A REVIEW OF THE KINETIC MODELINGS FOR NON-REACTIVE AND REACTIVE DENSE FLUIDS: QUESTIONS AND PROBLEMS

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ABSTRACT. A review of various kinetic models for non-reactive and reactive dense fluids, including possible detonation and combustion processes.

1. Introduction

One of the most challenging goals in physics is gaining an understanding of relations between alternative descriptions of matter: microscopic, statistical, and macroscopic. From the phenomenological point of view the state of a system (for example, air in a room, or fluid in a glass) is given in terms of the variables that describe space distribution of physical quantities, e.g., local density, local velocity or local temperature. These quantities are related to each other through the basic equations of the macroscopic theory: the Euler and Navier-Stokes equations. The equations reflect the balance of certain physical quantities such as mass, momentum, energy, and possibly higher order quantities, if one considers the extended thermodynamics.

However, in order for this macroscopic theory to work, we must supplement not only the appropriate boundary conditions, but also the values of **thermophysical constants** such as

- equation of state data: e.g., $p = nk_BT$ for ideal gas;
- transport and structure coefficients (as well as constitutive relations: e.g.,

$$P_{xy} = -\eta \frac{\partial u_x}{\partial y}, \tag{1.1}$$

  where P_{xy} is the shear stress, $\dfrac{\partial u_x}{\partial y}$ is the strain rate, and η is the shear viscosity).

These data **cannot** be obtained from the macroscopic theory. Historically, they have been supplied by experiments and/or various phenomenological, often ad hoc, considerations. One of the most important goals of the statistical mechanics

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and the kinetic theory of fluids is to predict these thermophysical constants from knowledge of molecules' interaction potentials.

The above described goal is particularly challenging for a special class of chemical reactions: combustion and detonation processes. Combustion and detonation have a long tradition in human endevours and great economic and technical importance (see, e.g., [1], [2], and [3] and references there). However, until recently very little scientific investigations has been done in this area from the **statistical mechanics** and/or the **kinetic theory** point of view.

One would like to construct robust and viable microscopic models for non-reacting and reacting dense fluids that

- provide consistent macroscopic theory (in the hydrodynamic limit);
- predict transport and structural coefficients for difficult to measure processes (e.g., exothermic shock waves);
- describe well large heat and mass transfers and large activation energies (combustion/detonation processes) for the reactive fluids.

These very challenging goals cannot be accomplished without initial modelings of inert dense fluids. Indeed, existent kinetic models, based mainly on the Boltzmann equation, are valid only for dilute gases. Furthermore, very often colliding molecules are treated as mass points without any internal geometry and zero excluded volume. Finally, good understanding of inert dense fluids will allow one to use it as a consistency check when in more complicated models (that involve chemical reactions) the reactions are *turned off*. This *turning off* is usually done by setting to zero suitable parameters of the model. In the process of developing kinetic models of inert dense fluids one encounters several outstanding problems. Some of them are related to polydisperse fluids (section 2.3), phase transitions (section 2.4), and hydrodynamic limits (section 2.6). Good understanding of these problems in the inert case is crucial in studying more complicated chemically reacting fluids (section 3). In addition, mathematical problems encountered in chemically reacting fluids, although more intricate, belong to the same category as in the case of inert fluids, at least for the models considered here. That is why a success in inert cases can be considered as a good indicator of proving similar results for reactive fluids.

In the kinetic theory approach, one abandons detailed description of each particle of the system in favor of knowing only particles' probability distribution (of positions and velocities) as a function of time. Time evolution of the probability distribution is governed by a corresponding kinetic equation (e.g., the Boltzmann equation). Although the Boltzmann equation is a good model for a rarefied gas, another approach is needed in the case of dense gases.

A *good* kinetic theory possesses a Liapunov functional (often called an H-function) that drives an initial distribution to the equilibrium state. I plan to study physical and mathematical aspects of the Liapunov functionals in non-reacting and chemically reacting **dense** gas mixtures. These functionals arise in the kinetic theories as the indicators of the dissipativity of a physical system and, in many situations, describe the way the system approaches an equilibrium state. The most celebrated example of the above-mentioned functionals is the H–function for the Boltzmann equation. They provide the information about the unifying notion underlying each dynamical system considered in the kinetic theory, i.e. its *irreversibility in the limit* when $t \to \infty$ ([4], [5]). In addition, they play an essential role ([6], [7]) in the methods used to obtain existence theorems and asymptotic and stability results.

In contrast to the kinetic theory of dilute gases (based on the Boltzmann equation), the kinetic theories of dense fluids **do not** neglect configurational correlations of the particles in the system. This results in the **desired departure** from the ideal fluid model, on the macroscopic level, and much better prediction of transport coefficients For example, the transport coefficients based on the Enskog equation are correct within 5% error for densities up to 3/4 of close packing density ([8]). I point out that Boltzmann's transport coefficients do **not** depend on density!

Furthermore, in order to have any chance of describing even simple fluids (i.e., chemically inert fluids with spherically symmetric interaction potentials), not to mention molecular or macromolecular liquids, one needs to go beyond the kinetic models that are obtained from the dilute-gas limit procedure (e.g., the Boltzmann equation). In the case of N hard spheres with the diameter a, the dilute-gas limit is equivalent to taking the following limits (an analog of the thermodynamic limit in equilibrium statistical mechanics):

$$a \to 0, \quad N \to \infty, \quad \text{and} \quad Na^2 \to const > 0. \tag{1.2}$$

The limit in (1.2) is also called the Boltzmann-Grad limit. In a fluid obtained through the dilute-gas limit (or zero-density limit) the volume occupied by fluids' particles (excluded volume) is zero. Indeed, in the limit (1.2), $N\frac{4}{3}\pi\left(\frac{a}{2}\right)^3$, the volume of hard spheres is zero.

In order to appreciate further inadequacy of the zero-density limit in describing more complicated fluids, it is interesting to consider the dilute-gas limit of the (hydrostatic) equilibrium pressure for systems with pairwise additive interaction potential, $\sum_{i<j} \phi(|r_i - r_j|)$, in the canonical ensemble:

$$p = \frac{Nk_BT}{V} - \frac{1}{6V}\iint |r_1 - r_2|\frac{d\phi(|r_1 - r_2|)}{dr} n_2(r_1, r_2) dr_1 dr_2, \tag{1.3}$$

where $n_2(r_1, r_2)$ is the two-body density function (also called the pair density). The dilute-gas limit of (1.3) can be most easily obtained for an isotropic fluid $n_2(r_1 - r_2) = n^2 g_2(|r_1 - r_2|)$, $n = N/V$, and hard-sphere potentials

$$\phi^{HS}(r) = \begin{cases} +\infty, & \text{if } r \leq a; \\ 0, & \text{if } r > a, \end{cases} \tag{1.4}$$

Indeed, one quickly obtains,

$$\frac{p}{nk_BT} = 1 - \frac{2\pi n}{3k_BT}\int_0^\infty r^3 \frac{d\phi^{HS}(r)}{dr} g_2(r)\, dr \tag{1.5}$$

$$= 1 + \left(\frac{2}{3}\pi a^3 n\right) g_2(a^+) \underset{\substack{\frac{2}{3}\pi n a^3 \to 0 \\ \text{(dilute-gas limit)}}}{\longrightarrow} 1, \tag{1.6}$$

where $g(a^+)$ (see (2.5)) denotes the contact value of the equilibrium radial distribution function for hard-spheres system and formally approaches 1 in the above limit. Thus, (1.3) reduces to the equation of state for an ideal gas! As before, $\frac{2}{3}\pi a^3 n = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 n = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 \frac{N}{V}$ is just the excluded volume that approaches zero in the dilute-gas limit. It was Enskog, in 1921 ([9]), who first noticed the importance of **nonzero** excluded volume in description of the behavior of dense systems. In analogy to (1.2) the (moderately) dense gas limit can be formulated as

$$a \to 0, \quad N \to \infty, \quad \text{and} \quad Na^3 \to \mathit{const} > 0. \tag{1.7}$$

The presence of the excluded volume increases the pressure of the system. This easily follows from (1.7) applied to (1.5)-(1.6).

