

H-Theorems in some kinetic models of chemically reacting dense gases

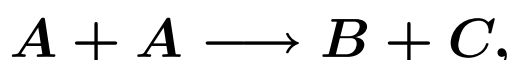
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- Kinetic theories of a dilute reactive gas:
 - Boltzmann-like theories
 - Other approaches: diffusion eq. or transition state theory
- Simple reacting spheres models
- Kinetic theories of reactive (moderately) dense gases:
 - search for the RET (Revised Enskog Theory) analog's of the reacting hard-sphere system
 - *H* theorems
 - global existence results
- Extensions:
 - local versions of the *H* theorems
 - reacting hard-spheres + square-well potential system (???)

Kinetic theories of a dilute reactive gas

- First attempts done by I.Prigogine and E.Xhrouet (Physica, 1949) and independently by C.F.Curtiss (1949) for very simple reactions where the presence of reaction products were ignored. Encounter between two particles A has the probability $1 - \sigma(|v - w|)$, ($0 < \sigma < 1$) of being inelastic



where all encounters between A and B or A and C are neglected. The result is one (Boltzmann-like) equation for the density distribution of particles A .

- Often the cross sections of (gas) reactions are much smaller than for those for non-reactive events. Therefore, many chemical reactions can be treated as perturbations to the non-reactive terms. This was confirmed in a series of papers by B.Shizgal and M.Karplus (J. Chem. Phys., 1970-1971). Significant effects are likely to occur only for reactions with large cross sections; this requires that both reactive and non-reactive collisions be treated on equal par.

Therefore one needs the full knowledge of the dynamics of reactions. (Shizgal and Karplus needed only the total averaged cross sections for reactions.)

- In a series of papers N.Xystris and J.S.Dahler (J. Chem. Phys., 1978) introduced several dynamical reactive models, including an extension of DIPR (*direct interaction, product repulsion model, proposed by P.J.Kuntz, M.H.Mok, and J.C.Polanyi, 1969*) model. The model (*MIRS, multiple interaction reacting spheres*) takes into account rotational-translational exchanges of energy for chemical reactions $A + BC \rightleftharpoons AB + C$.
- Knowing chemical reactions, among other things, means knowledge of the coupling between the dynamics of the reactive events (involving solute molecules) and the dynamics of the solvent molecules. This is a very difficult problem. Sometimes it is assumed that the dynamics of the solute molecules is described by the diffusion equation (Fokker-Planck) while the solvent dynamics is not considered. Here, the reactive events are determined by suitable boundary conditions.
- Still another approach is to use the *transition state theory* to compute the reaction rate coefficient. Here, the dynamic problem is completely avoided, and replaced by an equilibrium computations, where solvent effects enter through the free energy at the transition state. (for reviews see, e.g., R.Kapral, Adv. Chem. Physics, 1981, or R.D.Levine and R.B.Bernstein, *Molecular and Reaction Dynamics and Chemical Reactivity, 1987*, or M.J.Pilling, P.W.Seakins, *Reaction Kinetics, 1995*)

Boltzmann-like theories

In a series of papers C. P. Grünfeld and E. Georgescu (C.R.Acad.Sci.Paris 1993, *Mathematische Fizika, Analiz, Geometria*, 1995) consider a general class of Boltzmann-like kinetic equations with multiple inelastic collisions, where they prove existence and uniqueness of vacuum-type solutions for small initial data.

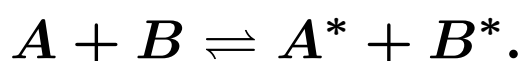
M. Groppi, A. Rossani, and G. Spiga (*Physica A*, 1998 and *J. of Mathematical Chemistry*, 1999) formally analyze various kinetic theories of chemically reacting dilute gases, including gas-photon interactions. They show existence of an H -function and described possible equilibrium solutions. Their results are based on the micro-reversibility conditions that relate the differential cross-section scattering kernels before and after reactive collisions. In the case of simple reacting spheres, however, the reacting molecules behave like hard spheres before and after reactive collisions. Thus, the micro-reversibility conditions reduce themselves to the symmetries of the separation distances $\sigma_{12} = \sigma_{34}$ and the steric factors $\beta_{ij} = \beta_{ji}$

Criteria for chemically reacting kinetic theories

- built in conservation laws;
- built in trend to equilibrium (*H*-theorem);
- their equilibrium states are **different** from the equilibrium states corresponding to noninteracting particles system (the case of the dilute gas as viewed from the statistical mechanics of view). In other words, I want to consider kinetic models whose underlying fluid (on the hydrodynamic level) is **NOT** an ideal gas.

