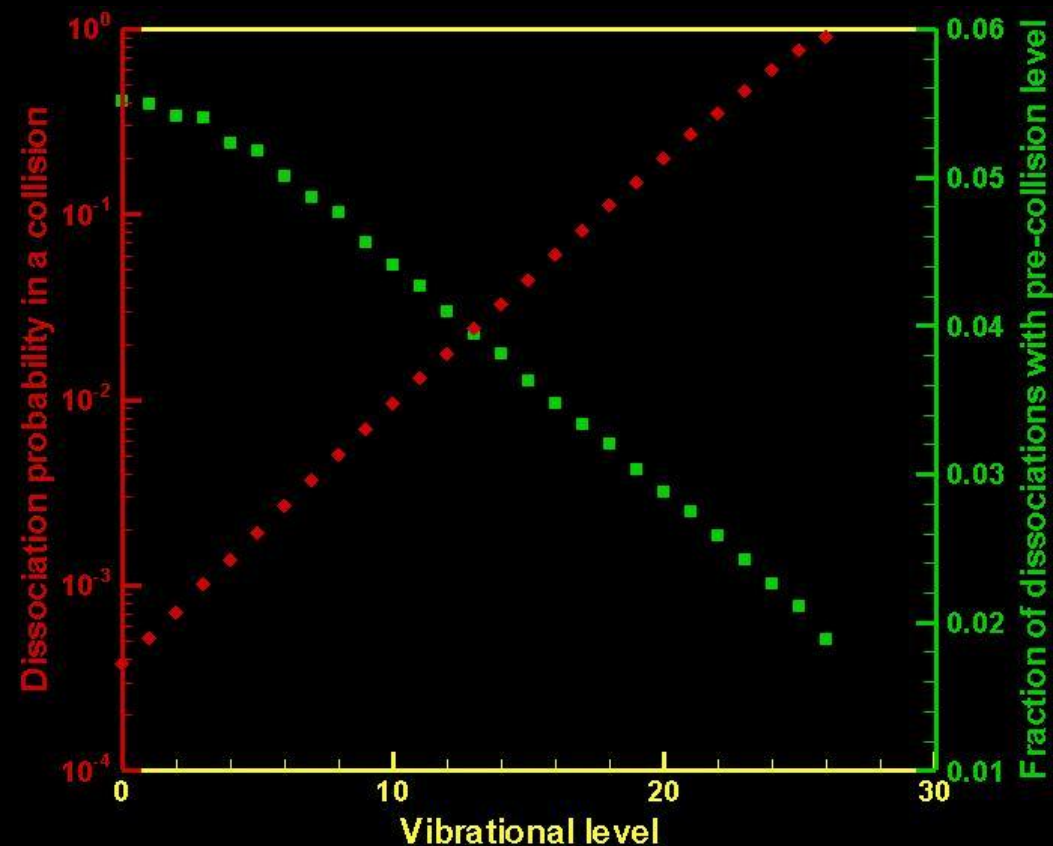
These figures show the probabilities associated with the case with the most rapid dissociations and recombinations ($T=6,500$ K at standard number density).

Even though the vibrational levels are truncated at level 26, the distribution of levels continues to be in good agreement with the Boltzmann distribution.

