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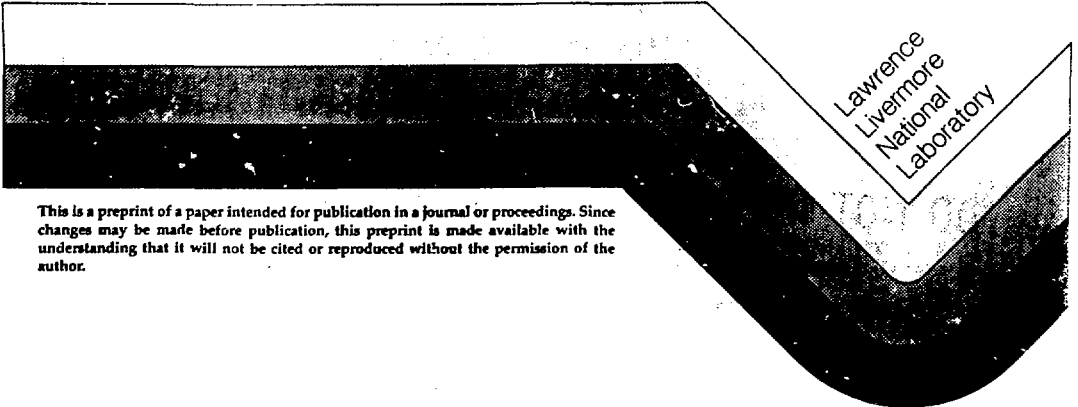
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**STATISTICAL THEORY  
OF ELECTRONIC ENERGY RELAXATION**

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## STATISTICAL THEORY OF ELECTRONIC ENERGY RELAXATION

J. B. Anderson\*\*, J. D. Foch, M. J. Shaw, R. C. Stern &amp; B. J. Wu

## ABSTRACT

A 'statistical method' is developed for treating electronic and electronic-translational energy transfer in systems of atoms having multiple electronic states. This method is based on the assumption that the states produced in a collision are distributed according to the equilibrium distribution for the energy available to the collision partners. The approach is readily incorporated into Monte Carlo gas dynamic calculations. Results of such calculations are reported for several cases of relaxation of electronic energy in a static gas and in a cylindrical source flow.

1. Introduction.

Our interest in the collisional exchange of electronic energy is directed primarily to the problems encountered in the expansion of gases for various isotope separation processes, but there are many systems in which electronic energy exchange plays an important role. The statistical theory developed here is applicable to expanding gases as well as to a number of systems of practical interest.

The statistical approach has been applied previously [1] to cases of vibrational and rotational energy exchange; but, to our knowledge, this is the first application to electronic energy exchange. It has also been applied in treating chemical reactions [4] and found to predict experimental observations in at least a few cases. For collisions of light atoms at low energies one should not, in general, expect the statistical approach to be useful in predicting behavior. However, for heavy atoms at higher energies, the strong interactions are likely to produce 'statistical' results and the approach may be expected to be useful.

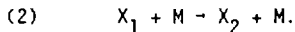
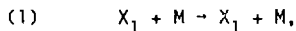
The method satisfies all requirements of momentum and energy conservation, microscopic reversibility, and equilibrium. The Boltzmann distribution of electronic states and the Maxwellian distribution of velocities are predicted correctly for thermal equilibrium. Since the energies and degeneracies of each state are included explicitly, the thermal properties--energy, enthalpy, heat capacity--are correct.

In the sections following, we outline the theoretical basis for the method, describe its use in Monte Carlo simulations (Bird type) of gas dynamics, and report results for relaxation of electronic energy in a static gas system and in cylindrical source flows.

2. Statistical Theory.

The method is based on the assumption that the states, translational and electronic, produced in a collision of two atoms are distributed according to the equilibrium distribution for the energy available to the collision partners. The distribution of states produced is random among the allowed possibilities with each possible combination of electronic states given a weight proportional to the relative translational energy of the separating atoms. Degenerate states are considered to be individual states.

