Molecular dynamics simulations of a chemical reaction; conditions for local equilibrium in a temperature gradient

Jing Xu, Signe Kjelstrup and Dick Bedeaux

Received 24th November 2005, Accepted 28th February 2006
First published as an Advance Article on the web 16th March 2006
DOI: 10.1039/b516704c

We have examined a simple chemical reaction in a temperature gradient, $2F \rightleftharpoons F_2$. A mechanical model was used, based on Stillinger and Weber’s 2- and 3-body potentials. Equilibrium and non-equilibrium molecular dynamics simulations showed that the chemical reaction is in local thermodynamic as well as in local chemical equilibrium ($\Delta G = 0$) in the supercritical fluid, for temperature gradients up to $10^{12}$ K m$^{-1}$. The reaction is thus diffusion-controlled. The velocity distributions of both components were everywhere close to being Maxwellian. The peak distributions were shifted slightly up or down from the average velocity of all particles. The shift depended on the magnitude of the temperature gradient. The results support the assumption that the entropy production of the reacting mixture can be written as a product sum of fluxes and forces. The temperature gradient promotes interdiffusion of components in the stationary state, a small reaction rate and an accumulation of the molecule in the cold region and the atom in the hot region.

1. Introduction

A chemical reaction that occurs far from global equilibrium, has a rate that is highly nonlinear in its driving force. Such reactions occur normally, not only in the presence of concentration gradients, but also in the presence of pressure and temperature gradients, e.g. in flames, combustors, turbines, reactors, in micro-porous or turbulent flow fields. For the modelling of these phenomena, it is important to have a well founded non-equilibrium description of the coupled transport processes. In non-equilibrium thermodynamics, it is assumed that, although the total system is not in equilibrium, there exists within a small volume element a state of ‘local equilibrium’, for which all normal thermodynamic relations hold. We then know that it is possible to write the entropy production of the system, the quantity that governs the transport, in terms of product sums of fluxes and forces.

The objective of the present work is to examine conditions for local equilibrium in a reacting system, to see how far these conditions can be assumed to be valid. Unless this assumption holds true, we cannot write the classical flux–force relations. The assumption is used in practice, in all calculations of combustion processes. Local equilibrium does not imply that the chemical reaction necessarily is in equilibrium. When a system that is in local thermodynamic equilibrium, also is in chemical equilibrium, the system is said to be in ‘local chemical equilibrium’. There is local thermodynamic equilibrium in a local volume element of the system, when all thermodynamics relations are valid in the volume element. Local chemical equilibrium means that in addition, the reaction Gibbs energy is equal to zero in the volume element. Local chemical equilibrium is thus a subclass of local thermodynamic equilibrium. This special condition is also frequently used.

Local thermodynamic equilibrium was found to hold in systems exposed to large driving forces for heat and mass transport and at surfaces. For a homogeneous phase, non-equilibrium molecular dynamics (NEMD) simulations with Lennard-Jones spline particles were used to verify that local thermodynamic equilibrium was valid in a two-component mixture with a temperature gradient up to $10^8$ K m$^{-1}$. It was also found to apply to a heterogeneous system, a gas–liquid interface in a one-component system. Chemical reactions have not been investigated before from this perspective, and one may wonder how good the assumption of local equilibrium is in, for instance, flame composition calculations. The temperature gradient in flames is thought to be around $10^8$ K m$^{-1}$. NEMD simulations are suitable for investigating problems of a thermodynamic nature, with the purpose of gaining molecular and statistical insight. For instance, one can find velocity distributions and compare them to a Maxwell distribution, a measure for thermodynamic equilibrium. This shall be done here. According to Ross and Mazur, the entropy production is bilinear in the fluxes and forces when the law of mass action holds. This is the case for reactions which do not disturb appreciably the Maxwell velocity distribution of the chemical components.

The purpose of this work is thus to use NEMD to study the precise nature of a chemical reaction exposed to large temperature gradients, up to $10^{12}$ K m$^{-1}$. How far is the reaction from local chemical equilibrium in the gradient? How can we characterize the behavior in the volume element, with an enormous energy flux, of about $10^8$ kJ m$^{-2}$ s$^{-1}$, across it?

In order to accomplish such a study, we first have to establish NEMD procedures for a chemical reaction. For
studies of the type we are after, quantum effects are not essential. A mechanical model may then be convenient for computational reasons. In order to capture the main thermodynamic property of the chemical reaction, namely its microscopic reversibility, the mechanical model must include not only 2, but also 3-body potentials.\textsuperscript{8–11} We chose therefore to use the reversible reaction;

\[ 2F \rightleftharpoons F_2 \]  

(1)

for method developments and first studies, as the 2 and 3-body interaction potentials of fluorine atoms and fluorine molecules are well known and documented at equilibrium.\textsuperscript{12–16}

We shall thus report a first computational effort to build an effective reaction model to be used with NEMD. The impact of the 2 and 3-body potential on the calculation of fluxes and forces, and the algorithms used, shall first be reported. The state of the reaction shall next be studied for a large range of conditions, within the accuracy of the calculation, and in spite of the net movement of components between the hot and the cold regions. The laws of thermodynamics at a local level can thus be safely applied, in spite of the extreme conditions.