Simple reacting spheres model (SRS)

The kinetic theory of simple reacting spheres (SRS) had been proposed by M.T.Marron (J.Chem.Phys., 1970) and further developed by N.Xystris and J.S.Dahler (J.Chem.Phys., 1978). In the model the molecules behave as if they were single mass points with two internal states of excitation. Collisions may alter the internal states: this occurs when the kinetic energy associated with the reactive motion exceeds the activation energy. Reactive and non-reactive collision events are considered to be hard spheres-like. In a four component mixture A , B , A^* , B^* , the chemical reactions are of the type



Here, A^* and B^* are the distinct species from A and B . Indices $1, 2, 3, 4$ are for the particles A, B, A^*, B^* , respectively. There is **NO** net mass transfer in reactive collisions. This implies $m_1 = m_3$ and $m_2 = m_4$, where m_i denotes the mass of the i -th particle, $i = 1, \dots, 4$. Reactions take place when the reactive particles are separated by a distance $\sigma_{12} = \frac{1}{2}(d_1 + d_2)$, where d_i denotes the diameter of the i -th particle. In the SRS model, reactions do not change diameters of the particles, $d_1 = d_3$ and $d_2 = d_4$, thus $\sigma_{34} = \sigma_{12}$. By not allowing the hard sphere diameter to change upon reaction one avoids complications of producing overlapping configurations.

Elastic encounters

In the case of elastic collisions between a pair of particles from species i and s , the initial velocities v , w take post-collisional values

$$v' = v - 2\frac{\mu_{is}}{m_i}\epsilon\langle\epsilon, v - w\rangle, \quad w' = w + 2\frac{\mu_{is}}{m_s}\epsilon\langle\epsilon, v - w\rangle.$$

Here, $\langle\cdot, \cdot\rangle$ is the inner product in \mathbb{R}^3 , ϵ is a vector along the line passing through the centers of the spheres at the moment of impact, i.e.,

$$\epsilon \in \mathbb{S}_+^2 = \{\epsilon \in \mathbb{R}^3 : |\epsilon| = 1, \langle\epsilon, v - w\rangle \geq 0\},$$

and

$$\mu_{is} = \frac{m_i m_s}{m_i + m_s}$$

is the reduced mass of the colliding pair, where m_i and m_s are the masses of particles from i -th and s -th species, respectively ($i, s = 1, 2, 3, 4$).

Finally, the assumptions $m_1 = m_3$ and $m_2 = m_4$ imply

$$\mu_{12} = \mu_{34}.$$

NOTE: *Presently, this property seems to be important in proving the existence of an H -functional for the SRS model.*

Reactive encounters

For the reactive collision between particles of species i and s to occur ($i, s = 1, \dots, 4$), the kinetic energy associated with the relative motion along the line of centers must exceed the activation energy γ_i (defined below),

$$\frac{1}{2}\mu_{is}(\langle \epsilon, v - w \rangle)^2 \geq \gamma_i,$$

with ϵ having the same meaning as above. In the case of the (endothermic) reaction $A + B \rightarrow A^* + B^*$ the velocities v, w take their post-reactive values

$$v^\ddagger = v - \frac{\mu_{12}}{m_1} \epsilon \left[\langle \epsilon, v - w \rangle - \alpha^- \right],$$

$$w^\ddagger = w + \frac{\mu_{12}}{m_2} \epsilon \left[\langle \epsilon, v - w \rangle - \alpha^- \right],$$

with $\alpha^- = \sqrt{(\langle \epsilon, v - w \rangle)^2 - 2E_{abs}/\mu_{12}}$ and, E_{abs} , the energy absorbed by the internal degrees of freedom. The absorbed energy E_{abs} has the property

$$E_{abs} = E_3 + E_4 - E_1 - E_2 > 0,$$

where $E_i > 0$, $i = 1, \dots, 4$, is the energy of i -th particle associated with its internal degrees of freedom.

Now, in order to complete the definition of the model, the activation energies γ_1 , γ_2 for A and B are chosen to satisfy $\gamma_1 \geq E_{abs} > 0$, and by symmetry, $\gamma_2 = \gamma_1$.

For the inverse (exothermic) reaction, $A^* + B^* \rightarrow A + B$, the post-reactive velocities are given by

$$v^\dagger = v - \frac{\mu_{34}}{m_3} \epsilon \left[\langle \epsilon, v - w \rangle - \alpha^+ \right],$$

$$w^\dagger = w + \frac{\mu_{34}}{m_4} \epsilon \left[\langle \epsilon, v - w \rangle - \alpha^+ \right],$$

with $\alpha^+ = \sqrt{(\langle \epsilon, v - w \rangle)^2 + 2E_{abs}/\mu_{34}}$, and the activation energies for A^* and B^* , $\gamma_3 = \gamma_1 - E_{abs}$ and, $\gamma_4 = \gamma_3$.

NOTE: *The model allows for the exothermic reaction to have nonzero activation energy.*

Post- and pre-collisional velocities of reactive pairs satisfy conservation of the momentum

$$m_1 v + m_2 w = m_3 v^\ddagger + m_4 w^\ddagger, \quad m_3 v + m_4 w = m_1 v^\dagger + m_2 w^\dagger.$$

A part of kinetic energy is exchanged with the energy absorbed by the internal states. The following equalities hold:

$$m_1 v^2 + m_2 w^2 = m_3 v^\ddagger^2 + m_4 w^\ddagger^2 + 2E_{abs},$$

$$m_3 v^2 + m_4 w^2 = m_1 v^\dagger^2 + m_2 w^\dagger^2 - 2E_{abs}.$$

The system of equations

For $i = 1, 2, 3, 4$, $f_i(t, x, v)$ denotes the one-particle distribution function of the i th component of the reactive mixture. The function $f_i(t, x, v)$, which changes in time due to free streaming and collisions (elastic and reactive), represents at time t the number density of particles at point x with velocity v .

