On the Entangling of the Reactions and Relaxation Processes in Chemical Gas-dynamics

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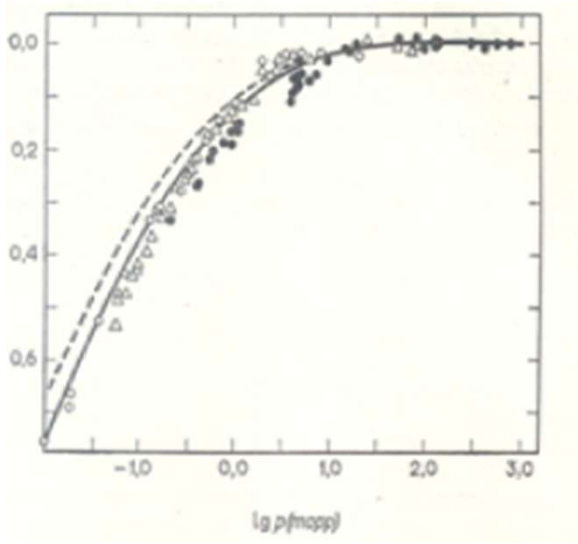
Problems of Traditional Approach

- Impossibility to reproduce the pressure dependence for the reaction rates, known from unimolecular reaction theory
- No basis for consideration of “chemical” part of collisional integral as a **small perturbation term**. First of all it concerns the high threshold chemical reactions: for high threshold chemical reactions perturbation of the distribution function near the threshold can be of the order of this function itself ($\delta f \sim f$ for $E >> kT$)
- Gas-dynamic variables should be calculated by *averaging of the variables, that are the summational invariants*.



Dissociation rate constant for cyclobutane

Results

1. Reaction and relaxation rate ‘constants’ depend on the partial pressures (number densities) of all species participating in the reaction. It is not an exception for unimolecular reaction rates
2. Generalized relaxation characteristics (reaction and relaxation rates) are linear combinations of each other, that mean the interdependency of chemical and relaxation processes (**chemical-relaxation entangling**)
3. Described features can not be derived in any order of Chapman-Enskog expansion within the traditional approach

Asymptotic procedure for generalized Boltzmann equation (Wang Chang – Uhlenbeck) solution

Procedure is based on three key positions

1. Collisional integral is not expanded into the series over the Knudsen number (no assumption is made that the part of the collisional integral, responsible for the chemical reactions, can be treated as the perturbation of its 'elastic' part)
2. Slow (gas-dynamic) variables are introduced via approximate summational invariants, defined within the method
3. Kinetic equations are presented in the form of a singularly perturbed system for gas-dynamic (slow) variables and for the 'fast' part of the distribution function

Asymptotic Procedure

1. Small parameter introduction: assumption on small impact of chemical reactions (since Prigogine's publication) is discarded

$$\frac{\partial F}{\partial t} + \vec{v} \cdot \frac{\partial F}{\partial \vec{r}} = \frac{1}{\varepsilon} I(F), \qquad \varepsilon = t_f / t_s << 1,$$

2. Approximate Summational Invariants (ASI):

$$\langle \psi_i, I(F) \rangle \le O(\varepsilon), \quad i = 1, \ldots, M.$$

$$\langle \xi, \eta \rangle \equiv \sum_{\alpha=1}^{N} \sum_{k_\alpha} \int d\vec{v}_\alpha \xi_\alpha(\vec{v}_\alpha, k_\alpha) \eta_\alpha(\vec{v}_\alpha, k_\alpha).$$

Slaw (gas-dynamic) variables

$$\Gamma_i = \langle \psi_i, F \rangle.$$

Asymptotic Procedure (continued)

3. $$F_\alpha = F_\alpha^{qe}\left(\Gamma_1,\ldots,\Gamma_M\right)+\Phi_\alpha,$$