2. Theory

2.1. Governing equations

De Groot and Mazur\textsuperscript{1} give the expression for the entropy production rate for a two-component system with transports of heat and mass, and a chemical reaction:

\[ \sigma = J_q \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} \sum_k J_k \cdot \nabla \mu_{k,T} - \frac{r}{T} \Delta G \geq 0 \]  

(2)

As is standard in non-equilibrium thermodynamics, \( \sigma \) is the sum of products of flux–force pairs. Here \( J_q \) is the measurable heat flux, \( T \) the absolute temperature, \( J_k \) the molar component fluxes with respect to the wall (or the net movement of \( F \) and \( F_2 \)), \( \nabla \mu_{k,T} \) the gradient in chemical potential at a constant temperature, \( r \) the reaction rate, and \( \Delta G \) is the reaction Gibbs energy. The symbol \( \cdot \) between two vectors indicates a contraction of two vectors (a scalar product). The first two flux–force pairs are vectors. The reaction has one scalar flux–force pair, \( r \) and \( \Delta G/T \). Our simple reaction is:

\[ 2F \rightleftharpoons F_2 \]  

(3)

In the molecular dynamics simulations we only considered gradients and fluxes in the \( x \)-direction. In that case the entropy production rate simplifies to

\[ \sigma = J_q \frac{\partial}{\partial x} \left( \frac{1}{T} \right) - \frac{1}{T} \sum_k J_k \frac{\partial}{\partial x} \mu_{k,T} - \frac{r}{T} \Delta G \geq 0 \]  

(4)

The balance equations for the molar densities are thus:

\[ \frac{\partial c_F(x, t)}{\partial t} = - \frac{\partial J_F(x, t)}{\partial x} - 2r(x, t) = 0 \]  

(5)

\[ \frac{\partial c_{F_2}(x, t)}{\partial t} = - \frac{\partial J_{F_2}(x, t)}{\partial x} + r(x, t) = 0. \]  

Here \( c_F \) and \( c_{F_2} \) are molar densities of component \( F \) and \( F_2 \), respectively. In our analysis we will focus on stationary states alone. The molar fluxes and the reaction rate are then only functions of \( x \). No external forces were applied during the simulations, and there was no mass flux out of the box. Mass conservation gives in a stationary state:

\[ \frac{\partial J_F(x)}{\partial x} = -2 \frac{\partial J_{F_2}(x)}{\partial x} = -2r(x) \]  

(6)

At every position, the divergence of each flux is therefore balanced by the reaction rate. From reaction kinetics, we can express the net reaction rate as

\[ r = r_t - r_b \]  

(7)

where \( r_t \) and \( r_b \) are unidirectional forward and backward reaction rates, respectively. By integrating eqn (6), we have \( J_F(x) = -2J_{F_2}(x) + C \), where \( C \) depends on the system boundaries. In this system, \( C = 0 \), and as a consequence

\[ J_F(x) = -2J_{F_2}(x) \]  

(8)

We shall find that the divergences of the fluxes are finite and lead to non-zero molar fluxes in the system, of atoms to the cold side and molecules to the hot side.

In the stationary state, the measurable heat flux is related to the reaction enthalpy. This can be seen from the expression for the total heat flux, or energy flux:

\[ J_q = J'_q + J_F H_F + J_{F_2} H_{F_2} = J'_q + J_{F_2} \Delta H \]  

(9)

Here \( H_F \) and \( H_{F_2} \) are partial molar enthalpies of \( F \) and \( F_2 \), respectively. We have used eqn (8) and \( \Delta H = H_{F_2} - 2H_F \). At the boundaries used, both mass fluxes were zero. This allows us to use \( J'_q = J_q \) at these locations. The energy flux through the system is constant.

2.2. Defining local equilibrium and local chemical equilibrium

There is local thermodynamic equilibrium in a volume element of a system when:

- All normal thermodynamic relations are valid in the volume element.\textsuperscript{17}

Criteria for local thermodynamic equilibrium were investigated by Hafskjold and Kjelstrup.\textsuperscript{5} They found that the assumption was valid even when the temperature gradient was \( \nabla T = 10^8 \text{ K m}^{-1} \). On the statistical level, local thermodynamic equilibrium means:

- The probability distribution of particle velocities is close to being Maxwellian everywhere in the system.

The Maxwell distribution of the \( x \)-component of the velocity is:

\[ M(v_x) = \sqrt{\frac{m}{2\pi k_B T_x}} \exp\left(-\frac{m(v_x^2 - \langle v_x \rangle^2)}{2k_B T_x}\right). \]  

(10)
Here $k_B$ is Boltzmann’s constant, $m$ is the mass of the particle in question, $v_x$ is the $x$-component of the particle’s velocity, $(v_x)$ is its average and $T_x$ is the temperature in the volume element calculated from the average kinetic energy in the $x$-direction. The distributions in the $y$ and $z$ direction were similar.

There is local chemical equilibrium in a volume element of a system when:

- In addition to the two criteria above, the reaction Gibbs energy is zero, $\Delta_r G(x) = 0$.

This is a special case of local thermodynamic equilibrium. The velocity distribution should be close to Maxwellian for both particles also in this case in order for the law of mass action to be valid. We can finally state that a system is in global equilibrium when all volume elements have the same thermodynamic state. This is what we normally understand as equilibrium.

### 2.3. The equilibrium constant and the reaction Gibbs energy

The chemical potentials of F and F$_2$ are needed to define the reaction Gibbs energy. For each of the components, we have:

$$\mu_k = \mu_k^\ominus + RT \ln f_k/p^\ominus \quad (11)$$

where $f_k$ is the fugacity and $k$ represents F or F$_2$ and the standard state is $p^\ominus = 1$ bar.