The SRS kinetic system has the form

$$\frac{\partial f_i}{\partial t} + v \frac{\partial f_i}{\partial x} = J_i^E + J_i^R, \quad i = 1, 2, 3, 4,$$

where J_i^E is the non-reactive (hard-sphere) collision operator

$$J_i^E = \sum_{s=1}^4 \left\{ \sigma_{is}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_{is}^{(2)}(t, x, v', x - \sigma_{is}\epsilon, w') - f_{is}^{(2)}(t, x, v, x + \sigma_{is}\epsilon, w) \right] \langle \epsilon, v - w \rangle d\epsilon dw \right\},$$

where $\mathbb{S}_+^2 = \{\epsilon \in \mathbb{R}^3 : |\epsilon| = 1, \langle \epsilon, v - w \rangle \geq 0\}$, and $f_{ij}^{(2)}$ approximates the density of pairs of particles in collisional configurations.

For $i = 1, 2, 3, 4$, the reactive terms $J_i^R =$

$$\mathcal{R}_{ij}^{kl} \left\{ \begin{array}{l} \beta \sigma_{ij}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_{kl}^{(2)}(t, x, v_{ij}^\odot, x - \sigma_{ij}\epsilon, w_{ij}^\odot) \right. \\ \left. - f_{ij}^{(2)}(t, x, v, x + \sigma_{ij}\epsilon, w) \right] \Theta(\langle \epsilon, v - w \rangle - \Gamma_{ij}) \times \\ \langle \epsilon, v - w \rangle d\epsilon dw \\ \\ - \beta \sigma_{ij}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_{ij}^{(2)}(t, x, v', x - \sigma_{ij}\epsilon, w') \right. \\ \left. - f_{ij}^{(2)}(t, x, v, x + \sigma_{ij}\epsilon, w) \right] \Theta(\langle \epsilon, v - w \rangle - \Gamma_{ij}) \times \\ \langle \epsilon, v - w \rangle d\epsilon dw, \end{array} \right.$$

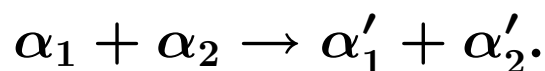
Here, $0 \leq \beta \leq 1$ is the steric factor, $\Gamma_{ij} = \sqrt{2\gamma_i/\mu_{ij}}$, and Θ is the Heaviside step function. The pairs of velocities (v_i^\odot, v_j^\odot) refer to post-reactive velocities, i.e., $(v_{ij}^\odot, w_{ij}^\odot) = (v^\ddagger, w^\ddagger)$ for $i, j = 1, 2$, and $(v_{ij}^\odot, w_{ij}^\odot) = (v^\dagger, w^\dagger)$ for $i, j = 3, 4$. The pairs of indices (i, j) and (k, l) are associated with the following set of quadruples (i, j, k, l) :

$$\{(1, 2, 3, 4), (2, 1, 4, 3), (3, 4, 1, 2), (4, 3, 2, 1)\}$$

Reactive hard sphere dynamics

S.Bose and Ortoleva, J.Chem.Phys., 1979
R.Kapral, Adv.Chem.Phys., 1981

We consider a collection of N hard spheres labeled $i = 1, 2, \dots, N$. With each hard sphere we associate a label α_i which may take values $1, 2, \dots, s$ indicating the s possible species in the system. Each species has a mass $m(\alpha)$, internal energy $E(\alpha)$, and diameter $d(\alpha)$. The binary reactions are



Mass is conserved so we have

$$m(\alpha_1) + m(\alpha_2) = m(\alpha'_1) + m(\alpha'_2).$$

The energy change upon reaction: $\Delta E(\alpha_1 + \alpha_2 \rightarrow \alpha'_1 + \alpha'_2)$

$$\Delta E(\alpha_1 + \alpha_2 \rightarrow \alpha'_1 + \alpha'_2) = E(\alpha'_1) + E(\alpha'_2) - E(\alpha_1) - E(\alpha_2).$$

Let $E_b(\alpha_1 + \alpha_2 \rightarrow \alpha'_1 + \alpha'_2)$ be the barrier for the above process. In addition,

- hard spheres diameters do **NOT** change upon reaction;
- zero mass is exchanged $m(\alpha_1) = m(\alpha'_1)$, $m(\alpha_2) = m(\alpha'_2)$;
- Between hard spheres encounters particles evolve classically with an arbitrary smooth potential. No change of continuous potential (if it exists) with reaction.
- criteria determining reactivity are only energetic.