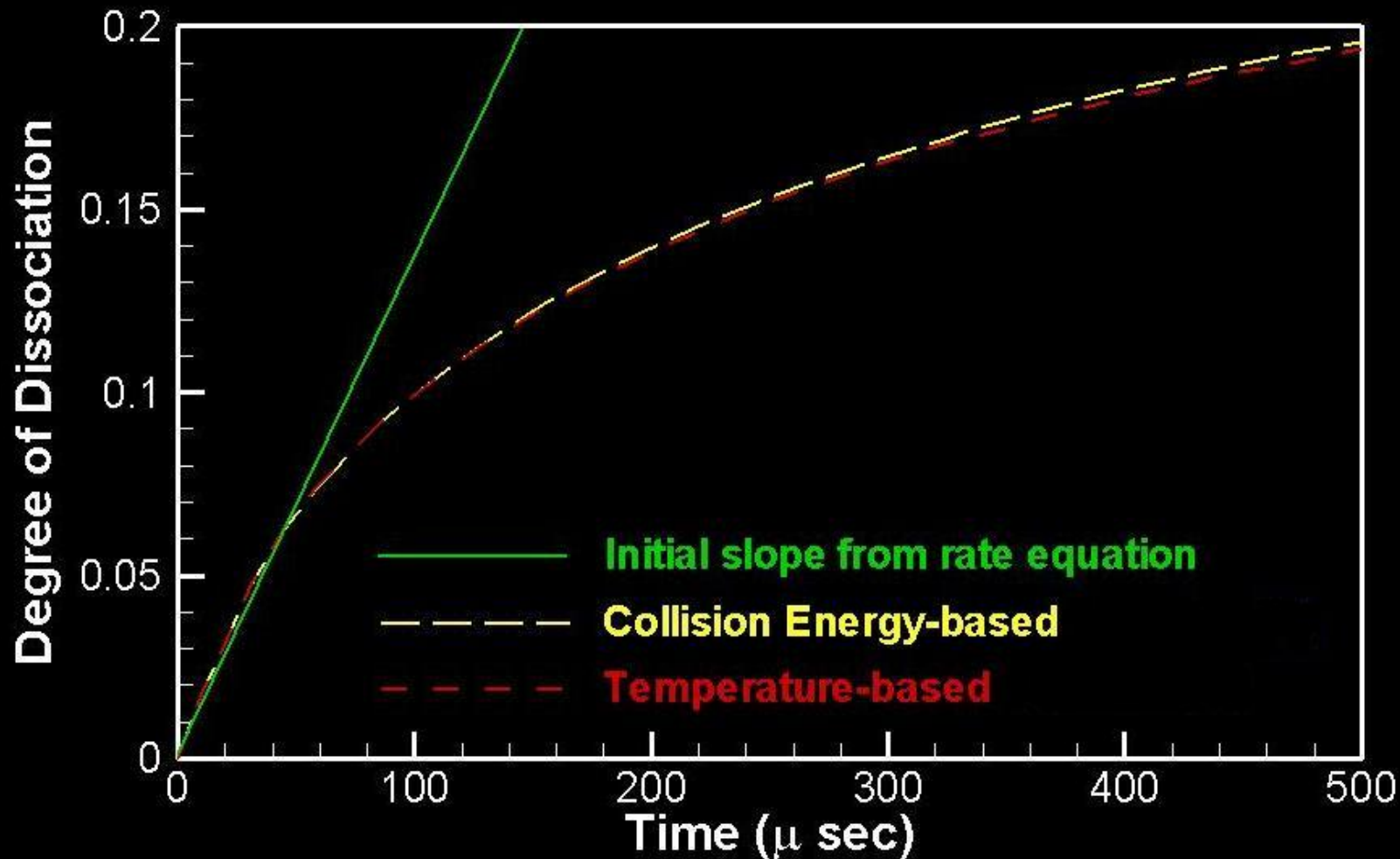


The probability $P_{diss}(i)$ is shown in red in the figure at left.

While a molecule in level 26 has a dissociation probability over 90% compared with 0.03% for a ground state molecule, more dissociations occur from the ground state than from level 26.



The vibrational relaxation rate strongly depends on whether T_{coll} or T is used in the quantum vibration procedures and is necessary to check whether this choice also affects the dissociation rate. DSMC calculations based on $i_{max} > \Theta_d / \Theta_v$ have been used to study the dissociation rate in molecular oxygen that is initially in equilibrium at $T=10,000$ K. and $n = 10^{20}/m^3$ (the recombination probability in each collision is then less than one in 10^{10}).



This choice has no effect (note that i_{max} must employ T_{coll}). Also the initial dissociation rate based on $i_{max} > \Theta_d / \Theta_v$ is consistent with the continuum rate equation based on experiment.

Unlike dissociation, there is no obvious physical model on which to base a DSMC condition for an **endothermic exchange reaction** such as $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$, but there are several desirable properties for a phenomenological model :-

- (1) Its analytical representation should conform to the Arrhenius equation and it arguably must include the exponential term of this equation.
- (2) Ideally, it should be based on a single vibrational state in order to facilitate the development of a model of the reverse reaction based on the principle of detailed balance.

The simplest model is to assume that the reaction with activation energy E_a occurs in a collision of N_2 and O if the vibrational level of N_2 after a trial Larsen-Borgnakke redistribution of the sum of the relative translational energy in the collision and the vibrational energy of N_2 is $i = i_a$, where i_a is the first level above E_a .