The fluid that we are dealing with, has a relatively high overall density, 11 kmol m$^{-3}$. We are working with temperatures from 400 K and up, with high pressures. At the critical point, the molar density of molecular fluorine is for comparison, near 15 kmol m$^{-3}$, the critical temperature is 144 K, and the critical pressure is 52 bar. It is thus necessary to use fugacities rather than partial pressures alone. The fugacity of the component with partial pressure $p_k$, is:

$$f_k = \gamma_k p_k = \gamma_k \frac{N_k}{N_N + N_{F_2}} p \quad (12)$$

We use particle numbers $N_k$ to calculate the mole fraction $x_k$. The reaction Gibbs energy is:

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q \quad (13)$$

where $\Delta_r G^\ominus = \mu_{F_2}^\ominus - 2\mu_F^\ominus$ is the standard reaction Gibbs energy and $Q$ is the reaction quotient, defined by

$$Q = \frac{N_{F_2}(N_F + N_{F_2})}{(N_F)^2} \quad (14)$$

and $\gamma_p$ is the activity coefficient ratio $\gamma_F/\gamma_{F_2}$. When $\Delta_r G = 0$ we obtain

$$\Delta_r G^\ominus = -RT \ln K_{eq} \quad (15)$$

and

$$K_{eq} = \left[ 1 + \frac{N_{F_2}(N_F + N_{F_2})}{(N_F)^2} \right]. \quad (16)$$

The equilibrium constant is only a function of the temperature (with 1 bar standard state). When the activity coefficient ratio is unity, $K_{eq} = K_p$:

$$K_p = \left[ \frac{N_{F_2}(N_F + N_{F_2})}{(N_F)^2} \right]. \quad (17)$$

The value of $K_p$ can be found from simulation data; components numbers and the pressure of the mixture. We can calculate

$$K_p^\prime = \frac{N_{F_2}(N_F + N_{F_2})}{(N_F)^2} \quad (18)$$

also in simulations of systems which are not in global equilibrium. If $K_p^\prime$ is the same function of $T$ as $K_p$ is, one may conclude that the mixture in question is in chemical equilibrium, without having knowledge of $\gamma_p(T)$.

### 3. Model and simulation details

#### 3.1. The reaction model

The reaction given in eqn (3), is simple. Fluorine atoms and molecules react and form a mixture. In order to see why 2- and 3-body potential interactions are essential, we write the reaction mechanism for eqn (3) as:

$$F + F_2 \iff F_2 + F \quad (19)$$

This equation indicates that an atom can constantly hit a molecule, and form a new bond (a molecule) plus a new single atom. Alternatively, one may also write:

$$\ldots F - F - F \iff F - F - F - F. \quad (20)$$

Stillinger and Weber$^{15}$ gave the potential surface $\Phi$ for the reaction as:

$$\Phi(r_1, ..., r_N) = \sum_{i,j} u_2(r_{ij}) + \sum_{i,j,k} u_3(r_{ij}, r_{ik}, r_{jk}) \quad (21)$$

Here $u_2$ is the two-atom potential— a function of the atom–atom distance $r_{ij} \equiv |r_i - r_j|$, and $u_3$ is the three-atom potential determined by three-atom distances $r_{jk}, r_{ik}$, and $r_{jk}$. The subscripts $i, j,$ and $k$ indicate different atoms. The pair potential $u_2$ was selected to give a good representation of isolated diatomic fluorine:

$$u_2(r_{ij}) = \begin{cases} A_0 [2(r_{ij}/r_0) - (r_{ij}/r_0)^4] \exp[\alpha_0/(r_{ij} - r_c)] & 0 < r_{ij} < r_c \ \
0 & r_{ij} \geq r_c \end{cases} \quad (22)$$

The value $A = 6.052463017$ causes the reduced pair potential $u^* = u_2/\epsilon_0$ to have a minimum with depth $-1$ at the normal fluorine bond distance $1.181999\epsilon_0$ (1.435 Å). The function vanishes at a cutoff distance of $r_c = 3.6\epsilon_0$. For the choice of these coefficients and a discussion of this choice we refer to Stillinger and Weber.$^{15}$ The reduced pair potential is plotted in Fig. 1.

Reduced units were used in the calculation. Basic units were the diameter of the fluorine atom, $\sigma_0 = 1.214 \ \text{Å}$, its potential energy depth $\epsilon_0 = 2.659 \times 10^{-19} \text{J}$ and its particle mass, $m_0 = 3.155 \times 10^{-26} \ \text{kg}$. Reduced units are indicated by a star symbol. The variables in real and reduced form are listed in Table 1. Using these reduced units the expression for the pair
The three-atom potential was scaled to fit fluorine, from the aforementioned scaling.\textsuperscript{15} Using the 2-atom and 3-atom reaction model, we computed first the potential energy for the linear configuration of three fluorine atoms. The results were compared with those of Stillinger and Weber.\textsuperscript{15} We found the same value as they, \(-1.04\) (in reduced units), for the two triple potential minima. Fig. 3 shows the contour plot of the potential energy for the linear 3-F configuration. Contours are given for reduced values \(-1.04\), \(-1.01\), and up. In this symmetrical configuration, the transition state for the reaction is found on the diagonal in the figure that separates the potential minima.

Stillinger and Weber\textsuperscript{15} used a distance cutoff criterion to identify chemical bonds, and by default also identifying unbonded atoms produced by dissociation. The value was chosen in the low temperature pair correlation function gap, which gave the cutoff diameter \(r_c = 1.7\sigma_0\). Any pair of atoms with atom–atom distance less than or equal to \(r_c\) were thus defined as molecules, i.e. chemically bonded. Pairs with atom–atom distance larger than this value were considered as free atoms. An important role of the chosen three-atom potential is to prevent the formation of more than one covalent bond to each fluorine atom.\textsuperscript{15}

\begin{table}[h]
\centering
\caption{Relations between reduced and real variables for fluorine}
\begin{tabular}{ll}
\hline
Reduced variable, symbol & Formula \\
\hline
Mass & \(m^\prime = m/n_0\) \\
Distance & \(r = r/\sigma_0\) \\
Energy & \(U' = U/n_0\) \\
Time & \(T' = k_BT/\hbar_0\) \\
Molar density of \(k\) & \(c_k = N_k\sigma_0^3\) \\
Pressure & \(p^* = \rho g\hbar_0/n_0\) \\
Velocity & \(v^* = \sqrt{n_0/\hbar_0}\) \\
\hline
\end{tabular}
\end{table}