Quasi-equilibrium distribution function (maximizes the entropy density of the gas mixture with fixed slow variables Γ_i)

$$F^{qe} = \exp\left(\ln s_\alpha(k_\alpha) - \sum_{i=1}^{M}\gamma_i\psi_{i\alpha}(\vec{v}_\alpha,k_\alpha)\right)$$

$$= \exp\left[\ln s_\alpha(k_\alpha) - \gamma_\alpha + \frac{m_\alpha}{2\gamma_E}\gamma_{\vec{p}}^2 - \gamma_E\frac{m_\alpha}{2}\left(\vec{v}_\alpha + \frac{\gamma_{\vec{p}}}{\gamma_E}\right)^2 - \gamma_E e_\alpha(k_\alpha) - \sum_{i=N+5}^{M}\gamma_{ai}\psi_{ai\alpha}(\vec{v}_\alpha,k_\alpha)\right]$$

Φ_α should satisfy the orthogonality conditions

$$\left\langle \psi_i, \Phi \right\rangle = 0, \quad i = 1,\ldots,M.$$

Asymptotic Procedure (continued)

3. (continued) Singularly perturbed set of equations

$$\frac{\partial \Gamma_i}{\partial t} = -\nabla \cdot \left\langle \vec{v}\,\psi_i, \left(F^{qe} + \Phi\right)\right\rangle + \left\langle \psi_i, I\left(F^{qe} + \Phi\right)\right\rangle \Big/ \varepsilon$$

$$\varepsilon \frac{\partial \Phi}{\partial t} = J_{F^{qe}}\left(F^{qe} + \Phi\right) - \varepsilon \vec{v} \cdot \nabla \Phi - \varepsilon \sum_{i=1}^{M} \frac{\partial F^{qe}}{\partial \Gamma_i}\left[\vec{v} \cdot \nabla \Gamma_i - \nabla \cdot \left\langle \vec{v}\,\psi_i, \left(F^{qe} + \Phi\right)\right\rangle\right]$$

$$J_\eta(F) \equiv I(F) - \sum_{i}^{M} \frac{\partial \eta}{\partial \Gamma_i}\left\langle \psi_i, I(F)\right\rangle$$

Kolesnichenko's generalized collisional operator coincides with the traditional only if all summational invariants are exact. Additional terms in the modified collisional operator are due to the slow evolution of the system: relaxation of slow variables adiabatically impacts the collision process.

Asymptotic Procedure (continued)

We are looking for the solution in a form as in Chapman-Enskog method

$$\Phi = \Phi^{(0)}(\Gamma) + \sum_{n=1}^{\infty} \varepsilon^n \Phi^{(n)}\left(\Gamma, \nabla\Gamma, \ldots, \nabla^n \Gamma\right) \equiv \Phi^{(0)} + \varepsilon\tilde{\Phi}$$

$$\frac{\partial \Gamma_i}{\partial t} = \sum_{k=0}^{\infty} \varepsilon^k B_i^{(k)}\left(\Gamma, \nabla\Gamma, \ldots, \nabla^{k+1}\Gamma\right)$$

General case: $$F_\alpha = F_\alpha^{qe} + \Phi_\alpha^{(0)} + \varepsilon\Phi_\alpha^{(1)},$$

'Weak' non-equilibrium: $$F_\alpha = F_\alpha^{qe} + \varepsilon\Phi_\alpha, \; i.e. \; \Phi^{(0)} = O(\varepsilon)$$

Equations for DF Corrections: General and 'Weak' Non-equilibrium Cases

General case: $J_{F^{qe}+\Phi^{(0)}}\left(F^{qe}+\Phi^{(0)}\right)=0;$

$$J'_{F^{qe}+\Phi^{(0)}}\left(F^{qe}+\Phi^{(0)}\right)\Phi^{(1)}$$

$$=\sum_{i=1}^{M}\frac{\partial F^{qe}+\Phi^{(0)}}{\partial\Gamma_i}\left[\vec{v}\cdot\nabla\Gamma_i-\nabla\cdot\left\langle\vec{v}\psi_i,\left(F^{qe}+\Phi^{(0)}\right)\right\rangle\right];$$

$$\Phi_{\alpha}^{(1)}=\Phi_{\alpha d}^{(1)}\nabla\cdot\vec{u}+\Phi_{\nabla\alpha}^{(1)},$$

