

# Transport properties of a reacting binary fluid, from non-equilibrium molecular dynamics simulations.

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## Summary

Molecular dynamics (MD) simulations have been performed of the exothermic reaction



in a temperature gradient, see Fig.1. This is of our knowledge the first molecular dynamics study of a reacting system submitted to non-equilibrium conditions. The reaction, which is diffusion controlled, was investigated at and close to local chemical equilibrium. The transport properties are determined; i.e. diffusion, thermal conductivity and the coupling between transport of heat and mass. The assumptions that are used to write down the equations of transport are verified.

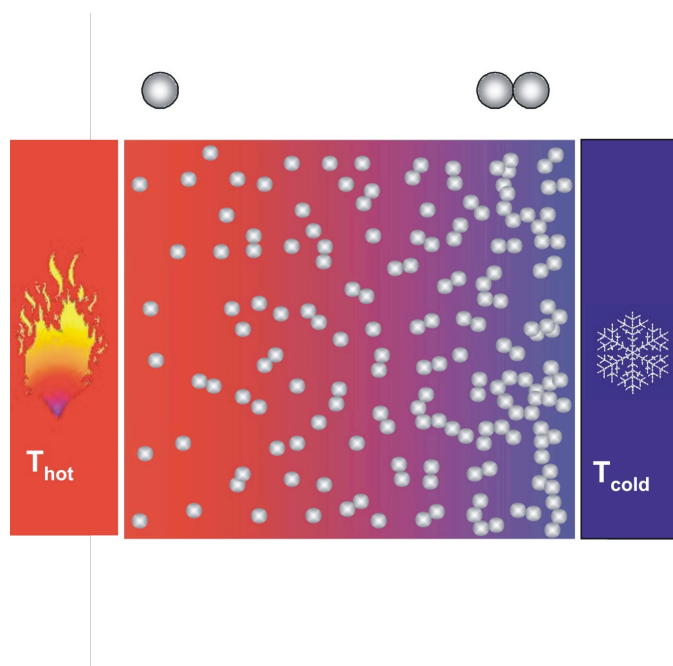


Figure 1. A schematic illustration of the reacting system. The closed system contains 1000 fluorine atoms partially reacted to molecules. The simulation box was divided into layers

perpendicular to the temperature gradient to allow analysis and apply thermostats in the so-called cold and hot layers.

### Molecular dynamics simulations

The fluorine atoms and molecules were simulated with a three body potential, which was developed by Stillinger and Weber [1] for the study of equilibrium properties of the reacting mixture (1) under different conditions. We reproduced these simulations at different temperatures and pressures as well as the chemical equilibrium constant. These systems were then forced out of equilibrium by applying different temperatures to the ends of the box, cf. figure 1. The hot and the cold zones were applied following the procedure described in [2]. A temperature gradient rapidly settled across the simulation box and became stationary. The temperature gradients were of the order of  $10^{11}$  K/m. and probably larger than those that occur in flames.

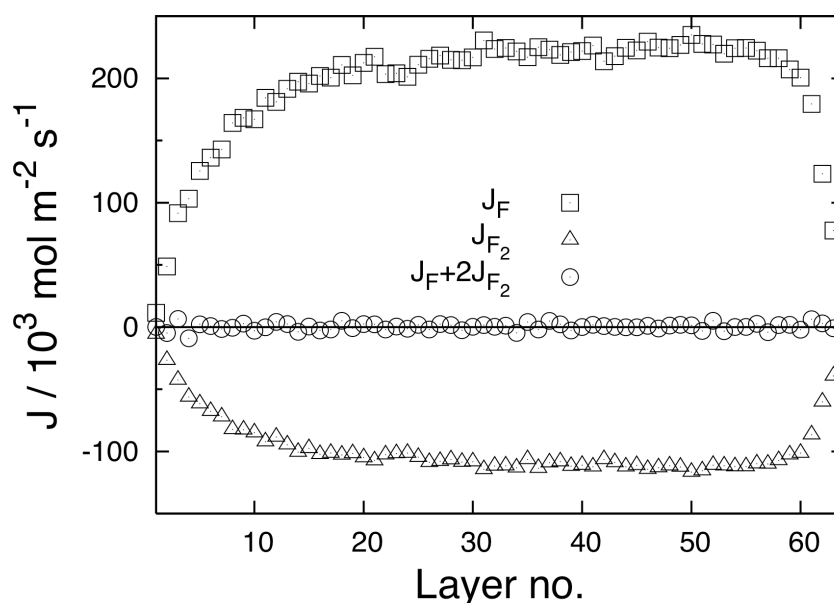


Figure 2. The molar fluxes in the reacting system simulated with a temperature gradient of  $2 \cdot 10^{11}$  K/m. The squares give the molar flux of F and the triangles give the molar flux of  $F_2$ . The circles give the total molar flux, which is the sum of two times the atomic flux and the molecular flux.

### System description

After a short period of around 10 picoseconds, the system exhibited a stationary state with a homogeneous non-zero energy flux directed towards the cold zone. As expected the temperature gradients lead to variations in the density as in the mole fraction profiles. The mass density and the mole fraction molecule  $F_2$  were higher in the cold zone. Mechanical equilibrium was verified, with the pressure being homogeneous across the simulation box. The simulations showed that locally, the system is in local thermodynamic equilibrium (all thermodynamic relations are valid) as well as in local chemical equilibrium (the reaction Gibbs energy,  $\Delta_r G$ , was zero). At the stationary state the net mass flux also vanished, but a net diffusive flux of fluorine atoms to the cold side and of molecules to the hot side was observed. The reaction took place everywhere along the system, and was faster than diffusion.

## Method of analysis

The simulation data were analysed using non-equilibrium thermodynamics theory [3,4] after verifying that all conditions for such a description were fulfilled [2]. For instance, the particles Maxwell distributions were shifted only slightly by the reaction and in the temperature gradient [2], meaning that the assumption of local equilibrium is good, and that the entropy production is bilinear in the fluxes and forces. The system was also described in detail by an analytical solution of the systems transport equations. These equations were derived from the entropy production. Transport properties were derived by fitting simulation data to the analytical solutions for conditions at and near chemical equilibrium.

## Results

The thermal conductivity, the interdiffusion coefficient, and the heat of transfer that quantify the coupling between heat and mass fluxes, have been calculated for conditions 1) at and 2) near equilibrium. The equilibrium composition was shifted according to the Le Chatelier principle by the changing temperature. A particle diffuses on the average  $4 \cdot 10^{-10}$  m before it reacts, a distance which explains why there is time for equilibration of the chemical reaction under most conditions.

We show that kinetic theory applies for the thermal conductivity derived from the overall (total) heat flux. The effective thermal conductivity increases due to the presence of the reaction. At equilibrium, we show that the heat of transfer is equal to the enthalpy of reaction. Near equilibrium the heat of transfer becomes larger.

## Discussion and conclusions

We demonstrate for a typical example that a chemical reaction in an enormous temperature gradient obeys the normal thermodynamic relations, so that all transport equations of the system can be derived from these. For the particular reaction in question, we can determine the interdiffusion coefficient of reactants and product, the thermal diffusion (or the heat of transfer) as well as the thermal conductivity of the mixture. We also give molecular interpretations of these values.

The reaction is fast and therefore controlled by thermal diffusion only. While the reaction rate does not couple to heat and mass fluxes, directly, the presence of the reaction gives a large *contribution* to the heat of transfer, equal to the negative reaction enthalpy. This explains i.e. the results of Fig.2.

## Acknowledgements

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## References

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