The three-atom potential \(u_3\) is the sum of three \(h\)-functions:

\[
\begin{align*}
\text{if} & , 0 < r_{ij} < r_{ij}^* \\
\end{align*}
\]

The three-atom potential was scaled to fit fluorine, from the well-known potential surface of \(H + H_2\).\textsuperscript{15} The three \(h\)-functions are symmetric in their first two variables, while \(\theta_i\) in \(h_i\) represents the angle between \(r_{ij}\) and \(r_{jk}\), and similarly for \(\theta_j\) and \(\theta_k\). Fig. 2 gives notations for the triple fluorine configuration. The expression for the reduced \(h\)-function is:

\[
h^*(a', b', \theta) = \\
\begin{cases}
8.4(a' b')^{-4} \exp[(a' - r_{ij}^*)^{-1} + (b' - r_{ij}^*)^{-1}] + (50 - 25 \cos^2 \theta) \exp[3(a' - r_{ij}^*)^{-1}], \\
0 < a' b' < r_{ij}^* + 3(b' - r_{ij}^*)^{-1} \\
8.4(a' b')^{-4} \exp[(a' - r_{ij}^*)^{-1} + (b' - r_{ij}^*)^{-1}], \\
either a' or b' exceeds r_{ij}^*, 0 \\
either a' or b' exceeds r_{ij}^* \\
\end{cases}
\]

Here \(a (a = a' \sigma_0)\) and \(b (b = b' \sigma_0)\) are adjacent sides of the angle \(\theta\). The expression for \(\cos^2 \theta = (a^2 + b^2 - c^2)/(2ab)\), where \(c (c = c' \sigma_0)\) is the third side of the triangle, was used to make the formula for \(h\) dependent on positions only. The second cutoff distance \(r_{ij}^* = 2.8\sigma_0\) was obtained from the aforementioned scaling.\textsuperscript{15}

Fig. 2 Notations used for a triple configuration.

Fig. 3 Potential energy contours for a linear arrangement of three fluorine atoms.
3.2. Simulation details

3.2.1. The molecular dynamics box. Algorithms. The system had \( N = 1000 \) fluorine atoms in a box with dimensions \( L_x, L_y, L_z \) in the \( x, y \) and \( z \) directions, respectively. Stillinger and Weber\textsuperscript{15} used the same number of fluorine atoms. The volume of the box was \( V = L_x L_y L_z = 1000/(c N_A) \), where \( c \) is the overall molar density (11 270.9 mol m\(^{-3}\)), and \( N_A \) is Avogadro’s number. The molecular dynamics (MD)-box was non-cubic, with lengths \( L_y = L_z = L_x/2 \). It was divided into 128 equal planar volume layers in the \( x \)-direction, with a symmetry plane between layers 64 and 65. The volume of each layer is \( V_L = V/128 \).

When the system was thermostatted, equilibrium MD simulations produced a canonical ensemble (with constant number of particles \( N \), volume \( V \) and temperature \( T \)). In order to test system size dependence, we did some of the equilibrium simulations with 1728 particles and \( L_y = L_z = L_x/8 \). Ikeshoji–Hafskjold\textsuperscript{18} periodic boundary conditions were applied to the \( x \)-direction and regular periodic boundary conditions were used in the \( y \)- and \( z \)-directions. In a stationary state the system is symmetric. Fig. 4 shows a 3-dimensional snapshot of 1000 fluorine particles in the MD box. Layers 1–4 and 125–128 (the hot layers) at the ends of the box were thermostatted to the temperature \( T_H \) using the HEX algorithm.\textsuperscript{5} The layers 61–69 (the cold layers) in the middle of the box were thermostatted to the temperature \( T_C \), where \( T_C \leq T_H \). Thermodynamic properties were found by time averaging over the instantaneous values in elements that lie symmetric to the central plane in the box.

The Verlet ‘Leap Frog’ algorithm was used. Many particle pairs are out of the range \( r^*_{12} = 3.6 \) of each others pair potential, see eqn (22). To restrict the computation time a list of pairs was made with a distance from each other smaller than a cut-off distance, \( r^*_{\text{list}} = 4 \). Pair interactions were calculated when \( r^* \) was equal to or smaller than this value. A similar algorithm, called NEIGHBOUR3, was made to compute 3-body interactions. For this, a list of triplets was made by combining pairs from the pair list, which had one particle in common.

As long as the displacement of the particles was less than half of \( r^*_{\text{list}} = 4 \), we did not need to update the two lists. This procedure avoided unnecessary calculation of particle interactions. A time step length of 0.01 in reduced units (see Table 1) was used. This corresponds to \( 4.1817 \pm 10^{-16} \) s in real time.

3.2.2. Equilibrium molecular dynamics simulations. Equilibrium simulations were first done. These results are called EMD results. We used the NEMD program (see next section) thermostating the hot and the cold layers to the same temperature, to find the EMD results. In the EMD simulations, the program gave the temperatures of each layer within 0.1%. A standard thermostat method (the velocity scaling algorithm\textsuperscript{5}) was applied during the first 1000 time steps.

Thirteen equilibrium cases were studied, all with the same overall density, \( c^* = 0.012 \) 147:

- Case 1: This case is identical to one of the cases of Stillinger and Weber.\textsuperscript{15} The triple point of molecular fluorine is \( T^* = 0.002 \) 779 and \( \rho^* = 0.097 \) 173,\textsuperscript{15} and we chose a state well above this point, with a temperature \( T^* = 0.019 \).
- Cases 2–13 had temperatures varying from \( T^* = 0.25 \), in steps of 0.05 to 0.80 in reduced units.