'weak' non-equilibrium $J'_{F^{qe}}\left(F^{qe}\right)\Phi^{(0)}=J_{F^{qe}}\left(F^{qe}\right);$

$$\Phi_{\alpha}^{(0)}=\Phi_{\alpha s}^{(0)}+\Phi_{\alpha d}^{(0)}\nabla\cdot\vec{u}+\Phi_{\nabla\alpha}^{(0)},$$

'Gradient' terms don't contribute the zero-order (Euler) gas-dynamic equations

Gas-dynamic Equations:
‘Weak’ Non-equilibrium Case

Approximate Summational Invariants & Gas-dynamic Variables

$$\psi_{n_\alpha,\gamma} = \delta_{\alpha\gamma}, \quad \Gamma_{n_\alpha} = n_\alpha;$$

$$\psi_{\vec{p},\alpha} = m_\alpha \vec{v}_\alpha, \quad \Gamma_{\vec{p}} = \rho\vec{u};$$

$$\psi_{E,\alpha} = e_\alpha^{(t)}(\vec{v}_\alpha) + e_\alpha^{(\mathrm{int})}(k_\alpha),$$

$$\Gamma_E = \rho\left(E_{kin} + u^2/2 + E_{\mathrm{int}}\right) = E;$$

$$\psi_{ai}, \quad \Gamma_{ai}.$$

Zero-order (Euler) Gas-dynamic Equations
Reaction Rates & Relaxation Rates

$$F_\alpha = F_\alpha^{qe} + \varepsilon\Phi_\alpha,$$

$$\frac{\partial n_\alpha}{\partial t} + \nabla\cdot\left(\vec{u}n_\alpha\right) = R_\alpha\left(\{\Gamma_i\}\right) = R_\alpha^{qe} + R_{s\alpha} + R_{d\alpha}\nabla\cdot\vec{u};$$

$$R_\alpha = \left\langle \psi_{n_\alpha}, I\left(F^{qe}\right)\right\rangle + \left\langle \psi_{n_\alpha}, I^l\left(F^{qe}\right)\left(\Phi_s + \Phi_d\nabla\cdot\vec{u}\right)\right\rangle;$$

$$\frac{\partial \rho\vec{u}}{\partial t} + \nabla\cdot\left(\rho\vec{u}\vec{u}\right) + \nabla p = 0; \qquad p = \frac{1}{3}\left\langle mc_\alpha^2, f^{(qe)}\right\rangle;$$

$$\frac{\partial E}{\partial t} + \nabla\left(\left(E + p\right)\vec{u}\right) = 0;$$

In one-temperature case

$$\frac{\partial \Gamma_{ai}}{\partial t} + \nabla\cdot\left(\vec{u}\Gamma_{ai}\right) = R_{ai}\left(\{\Gamma_i\}\right) = R_{ai}^{qe} + R_{ais} + R_{aid}\nabla\cdot\vec{u};$$

$$R_{ai} = \left\langle \psi_{ai}, I\left(F^{(qe)}\right)\right\rangle + \left\langle \psi_{ai}, I^l\left(F^{(qe)}\right)\left(\Phi_s + \Phi_d\nabla\cdot\vec{u}\right)\right\rangle;$$

Generalized Relaxation Rates and Renormalization Procedure

Equations for DF Corrections: Scalar Part

$$\left[I'\left(F^{qe}\right)\Phi_s\right]_\alpha = -I_\alpha\left(F^{qe}\right) + \sum_{i=1}^{N+M_a} \frac{\partial F_\alpha^{qe}}{\partial \Gamma_i} R_i^{sh};$$

$$\Phi_{\alpha s} = \Phi_{\alpha s}^0 + \sum_{i=1}^{N+M_a} \Phi_{\alpha i s}^a R_i^{sh};$$