The dilute-gas case of the SRS model

In the dilute gas case

$$f_{ij}^{(2)}(t, x_1, v_1, x_2, v_2) = f_i(t, x_1, v_1) f_j(t, x_2, v_2)$$

and the SRS kinetic system has the form

$$\frac{\partial f_i}{\partial t} + v \frac{\partial f_i}{\partial x} = J_i^E + J_i^R, \quad i = 1, 2, 3, 4,$$

where J_i^E is the non-reactive (hard-sphere) collision operator

$$J_i^E = \sum_{s=1}^4 \left\{ \sigma_{is}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_i(t, x, v') f_s(t, x, w') - f_i(t, x, v) f_s(t, x, w) \right] \langle \epsilon, v - w \rangle d\epsilon dw \right\},$$

with the reactive terms $J_i^R =$

$$\mathcal{R}_{ij}^{kl} \left\{ \begin{array}{l} \beta \sigma_{ij}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_k(t, x, v_{ij}^\odot) f_l(t, x, w_{ij}^\odot) \right. \\ \left. - f_i(t, x, v) f_j(t, x, w) \right] \Theta (\langle \epsilon, v - w \rangle - \Gamma_{ij}) \times \\ \langle \epsilon, v - w \rangle d\epsilon dw \\ \\ \mathcal{R}_{ij} \left\{ \begin{array}{l} - \beta \sigma_{ij}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_i(t, x, v') f_j(t, x, w') \right. \\ \left. - f_i(t, x, v) f_j(t, x, w) \right] \Theta (\langle \epsilon, v - w \rangle - \Gamma_{ij}) \times \\ \langle \epsilon, v - w \rangle d\epsilon dw, \end{array} \right. \end{array} \right.$$

For a nonnegative solution f_i the convex function $H(t)$ defined by

$$H(t) = \sum_{i=1}^4 \iint_{\Omega \times \mathbb{R}^3} f_i(t, x, v) \log f_i(t, x, v) dv dx$$

is non-increasing in t .

The standard macroscopic quantities (the moments of f_i), the number densities $n(t, \mathbf{x})$, the macroscopic velocity $\mathbf{u}(t, \mathbf{x})$, and the macroscopic temperature $T(t, \mathbf{x})$, are defined by

$$n_i(t, \mathbf{x}) = \int_{\mathbb{R}^3} f_i(t, \mathbf{x}, \mathbf{v}) d\mathbf{v}, \quad n(t, \mathbf{x}) = \sum_{i=1}^4 n_i(t, \mathbf{x}),$$

$$\mathbf{u}(t, \mathbf{x}) = \frac{\sum_{i=1}^4 m_i n_i(t, \mathbf{x}) \mathbf{u}_i(t, \mathbf{x})}{\sum_{i=1}^4 m_i n_i(t, \mathbf{x})},$$

$$\mathbf{u}_i(t, \mathbf{x}) = \frac{\int_{\mathbb{R}^3} \mathbf{v} f_i(t, \mathbf{x}, \mathbf{v}) d\mathbf{v}}{n_i(t, \mathbf{x})},$$

$$3kn(t, \mathbf{x})T(t, \mathbf{x}) = \sum_{i=1}^4 m_i \int_{\mathbb{R}^3} [\mathbf{v} - \mathbf{u}(t, \mathbf{x})]^2 f_i(t, \mathbf{x}, \mathbf{v}) d\mathbf{v},$$

where k is the Boltzmann constant.

The equilibrium states in the dilute-gas case

For nonnegative solutions f_i ($i = 1, 2, 3, 4$) the following statements are equivalent:

$$1. f_i = n_i(t, x) \left(\frac{m_i}{2\pi kT(t, x)} \right)^{3/2} \exp \left(-\frac{m_i(v - u(t, x))^2}{2kT(t, x)} \right)$$

and

$$n_1(t, x)n_2(t, x) = n_3(t, x)n_4(t, x) \exp \left(\frac{E_{abs}}{kT(t, x)} \right),$$

$$2. J_i^E(\{f_i\}) = 0 \text{ and } J_i^R(\{f_i\}) = 0, i = 1, \dots, 4,$$

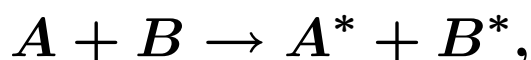
$$3. \sum_{i=1}^4 \int_{\mathbb{R}^3} [J_i^E(\{f_i\}) + J_i^R(\{f_i\})] \log f_i dv = 0.$$

Recently, global existence and convergence to equilibrium results have been obtained (J.Polewczak, J.Stat.Phys., 2000).

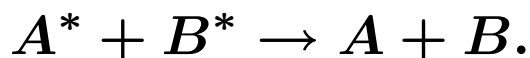
Back to the reactive (moderately) dense gases

Can one construct an analog of the RET (Revised Enskog Theory) for the reacting hard-spheres ?

I start with a simple caricature model. Assume that when a hard-sphere A collides with another hard-sphere B , there is a probability α_R that



i.e., A^* and B^* are formed. I apply the same rule for the reverse reaction



This simple dynamic model amounts to a *coloring* process with probability α_R .

The corresponding kinetic system has the form

$$\frac{\partial f_i}{\partial t} + v \frac{\partial f_i}{\partial x} = J_i^E + J_i^R, \quad i = 1, 2, 3, 4,$$

with J_i^E the non-reactive (hard-sphere) collision operator

$$J_i^E = \sum_{s=1}^4 \left\{ \sigma_{is}^2 \lambda_{is}^E \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_{is}^{(2)}(t, \mathbf{x}, \mathbf{v}', \mathbf{x} - \sigma_{is}\boldsymbol{\epsilon}, \mathbf{w}') \right. \right. \\ \left. \left. - f_{is}^{(2)}(t, \mathbf{x}, \mathbf{v}, \mathbf{x} + \sigma_{is}\boldsymbol{\epsilon}, \mathbf{w}) \right] \langle \boldsymbol{\epsilon}, \mathbf{v} - \mathbf{w} \rangle d\boldsymbol{\epsilon} d\mathbf{w} \right\},$$