Case 1 was done to check the reproducibility of the earlier EMD results with our NEMD code. In all cases, we calculated compositions and velocities of atoms and molecules.
temperature and pressure (see section on Calculation details). We also calculated the velocity distribution of the x-component of the velocity of atoms and molecules in equilibrium. They are given for Cases 4 and 13 in Fig. 5 for a position where the reduced temperatures were $T^* = 0.35$ and $T^* = 0.8$, respectively.

3.2.3. Non-equilibrium molecular dynamics simulations. Details of the NEMD program have been described in earlier work.5-6,19-21 Here we shall only give the main properties as well as the expressions which are modified due to contributions from the three particle interactions.

The thermostating algorithm was now used to control the temperatures in the hot and in the cold layers. All NEMD simulations were performed over $10^7$ time steps. We omitted the first $2 \times 10^6$ time steps, which showed transient effects. Mean values of properties, such as temperature and density, were computed for each layer of the box. The average value was then taken for mirror symmetric layers. Time averages were done every $5 \times 10^5$ time steps.

Nine NEMD simulations were performed, Cases 14–22. The temperatures in the hot and the cold layers for these cases, are listed in Table 2. Cases 14, 15 and 16 had the smallest temperature difference, while Case 22 had the largest temperature difference. In the last case the temperature gradient was $1.1 \times 10^{12}$ K m$^{-1}$ and the heat flux through the system was then $9.9 \times 10^8$ kJ m$^{-2}$ s$^{-1}$. For even larger temperature differences the velocity distribution would no longer relax to a nearly Maxwellian distribution, so that nothing comparable to local equilibrium developed. In all cases the NEMD simulations were very far from global equilibrium. The velocity distributions of the x-component of the velocity of atoms and molecules were studied. They are given for Cases 19 and 22 in Fig. 6 for a position where the reduced temperatures were $T^* = 0.488$ and $T^* = 0.511$, respectively.

3.2.4. Calculation details. The same NEMD program was used to calculate all properties, also equilibrium properties. In EMD simulations, the overall temperature, pressure and densities were determined by averaging layer properties over all 128 layers in the MD box. In NEMD simulations, local properties, such as temperature, pressure and density, were calculated for each layer, and an average was then taken for pairs of layers that were mirror symmetric around the center of the box.

The molar density of component $k$ in layer $l$, with $l = 1, \ldots, 128$, is:

$$c_{kl} = \frac{N_{kl}}{N_A V_L}$$

(26)

where $N_{kl}$ is the number of particles of component $k$ (F or F$_2$) in the layer $l$. All the layers have the volume $V_L = V/128$. Furthermore $N_A$ is Avogadro’s number.

The temperature $T_l$ of layer $l$ was found from the average kinetic energy per degree of freedom:

$$T_l = \frac{1}{3 k_B N_l} \sum_{i \in l} m_i v_i^2$$

(27)

where $N_l = \sum_k N_{kl}$ is the total number of particles in the layer $l$ and $v_i^2 = v_x^2 + v_y^2 + v_z^2$.

From the virial theorem, the expression for the pressure tensor for layer $l$ in the presence of 2- and 3-body interactions is:

$$p_l = \frac{k_B T N_l}{V_L} - 1 + \frac{1}{V_L} \sum_{i \in l} \left( \sum_{j \text{ pair with } i} w_{ij} + \sum_{j < k \text{ triplet with } i} w_{ijk} \right)$$

(28)

Table 2  NEMD simulation conditions. The temperature is given in reduced units

<table>
<thead>
<tr>
<th>Case no.</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^*_H$</td>
<td>0.30</td>
<td>0.35</td>
<td>0.40</td>
<td>0.40</td>
<td>0.50</td>
<td>0.60</td>
<td>0.80</td>
<td>1.00</td>
<td>0.80</td>
</tr>
<tr>
<td>$T^*_L$</td>
<td>0.25</td>
<td>0.30</td>
<td>0.35</td>
<td>0.30</td>
<td>0.40</td>
<td>0.40</td>
<td>0.60</td>
<td>0.70</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Fig. 6 Distribution of the x-component of the velocity in layer number 35 of the MD box in a temperature gradient. The dash-dotted and dashed lines are Maxwell distributions (eqn (10)) in the layer around the average velocity of the two components. Symbols denote NEMD simulations, Case 19 and 22. (a) Case 19: $\langle T^* \rangle = 0.488$. (b) Case 22: $\langle T^* \rangle = 0.511$. 

This journal is © the Owner Societies 2006
where \( \mathbf{I} \) is the unit tensor. The first contribution on the right hand side is the kinetic contribution. The second and the third contributions are due to the two and the three particle interaction, respectively. The summands in these terms are given by:

\[
\begin{align*}
\mathbf{w}_{ij} &= -\frac{1}{2} \frac{\partial u_2(r_{ij})}{\partial r_{ij}} r_{ij} r_{ij} \\
\mathbf{w}_{ijk} &= - \left[ \frac{\partial h_i}{\partial r_{j}} r_{ij} r_{ik} - \frac{\partial h_i}{\partial r_{jk}} r_{jk} r_{ik} + \frac{\partial h_i}{\partial r_{jk}} r_{jk} r_{jk} \right]
\end{align*}
\]  