$$\left[I'\left(F^{qe}\right)\Phi_s^0\right]_\alpha = -I_\alpha\left(F^{qe}\right); \qquad \left[I'\left(F^{qe}\right)\Phi_{is}^a\right]_\alpha = \frac{\partial F_\alpha^{qe}}{\partial \Gamma_i};$$

$$R_i^{sh} = R_{is}^0 + \sum_{j=1}^{N+M_a} A_{ijs} R_j^{sh}; \qquad R_{is}^0 = R_i^{qe} + R_{is}^{ne0};$$

$$R_{is}^{ne0} = \left\langle \psi_{\Gamma_i}, I^l\left(F^{qe}\right)\Phi_{\alpha s}^0 \right\rangle; \qquad A_{ijs} = \left\langle \psi_{\Gamma_i}, I^l\left(F^{qe}\right)\Phi_{\alpha js}^a \right\rangle;$$

$$R^{sh} = \left(I - A_s\right)^{-1} R_s^0;$$

Equations for DF Corrections: Divergency Part

$$\left[I'\left(F^{qe}\right)\Phi_d\right]_\alpha = \sum_{i=1}^{N+M_a} \frac{\partial F_\alpha^{qe}}{\partial \Gamma_i} R_i^{sh} - \sum_{i=1}^{M} \frac{\partial F_\alpha^{qe}}{\partial \Gamma_i} \Gamma_i - p \frac{\partial F_\alpha^{qe}}{\partial \Gamma_E} + \frac{\gamma_E m_\alpha c_\alpha^2}{3} F_\alpha^{qe};$$

$$\Phi_{\alpha d} = \Phi_{\alpha d}^0 + \sum_{i=1}^{N+M_a} \Phi_{\alpha i d}^a R_{id}^{ne};$$

$$\left[I'\left(F^{qe}\right)\Phi_d^0\right]_\alpha = -\sum_{i=1}^{M} \frac{\partial F_\alpha^{qe}}{\partial \Gamma_i} \Gamma_i - p \frac{\partial F_\alpha^{qe}}{\partial \Gamma_E} + \frac{\gamma_E m_\alpha c_\alpha^2}{3} F_\alpha^{qe};$$

$$\Phi_{id}^a = \Phi_{is}^a, \Rightarrow A_{ijs} = A_{ijd} = A_{ij}; \qquad A_{ij} = \left\langle \psi_{\Gamma_i}, I^l\left(F^{qe}\right)\Phi_{\alpha j}^a \right\rangle;$$

$$R_d^{ne} = \left(I - A\right)^{-1} R_d^{ne0}; \qquad R_{id}^{ne0} = \left\langle \psi_{\Gamma_i}, I^l\left(F^{qe}\right)\Phi_{\alpha d}^0 \right\rangle; \qquad R_d^0 = R_d^{ne} \nabla \cdot u;$$

$$R = \left(I - A\right)^{-1}\left(R_s^0 + R_d^0\right)$$

Comparison with Navier-Stoks Approximation

$$\left[I^{nr\prime}\left(F^{qe}\right)\Phi^{NS}\right]_\alpha = -I_\alpha^r\left(F^{qe}\right) + \sum_{i=1}^{N+M_a} \frac{\partial F_\alpha^{qe}}{\partial \Gamma_i} R_i^{qe};$$

$$\Phi_a^{NS} = \Phi_\alpha^{NS0} + \sum_{i=1}^{N+M_a} \Phi_{\alpha i}^a R_i^{qe};$$

$$\left[I^{nr\prime}\left(F^{qe}\right)\Phi^{NS0}\right]_\alpha = -I_\alpha\left(F^{qe}\right); \qquad \left[I^{nr\prime}\left(F^{qe}\right)\Phi_i^{NSa}\right]_\alpha = \frac{\partial F_\alpha^{qe}}{\partial \Gamma_i};$$

$$R_i^{NS} = R_i^{qe} + R_i^{NS0} + \sum_{j=1}^{N+M_a} A_{ij} R_j^{qe} = \sum_{j=1}^{N+M_a} \left(\delta_{ij} + A_{ij}\right) R_j^{qe} + R_i^{NS0};$$