Consider first the simplest of cases: a two-state system for atom X, with electronic states  $X_1$  and  $X_2$  of energies  $E_1$  and  $E_2$  and degeneracies  $g_1$  and  $g_2$ . For a collision of  $X_1$  with an inert atom M the result is either  $X_1 + M$  or  $X_2 + M$ :



With a total available energy  $E$  given by the sum of  $E_1$  and the relative translational energy  $E_{rel}$ , the probability of outcome  $(X_1 + M)$  is proportional to  $g_1$  and  $E_{rel}$  for the departing atoms,

$$(3, 4) \quad P(X_1 + M) \sim g_1 E_{rel} \sim g_1 (E - E_1)$$

Similarly, if  $(E - E_2) > 0$ ,

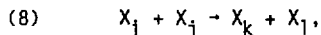
$$(5) \quad P(X_2 + M) \sim g_2 (E - E_2).$$

Since the sum of the probabilities is unity, the probabilities are

$$(6) \quad P(X_1 + M) = \frac{g_1 (E - E_1)}{g_1 (E - E_1) + g_2 (E - E_2)},$$

$$(7) \quad P(X_2 + M) = \frac{g_2 (E - E_2)}{g_1 (E - E_1) + g_2 (E - E_2)}.$$

Next is the general case involving atoms with states 1, 2, 3, . . . , electronic energies  $E_1, E_2, E_3 \dots$ , and degeneracies  $g_1, g_2, g_3 \dots$ . For a collision of  $X_i$  and  $X_j$ ,



the probability of a given pair of product states is given by

$$(9) \quad P(X_k + X_1) = \frac{g_k g_1 (E - E_k - E_1)}{\sum g_k g_1 (E - E_k - E_1) +}$$

where the subscript (+) indicates the summation over positive values only.

The rates of production of species may be calculated for a system at equilibrium. It is convenient, but not necessary, to fix the collision cross-section at a constant value  $S$ . For the two-state system at thermal equilibrium, the distribution function for relative velocities of collision partners is given by

$$(10) \quad f(v_{rel}) = \frac{1}{2} \left( \frac{\mu}{kT} \right)^2 e^{-\frac{\mu v_{rel}^2}{2kT}} v_{rel}^3$$

and the distribution function for energy associated with relative velocity is

$$(11) \quad f(E_{rel}) = \left( \frac{1}{kT} \right)^2 e^{-\frac{E_{rel}}{kT}} E_{rel}.$$

For collisions of  $X_1$  with  $M$  at energy  $E = E_1 + E_{rel}$  in the interval  $dE = dE_{rel}$  the collision rate is given by

$$(12) \quad r_c = A n_1 n_m S e^{-\frac{E - E_1}{kT}} (E - E_1) dE$$

where A is a group of constants. The rate of formation of  $X_2$  is given by

$$(13) \quad r_{12} = An_1n_m S e^{-\frac{E-E_1}{kT}} \frac{g_2 (E-E_2) (E-E_1)}{g_1 (E-E_1) + g_2 (E-E_2)} dE$$

where A is a constant.

Similarly, the rate of the reverse reaction in the same interval  $dE$  is

$$(14) \quad r_{21} = An_2n_m S e^{-\frac{E-E_2}{kT}} \frac{g_1 (E-E_1) (E-E_2)}{g_1 (E-E_1) + g_2 (E-E_2)} dE$$

At equilibrium, the forward and reverse reactions are equal and the combination of the two equations yields

$$(15) \quad \frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\frac{E_2-E_1}{kT}},$$

as required by the Boltzmann equation.

Consideration of the direction of change after a perturbation from an equilibrium distribution indicates the system will approach equilibrium with increasing time. Extension of these arguments to the general case of multiple states is straightforward.

We note that for collisions at a fixed total energy, the rate of production of a specific state  $X_1$  is proportional to the energy  $E_{rel} = E - E_i$  rather than the momentum  $(2\mu E_{rel})^{1/2}$  associated with the departing atoms. This is as it should be. The density of the state  $X_1$  is given by its rate of production divided by the relative velocity and is thus proportional to the momentum.

The cross-section  $S$  may be made dependent on the states colliding and their relative velocity if such detailed information is available. When specific exchanges may be eliminated on the basis of experimental evidence or selection rules, their cross-sections may be specified as zero. The principle of microscopic reversibility places certain restrictions on the choices of cross-sections.