Below, I list the criteria that are used in this review to construct various kinetic models of dense fluids:

- 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.

Once the model is constructed, I will be also interested in the responses of the model, on the kinetic and on the hydrodynamic levels, to various (stochastic) perturbations imposed on the original model. A *good* perturbation is another kinetic model that preferably satisfies the above criteria together with certain stability conditions.

First, I start with the revised Enskog theory (RET, see section 2.1) and the square-well kinetic theory (KVTIII, see section 2.2). Next, I consider perturbations of these models. I will be particularly interested in controlling the equation of state, the internal energy, the specific heats, and the transport and structure coefficients of the underlying fluids through the (often stochastic) inputs (see sections 2.3 and 2.6) that characterize these perturbations. These goals are very important in understanding the microscopic roots of the fluid's properties. This is particularly true when one adds reactive terms to the model. Some of these new models correspond to the class of polydisperse systems, including polydispersity in mass. A new frontier in the kinetic theory would be to consider models of convex bodies (spheroids, spherocylinders, or truncated spheres). The equilibrium statistical mechanics of some convex bodies [10] is rather well known. This raises hopes for the development of their non-equilibrium counterpart: the kinetic theory of convex bodies. Such a theory would play a very important role in understanding the behavior of macromolecules and liquid crystals. This is particularly interesting for chemically reacting macromolecules or liquid crystals.

The construction of a kinetic theory for chemically reacting fluids is the most challenging one. With very few exceptions (most notably hard-sphere-like models) only Boltzmann-like models have been considered in the literature. From the physical point of view, the most important goal is to find possible analogs of the RET and the KVTIII for chemically reacting fluids that satisfy the above criteria of the well behaved kinetic theories. Relative simplicity of hard-spheres and square-well potentials increases chances of a success in this area. Finally, the regimes of combustion/detonation fall naturally into the problems of shock waves (already known in an inert case) for chemically reacting mixtures corresponding to large mass and heat transfer, and/or large activation energies.

In addition to the kinetic modeling, there are many outstanding mathematical problems that appear in a natural way and their resolution would strengthen the physical foundations of the considered models. I list them in the framed-boxes of the diagram below.

BBGKY hierarchy: reduced distribution functions

$\downarrow$

Dense gas limit:

$$\left\{\begin{matrix} a \to 0,\ N \to \infty \\ Na^3 \to\ const > 0 \end{matrix}\right\} \Longrightarrow^{Na^2 \to \infty}$$

$\downarrow$

Kinetic level: one-particle distribution functions

convergence of g_2
existence and uniqueness
trend to equilibrium
phase transitions
spectral analysis

$\downarrow$

Hydrodynamic limit:
Euler level
Navier-Stokes level

Macroscopic equations

The rigorous derivation of Boltzmann equation from the BBGKY hierarchy in the dilute-gas limit (1.2) is relatively well established ([11], [12], [13]). This is to be contrasted with almost no results in this direction for the dense gas limit, whether for the RET or the KVTIII equations. Initial progress for the Boltzmann-Enskog equation, where only the first term of the density expansion of the pair correlation function g_2 is retained (see (2.7)), has been done in [14] and [15]. Likely, the convergence of the Mayer cluster expansion for g_2 (in (2.7) and (2.20)) is one of the important ingredients to the solution of this problem.

In the last 15 years there has been important progress in the fundamentals of statistical mechanics of dense gases and liquids ([16], [17], [18], [19]). This research, carried out mainly by physicists and chemists, begins to provide for the first time the physical framework and computational analysis for the models of dense fluids. Following the breakthrough work of DiPerna and Lions [6] on the global existence theorem for the Boltzmann equation, many authors applied their ideas to the Enskog (or the Boltzmann-Enskog) equation ([20], [7], [33], [35], [34], [21]), the KVTIII theory ([22], [23]), and the chemically reacting kinetic theory ([24]).

I end this introduction by listing some of the outstanding problems and questions in the kinetic theory of non-reactive and reactive dense gases and liquids.

- Does there exist a model of the kinetic theory whose underlying fluid has features similar to the fluids described by the van der Waals equation of state
$$p = \frac{nk_BT}{1-bn} - an^2,$$
or by the van der Waals–Maxwell equation of state,
$$p = p_{HS} - an^2\,?$$
Remark: Here, p_{HS} is given in (2.6) and $p_{HS} \neq (nk_BT)\,/\,(1-bn)$, except for hard rods. This problem is particularly interesting in view of the fact that the van der Waals equation is rigorously valid in the thermodynamic limit of the system with the Kac's potential (hard-core plus a smooth and rapidly decreasing tail, see, for example, [25]).
- Find a model of the kinetic theory whose transport coefficients behave similarly to the transport coefficients of the realistic gases and liquids, for example,
shear viscosity η increases as $T\uparrow$; (for gases)
shear viscosity η decreases as $T\uparrow$. (for liquids)
- Find models of the kinetic theory that describe *well* chemically reacting gases and liquids that also undergo fast chemistry, large heat and mass transfer, and large activation energies (combustion/detonation processes).

2. Non-reactive kinetic theories.

2.1. **The revised Enskog theory.** In an attempt to generalize the Boltzmann equation to moderately dense gases, Enskog [9] proposed a kinetic theory that generalized Boltzmann's original *stosszahlansatz* in two ways:

(1) by taking into account the fact that the centers of two colliding spheres are at a distance a, equal to the diameter of hard spheres.
(2) by increasing the collision frequency by a factor Y_0 which nowadays is identified with the radial pair correlation function $g_2(r)$ for the system of hard spheres at a **uniform** equilibrium.

I want to note that the advantage of considering hard sphere systems resides in two facts: the collisions are instantaneous and influence of multiple collisions (i.e. simultaneous encounters of more than two spheres) is negligible. In fact, the volume of the phase space corresponding to triple, quadruple, and n-tuple collisions is zero; at least for integrable functions.

Furthermore, in moderately dense gases the molecular diameter is no longer small compared with the mean free path between collisions. An important consequence of this is that the transport of momentum and energy during collisions (negligible in the dilute-gas limit, and consequently in the Boltzmann equation) takes place over distances comparable to the separation of the molecules.

The standard Enskog equation (SET) [26] for the one–particle distribution function f is a nonlinear integro-partial differential equation

$$\frac{\partial f}{\partial t} + v_1 \frac{\partial f}{\partial r_1} = E(f) = E^+(f) - E^-(f), \tag{2.1}$$

with

$$E^+(f) = a^2 \iint\limits_{\mathbb{R}^3 \times \mathbb{S}^2_+} Y_0 \left[n \left(r_1 - \frac{a\epsilon}{2} \right) \right] f(t, r_1, v_1') \, f(t, r_1 - a\epsilon, w') \, \langle \epsilon, v_1 - w \rangle \, d\epsilon dw \tag{2.2}$$

and

$$E^-(f) = a^2 \iint\limits_{\mathbb{R}^3 \times \mathbb{S}^2_+} Y_0 \left[n \left(r_1 + \frac{a\epsilon}{2} \right) \right] f(t, r_1, v_1) \, f(t, r_1 + a\epsilon, w) \, \langle \epsilon, v_1 - w \rangle \, d\epsilon dw \tag{2.3}$$

where $\langle \cdot, \rangle$ is the inner product in $\mathbb{R}^3$, $\mathbb{S}^2_+ = \{\epsilon \in \mathbb{S}^2 : \langle \epsilon, v_1 - w \rangle \geq 0\}$, v_1', w' are post-collisional velocities

$$v_1' = v_1 - \epsilon \langle \epsilon, v_1 - w \rangle, \qquad w' = w + \epsilon \langle \epsilon, v_1 - w \rangle,$$

$n(r_1) = \int f(r_1, v_1) \, dv_1$, and

$$Y_0(n(r_1)) = 1 + \left(\frac{2\pi a^3}{3} \right) b_3 n(r_1) + \left(\frac{2\pi a^3}{3} \right)^2 b_4 n^2(r_1) + \cdots . \tag{2.4}$$