$$R_{is}^{ne0} = \left\langle \psi_{\Gamma_i}, I^l\left(F^{qe}\right)\Phi_{\alpha s}^0 \right\rangle; \qquad A_{ijs} = \left\langle \psi_{\Gamma_i}, I^l\left(F^{qe}\right)\Phi_{\alpha js}^a \right\rangle;$$

$$R^{sh} = \left(I - A\right)^{-1} R_s^0 \approx (I + A)\left(R_s^{qe} + R_s^{nr0}\right)$$

$$\approx (I + A) R_s^{qe} + R_s^{nr0} = R^{NS};$$

Two-temperature Cut-off Harmonic Oscillator Model

Approximate Summational Invariants, Gas-dynamic Variables & Reaction Rates

$$\psi_{n_\alpha,\gamma} = \delta_{\alpha\gamma}, \quad \Gamma_{n_\alpha} = n_\alpha; \qquad \psi_{\vec{p},\alpha} = m_\alpha \vec{v}_\alpha, \quad \Gamma_{\vec{p}} = \rho\vec{u};$$

$$\psi_{E,\alpha} = e_\alpha^{(t)}(\vec{v}_\alpha) + e_\alpha^{(\mathrm{int})}(k_\alpha), \quad \Gamma_E = \rho\left(E_{kin} + u^2/2 + E_{\mathrm{int}}\right) = E;$$

$\psi_V = q_1, \quad \Gamma_V$ – quantum number density.

$$R_1 = -\frac{R_1^{qe} - \left(P_{d,q_m}\Delta''_{q_m} + Q_{q_m}P_{r,q_m}n_3 n_4\right)X_{1,q_m}^{qe}}{1 - \left(P_{d,q_m}B'_{q_m} - Q_{q_m}\right)X_{1,q_m}^{qe}},$$

$$R_1^{qe} = -\left(P_{d,q_m}X_{1,q_m}^{qe} - P_{r,q_m}n_3 n_4\right),$$

$$R_V = R_{VV} + q_m R_1$$

$$\left(P_{d,q_m}B'_{q_m} - Q_{q_m}\right)X_{1,q_m}^{qe} \sim \tau_{VV}/\tau_{ch}$$

One-temperature case

Collisional Integral Representation

CI may be represented as a sum of two parts: a sum over non-reactive collisions and a sum over reversible reactions:

$$I_\alpha\left(F \mid \vec{v}_\alpha, k_\alpha\right) = I_\alpha^{nr} + I_\alpha^{r} = \sum_{\nu \in \nu_\alpha} \left(\xi_{\alpha\nu}^{Qnr}{}'\left(\vec{v}_\alpha, k_\alpha\right) - \xi_{\alpha\nu}^{Qnr}\left(\vec{v}_\alpha, k_\alpha\right)\right)\eta_\nu^Q$$

$$+ \sum_{\substack{r \in r_\alpha \\ \nu_r'' \neq \nu_\alpha'}} \left(\xi_{\alpha r}^{Q}{}''\left(\vec{v}_\alpha, k_\alpha\right)\eta_\nu^Q{}'' - \xi_{\alpha r}^{Q}{}'\left(\vec{v}_\alpha, k_\alpha\right)\eta_\nu^Q{}'\right)$$

$$\xi_{\alpha\nu}^{Qnr(\prime)} = \sum_{k_\nu, k_\alpha', k_\nu'} \int d\vec{v}_\nu d\vec{v}_\alpha' d\vec{v}_\nu' W_{\nu''}^{\nu''} \prod_{\beta \in \nu''} \frac{F_\beta^{(\prime)} Q_\beta}{s_\beta n_\beta}, \qquad \xi_{\alpha r}^{Q\prime(\prime\prime)} = \sum_{k_\nu, k_\nu'} \int d\vec{v}_\nu d\vec{v}_\nu' W_{\alpha,\nu}^{\nu'} \prod_{\beta \in \nu_r'^{(\prime\prime)}} \frac{F_\beta Q_\beta}{s_\beta n_\beta}$$