where, as before, $\mathbb{S}_+^2 = \{\boldsymbol{\epsilon} \in \mathbb{R}^3 : |\boldsymbol{\epsilon}| = 1, \langle \boldsymbol{\epsilon}, \mathbf{v} - \mathbf{w} \rangle \geq 0\}$, and $\lambda_{is}^E = \lambda_{si}^E =$

$$\begin{cases} (1 - \alpha_r) m_i m_s, & \text{if } (i, s) \in \{(1, 2), (2, 1), (3, 4), (4, 3)\}; \\ m_i m_s, & \text{otherwise.} \end{cases}$$

and

$$f_{ij}^{(2)}(\mathbf{x}, \mathbf{v}, \mathbf{x} \pm \sigma_{ij}, \mathbf{w}) = g_2^{(ij)}(\mathbf{x}, \mathbf{x} \pm \sigma_{ij}) f_i(\mathbf{x}, \mathbf{v}) f_j(\mathbf{x} \pm \sigma_{ij}, \mathbf{w}),$$

where $g_2^{(ij)}(\mathbf{r}_1, \mathbf{r}_2) = g_2^{(ij)}(\mathbf{r}_1, \mathbf{r}_2, \{\rho_i\})$ is a pair correlation function for the system at non-uniform equilibrium with

$$\rho_i = m_i n_i.$$

$$\begin{aligned}
 g_2^{(ij)}(r_1, r_2) = \exp(-\beta\phi_{ij}^{HS}(|r_1 - r_2|)) & \left\{ \right. \\
 1 + \sum_{s=1}^4 \int V(12 | 3) \rho_s(t, r_3) & \\
 + \frac{1}{2} \sum_{s=1}^4 \sum_{l=1}^4 \int \int V(12 | 34) \rho_s(t, r_3) \rho_l(t, r_4) dr_3 dr_4 & \\
 + \dots + & \\
 \frac{1}{(k-2)!} \sum_{i_1, \dots, i_k=1}^4 \int dr_3 \dots \int dr_k \rho_{i_1}(3) \dots \rho_{i_k}(k) \times & \\
 V(12 | 3 \dots k) & \\
 + \dots & \left. \right\},
 \end{aligned}$$

where $\rho_{i_j}(j) = \rho_{i_j}(t, r_j)$, $\beta = 1/k_B T$, $V(12 | 3 \dots k)$ (Husimi function) is the sum of all graphs of k labeled points which are biconnected when the Mayer factor $f^{ij}(r_1, r_2) = \exp(-\beta\phi_{ij}^{HS}(|r_1 - r_2|)) - 1$ is added. In the case of the hard-spheres mixture, the Mayer factors, f^{ij} , become

$$f^{ij}(r_1, r_2) = \Theta(|r_1 - r_2| - \sigma_{ij}) - 1, \quad \Theta \text{ is the step function.}$$

For $i = 1, 2, 3, 4$, the reactive terms $J_i^R =$

$$J_i^R = \frac{\alpha_R \mu_{ij}}{M} \sigma_{ij}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_{kl}^{(2)}(t, \mathbf{x}, \mathbf{v}', \mathbf{x} - \sigma_{ij} \boldsymbol{\epsilon}, \mathbf{w}') - f_{ij}^{(2)}(t, \mathbf{x}, \mathbf{v}, \mathbf{x} + \sigma_{ij} \boldsymbol{\epsilon}, \mathbf{w}) \right] \langle \boldsymbol{\epsilon}, \mathbf{v} - \mathbf{w} \rangle d\boldsymbol{\epsilon} d\mathbf{w}$$

The pairs (i, j) and (k, l) are associated with the following set of quadruples (i, j, k, l) :

$$\{(1, 2, 3, 4), (2, 1, 4, 3), (3, 4, 1, 2), (4, 3, 2, 1)\}$$

NOTE: $\sigma_{12} = \frac{d_1 + d_2}{2} = \frac{d_3 + d_4}{2} = \sigma_{34},$

since $d_1 = d_3$ and $d_2 = d_4$.

In contrast to a non-reactive four species RET, there is no mass conservation for the individual species in the above model.

The H -function

$$H(t) = \sum_{i=1}^4 \iint_{\Omega \times \mathbb{R}^3} f_i(t, \mathbf{x}, \mathbf{v}) \log f_i(t, \mathbf{x}, \mathbf{v}) d\mathbf{v} d\mathbf{x} - H_{corr}(t),$$

$$H_{corr}(t) = \frac{1}{2} \sum_{i=1}^4 \sum_{j=1}^4 \iint \rho_i(t, \mathbf{r}_1) \rho_j(t, \mathbf{r}_2) V(12) d\mathbf{r}_1 d\mathbf{r}_2$$

$$+ \sum_{k=3}^{\infty} \frac{1}{k!} \sum_{i_1, \dots, i_k=1}^4 \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_k \rho_{i_1}(1) \cdots \rho_{i_k}(k) \times$$

$$V(12 \cdots k),$$

where $\rho_{i_j}(j) = \rho_{i_j}(t, \mathbf{r}_j)$ and $V(12 \cdots k)$ is the sum of all irreducible Mayer graphs which doubly connect k particles.