The expansion in (2.4) is just the contact value density expansion (i.e., for $|r_1 - r_2| = a$) of the radial pair correlation function g_2 for the system of hard spheres at **uniform** equilibrium:

$$g_2(a^+) = 1 + \left(\frac{2\pi a^3}{3} \right) b_3 + \left(\frac{2\pi a^3}{3} \right)^2 b_4 n^2 + \cdots , \tag{2.5}$$

where b_k are expressed in terms of the virial coefficients B_k, appearing in the equation of state for the hard sphere system

$$\frac{p}{nk_BT} = 1 + \sum_{k=1}^{\infty} B_{k+1} n^k \underset{\text{see (1.6)}}{=} 1 + \left(\frac{2}{3}\pi a^3 n\right) g_2(a^+) \tag{2.6}$$

In 1973, H. van Beijeren and M. H. Ernst ([27]) modified the original Enskog theory by replacing the radial pair correlation function g_2 at **uniform** equilibrium by the exact pair correlation function $g_2(r_1, r_2 \,|\, n)$ that takes full account of spatial non-uniformities in the local equilibrium. The Mayer cluster expansion of $g_2(r_1, r_2 \,|\, n)$ ([28]) has the form

$$\begin{aligned} &g_2(r_1, r_2 \,|\, n) = \exp(-\beta\phi^{HS}(|r_1 - r_2|))\times \\ &\Big\{1 + \int V(12 \,|\, 3) n(t, r_3)\, dr_3 + \frac{1}{2}\int\int V(12 \,|\, 34) n(t, r_3)\, n(t, r_4)\, dr_3 dr_4 \\ &+ \cdots + \frac{1}{(k-2)!}\int dr_3 \cdots \int dr_k\, n(3) \cdots n(k)\, V(12 \,|\, 3 \ldots k) + \cdots\Big\}, \end{aligned} \tag{2.7}$$

where $n(k) = n(t, r_k)$, $\beta = 1/k_BT$, $V(12 \,|\, 3 \ldots k)$ is the sum of all graphs of k labeled points which are biconnected when the Mayer factor $f_{ij} = \exp(-\beta\phi^{HS}(|r_i - r_j|)) - 1$ is added. Here, ϕ^{HS} is the hard-sphere potential given in (1.4). For example, if Ω denotes the spatial domain, the second term in (2.7) has the form

$$\int n(r_3)\, V(12 \,|\, 3)\, dr_3 = \int n(r_3)\, f_{13}\, f_{23}\, dr_3 = \int_{\Omega\cap\left\{\substack{|r_1 - r_3| \le a \\ |r_2 - r_3| \le a}\right\}} n(r_3)\, dr_3, \tag{2.8}$$

and similarly for higher order coefficients.

Remark 2.1. *I want to point out that in the uniform equilibrium (when $n(r_1) = n$) the series* (2.7) *evaluated at contact value (i.e., when $|r_1 - r_2| = a$) becomes* (2.5). *It is at this point one can see that Y_0's dependence on r_1 in* (2.2)–(2.3) *and* (2.4) *is artificial.*

Now, the corresponding revised Enskog equation (RET) has the form (2.1) with $E^+(f)$ and $E^-(f)$ replaced by

$$\begin{aligned} E^+_{RET}(f) =& a^2 \iint_{\mathbb{R}^3\times\mathbb{S}^2_+} g_2(r_1, r_1 - a\epsilon \,|\, n(t)) f(t, r_1, v_1')\, f(t, r_1 - a\epsilon, w')\times \\ & \langle \epsilon\cdot, v_1 - w\rangle\, d\epsilon dw \end{aligned} \tag{2.9}$$

and

$$\begin{aligned} E^-_{RET}(f) =& a^2 \iint_{\mathbb{R}^3\times\mathbb{S}^2_+} g_2(r_1, r_1 + a\epsilon \,|\, n(t)) f(t, r_1, v_1)\, f(t, r_1 + a\epsilon, w)\times \\ & \langle \epsilon\cdot, v_1 - w\rangle\, d\epsilon dw. \end{aligned} \tag{2.10}$$

The RET has an H-functional [29] (and the corresponding local H functional [30])

$$\begin{aligned} H_{RET} = H_B(t) + H_{corr}(t) = & \iint f(t, r_1, v_1) \log f(t, r_1, v_1)\, dv_1 dr_1 \\ & - \sum_{k=2}^{\infty} \frac{1}{k!} \int dr_1 \cdots \int dr_k\, n(1) \dots n(k)\, V(1 \dots k), \end{aligned} \tag{2.11}$$

where $V(1 \dots k)$ is the sum of all irreducible Mayer graphs which doubly connect k particles.

In contrast to Botzmann's H–function, H_{RET} consists of two parts: the kinetic part ($H_B(t)$) and the correlational part. $-H_{RE}(t)$ (modulo an additive constant) is the equilibrium (non-uniform) entropy for the infinity system of hard–spheres. In addition, one recognizes that

$$-\beta H_{corr} = \mathcal{A}^{excess} \tag{2.12}$$

is the excess free energy for the system hard-spheres in the **non-uniform** equilibrium.

In spite of some progress made recently in obtaining rigorous results for the Enskog equation ([31], [32], [20], [33], [34], [7], [35], [21], and [36]), there are still basic and unresolved problems for both the standard and revised Enskog equations.

The first natural problem in the RET concerns the convergence of the series in (2.7). In the homogeneous case, i.e., when n does not depend on the spatial variable r, the series in (2.7) is convergent for sufficiently small densities n (e.g., [37]). It is not clear whether this result can be extended to the non-homogeneous case. But even if that is the case, there are still difficulties in applying this fact to the existence theorems for the RET. It is not clear whether the RET preserves the boundedness of the density with time evolution. Together with G. Stell, I elaborated further on this topic in [21] and its relation to Resibois' work [29].

The existence theorems obtained so far dealt only with the modifications of the revised or standard Enskog equations. In [31] and [32] the authors obtained small initial data and vacuum solutions with g_2 (given in equation (2.7)) assumed to be smooth and bounded. This condition cannot be checked for the series in (2.7) before its convergence is confirmed. The authors in [20], [7], [34] and [33] have obtained weak solutions in L^1, using the weak compactness method, originally applied to the Boltzmann equation by DiPerna and Lions [6]. They consider either the cases of $g_2 \equiv 1$ (the Boltzmann–Enskog equation) or the cases of g_2 that are bounded and with compact support. In [21] and [36] some progress has been made by considering the approximation of g_2

$$\begin{aligned} G = & \exp\left(-\beta \phi^{HS}(|r_1 - r_2|)\right) \times \\ & \left\{ 1 + \sum_{k=3}^{i} \frac{1}{(k-2)!} \int dr_3 \cdots \int dr_k n(3) \dots n(k) V(12 \,|\, 3 \dots k) \right\}, \end{aligned} \tag{2.13}$$

for $i \geq 2$, and with the convention that $G = \exp\left(-\beta\phi^{HS}(|r_1 - r_2|)\right)$ for $i = 2$. The case of $i = 2$ corresponds to the Boltzmann–Enskog equation, i.e., the case when $G \equiv 1$.

Finally, recent derivations of the two-particle dense kinetic theory in the context of maximum entropy formalism raise [39]-[42] hopes for possible extensions of the hard-spheres kinetic theory to its two-particles' version.

2.2. **Square-well kinetic theories.** While in the dilute–gas regime, the Boltzmann equation, and for moderately dense fluids the RET, are sufficient in providing accurate predictions of hard–sphere transport coefficients, the case of dense gases and liquids is rather different. Indeed, many–particle interactions and the fact that the energy density is **not** determined by the one–particle distribution function alone, but requires the two–particle distribution function, present us with difficulties that cannot be resolved on the one–particle level. (Although, interestingly enough, one of this complications is absent for hard–sphere systems, where the potential energy of inter-particle interactions is zero.) This together with the fact that real molecules are not hard spheres has led many in search of a generalization of the RET to the kinetic equations with more realistic potentials. Since smooth potentials can be approximated by a sequence of step functions, the square-well potential ϕ^{SW} can be considered as the lowest-order approximation of this type. For $\gamma > 0,\ 0 < a < R$, and

$$\phi^{SW}(r) = \begin{cases} \infty, & \text{for } r \leq a, \\ -\gamma, & \text{for } a < r < R, \\ 0 & \text{for } r \geq R. \end{cases} \tag{2.14}$$

the authors in [43], [44] and [45] have developed a new approach to partially remedy the above situation. It is based on the maximization of the fine–grained entropy, subject to appropriate constraints, which yields what has come to be called kinetic variational theory (KVT) [46], [47]. Use of a set of increasingly stringent constraints which is a subset of the exact constraints in the problem yields increasingly accurate quantitative assessments of transport coefficients and related macroscopic quantities. In particular, the version that is based upon a local energy–density constraint (called by the authors KVTIII, because it is generated by the third in the sequence of constraints mentioned above) has been investigated in detail and the transport coefficients obtained from the KVTIII are in good agreement with experimental data and computer simulation results for moderately dense fluids.