$$\eta_\nu^Q = \prod_{\beta \in \nu} \frac{n_\beta}{Q_\beta}, \qquad \eta_r^Q = \eta_r^Q{}' - \eta_r^Q{}'' = \prod_{\beta \in \nu_r'} \frac{n_\beta}{Q_\beta} - \prod_{\beta \in \nu_r''} \frac{n_\beta}{Q_\beta}, \qquad K_{cr}^e = \prod_{\beta \in \nu_r'} Q_\beta \Big/ \prod_{\beta \in \nu_r''} Q_\beta$$

$$\xi_{\alpha r}^{Qqe} = \sum_{k_\nu, k_{\nu'}}{}' \int{}' d\vec{v}_\nu d\vec{v}_{\nu'} W_{\alpha,\nu}^{\nu'} \exp\left(-\gamma_E e_\nu\right), \qquad \xi_{\alpha r}^{Qqe}{}' = \xi_{\alpha r}^{Qqe}{}'' = \xi_{\alpha r}^{Qqe}$$

Non-equilibrium Reaction Rates for Spatially Homogeneous Case

$$\left[J'_{F^{qe}}\left(F^{qe}\right)\Phi_s\right]_\alpha = -\sum_{r\in r_\alpha}\left(\left(\xi^{Qqe}_{\alpha r} - \sum_{r\in r_\alpha}\left(\nu''_{\alpha r} - \nu'_{\alpha r}\right)K^{Qqe}_r\right)\eta^Q_r\right);$$

$$K^{Qqe}_r = \sum_{k_{\nu''},k_{\nu'}}{}' \int{}' d\vec{v}_{\nu''} d\vec{v}_{\nu'} W^{\nu'}_{\nu''} \exp\left(-\gamma_E e_\nu\right)$$

$$\Phi_{s\alpha} = F^{qe}_\alpha \sum_{r=1}^{r_\alpha} \varphi_{s\alpha r}\left(\vec{v}_\alpha, k_\alpha\right)\eta^Q_r$$

$$R^0_{s\alpha} = R^{qe}_\alpha + R^{ne0}_{s\alpha} = \sum_{r,r'\in r_\alpha}\left(\nu''_{\alpha r} - \nu'_{\alpha r}\right)\left(K^{Qqe}_r \delta_{rr'} + \tilde{K}^{Qne0}_{srr'}\right)\eta^Q_{r'};$$

$$\tilde{K}^{Qne0}_{srr'} = K^{ne0}_{srr'}{}'\eta^Q_{r'}{}' - K^{ne0}_{srr'}{}''\eta^Q_{r'}{}''$$

$$K^{Qne0\,'(\,''\,)}_{srr'} = \sum_{k_{\nu''},k_{\nu'}}{}' \int{}' d\vec{v}_{\nu''} d\vec{v}_{\nu'} W^{\nu'}_{\nu''} \exp\left(-\gamma_E e_\nu\right) \sum_{\beta\in\nu'^{(\,''\,)}_{r'}} \varphi^0_{s\beta r}$$

Conclusions

1. All generalized relaxation processes described by Euler equations become entangled (affecting each other)
2. Concept of individual reaction rates is not universal. In general for each mixture the specific expressions for the reaction rates for each species should be calculated. This is similar to the widely used procedure of applying the Stefan–Maxwell equations for the diffusion description in multi-component mixtures

Conclusions (continued)

3. Great achievements of the traditional physical-chemical gas-dynamics may be the result of the fact that the spatially-homogeneous effects don't shift the local chemical equilibrium. Their role mainly reduces to the change of the rate of equilibrium approaching. Besides, the non-equilibrium effects are localized in the narrow zones of gas-dynamic parameters, so that there could be expectation of their small impact and of getting the accurate results within the traditional description, but it can be ascertained only after applying the proposed generalized description. Thus, to make predictions on the basis of gas-dynamics for high-enthalpy flows more reliable, further research is needed.

Questions please

Thank you for your attention

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