$$\rho_i(t, \mathbf{r}_1) \rho_j(t, \mathbf{r}_2) V(12) = \rho_i(t, \mathbf{r}_1) \rho_j(t, \mathbf{r}_2) f^{ij}(r_1, r_2)$$

$$\rho_i(t, \mathbf{r}_1) \rho_j(t, \mathbf{r}_2) \rho_k(t, \mathbf{r}_3) V(123) =$$

$$\rho_i(t, \mathbf{r}_1) \rho_j(t, \mathbf{r}_2) \rho_k(t, \mathbf{r}_3) f^{ij}(r_1, r_2) f^{ik}(r_1, r_3) f^{jk}(r_2, r_3)$$

As in the case of non-reactive hard-sphere mixture one expects

$$-\beta H_{corr} = \mathcal{A}^{excess}$$

to be the excess free energy for the mixture of hard-spheres in the **non-uniform** equilibrium.

The equilibrium states

For nonnegative solutions f_i ($i = 1, 2, 3, 4$) the following statements are equivalent:

$$1. f_i = n_i(t, x) \left(\frac{m_i}{2\pi kT(t)} \right)^{3/2} \exp\left(-\frac{m_i(v - u(t))^2}{2kT(t)} \right)$$

and

$$n_1(t, x)n_2(t, x) = n_3(t, x)n_4(t, x),$$

$$2. \sum_{i=1}^4 \iint_{\Omega \times \mathbb{R}^3} [J_i^E(\{f_i\}) + J_i^R(\{f_i\})] \log f_i \, dv dx = 0.$$

The SRS system again

$$\frac{\partial f_i}{\partial t} + v \frac{\partial f_i}{\partial x} = J_i^E + J_i^R, \quad i = 1, 2, 3, 4,$$

where J_i^E is the non-reactive (hard-sphere) collision operator

$$J_i^E = \sum_{s=1}^4 \left\{ \sigma_{is}^2 \lambda_{is}^E \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_{is}^{(2)}(t, x, v', x - \sigma_{is}\epsilon, w') - f_{is}^{(2)}(t, x, v, x + \sigma_{is}\epsilon, w) \right] \langle \epsilon, v - w \rangle d\epsilon dw \right\},$$

where $\mathbb{S}_+^2 = \{\epsilon \in \mathbb{R}^3 : |\epsilon| = 1, \langle \epsilon, v - w \rangle \geq 0\}$, $\lambda_{is}^E = \lambda_{si}^E > 0$ are scaling factors (to be chosen), and

$$f_{ij}^{(2)}(x, v, x \pm \sigma_{ij}, w) = g_2^{(ij)}(x, x \pm \sigma_{ij}) f_i(x, v) f_j(x \pm \sigma_{ij}, w),$$

where $g_2^{(ij)}(r_1, r_2) = g_2^{(ij)}(r_1, r_2, \{\rho_i\})$ is a pair correlation function for the system at non-uniform equilibrium with

$$\rho_i = m_i n_i.$$

As before,

$$\begin{aligned}
 g_2^{(ij)}(r_1, r_2) = \exp(-\beta\phi_{ij}^{HS}(|r_1 - r_2|)) & \left\{ \right. \\
 1 + \sum_{s=1}^4 \int V(12 | 3) \rho_s(t, r_3) & \\
 + \frac{1}{2} \sum_{s=1}^4 \sum_{l=1}^4 \int \int V(12 | 34) \rho_s(t, r_3) \rho_l(t, r_4) dr_3 dr_4 & \\
 + \dots + & \\
 \frac{1}{(k-2)!} \sum_{i_1, \dots, i_k=1}^4 \int dr_3 \dots \int dr_k \rho_{i_1}(3) \dots \rho_{i_k}(k) \times & \\
 V(12 | 3 \dots k) & \\
 + \dots & \left. \right\},
 \end{aligned}$$

where $\rho_{i_j}(j) = \rho_{i_j}(t, r_j)$, $\beta = 1/k_B T$, $V(12 | 3 \dots k)$ (Husimi function) is the sum of all graphs of k labeled points which are biconnected when the Mayer factor $f^{ij}(r_1, r_2) = \exp(-\beta\phi_{ij}^{HS}(|r_1 - r_2|)) - 1$ is added. In the case of the hard-spheres mixture, the Mayer factors, f^{ij} , become

$$f^{ij}(r_1, r_2) = \Theta(|r_1 - r_2| - \sigma_{ij}) - 1, \quad \Theta \text{ is the step function.}$$

For $i = 1, 2, 3, 4$, the reactive terms $J_i^R =$

$$\mathcal{R}_{ij}^{kl} \left\{ \begin{array}{l} \beta \sigma_{ij}^2 \lambda_{ij}^R \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_{kl}^{(2)}(t, x, v_{ij}^\odot, x - \Delta_{ij} \sigma_{ij} \epsilon, w_{ij}^\odot) \right. \\ \left. - f_{ij}^{(2)}(t, x, v, x + \Delta_{ij} \sigma_{ij} \epsilon, w) \right] \Theta(\langle \epsilon, v - w \rangle - \Gamma_{ij}) \times \\ \langle \epsilon, v - w \rangle d\epsilon dw \\ \\ - \beta \sigma_{ij}^2 \lambda_{ij}^R \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_{ij}^{(2)}(t, x, v', x - \sigma_{ij} \epsilon, w') \right. \\ \left. - f_{ij}^{(2)}(t, x, v, x + \sigma_{ij} \epsilon, w) \right] \Theta(\langle \epsilon, v - w \rangle - \Gamma_{ij}) \times \\ \langle \epsilon, v - w \rangle d\epsilon dw, \end{array} \right.$$