(29)

where the hat (circumflex) indicates a unit vector, like \( \mathbf{r}_{ij} = \mathbf{r}_{ij} / r_{ij} \). In the expression for the contribution due to pair interactions we use the convention due to Irving and Kirkwood\textsuperscript{22} and assign half of the force moment due to the pair \( ij \) to particle \( i \) and the other half to particle \( j \). The interaction energy due to a triple, cf. eqn (24), is the sum of three terms, \( h_i, h_j \) and \( h_k \). In eqn (28) we have assigned the force moments due to particle \( i \) to particle \( j \) or \( h_i \) to particle \( j \) and those to \( h_k \) to particle \( k \). Though other choices are possible this seems like a natural choice. In the simulations we found the pressure to be independent of the position. A different choice would therefore lead to essentially the same results. Furthermore the pressure tensor was found to be diagonal and the same in all directions. Using eqn (29) we find for the hydrostatic pressure in layer \( l \) one third of the trace of the tensor given in eqn (28)

\[
p_l = \frac{k_b T N_l}{V_L} - \frac{1}{3V_L} \sum_{i<j} \left[ \frac{1}{2} \sum_{j \text{ pair with } i} \frac{\partial u_2(r_{ij})}{\partial r_{ij}} r_{ij} + \sum_{j<k \text{ triplet with } i} \left( \frac{\partial h_i}{\partial r_{j}} r_{ij} + \frac{\partial h_i}{\partial r_{jk}} r_{jk} \right) \right]
\]  

(30)

The positive direction of the fluxes is from the left to the right hand side of the MD-box. The molar flux of component \( k \) in layer \( l \) is:

\[
\mathbf{J}_{k,l} = \frac{1}{N_A V_L \sum_{i \in \text{component } k}} \mathbf{v}_i
\]  

(31)

The total molar flux in layer \( l \) is given by

\[
\mathbf{J}_l = \sum_k \mathbf{J}_{k,l}
\]  

(32)

The energy flux in layer \( l \) is

\[
\mathbf{J}_{q,l} = \frac{1}{V_L} \sum_{i \in \text{component } k} \left[ \mathbf{v}_i \frac{1}{2} m_i v_i^2 + \Phi_i \right] + \mathbf{v}_i \cdot \mathbf{p}_l
\]

\[
= \frac{1}{V_L} \sum_{i \in \text{component } k} \left[ \mathbf{v}_i \frac{1}{2} m_i v_i^2 + \Phi_i + p_l \right]
\]  

(33)

where \( \cdot \) now indicates a contraction of a vector and a tensor. Furthermore \( \Phi_i \) is the potential energy of particle \( i \)

\[
\Phi_i = \frac{1}{2} \sum_{j \text{ pair with } i} u_2(r_{ij}) + \sum_{j<k \text{ triplet with } i} h(r_{ij}, r_{jk}, \theta_{ijkl})
\]  

(34)

In the expression for the contribution due to pair interactions we assign half of the force moment due to the pair \( ij \) to particle \( i \) and the other half to particle \( j \). The interaction energy due to a triplet, cf. eqn (24), is the sum of three terms, \( h_i, h_j \) and \( h_k \). In eqn (34) we have assigned \( h_i \) to particle \( i \), \( h_j \) to particle \( j \) and \( h_k \) to particle \( k \). All these choices are analogous to the ones we made in the expression for the pressure, see eqn (28) and (30).

In the expression for the energy flux, eqn (33), it is crucial to use similar choices as those used in the pressure. This contributes to making the treatment self-consistent. It should be emphasized that other choices are possible, which should give essentially the same results.

The measurable heat flux in a volume element is related to the energy flux by

\[
\mathbf{J}_{q,l} = \mathbf{J}_{h,l} - \mathbf{J}_{F,F} H_{F,F} - \mathbf{J}_{F,F} H_{F,F} = \mathbf{J}_{h,l} - \mathbf{J}_{F,F} \Delta \mathbf{H}_l
\]  

(35)

where the reaction enthalpy in layer \( l \) is \( \Delta \mathbf{H}_l = H_{F,F} - 2H_{F,F} \).

It is impossible to calculate the partial enthalpies \( H_{F,F} \) and \( H_{F,F} \) by simulations. We can, however, find the total enthalpy of \( F \) and of \( F_2 \) in layer \( l \). The total enthalpy in J mol\(^{-1}\) is given by

\[
H_l = N_A \left\{ \frac{1}{N_l} \sum_{i \in l} \phi_i + \frac{p_l V_L}{N_l} + \frac{3}{2} k_b T \right\}
\]  

(36)

By allocating contributions to \( H_l \) from \( F \) or \( F_2 \), we found estimates for molar enthalpies. With this information, we estimated \( \Delta \mathbf{H}_l \) for each layer. With knowledge of the particle flux and total heat flux, we were then able to estimate the measurable heat flux. These estimates will be reliable when the gas is close to being ideal.

4. Results and discussion

4.1. An algorithm for a chemical reaction in a temperature gradient

The results of the EMD simulation for Case 1 are shown in Fig. 7. The results are identical to those of Stillinger and Weber\textsuperscript{15} up to 70 ps. We continued the simulation up to \( 4 \times 10^5 \) time steps (1672.8 ps), and found a stationary state with only two atoms left, see Fig. 7. The corresponding pair

![Fig. 7](image-url)
The pair correlation function (pcf) versus distance is shown for the long runs in Fig. 8. The sharp peak of the pcf curve is positioned at a reduced atom–atom distance of $r^* = 1.2$. This represents the chemically bonded pairs, and corresponds to the minimum in Fig. 1.

We have thus confirmed the equilibrium results of Stillinger and Weber\textsuperscript{15} and consider our computations to be reliable.

4.2. The chemical reaction in the temperature gradient

The system we investigated had no net mass flux. In order to obey mass conservation (eqn (8)), the flux of atoms was everywhere minus twice the flux of molecules. The calculations are reported for the stationary state. The fluxes in Case 18 are shown in Fig. 9. The flux of atoms was directed to the cold side, while the flux of molecules was directed to the hot side. It is interesting that they are not constant across the box. This situation is very unlike the situation in the absence of a chemical reaction, where the fluxes of both components will be zero in the stationary state. The variation is due to the chemical reaction. The total mass flux is proportional to two times the molar flux of F\textsubscript{2} plus the molar flux of F. This flux is, as expected within the accuracy of the calculation, equal to zero.