In contrast to the RET or the Boltzmann equation, the KVTIII consists of two coupled equations for the one-particle distribution function and the potential energy density u_p. The function $u_p(t, r_1)$ is given in terms of the two-particle distribution function f_2 by

$$u_p(t, r_1) = \frac{1}{2} \int\limits_{\Omega\times\mathbb{R}^3\times\mathbb{R}^3} \phi^{SW}(|r_1 - r_2|) f_2(t, r_1, v_1, r_2, v_2)\, dv_1 dv_2 dr_2. \tag{2.15}$$

The *collisions* are understood to be instantaneous and take place at the points where ϕ^{SW} is discontinuous. There are four different type of collisions that can be distinguished in the case of the square-well potential: (1) a collision at the hard core (at $r = a^+$), (2) a collision entering the square-well (at $r = R^-$), (3) a collision leaving the square-well (at $r = R^+$), and (4) a collision rebounding at the inner side of the square-well (at $r = R^-$). The last type of collision occurs when the radial relative velocity is too small for escape from the well, i.e., is smaller than $|v_{esc}| = \sqrt{4\gamma}$.

Similarly to the case of hard-sphere systems one can derive the pseudo-Liouville equation that governs the exact dynamics of the system interacting with the square-well potential ϕ^{SW}, as well as the corresponding analog of the BBGKY hierachy for hard-sphere systems (e.g., [8]). The first hierarchy equation for the one-particle distribution function f has the form

$$\frac{\partial f}{\partial t} + v_1 \frac{\partial f}{\partial r_1} = Q^{SW}(f_2) \equiv Q_1(f_2) + Q_2(f_2) + Q_3(f_2) + Q_4(f_2) \tag{2.16}$$

where Q_i, for $i = 1, 2, 3, 4$, are the collisions operators corresponding, respectively, to the four types of collisions mentioned above.

From the second hierarchy equation, the equation for $u_p(t, r_1)$ has the form

$$\frac{\partial}{\partial t} u_p(t, r_1) + \frac{1}{2} \frac{\partial}{\partial r_1} \iiint\limits_{\Omega \times \mathbb{R}^3 \times \mathbb{R}^3} \phi^{SW}(|r_1 - r_2|) f_2(t, r_1, v_1, r_2, w)\, dw\, dv_1\, dr_2 = J(f_2) \tag{2.17}$$

where, as in (2.16), J is an explicit operator depending on f_2. Next, the just mentioned maximization of fine-grain entropy yields the expression for f_2,

$$f_2(t, r_1, v_1, r_2, v_2) = f(t, r_1, v_1)\, f(t, r_2, v_2)\, g_2(r_1, r_2 \,|\, n(t, \cdot), \beta(t, \cdot)), \tag{2.18}$$

and this closes the system of equations (2.16)-(2.17) for $f(t, r_1, v_1)$ and $u_p(t, r_1)$. Indeed, as in the case of the RET the pair correlation function g_2 is a functional of $n(t, r_1) = \int_{\mathbb{R}^3} f(t, r_1, v_1)\, dv_1$ and $\beta(t, r_1)$, can be expressed in terms of the Mayer expansion, where each vertex is weighted by the density field $n(t, r_1)$ and the Mayer factors assume the form

$$f_{ij} = \exp\left\{ \frac{1}{2} \left[\beta(t, r_i) + \beta(t, r_j)\right] \phi^{SW}(|r_i - r_j|) \right\} - 1. \tag{2.19}$$

The field $k_B \beta(t, r_1)$ can be interpreted as the inverse of the local potential energy temperature that in equilibrium coincides with the usual kinetic energy temperature.

Furthermore,

$$g_2(r_1, r_2 \,|\, n, \beta) = \exp\left(-\frac{1}{2} \left[\beta(t, r_1) + \beta(t, r_2)\right] \phi^{SW}(|r_1 - r_2|) \right) \chi(r_1, r_2 \,|\, n, \beta) \tag{2.20}$$

where

$$\chi(r_1, r_2 \,|\, n, \beta) = 1 + \sum_{k=3}^{\infty} \frac{1}{(k-2)!} \int\limits_{\Omega} dr_3 \,\cdots \int\limits_{\Omega} dr_k \, n(3) \,\ldots\, n(k) \, V(12 \,|\, 3 \ldots k). \tag{2.21}$$

Here, $n(k) = n(t, r_k)$, $V(12 \,|\, 3 \ldots k)$ is the sum of all graphs of k labeled points which are biconnected when the Mayer factor

$$f_{12} = \exp\left[-\beta_{12}\phi^{SW}(|r_1 - r_2|)\right] - 1$$

is added. Except for a different expression of the Mayer factors f_{ij}, the above expansion has the same algebraic structure as the Mayer expansion of g_2 in the RET !

From (2.15), $u_p(t, r_1)$ is also a functional of $n(t, r_1)$ and $\beta(t, r_1)$, and by formally inverting this relation, one can express $\beta(t, r_1)$ as a functional of $u_p(t, r_1)$ and $n(t, r_1)$. Therefore, inserting (2.18) and (2.20) into (2.16) and (2.17) yields the square-well kinetic theory consisting of the coupled equations for f and u_p. Equivalently, instead of $f(t, r_1, v_1)$ and $u_p(t, r_1)$, one has an option of switching to $f(t, r_1, v_1)$ and $\beta(t, r_1)$ as the unknown functions appearing in equations (2.16) and (2.17).

The resulting kinetic theory has an H-functional [43] (and the corresponding local H-functional [45])

$$\begin{aligned} H_{SW}(f, \beta)(t) = H_B(t) + H_{corr}^{SW}(t) + H_p(t) = \\ \iint\limits_{\Omega \times \mathbb{R}^3} f(t, r_1, v_1) \log f(t, r_1, v_1) \, dv_1 dr_1 \\ - \sum_{k=2}^{\infty} \frac{1}{k!} \int\limits_{\Omega} dr_1 \,\cdots \int\limits_{\Omega} dr_k \, n(1) \ldots n(k) \, V(1 \ldots k) - \int\limits_{\Omega} \beta(t, r_1) u_p(t, r_1) \, dr_1, \end{aligned} \tag{2.22}$$

where $V(1 \ldots k)$ is the sum of all irreducible Mayer graphs (2.19), which doubly connect k particles.

Similarly to RET's H function (see (2.11) and relation (2.12))

$$-\beta H_{corr}^{SW} + \int\limits_{\Omega} \beta(t, r_1) u_p(t, r_1) \, dr_1 = \mathcal{A}^{excess} \tag{2.23}$$

is the excess free energy for the system with the square-well interaction potential (2.14) at **non-uniform** equilibrium.

The existence of an H-function raises hopes for existence and stability results for this important set of kinetic equations; an initial progress has been reported in [22]. As in the case of the RET the convergence of (2.21) is of prime concern. Fortunately, due the same algebraic structure of both of H_{corr} in (2.11) and H_{corr}^{SW} in (2.21), the methods that imply convergence of the former should most likely yield the convergence of the latter series too.

2.3. **Perturbations of the basic models and polydisperse extensions.** The simplicity of geometry and the finite total cross-section were always main advantages in considering hard-sphere systems. However, hard-sphere's scattering law implying that the cross-section is independent of the relative translational kinetic energy in the collision, is its disadvantage. Several ad hoc remedies had been proposed: the variable hard sphere [48], the variable soft sphere [49], [50] and generalized hard sphere models [51]. All of them, however, were concentrated on better computations of the transport coefficients as compared to with realistic gases and not the actual properties of the models.