Here, $0 \leq \beta \leq 1$ is the steric factor, $\lambda_{ij}^R = \lambda_{ji}^R > 0$ are reactive scaling factors, $\Gamma_{ij} = \sqrt{2\gamma_i/\mu_{ij}}$, and Θ is the Heaviside step function. The pairs (v_i^\odot, v_j^\odot) refer to post-reactive velocities, i.e., $(v_{ij}^\odot, w_{ij}^\odot) = (v^\ddagger, w^\ddagger)$ for $i, j = 1, 2$, and $(v_{ij}^\odot, w_{ij}^\odot) = (v^\dagger, w^\dagger)$ for $i, j = 3, 4$. Also $\Delta_{ij} = \Delta_{ji}$, with $\Delta_{12} = 1$ and $\Delta_{34} = -1$. The pairs (i, j) and (k, l) are associated with the following set of quadruples (i, j, k, l) :

$$\{(1, 2, 3, 4), (2, 1, 4, 3), (3, 4, 1, 2), (4, 3, 2, 1)\}$$

The H -functional

I consider only a simplified case where the activation energies

$$\gamma_1 = \gamma_2 = E_{abs} \quad \text{and} \quad \gamma_3 = \gamma_4 = 0.$$

and scaling factors in the reactive terms satisfy

$$\lambda_{12}^R = \lambda_{34}^R \quad \text{with} \quad \beta \lambda_{34}^R \leq \lambda_{34}^E.$$

The H -functional that formally drives the system to an equilibrium has the form

$$\Gamma(t) = \sum_{i=1}^4 \iint_{\Omega \times \mathbb{R}^3} f_i(t, x, v) \log f_i(t, x, v) dv dx - \int_0^t I(s) ds.$$

At equilibrium the following statements are equivalent:

$$1. \quad f_i = n_i(t, x) \left(\frac{m_i}{2\pi kT(t)} \right)^{3/2} \exp \left(-\frac{m_i(v - u(t))^2}{2kT(t)} \right)$$

and

$$n_1(t, x)n_2(t, x) = n_3(t, x)n_4(t, x) \exp \left(\frac{E_{abs}}{kT(t)} \right);$$

$$2. \quad \sum_{i=1}^4 \iint_{\Omega \times \mathbb{R}^3} [J_i^E(\{f_i\}) + J_i^R(\{f_i\})] \log f_i dv dx = 0.$$

The function $I(t)$ is given by

$$\begin{aligned}
 I(t) = & \sum_{\substack{i \leq j=1 \\ (i,j) \neq (3,4)}}^4 C_{ij} \lambda_{ij}^E \sigma_{ij}^2 \iiint\limits_{\Omega \times \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{S}_+^2} f_i(t, x, v) \langle \epsilon, v - w \rangle \times \\
 & \left[f_j(t, x - \sigma_{ij} \epsilon, w) g_2^{(ij)}(x, x - \sigma_{ij} \epsilon) \right. \\
 & \left. - f_j(t, x + \sigma_{ij} \epsilon, w) g_2^{(ij)}(x, x + \sigma_{ij} \epsilon) \right] d\epsilon dw dv dx \\
 & + \sigma_{34}^2 (\lambda_{34}^E - 2\beta \lambda_{34}^R) \iiint\limits_{\Omega \times \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{S}_+^2} f_3(t, x, v) \langle \epsilon, v - w \rangle \times \\
 & \left[f_4(t, x - \sigma_{34} \epsilon, w) g_2^{(34)}(x, x - \sigma_{34} \epsilon) \right. \\
 & \left. - f_4(t, x + \sigma_{34} \epsilon, w) g_2^{(34)}(x, x + \sigma_{34} \epsilon) \right] d\epsilon dw dv dx,
 \end{aligned}$$

where

$$C_{ij} = \begin{cases} \frac{1}{2}, & \text{if } i = j; \\ 1, & \text{otherwise.} \end{cases}$$

By choosing $\lambda_{ij}^E =$

$$\begin{cases} m_3 m_4 (1 + 2\beta \lambda_{34}^R), & \text{if } (i, j) = (3, 4) \text{ or } (i, j) = (4, 3); \\ m_i m_j, & \text{otherwise.} \end{cases}$$

we obtain

$$\begin{aligned} \int_0^t I(s) ds &= \frac{1}{2} \sum_{i=1}^4 \sum_{j=1}^4 \iint \rho_i(t, r_1) \rho_j(t, r_2) V(12) dr_1 dr_2 \\ &+ \sum_{k=3}^{\infty} \frac{1}{k!} \sum_{i_1, \dots, i_k=1}^4 \int dr_1 \cdots \int dr_k \rho_{i_1}(1) \cdots \rho_{i_k}(k) \times \\ &V(12 \cdots k), \end{aligned}$$

where $\rho_{i_j}(j) = \rho_{i_j}(t, r_j)$ and $V(12 \cdots k)$ is the sum of all irreducible Mayer graphs which doubly connect k particles.