### 3. Monte Carlo Calculations.

The method is easily incorporated into Monte Carlo calculations of rarefied gas dynamics such as those based on Bird's direct simulation method. The electronic states are simply treated as different species and the calculation of the effects of a collision is altered to allow for energy exchange. The extensions to earlier calculations are straightforward and only a few details are required here.

We specify a cross-section  $S$  for translational energy exchange together with an electronic energy exchange or relaxation probability  $P_r$  in the range (0,1). Collision partners are selected in the usual way and electronic relaxation is chosen with probability  $P_r$ . If *electronic relaxation is not chosen, the departing atoms are the same as the colliding atoms, and their relative velocity is unchanged except for its direction.* If electronic relaxation is chosen, the selection of departing atoms is made according to Eqn. (9), and the relative velocity for the pair is altered as required for energy conservation.

### 4. Static Gas.

We have examined a number of cases of electronic energy relaxation in a static gas of fixed volume. The examples here are those of hard-sphere atoms (isotropic scattering in the center of mass) having five electronic states of energies 0, 5, 10, 15, and 20 kJ/mole. The temperatures reported below are energy-based and correspond to the temperatures for equilibrium systems having the same energies as the calculated system regardless of the distribution of velocities (for translational) or states (for electronic). The collision number  $N_C$  used is twice the number of collisions divided by the number of molecules. One collision in a system of two molecules increases the collision number by 1.0.

In Case A (Fig. 1) the gas has an initial translational temperature  $T_{tr}$  of 1000 K, and an electronic temperature  $T_{e1}$  of 100 K with an equilibrium distribution of electronic states. The relaxation probability  $P_r$  is unity. As may be seen in Fig. 1, the half-life for relaxation is about one collision per molecule and the relaxation is essentially complete by the time  $N_C = 8$ .

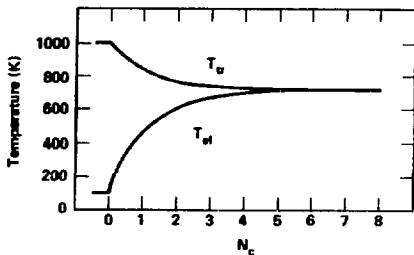


Fig. 1. Case A. Variation of electronic and translational temperature with collision number.

In Case B (Figs. 2 and 3) the initial temperatures of case A are reversed:  $T_{tr} = 100$  K,  $T_{el} = 1000$  K,  $P_r = 1.0$ . Again the half-life for relaxation is about one collision per molecule and relaxation is nearly complete by  $N_c = 8$ . The variation in the distribution of states is shown in Fig. 3 and the approach to equilibrium may be seen.

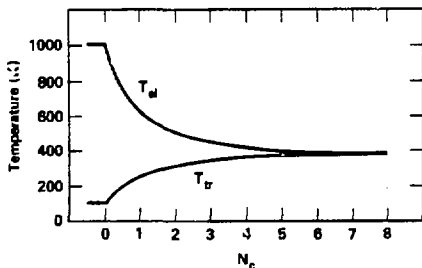


Fig. 2. Case B. Variation of temperatures.

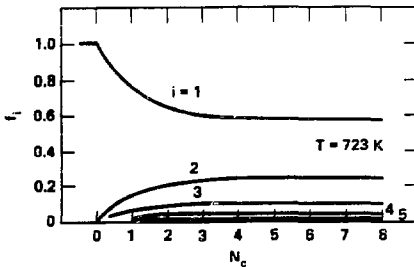


Fig. 3. Case B. Variation of electronic state populations.

In Case C (Fig. 4) all the atoms begin in the highest electronic level  $i = 5$  at a translational temperature of 100 K. The relaxation probability is unity. Again relaxation is nearly complete by  $N_c = 8$ . A translational temperature overshoot of the type observed by Koura (3) is seen as the translational temperature of species  $i = 1$  is near 1400 K in the early stages and decreases thereafter toward the final temperature of 1223 K. The greater release of electronic energy to translation for the lowest electronic state is the cause of the overshoot.

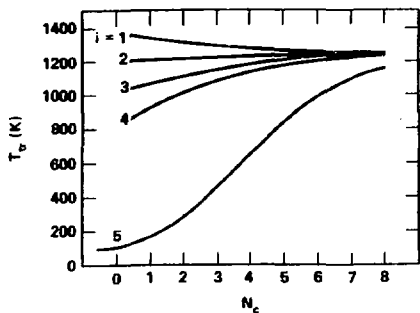


Fig. 4. Case C. Translational temperature overshoot with  $P_r = 1.0$ .