Recently, the authors in [52] considered the kinetic models that address some of the drawbacks mentioned above, and at the same time constitute the well defined kinetic theories with built in conservation laws and trend to equilibrium. The main idea is to introduce a *smearing-type* effect in the collision process by introducing varying diameters of hard spheres and the widths of the square-well in the KVTIII. For example, the perturbation of the RET has the form

$$\frac{\partial f}{\partial t} + v_1 \frac{\partial f}{\partial r_1} = E_{stoch}(f) \equiv E^{+}_{stoch}(f) - E^{-}_{stoch}(f), \tag{2.24}$$

with

$$\begin{aligned} E^{+}_{stoch}(f) = \iiint\limits_{[\alpha,\beta]\times\mathbb{R}^3\times\mathbb{S}^2} & f(t, r_1, v_1')f(t, r_1 - a\epsilon, w')a^2 P(a, \theta, |v - w|)\times \\ & g_2(r_1, r_1 - a^{+}\epsilon)\langle\epsilon, v_1 - w\rangle d\epsilon dw da, \end{aligned} \tag{2.25}$$

$$\begin{aligned} E^{-}_{stoch}(f) = \iiint\limits_{[\alpha,\beta]\times\mathbb{R}^3\times\mathbb{S}^2} & f(t, r_1, v_1)f(t, r_1 + a\epsilon, w)a^2 P(a, \theta, |v - w|)\times \\ & g_2(r_1, r_1 + a^{+}\epsilon)\langle\epsilon, v_1 - w\rangle d\epsilon dw da, \end{aligned} \tag{2.26}$$

where θ is the angle between ϵ and $v_1 - w$. The function P is a given nonnegative probability density. In the case $P(a, \theta, |v-w|) = \delta(a-d)$, equation (2.24) reduces to revised Enskog equation. Similarly, one can introduce this *smearing-type* effect to the square-well kinetic theory (KVTIII) (2.16)-(2.17). In the KVTIII however, this smearing effect can take place not only at the hard-core but also at the square-well edge. Thus, the width of square-well can vary according to an additional probability density $P_{SW}(R, \theta, |v_1 - w|)$.

Similar models to (2.24) had been known for the Boltzmann equation [53]. From the mathematical point of view, the authors in [54] (see also references in [55]) utilized similar searing-type effects to pass to the Euler level from a stochastic BBGKY-hierachy equations, while the authors in [56] proved the convergence to absolute equilibrium for the stochastic (Povzner-like) Boltzmann equation.

One of the important goals in developing the above model (both for the RET and KVTIII) is to provide prescriptions for functions P and/or P_{SW}. This is precisely at this point where the attractiveness of (2.24) becomes apparent. It turns out [52] that the self-diffusion coefficient computed from (2.24) (or more precisely, from the corresponding stochastic mixture model, when $P = P(a)$),

$$D_{stoch} = \frac{3}{8n} \frac{1}{\left(\int_0^\infty a^2 P(a) g_2(a^+)\, da\right)} \left(\frac{k_B T}{\pi m}\right)^{1/2}, \tag{2.27}$$

(2.28)

is strikingly similar to the self-diffusion coefficient, obtained by J. A. Leegwater [57]

$$D = \frac{3}{8n} \frac{1}{\left(\int_\alpha^\beta W(a) g_2(a^+)\, da\right)} \left(\frac{k_B T}{\pi m}\right)^{1/2}. \tag{2.29}$$

The authors in [58] and [57] tried to improve the hard-spheres's transport coefficients by considering more realistic Lenard-Jones interactions through the method similar to Green-Kubo's approach, without, of course, considering the kinetic model (2.24). They also indicated how to construct $W(a)$ (or $a^2 P(a)$ in our case) for a variety of potentials. This unexpected link allows one to obtain all other transport coefficients!

Polydisperse extensions.

In a series of papers [59], [60], and [61] J.Xu and G.Stell generalized the hard-sphere mixture revised Enskog transport coefficients to the case in which one the species (for example, the solute) becomes polydisperse. They started with the hard-sphere finite-species mixture (indexed by i) transport coefficients and formally generalized it to the case of infinite (uncountable) species mixture by replacing sums with the integrals over new random variable σ that denotes particle's diameter. They also replaced concentrations x_i by the probability $h(\sigma)d\sigma$ of finding a particle with diameter in the range σ to $\sigma + d\sigma$. Here, $h(\sigma)$ is the probability density of the random variable σ. The formulas for transport coefficients of polydisperse fluid collapse to a single-component hard-sphere fluid when $h(\sigma) = \delta(\sigma - d)$.

The following important question arises:

Is it possible to find a kinetic model, with built in conservation laws and trend to equilibrium, whose transport coefficients coincide with the transport coefficients of the above polydisperse fluids ?

2.4. **Stationary solutions and their connections to the BBGY hierarchy.**

One of most interesting features of the revised Enskog (RET) and square-well (KVTIII) kinetic equations (but **not** the Boltzmann and standard Enskog equations) is their exactness at a local equilibrium. Indeed, for $f = \omega$ with

$$\omega = \frac{n(r_1)}{(2\pi k_B T)^{3/2}} \exp\left(-\frac{v_1^2}{2k_B T}\right), \tag{2.30}$$

$T = const$, and and some external potential $F_{external} = -d\Phi/dr$, the RET and the KVTIII become

$$\frac{\partial \log n}{\partial r_1} + \frac{\partial}{\partial r_1}\left(\frac{\Phi(r_1)}{T}\right) = \int_\Omega \left(\frac{\partial f_{12}}{\partial r_1}\right) \overline{g}_2(r_1, r_2 \,|\, n)\, n(r_2)\, dr_2, \tag{2.31}$$

where

$$\begin{aligned}\overline{g}_2 =& 1 + \int_\Omega f_{13} f_{23} n(t, r_3)\, dr_3 + \cdots + \\ & \frac{1}{(k-2)!} \int_\Omega dr_3 \cdots \int_\Omega dr_k\, n(3)\, \ldots\, n(k)\, V(12 \,|\, 3 \ldots k) \cdots ,\end{aligned} \tag{2.32}$$

with $V(12\,|\,3\ldots k)$ given in (2.7) for the RET, and by (2.20)-(2.21) for the KVTIII. The Mayer functions in $V(12\,|\,3\ldots k)$ are equal to the corresponding factors in the hard-sphere and square-well systems. In particular,

$$\frac{\partial f_{12}}{\partial r_1} = \tag{2.33}$$

$$\begin{cases} \delta(|r_1 - r_2| - a^+)\hat{r}_{12}, & \text{(RET)} \\ \delta(|r_1 - r_2| - a^+)\hat{r}_{12} + \left[1 - \exp\left(\dfrac{\gamma}{k_B T}\right)\right] \delta(|r_1 - r_2| - R^+)\hat{r}_{12}, & \text{(KVTIII)}, \end{cases}$$

where $\hat{r}_{12} = (r_1 - r_2)/|r_1 - r_2|$ and Ω is a spatial domain of the fluid. The system of three equations (2.31) is the first member of the BBGY equilibrium hierarchy for the system of hard-spheres or for the square-well interaction potential. Since $\overline{g}_2$ is expressed only in terms of n (and also in terms of $T = const$ for the KVTIII), the above equations are **closed** and **exact**.

From the mathematical point of view almost nothing is known about the system (2.31). For the one-dimensional hard-sphere system (i.e., hard-rods) H.J.Ravache and C.A.Stuart [62] proved the uniqueness of solutions to (2.31) when the external potential $\Phi = 0$. It is easy to check that for $\Phi = 0$, $n = const$ is always a solution of (2.31).