A net and varying reaction rate $r(x)$, was observed through the system, see Fig. 10 for Case 22. The series of events can be understood as the reaction being controlled by diffusion. The transport in and out of a volume element is limited by the fluxes. As soon as a composition is perturbed from its equilibrium value by an incoming flux, the reaction rate will bring the mixture back to equilibrium.

The largest temperature gradient used in the simulations was around 1.1 × 10\textsuperscript{12} K m\textsuperscript{-1} and the corresponding total heat flux was 9.9 × 10\textsuperscript{8} kJ m\textsuperscript{-2} s. The temperature gradient is larger by several orders of magnitude from what one may expect in flames. This gradient drives the chemical reaction by setting up thermal diffusion and interdiffusion of components. The effect of the chemical reaction may have an impact on flame modelling through this. We shall elaborate on this in our next study.

4.3. The effect of the 3-body potential on calculation of thermodynamic properties

The model used to simulate the chemical reaction was described in the theoretical Section 3.1. Unless a third particle is there to take away excess kinetic energy, a stable pair cannot be formed. Similarly, a molecule needs to be hit by a third particle, in order to break open and at the same time change its interaction potential. Calculations of system’s properties are consistent with this. As our NEIGHBOUR\textsuperscript{3} algorithm and the expressions of the section reproduced earlier results we believe that it performs satisfactorily. The 3-body potential interaction had a significant effect on the thermodynamic properties. This is illustrated for the pressure for one condition in Fig. 11. The figure shows the varying contributions to the pressure; that is the ideal gas-, the 2-body interaction-, and the 3-body interaction-contribution. The different contributions have different temperature dependences. The three-body contribution is more sensitive to the temperature than the two-
body contribution. This is expected, as this potential reflects much of the properties of the reaction.

### 4.4. Maxwell velocity distributions

The probability distributions for the $x$-components of the velocities of the atoms, $F$, and the molecules, $F_2$ in the system, $P(v_x)=N(v_x)/N$, are shown in Fig. 5 and 6. Fig. 5 presents the equilibrium Cases 4 and 13, while Fig. 6 presents the non-equilibrium Cases 19 and 22, for layer 35 together with its mirror image. The Maxwell velocity distributions for the two components, $M(v_x)$, were calculated from eqn (10) using the average temperatures of the symmetric layers in question. These results are also shown in Fig. 5 and 6. These temperatures were found from the average kinetic energy in the $x$ direction. Temperatures obtained from the average kinetic energies in the $y$ and the $z$ direction were found to be the same (as they should be).

Fig. 5 shows results for global equilibrium, at a low and a high temperature, respectively ($T^*=0.35$ and $T^*=0.8$). The figure shows that the velocity distribution of the atoms and molecules have average velocity 0.0000 $\pm$ 0.0001, and both are Maxwellian within 1% accuracy. This result is what we expect for equilibrium.

The non-equilibrium studies were done at a small temperature difference, $\Delta T^* = 0.2$, and the largest possible temperature difference, $\Delta T^* = 0.5$. The temperatures and velocities of the atoms and the molecules in the layer were calculated (Cases 19 and 22). We observed that a temperature gradient across the system shifted the velocity distributions. The shift for $F_2$ gave $J_{F_2}$ as pictured in Fig. 9, while the shift for $F$ gave $J_F$ in this figure. The molecules had a sharper distribution than the atoms had in Fig. 6, and the molecules gave a negative average velocity, while the atoms gave a positive average velocity. Each distribution was still close to a Maxwellian one. The simulations in sub-Fig. 6(a) and (b) agreed with their respective Maxwell distribution within $\pm 3\%$ (6(a)) and $\pm 5\%$ (6(b)). The shift increased with the temperature gradient. For temperature gradients larger than $10^{12}$ K m$^{-1}$, we found that the velocity distribution did no longer relax to a nearly Maxwellian distribution.

We can thus conclude that the system is always in local thermodynamic equilibrium. This is true even for the largest temperature gradient investigated, $1.1 \times 10^{12}$ K m$^{-1}$. The situation fits well with the situation described by Ross and Mazur. We see that the chemical reaction perturbs the Maxwellian distribution of velocities. The reason is removal (supply) of molecules with high (low) kinetic energy. The perturbation observed here does not alter the law of mass action (see section below) and must therefore be considered small enough. The small shift in the velocity distribution up or down, equal to the mean velocity of the component, does thus not affect the entropy production. It maintains its bilinear form in the fluxes and driving forces. This is comforting to know for a further development of the transport properties of the system. We can use the familiar expression for the entropy production from classical non-equilibrium thermodynamics to define the fluxes and forces in the system. This shall be done in our next paper, when we discuss the transport properties of the mixture.

### 4.5. A distance from local chemical equilibrium?

The question is now whether one can speak of local chemical equilibrium in a system that has internal diffusion as described above. This question was investigated by comparing Cases 14–22 to Cases 2–13 (see the theoretical Section 2.3). The ratio $K_p$ was calculated as a function of $T^*$ for all EMD simulations and plotted in Fig. 12. It was verified that $K_p$ was independent of the size of the system by an extra study with 1728 fluorine atoms in an elongated box. We found the same results as the EMD results with 1000 fluorine atoms (Fig. 12), within $\pm 1\%$.