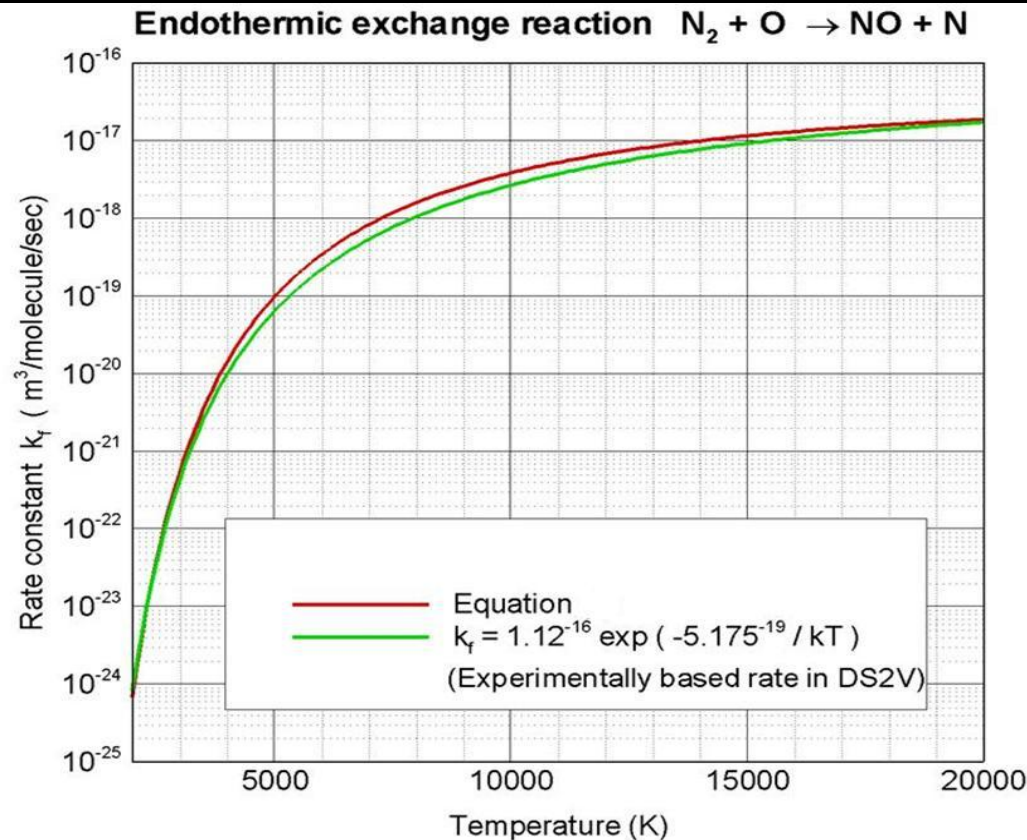
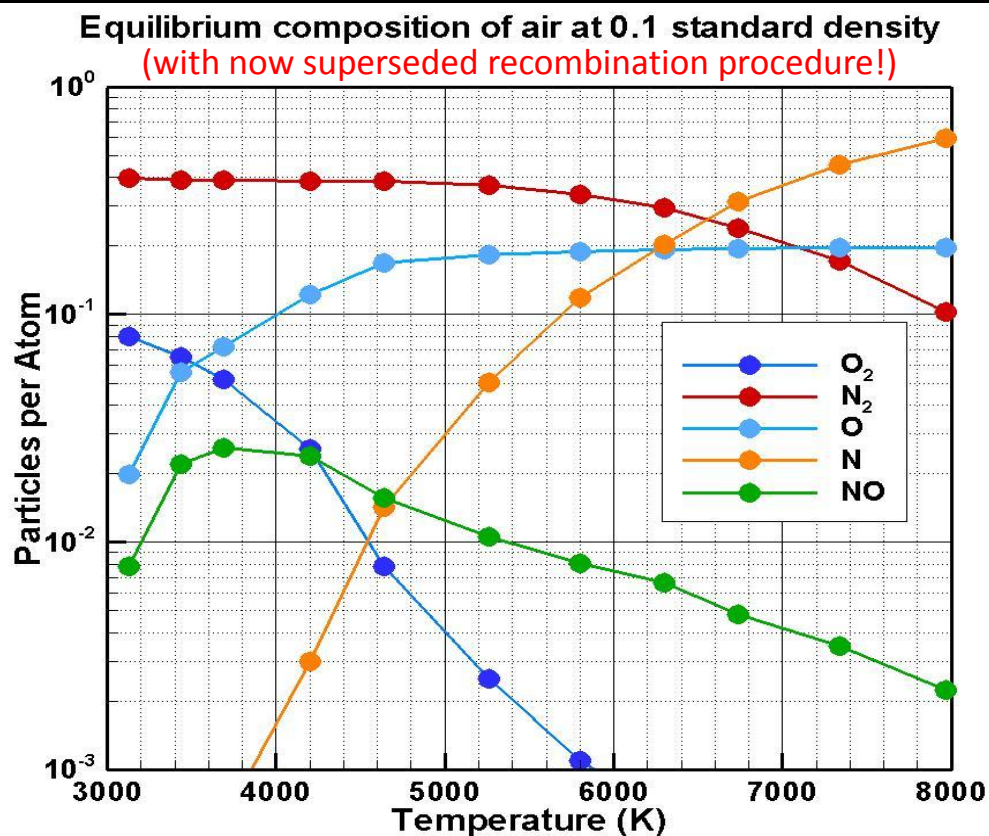
The trial redistribution is made to avoid an unphysical depletion of the i_a state.