$$\begin{aligned} \rho_i(t, r_1) \rho_j(t, r_2) V(12) &= \rho_i(t, r_1) \rho_j(t, r_2) f^{ij}(r_1, r_2) \\ \rho_i(t, r_1) \rho_j(t, r_2) \rho_k(t, r_3) V(123) &= \\ \rho_i(t, r_1) \rho_j(t, r_2) \rho_k(t, r_3) f^{ij}(r_1, r_2) f^{ik}(r_1, r_3) f^{jk}(r_2, r_3) \end{aligned}$$

Basic apriori estimation: L^1 -weak compactness

If initial values $f_{i0} \geq 0$ ($i = 1, 2, 3, 4$) satisfy

$$\iint_{\Omega \times \mathbb{R}^3} (1 + v^2 + x^2 + |\log f_{0i}(x, v)|) f_{0i}(x, v) \, dv dx \leq C_0,$$

then a nonnegative solution $\{f_i\}_{i=1}^4$ satisfies

$$\iint_{\Omega \times \mathbb{R}^3} (1 + v^2 + x^2 + |\log f_i(t, x, v)|) f_i(t, x, v) \, dv dx \leq C_{\mathcal{T}},$$

for $i = 1, 2, 3, 4$, uniformly in $t \in [0, \mathcal{T}]$, and any \mathcal{T}

Here, $\Omega = \mathbb{R}^3$ or $\Omega = [0, L_1] \times [0, L_2] \times [0, L_3]$ (plus periodic conditions). In the latter case, x^2 is superfluous in the above estimation, and, in addition, $C_{\mathcal{T}}$ is independent of \mathcal{T} .

Compactness lemma (Golse, Lions, Perthame, Sentis, 1988)

Suppose that $f_n, g_n \in L^1_{\text{loc}}((0, \mathcal{T}) \times \Omega \times \mathbb{R}^3)$ satisfy

- $$\mathbf{T}_v f_n \stackrel{\text{def}}{=} \frac{\partial f_n}{\partial t} + v \frac{\partial f_n}{\partial x} = g_n$$

in $\mathcal{D}'((0, \mathcal{T}) \times \Omega \times \mathbb{R}^3)$;

- for each compact set K of $(0, \mathcal{T}) \times \Omega \times \mathbb{R}^3$, the sequences $\{f_n\}$ and $\{g_n\}$ are weakly compact in $L^1((0, \mathcal{T}) \times \Omega \times \mathbb{R}^3)$ and $L^1(K)$, respectively.

Then for all $\phi \in L^\infty((0, \mathcal{T}) \times \Omega \times \mathbb{R}^3)$ the set

$$\left\{ \int_{\mathbb{R}^3} \phi f_n dv \right\}_{n=1}^{\infty} = \left\{ \int_{\mathbb{R}^3} \phi \mathbf{T}_v^{-1} g_n dv \right\}_{n=1}^{\infty}$$

is compact in $L^1((0, \mathcal{T}) \times \Omega)$.

\mathbf{T}_v^{-1} resembles the inverse of an elliptic operator. \mathbf{T}_v^{-1} may be singular only on the set of the characteristic direction. Velocity averaging compensates for the lack of regularity in the characteristic direction of the hyperbolic operator \mathbf{T}_v .

Renormalized solutions (DiPerna and Lions, 1989)

A nonnegative $f \in L^1_{\text{loc}}((0, \mathcal{T}) \times \Omega \times \mathbb{R}^3)$

is a renormalized solution if

$$\frac{1}{1+f} E^\pm(f) \in L^1_{\text{loc}}((0, \mathcal{T}) \times \Omega \times \mathbb{R}^3)$$

and

$$\frac{\partial}{\partial t} \log(1+f) + v \frac{\partial}{\partial x} \log(1+f) = \frac{1}{1+f} E(f)$$

in $\mathcal{D}'((0, \infty) \times \Omega \times \mathbb{R}^3)$.

Theorem. *If initial values $f_{0i} \geq 0$ satisfy*

$$\iint_{\Omega \times \mathbb{R}^3} (1 + v^2 + x^2 + |\log f_{0i}(x, v)|) f_{0i}(x, v) dv dx \leq C_0,$$

then there exists a nonnegative renormalized solution $\{f_i\}_{i=1}^4$ of the truncated SRS system on $[0, \mathcal{T}]$ for any $\mathcal{T} > 0$.

Furthermore, for some sequence $\{t_n\}$ with $t_n \xrightarrow{n \rightarrow \infty} \infty$

$$f_i(t_n, x, v) \xrightarrow{n \rightarrow \infty} \omega_i(x, v), \text{ almost everywhere in } x, v,$$

$$\text{where } \omega(x, v) = \frac{n_i(x)}{(2\pi k_B X)^{3/2}} \exp\left(-\frac{|v - u|^2}{2k_B X}\right).$$

Remark:

Here $n_i(x)$ and u are macroscopic density and velocity of the gas, respectively.

However, X may not necessary the macroscopic temperature of the gas. This due to the fact that (technical problems ?) the convergence above is in $L^1[(1 + |v|)^k]$ for only $0 \leq k < 2$, not including $k = 2$.