We next calculated the same ratio for Cases 14 ($\Delta T^* = 0.05$), 21 ($\Delta T^* = 0.3$) and 22 ($\Delta T^* = 0.5$), all as a function of the reduced temperature, $T^*$, in the box. These results are also shown as points in Fig. 12. We observed then that $K_p$ of the EMD simulations and $K'_p$ of the NEMD simulations coincided to a large extent, see Fig. 12. There was reasonable agreement ($\pm 5\%$) between the ratios from NEMD and EMD in the central part of the half-box, and less agreement ($\pm 10\%$) close
to the thermostatted regions. Deviations were larger for the largest gradient (see Fig. 12). We can say on the basis of this, that the reaction is very close to local chemical equilibrium away from the boundaries.

By counting the formation of molecules over several thousand time steps in the stationary state, we found a forward reaction rate, \( r_f \), in case 22 of around \( 10^{16} \) to \( 10^{17} \) mol m\(^{-3}\) s\(^{-1}\), see Fig. 10. Compared to the value of the forward reaction rate \( r_f \), a net rate of \( 10^{13} \) mol m\(^{-3}\) s\(^{-1}\) is small. The system is therefore also very close to microscopic reversibility, in spite of having a net reaction rate. We verified this by plotting also the ratio \( c_{F_2}^*/(c_F^*)^2 \) for EMD and NEMD conditions, shown in Fig. 13. Also these ratios were very similar.

### 4.6. Comment on the system’s transport properties

The system with the reacting mixture has an enthalpy flux associated with the transport of each component, and therefore a substantial transfer of enthalpy takes place between the ends. The local reaction enthalpy was estimated using eqn (36) for the separate components. The value varied across the box from \(-340\) to \(-190\) kJ mol\(^{-1}\). The large enthalpy change has an effect on the measurable heat flux, estimated to be 5% for the largest heat flux. We shall return to a quantitative determination of the transport properties in the future.

### 5. Conclusion

NEMD simulations with various temperature gradients have been done to study the chemical reaction, \( 2F \rightleftharpoons F_2 \) using the 2-body and 3-body potentials of Stillinger and Weber,\(^{15}\) adding for an efficient MD program the NEIGHBOUR3 algorithm. Our NEMD code reproduced some of the equilibrium results obtained by others,\(^{15}\) indicating that our results can be trusted. Temperature gradients up to \( \nabla T = 1.1 \times 10^{12} \) K m\(^{-1}\) were investigated.

The non-ideal reacting mixture was always in local thermodynamic as well as in local chemical equilibrium. This means that the reaction Gibbs energy is zero and all normal thermodynamic relations hold. Component velocity distributions remained close to Maxwellian. Statistical and thermodynamic evidence was presented that the transport processes are governed by an entropy production which is bilinear in the fluxes and forces of the system. The stationary state was characterized by non-zero average velocities of the components. Thermal diffusion and interdiffusion of components were set up in the temperature gradient. A net reaction rate was observed much smaller than the forward and the backward reaction rates. The reaction was diffusion controlled.

### Symbols

- \( c_k \) Molar density of component \( k/\)mol m\(^{-3}\)
- \( f_k \) Fugacity of component \( k/\)bar
- \( \Delta_G \) Standard reaction Gibbs energy/J mol\(^{-1}\)
- \( \Delta_H \) Reaction enthalpy/J mol\(^{-1}\)
- \( J_q \) Total heat flux or energy flux/J m\(^{-2}\) s\(^{-1}\)
- \( K_p \) Equilibrium constant
- \( L_a \) Boltzmann’s constant, \( 1.381 \times 10^{-23} \) J K\(^{-1}\)
- \( m_t \) Mass of particle \( i/\)kg
- \( \rho_\text{std} \) Standard pressure, 1 bar
- \( \rho \) Standard pressure, 1 bar
- \( Q \) Reaction quotient
- \( r \) Net reaction rate/mol m\(^{-3}\) s\(^{-1}\)
- \( r_{f0} \) Forward reaction rate/mol m\(^{-3}\) s\(^{-1}\)
- \( r_{b} \) Backward reaction rate/mol m\(^{-3}\) s\(^{-1}\)
- \( r_{c1} \) Cutoff distance for bonded fluorine molecule, 1.7\( \sigma_o \) m
- \( r_{c2} \) First cutoff distance for \( \Phi, 3.6\sigma_o \) m
- \( r_{c3} \) Second cutoff distance for \( \Phi, 2.8\sigma_o \) m
- \( r_{f1} \) Forward reaction rate/mol m\(^{-3}\) s
- \( r_{fj} \) Distance between particle \( i \) and particle \( j/\)m
- \( r_{\text{int}} \) Cutoff distance for neighbour list
- \( T \) Temperature/K
- \( T_f \) Temperature at the triple point/K
- \( u_2 \) 2-body potential/J
- \( u_3 \) 3-body potential/J
- \( V \) Volume of the MD box/m\(^3\)
- \( V_L \) Volume of the layer of the MD box/m\(^3\)
- \( v_k \) Velocity of component \( k/\)m s\(^{-1}\)
- \( \Phi \) The total potential energy/J
- \( \mu_k \) Chemical potential of component \( k/J \) mol\(^{-1}\)
- \( \sigma \) Entropy production rate/W K\(^{-1}\) m\(^{-3}\)
- \( \sigma_o \) Diameter of fluorine, 1.214 \( \times 10^{-10} \) m
- \( \sigma_o \) Potential energy depth to keep \( u_2 \) \( -1, 2.659 \times 10^{-19} \) J
- \( \rho \) Density at the triple point/bar
- \( \gamma_k \) Activity coefficient of component \( k\)
- \( \gamma_p \) Activity coefficient ratio
Acknowledgements

J. Xu is grateful for support from The Research Council of Norway (grant no. 153305/432). Discussions with J. M. Simon are gratefully acknowledged.

References