The attractive part of the square-well interaction potential makes equations (2.31) particularly interesting. Indeed, these equations should describe phase transitions of the corresponding equilibrium square-well system. To check for this possibility one needs to show that, in addition to constant solutions, the BBGY hierarchy allows also for periodic (in r_1) solutions (a bifurcation problem). If true, this would provide the first kinetic description of phase transitions! An initial progress in this direction has already been reported by J. Polewczak in [23] and [63], where for some truncated cases of $\overline{g}_2$ in (2.32) and small enough $(Na^3)/vol(\Omega)$, $n = const$ is the only solutions, while for some other choices of Ω, the parameter $N/vol(\Omega)$ and the diameter a, there are also periodic solutions. Here, $N = \int_\Omega n(r_1)\, dr_1$. For the solutions obtained in [63], the following situation arises. We already know that this solution $f(t_n, r_1, v_1)$ converges (pointwise) to ω, given in

(2.30), as $t_n \to \infty$, where

$$n(r_1) = \begin{cases} \text{is constant,} & \text{for } \dfrac{N}{\mathrm{vol}(\Omega)} a^3 \text{ small;} \\ \text{is periodic,} & \text{for some choices } N,\ \mathrm{vol}(\Omega), \text{ and } a. \end{cases} \tag{2.34}$$

Suppose that we pick initial data with $N = \int_\Omega n(r_1)\,dr_1$, $\mathrm{vol}(\Omega)$, and the diameter a corresponding to the case where (2.31) has, in addition, also a periodic solution $n(r_1)$. The next question is of great interest:

Does $f(t_n, r_1, v_1)$ converge to $\omega(r_1, v_1)$ with $n(r_1) = const$, or a periodic function in r_1 ?

Since the H-theorem already did its job we must find another way to answer this question. Of course, from the physical point of view we would choose n in (2.30) with the lowest excess free energy (see, for example, [64]) How this could be translated into a mathematical argument is not yet clear.

Finally, I want to add that the stochastic models' versions (see section 2.3) of the BBGY equilibrium hierarchy have a very similar form to (2.31), except for appearance of the stochastic input functions P and P_{SW} and additional integrations with respect to a and R. The following question arises:

For what choices of P and P_{SW} can one induce or suppress the bifurcation of solutions in (2.31) ?

2.5. **Problems in the transport theory of dense fluids.** One of the most desirable features in a kinetic theory is to provide theoretical predictions of transport coefficients. This problem is intrinsically related to the study of the spectrum of the corresponding linearized kinetic equation (linearized about an absolute maxwellian). Knowledge of the spectrum of the linearized Boltzmann operator is rather complete ([65] and [66] are good reviews of the topic). In particular, [67] and [68] provide a rigorous analysis of the linearized Boltzmann equation with respect to those aspects of its behavior that are important to a hydrodynamic description of a fluid.

The works of B. Cichocki and J. Bławzdziewicz ([69] and [70]) for the linear RET, and the works of H. van Beijeren, J. A. Leegwater, and J. P.J.Michels ([71] and [8]) for the linear KVTIII, provide good physical backgrounds for the subject; at the same time a rigorous analysis of the linearized RET or KVTIII is not available at this time. I intend to work on this problem.

The linearized (about an absolute Maxwellian) revised Enskog equation has the form

$$\frac{\partial f}{\partial t} + v_1 \frac{\partial f}{\partial r_1} = L^E(f), \tag{2.35}$$

where $L^E(f)$, after taking the Fourier transform with respect to the spatial variable r_1, can be written as

$$\hat{L}^E(f) \equiv L^E_k(f) = L^B_k(f) + A_k(f). \tag{2.36}$$

For simplicity, in the right hand side of (2.36) I have suppressed the Fourier variable k (conjugate to r_1). The operator $L_k^B(f)$ is essentially the linearized Boltzmann operator corresponding to the hard–sphere potential, and $A_k(f)$ is the Enskog perturbation. In particular, $L_k^B(f)$ is a closed and nonpositive operator in the $L^2(R^3)$ space weighted by a Maxwellian and, for each k, the closed operator $A_k(f)$ is a relatively compact perturbation of $L_k^B(f)$. Hence, by a variant of Weyl's theorem, the essential spectrum of $A_k(f)$ is the same as the essential spectrum of $L_k^B(f)$. In other words, except for a finite number of eigenvalues with finite multiplicities, the study of the spectrum of $L_k^E(f)$ is reduced to the study of the spectrum of $L_k^B(f)$. It is not clear at this time whether $L_k^E(f)$ is dissipative in the scalar product of L^2 weighted by the absolute Maxwellian. Recently, M. Lachowicz ([72]) has shown that, in fact, the Boltzmann-Enskog linearized operator, corresponding to the truncation of g_2 in (2.7) to the first term only, is not necessarily dissipative in the above scalar product. Possibly, some changes in the weight of $L^2(R^3)$ are necessary to obtain a desired dissipativity of $L_k^E(f)$ for the original (un-truncated) g_2. From the physical point of view, the last property is related to the stability of the system.

It seems likely that a study of the linearized KVTIII operator, with some necessary changes, can be investigated along the lines indicated above for the revised linearized Enskog operator.

2.6. **Hydrodynamic limits.** The goal of any kinetic theory is not complete without understanding the properties of the underlying fluid. In our case, this is done by investigating the hydrodynamic level of the revised Enskog and the KVTIII equations. The fluids described by the RET and the KVTIII are **not** ideal fluids. In the case of the RET the equation of state is given in (2.6). For the KVTIII the equation of state has the form

$$\frac{p}{nk_BT} = 1 + \left(\frac{2}{3}\pi a^3 n\right) g_2(a^+) + \left(\frac{2}{3}\pi R^3 n\right)\left[1 - \exp\left(\frac{\gamma}{k_BT}\right)\right] g_2(R^+), \quad (2.37)$$

where $g_2(a^+)$ and $g_2(R^+)$ denote the contact values of the (uniform) equilibrium radial correlation function of the square-well system, evaluated at the hard core and square-well edge, respectively. Furthermore, both $g_2(a^+)$ and $g_2(R^+)$ depend on the density n and the temperature T.

Below, I present some of the ideas of how to attack the problem by considering only the Euler level for the revised Enskog equation. The Euler level for the KVTIII and the Navier-Stokes level require further adjustments and for brevity are not presented here.

First, the usual time-space scaling (hyperbolic or Euler scaling)

$$t \longmapsto \frac{t}{\delta}, \qquad x \longmapsto \frac{x}{\delta} \quad (2.38)$$

does not work here due to existence of the factors $g_2(r_1, r_1 \pm a\epsilon \,|\, n) \neq 1$ in the revised (or standard) Enskog equation. In addition, we have to deal with two small parameters $a > 0$ and $\delta > 0$:

$$\begin{array}{ll} a \to 0 & \delta \to 0 \\ \text{(diameter of hard spheres)} & \text{(mean free path, } \delta \approx 1/(na^2)\text{)}. \end{array} \tag{2.39}$$

If we recall that the Enskog theory is valid in the limit

$$a \to 0, \quad n \to \infty, \quad \text{(dense gas limit)} \quad na^3 \to const > 0, \tag{2.40}$$

then the following scaling of the revised Enskog equation might be of interest

$$f \longmapsto \frac{f}{\delta^3} \qquad \text{with} \qquad \delta \approx \left(\frac{a}{d}\right)^m, \quad m > 0, \tag{2.41}$$

where $d > 0$ is fixed. Indeed, in recent work [63], I showed (without considering the convergence question of the density expansion for g_2) an important invariance of $g_2(r_1, r_1 \pm a\epsilon \,|\, n)$ (given in (2.7)) under the scaling (2.41).