The analytical representation for an equilibrium gas is easily written down

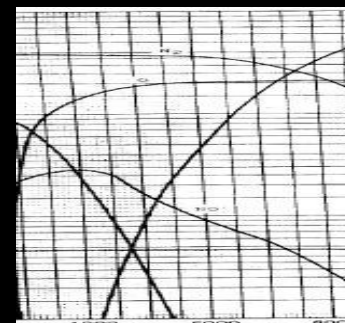
$$k_f(T) = \frac{2\sigma_{\text{ref}}}{\sqrt{\pi}} \left(\frac{T}{T_{\text{ref}}}\right)^{1-\omega} \left(\frac{2kT_{\text{ref}}}{m_r}\right)^{1/2} \exp\left(-\frac{i_a \Theta_v}{T}\right) / z_v(T)$$

The straightforward detailed balance condition for the occurrence of the reverse exothermic reaction $\text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O}$ is $i^* = i_a$. Here, i^* is the vibrational state of the potentially generated N_2 after a provisional Larsen-Borgnakke redistribution of the sum of the relative translational energy in the collision of NO with N , the pre-collision vibrational energy of NO and the reaction energy E_a . Note that, after any reaction, there is always a full Larsen-Borgnakke redistribution that is independent of any provisional or trial distribution that led to the reaction.

There is again (fortuitously ?) good agreement for this reaction between the analytical result for an equilibrium VHS gas and the experimentally-based rate equation that has been used in the DS2V implementation of the traditional DSMC chemistry model.



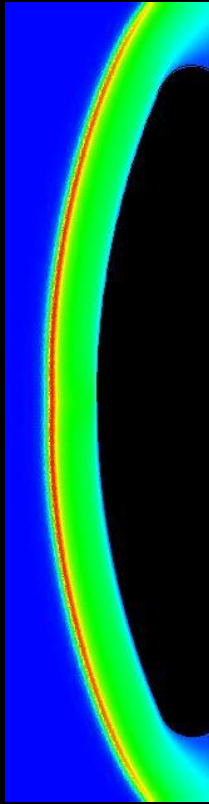
Preliminary DSMC calculations, using the new DS1 program, have been made for the equilibrium composition of air.



Directly comparable result from NACA TN 4265 (1958) by Moeckel & Weston (The main discrepancy is earlier N_2 dissociation with DSMC)

The DS1 program includes an option for stagnation streamline calculations (see Section 12.12 and program DSMC1T.FOR in 1994 book) and implements either the traditional or this new DSMC chemistry model. Using the shock-standoff distance from a DS2V calculation, it has been used to calculate the stagnation point quantities for the Orion re-entry at an altitude of 85 km.

For 3.5 million incident molecules	New DSMC model	Traditional DSMC model
Incident number flux (/sq m/sec)	7.72e24	7.60e24
Pressure (N/sq m)	437	437
Incident heat flux (kW/sq m)	358	360
Reflected heat flux (kW/sq m)	-275	-277
Net heat flux (kW/sq m)	83	83



The agreement is satisfactory, but this flow is near continuum and may be driven more by the energetics than by the rates of the reactions. Measurements of the interior structure of very strong shock wave in reacting gases are needed as decisive test cases. Entry flows are driven largely by the endothermic dissociation reactions. The most interesting applications of the new detailed balance exothermic procedures will be to flows driven by exothermic combustion processes (e.g. the oxygen- hydrogen system). It appears that DSMC can calculate entry flows without any need for reaction rate data based on experiment, but can DSMC be used to predict combustion wave speeds, flammability and explosion limits ?