The conditions for Case D (Fig. 5) are the same as for Case C except that the relaxation probability  $P_r$  is set to 0.1. The behavior is similar to that for Case C when the collision number is scaled by a factor of ten. The translational temperature overshoot is missing since there are many more collisions to give translational equilibration between the five electronic states. However, for  $N_c$  less than 0.2 there is insufficient data for a reliable determination of translational temperature.

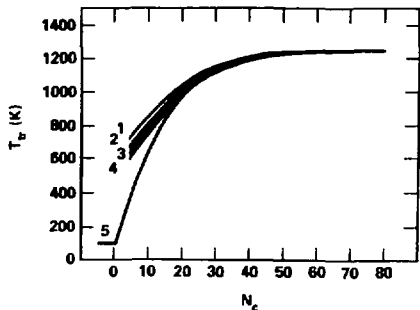


Fig. 5. Case D. Translational temperature variation with  $P_r = 0.1$ .



In Case E (Fig. 6) the degeneracies of the levels 1 to 5 are specified as 1, 2, 1, 4, and 7, respectively. At the start, all the atoms are in level 5 and the translational temperature is 100 K. The approach to equilibrium may be seen in Fig. 6 in which the fractions of atoms in each state are plotted. The final temperature is 1017 K.

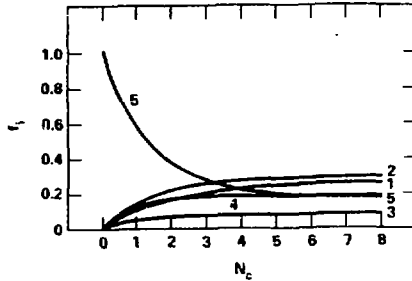


Fig. 6. Case E. Approach to equilibrium for degeneracies 1,2,1,4,7.

5. Cylindrical Source Flow Expansion.

The calculations for cylindrical expansion were carried out for the same five-state, hard sphere atoms as in Cases A-D. Two cases are given here: Case F, with  $P_r = 0.0$  corresponding to a simple hard-sphere gas; and Case G, with  $P_r = 1.0$  to give rapid electronic energy transfer. The Knudsen number, the ratio of stagnation mean free path to entering radius  $r_{in}$ , is 0.1 and the Mach number is 1.1 for the entering flow at 1000 K. Results are shown in Figs. 7 and 8 with temperatures  $T_{||}$  (parallel to flow),  $T_{\perp}$  (perpendicular to flow),  $T_z$  (parallel to axis of source cylinder), and  $T_{e1}$  (electronic).

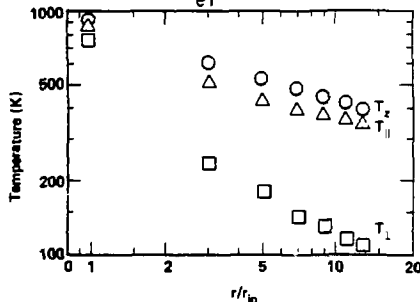


Fig. 7. Case F. Cylindrical flow with  $P_r = 0.0$ .

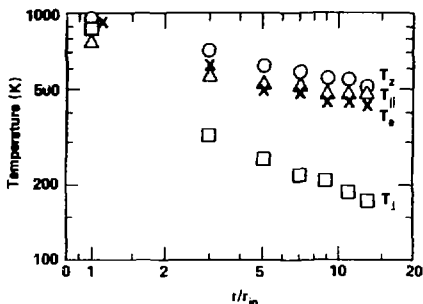


Fig. 8. Case G. Cylindrical flow with  $Pr = 1.0$ .

For  $Pr = 1.0$ , the relaxation allows  $T_{||}$ ,  $T_z$ , and  $T_{e1}$  to stay nearly the same as each other with  $T_{||}$  falling below as observed in prior calculations [2]. The additional energy available from higher electronic states results in higher temperatures than for  $Pr = 0.0$  as expected. An examination of the electronic state populations shows a mild departure from a Boltzmann distribution as  $r/r_{in}$  increases toward 20.

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