Invariance Lemma. *For smooth $n(r_1)$ and $\delta = (a/d)^m$, with $0 < m \leq 1$ and $d > 0$,*

$$\lim_{a \to 0\,,\,\delta \to 0} g_2\left(r_1, r_1 \pm a\epsilon \,|\, (1/\delta^3) n\right) = \begin{cases} 1, & 0 < m < 1; \\ g_2(d^+, n(r_1)), & m = 1; \end{cases} \tag{2.42}$$

*pointwise, where $g_2(d^+, n(r_1))$ is the pair correlation function for the system of hard spheres, in the **uniform** equilibrium, with diameter d and with density $n(r_1)$. Function $g_2(d^+, n(r_1))$ has the density expansion given in (2.5), with a replaced by d.*

Let us observe that the pair correlation function in (2.42), before the limit is taken, is the contact value of the **non-uniform** equilibrium pair correlation of the hard-sphere system that appears in the revised Enskog collision operator (2.9)-(2.10). Under the scaling (2.41), and in the hydrodynamic limit with $m = 1$, g_2 is being transformed into the uniform equilibrium object. This property yields the expected Euler level hydrodynamics with the equation of state of the underlying fluid given by (2.6). On the other hand, when $0 < m < 1$, g_2 collapses to the dilute-gas limit value 1, and thus, the corresponding fluid becomes an ideal fluid. This important interplay between two small parameters a and δ is at the center of the hydrodynamic limit in the RET. Indeed, in addition to the excluded volume of hard spheres taken into account, the RET, in contrast to the Boltzmann equation, does not ignore the difference in position between colliding particles. Therefore, collisional transfers of momentum and energy from the center of one colliding sphere to the other are taken into account. (Thus the differences in the transfer equations between the revised Enskog and the Boltzmann equations). These transfers take place over distances proportional to a, the diameter of hard spheres. This is to be contrasted with the convective transport over a distance of order δ (the mean free path between collisions). As a consequence, the convective transport dominates at low densities, where $\delta/a \gg 1$ (or $0 < m < 1$). On the other hand, at high densities $\delta/a \leq 1$, and the collisional transfer dominates the transport. Since the mean free path $\delta \approx 1/(na^2)$, the case of $m = 1$, i.e.,

$\delta \approx a$, corresponds to $na^3 \approx 1$. This is in a complete agreement with the scaling $f \longmapsto f/\delta^3$ as well as the dense gas limit (2.40).

The hydrodynamic limits for the stochastic models, considered in section 2.3, are particularly interesting from the point of view of the control the equation of state, the internal energy, and specific heats of the underlying fluids in terms of the stochastic inputs P and P_{SW}. For example, in the case of the stochastic RET (2.24)-(2.26) (with $\alpha = 0$ and $\beta = \sigma > 0$), it was shown [52] that under the scaling (2.41), and with a replaced by σ, the corresponding equation of state in the hydrodynamic limit has the form

$$\frac{p}{nk_BT} = 1 + \sum_{k=1}^{\infty} C_k B_{k+1} n^k, \tag{2.43}$$

where B_k are the virial coefficients for the hard sphere system of diameter d (see (2.6)) and C_k are just the moments of the limiting function $\lim_{\sigma \to 0} \sigma P(\sigma x)$.

Although the formal hydrodynamic limit for the Enskog equation has been known for many years, the approach based on the above Invariance Lemma does not invoke any approximation or truncation that are usually performed while using the Hilbert or Chapman-Enskog methods. The above approach, with some modifications, is expected to work for the KVTIII and other dense kinetic theories.

There has been important progress ([73], [74], [75]) in a rigorous passage to hydrodynamics starting from the Boltzmann equation. The recent work [13] (with extensive references) provides a source of various tools used in the case of the Boltzmann equation. One would like to hope that these ideas can be applied successfully to the RET and the KVTIII. M. Lachowicz in [76] and [77] has studied some variants of the standard Enskog equations (albeit with not physical Y_0) or the Boltzmann-Enskog equations [78]. In contrast to the work in [74] for the Boltzmann equation, M. Lachowicz presents convergence for times comparable to the mean time between collisions. It seems likely that in order to make a substantial progress in this direction for the full revised Enskog equation (with g_2 given in (2.7)) and the KVTIII one needs the convergence of the Mayer cluster expansion in (2.7) and additional (spectral) properties of the linearized Enskog and KVTIII operators (see section 2.5).

3. Reactive kinetic theories

A general nature of the methods described in sections 2.1–2.6 makes it possible to investigate important aspects of the kinetics of chemically reacting fluids within the framework I have already discussed. The starting point is the work done by a number of researchers in the late 1970's and early 1980's [79], [80], [81], and [82]. Reports on the progress in this and other directions can be found in [83], [84] and [85].

I consider the model in which molecules behave as if they were single mass points with two (or more) 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 collisional events are considered to be hard–spheres like. I start by considering a four component mixture A, B, A^*, B^*, and the chemical reaction of the type

$$A + B \rightleftharpoons A^* + B^*. \tag{3.1}$$

Here, A^* and B^* are distinct species from A and B, and I use the indices 1, 2, 3, and 4 for the particles A, B, A^*, and B^* respectively. 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 case of elastic encounters between a pair of particles from species i and s, the initial velocities v, w take post–collisional values

$$v' = v - 2\frac{\mu_{is}}{m_i}\epsilon\langle\epsilon, v - w\rangle, \quad w' = w + 2\frac{\mu_{is}}{m_s}\epsilon\langle\epsilon, v - w\rangle. \tag{3.2}$$

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., $\epsilon \in \mathbb{S}^2_+ = \{\epsilon \in \mathbb{R}^3 : |\epsilon| = 1, \langle\epsilon, v - w\rangle \geq 0\}$. Also, $\mu_{is} = \frac{m_i m_s}{m_i + m_s}$ 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. The conservation of mass requires that $m_1 + m_2 = m_3 + m_4$.

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

$$\frac{1}{2}\mu_{is}\big(\langle\epsilon, v - w\rangle\big)^2 \geq \gamma_i, \tag{3.3}$$

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

$$v^\ddagger = v - \frac{\mu_{12}}{m_1}\epsilon\Big[\langle\epsilon, v - w\rangle - \alpha^-\Big], \quad w^\ddagger = w + \frac{\mu_{12}}{m_2}\epsilon\Big[\langle\epsilon, v - w\rangle - \alpha^-\Big], \tag{3.4}$$

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

$$E_{abs} = E_3 + E_4 - E_1 - E_2 > 0, \tag{3.5}$$

where $E_i > 0$, $i = 1, \ldots 4$, 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 reaction, $A^* + B^* \to A + B$, the post–reactive velocities are given by

$$v^\dagger = v - \frac{\mu_{34}}{m_3}\epsilon\Big[\langle\epsilon, v - w\rangle - \alpha^+\Big], \quad w^\dagger = w + \frac{\mu_{34}}{m_4}\epsilon\Big[\langle\epsilon, v - w\rangle - \alpha^+\Big], \tag{3.6}$$

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

The pairs of velocities in (3.4) and (3.6) satisfy conservation of the momentum

$$\begin{aligned} m_1 v + m_2 w &= m_1 v^{\ddagger} + m_2 w^{\ddagger} = m_3 v^{\ddagger} + m_4 w^{\ddagger}, \\ m_3 v + m_4 w &= m_3 v^{\dagger} + m_4 w^{\dagger} = m_1 v^{\dagger} + m_2 w^{\dagger}; \end{aligned} \tag{3.7}$$

they do not, however, obey conservation of the kinetic energy. A part of kinetic energy is exchanged with the energy absorbed by the internal states. The following equalities hold:

$$\begin{aligned} m_1 v^2 + m_2 w^2 &= m_1 v^{\ddagger 2} + m_2 w^{\ddagger 2} + 2E_{abs} = m_3 v^{\ddagger 2} + m_4 w^{\ddagger 2} + 2E_{abs}, \\ m_3 v^2 + m_4 w^2 &= m_3 v^{\dagger 2} + m_4 w^{\dagger 2} - 2E_{abs} = m_1 v^{\dagger 2} + m_2 w^{\dagger 2} - 2E_{abs}. \end{aligned} \tag{3.8}$$

Now, for each i $(i = 1, \ldots, 4)$, let $f_i(t, x, v)$ denote the one-particle distribution function of the ith component of the reactive mixture. The function $f_i(t, x, v)$, which changes in time due to free streaming and collisions (both elastic and reactive), represents, at time t, the number density of particles at point x with velocity v.

The corresponding kinetic system can be expressed as follows

$$\frac{\partial f_i}{\partial t} + v \frac{\partial f_i}{\partial x} = J_i^E + J_i^R, \tag{3.9}$$

with

$$\begin{aligned} J_i^E = &\sum_{s=1}^{4} \Big\{ \sigma_{is}^2 \iint\limits_{\mathbb{R}^3 \times \mathbb{S}^2} \Big[f_{is}^{(2)}(t, x, v', x - \sigma_{is}\epsilon, w') - f_{is}^{(2)}(t, x, v, x + \sigma_{is}\epsilon, w) \Big] \times \\ &\Theta\left(\langle \epsilon, v - w\rangle\right) \langle \epsilon, v - w\rangle \, d\epsilon dw \Big\} \\ &- \beta_{ij}\sigma_{ij}^2 \iint\limits_{\mathbb{R}^3 \times \mathbb{S}^2} \Big[f_{ij}^{(2)}(t, x, v', x - \sigma_{ij}\epsilon, w') - f_{ij}^{(2)}(t, x, v, x + \sigma_{ij}\epsilon, w) \Big] \times \\ &\Theta\left(\langle \epsilon, v - w\rangle - \Gamma_{ij}\right) \langle \epsilon, v - w\rangle \, d\epsilon dw, \end{aligned} \tag{3.10}$$

and

$$\begin{aligned} J_i^R = \beta_{ij}\sigma_{ij}^2 &\iint\limits_{\mathbb{R}^3 \times \mathbb{S}^2} \Big[f_{kl}^{(2)}(t, x, v_{ij}^{\odot}, x - \sigma_{ij}\epsilon, w_{ij}^{\odot}) - f_{ij}^{(2)}(t, x, v, x + \sigma_{ij}\epsilon, w) \Big] \times \\ &\Theta\left(\langle \epsilon, v - w\rangle - \Gamma_{ij}\right) \langle \epsilon, v - w\rangle \, d\epsilon dw. \end{aligned} \tag{3.11}$$

Here, the function $f_{is}^{(2)}$ approximates the density of pairs of particles in collisional configurations, $0 \le \beta_{ij} < 1$ is the steric factor for reactive collisions between species i and j, $\Gamma_{ij} = \sqrt{2\gamma_i/\mu_{ij}}$, and Θ is the Heaviside step function. The prime velocities in (3.10) are given in (3.2). The pair of velocities $(v_i^{\odot}, v_j^{\odot})$ refers to post-reactive velocities described either in (3.4) or (3.6), 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, the index pairs (i,j) and (k,l) appearing in (3.10)-(3.11) are associated with the set of indices (i,j,k,l) specified below

$$(1,2,3,4), \quad (2,1,4,3), \quad (3,4,1,2), \quad (4,3,2,1). \tag{3.12}$$

The first term of (3.10) is a hard-spheres collision operator with the usual pre-collisional range of integration, while the second term of (3.10) singles out those pre-collisional states that are energetic enough to result in reaction. The collision operator in (3.11) is purely reactive.

When the steric factors $\beta_{ij}=0$, i.e., there are no reactive collisions. That is how one can *turn on* $(\beta_{ij}>0)$ or *turn off* $(\beta_{ij}=0)$ chemical reactions in the model in order to do the consistency checks mentioned in the Introduction.

Furthermore, when $\beta_{ij}=0$ and $f_{is}^{(2)}$ is the exact two–particle distribution function, system (3.9)–(3.11) becomes the exact first BBGKY hierarchy system for a four component hard–spheres mixture. As in the kinetic theory of non-reactive mixtures, different ways in which one approximates the two–particle distribution function $f_{ij}^{(2)}$ give rise, in the present case, to different **reactive** kinetic models. For our purpose it is convenient to write $f_{ij}^{(2)}$ in form of the closure relation

$$f_{ij}^{(2)}(t,x,v,y,w) = Y_{ij}\left(t,x,v,y,w \,|\, \{\Lambda_i f_i\}\right) f_i(t,x,v) f_j(t,y,w), \tag{3.13}$$

where Y_{ij} is assumed to be given, for each i and j and for each fixed $t \geq 0$, $\Lambda = (\Lambda_1, \Lambda_2, \Lambda_3, \Lambda_4)$ is an (possibly nonlinear) operator acting on (f_1, f_2, f_3, f_4), typically through one or more velocity moments, In [21] various forms of Λ and the resulting kinetic equations were considered. It seems that a reasonable choice of Y_{ij} is to take $Y_{ij} = Yij^{RET}$ as in the case of the revised Enskog system for non-reactive mixtures (see, [27] and [38]) Let us recall that it has the form

$$Y_{ij}^{RET} = g_{ij}^{(2)}\left(x_1, x_2 \,|\, \{n_i(t,\cdot)\}\right), \tag{3.14}$$

where $n_i(t,x) = \int_{\mathbb{R}^3} f_i(t,x,v)dv$ is the local number density of the component i and $g_{ij}^{(2)}$ is the pair correlation function for a **non-uniform** system at equilibrium with the local densities $n_i(t,x)$. The notation $g_{ij}^{(2)}(x_1, x_2 \,|\, \{n_i(t,\cdot)\})$ indicates that $g_{ij}^{(2)}$ is a functional of the local densities n_i. With the choice of Y_{ij} from (3.14), the reactive model, being a natural extension of the hard–sphere collisional model, reduces itself to the Enskog theory when the chemical reactions are *turned off*. Here again, one can see the importance of good understanding of inert dense cases in constructing the reactive models.

The ideas found in [86], especially the notion of the pseudo-Liouville equation for the reacting spheres, should make it possible to derive an analog of the BBGKY hierarchy for chemically reacting hard-spheres. This is the first step in obtaining an analog of the RET for the reacting hard-spheres. Finally, the progress in this direction should also help obtaining a KVTIII analog of the reacting kinetic theory.

The simplest cases of detonation/combustion regimes for the above model occur when the activation energies γ_1, γ_2 and the absorbed energy E_{abs} of the reaction are sufficiently large. This leads to well known (from inert fluids) problems of shock waves that should be treated on both the kinetic and hydrodynamic levels.

I want to point out that the following problems encountered in the study of inert fluids

- polydisperse extension (section 2.3),
- phase transition (section 2.4),
- transport coefficients (section 2.5),
- hydrodynamic limit (section 2.6),

can now be easily formulated for the reactive models. As before, good understanding of the inert models allows one to consider more interesting and challenging chemically reactive fluids. The case of hydrodynamic limit is of particular interest. Indeed, there are many phenomenological (macroscopic) models, often described in terms of the corresponding conservation equations (analogs of the Euler and Navier-Stokes equations), that deserve the microscopic confirmation (see, for example, [2], [95], or [96]). Furtheremore, as in the case of inert fluid, reactive kinetic modeling provides almost explicit formulas for transport coefficients. If they are found in agreement with available experimental values, these formulas can be used to further predict transport coefficients for difficult to measure regimes or for special mixtures.

I end with a review of relevant literature in the kinetic theories of chemically reacting fluids. Recently some progress has been made in treating reacting dilute gases, both from the mathematical and physical points of view. In a series of papers C. P. Grünfeld and E. Georgescu ([87], [88], and [89]) 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 in [90], [91] and [92] formally analyze various kinetic theories of chemically reacting gases, including gas-photon interactions. They show existence of an H-function and describe possible equilibrium solutions. R. Monaco, J. Polewczak, and A. Rossani in [93] and [94] provide stability analysis of some time-dependent and stationary gas–photon interactions. Finally, in [24], I analyze a simple reacting spheres model in the dilute-gas limit.

In all the works cited above the authors use either Boltzmann-type equations or the original standard Enskog theory. The replacement of the original SET, used in [81] and [82], by the RET should make the models more viable from the physical and mathematical point of views. An initial progress in this direction has been reported in [97].

Finally, two additional reacting models deserve further attention. The first is the work of J. A. McLennan [98], in which a three–body collision term has been included in the Boltzmann equation describing a dissociation/recombination model of a chemically reacting fluid. An analog of the H–function obtained in [83] will make it possible to prove an existence theorem for this rather special case of a kinetic equation with the three–body term explicitly included.

The second model is the Larsen-Borgnakke model [99] of inelastic collisions with the total energy split between the translational and internal modes. The authors in [100] and [101] showed the existence of an H-function and the possibility of obtaining the internal energy of the underlying fluid as an arbitrary function of the temperature. Larsen-Borgnakke model combined with the stochastic model (2.24)-(2.26), in which the pressure is well controlled, could result in a simple kinetic model where both the internal energy and the equation of state are fully controllable through the input functions characterizing the model.

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