First principle basis of the direct numerical simulation for turbulence of inert and reactive gases

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Abstract. An open question of whether phenomenological fluid equations to be used for direct numerical simulation of turbulence are warranted on ‘first principles’ is addressed, and the problem is posed using Klimontovich microscopic density to replace the Boltzmann function of the classical statistical mechanics. For inert monatomic gases, it is shown that all the gasdynamic equations, namely, the three conservation equations plus the Navier-Stokes stress law and the Fourier heat conduction law are retrieved as governing instantaneous quantities, without having recourse to any concepts of averaging or statistical equilibrium. For reactive gases, however, the Arrhenius reaction rate law written in terms of the fluctuating temperature is not justified, reflecting the fact that this rate law hinges crucially on these concepts.

1. Introduction

Molecular approach to macroscopic behavior of gases by means of the kinetic theory or nonequilibrium statistical mechanics has provided firmer basis for variety of fields of phenomenologies.

Most important contributions among them include;

i) derivation of the Navier-Stokes equation from Boltzmann’s equation [1] [2].

ii) proof that the classical ‘equilibrium’ thermodynamics remains exact to the first order in translational nonequilibrium, namely that it has the same region of validity as the Navier-Stokes equation, not the inviscid Euler equation [3], and

iii) Arrhenius’ rate law derived from the Boltzmann equation for simple classical molecules executing reactive collisions, where the activation energy is expressed by

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parameters of particle mechanics, namely, reduced mass and the threshold potential for inelastic collisions [4].

Hence, those widely used tools of phenomenologies are warranted on ‘first principles’.

If the flow is turbulent, however, it is not obvious that those equations remain valid for instantaneous flow quantities that are both stochastic and fractal [5]. In fact, as the matter of definition, the Boltzmann function is the mean number density in the six-dimensional phase(μ-)space, so is subject to statistical averaging. Therefore, the fluid velocity defined through a moment integral of the Boltzmann function may not resolve small eddies or fractal behavior.

Therefore, if the ‘first-principle’ ground of the Navier-Stokes equation to be used for the direct numerical simulation (DNS) is asked, we have to address to unaveraged Boltzmann function and to its governing equation that is free from statistical concept. Needs for the approach along this line reflect the observation that if we leave the binary (long range) correlation in the Boltzmann equation, the Chapman-Enskog procedure applied to this equation leads not to the ‘raw’ Navier-Stokes equation, but to Reynolds averaged one [3].

Such a function known as the microscopic density is advocated by Klimontovich in connection with plasma kinetic theory [7]. It represents exact number density in the μ-space, a deterministic function by nature.

The equation governing the microscopic density for a neutral ideal gas is derived in [8]. It is formulated as an equation of continuity in the μ-space, happens to be identical in form with Boltzmann’s equation with different implications. In what follows this equation will be called master Boltzmann equation (MBE). Molecular background for the fluid equations to be used for DNS should be a fluid version of the MBE.

The objective of this paper is to show how these fluid equations are derived on first principles of molecular dynamics for monatomic inert molecules, then how the situation differs crucially for reactive molecules.

2. A formalism on the microscopic density and the master Boltzmann equation

Let the microscopic density be defined by the following expression after Klimontovich [8]

\[ f(z, t) \equiv \sum_{1 \leq s \leq N} \delta(z - z^{(s)}(t)) \] (1)

where \( z \equiv (x, v) \) is a point in the μ-space, namely, a 6 dimensional space consisting of the physical- plus molecular-velocity spaces, \( z^{(s)}(t) \) is locus of the \( s \)-th molecule in this space, \( \delta \) denotes the 6-D delta function and the summation spans over total number of molecules \( N \) under consideration. If \( z^{(s)}(t) \) is given as the solution of Hamiltonian
mechanics of N-body system, formula (1) provides the most accurate expression for the instantaneous number density in the \( \mu \)-space.

According to this ‘Klimontovich formalism’ number density in the physical space is given by

\[
\mathcal{n}(x, t) \equiv \int f(z, t) dv = \sum_{1 \leq s \leq N} \delta(x - x^{(s)}(t)) \tag{2}
\]

In the same way fluid velocity \( \mathbf{u}(x, t) \) is defined by

\[
\mathcal{u}(x, t) \equiv \int \mathbf{v} f(z, t) dv = \sum_{1 \leq s \leq N} \mathbf{v}^{(s)}(t) \delta(x - x^{(s)}(t)) \tag{3}
\]

These expressions are to be compared with those of the Boltzmann formalism of the classical kinetic theory of gases:

\[
n = \int f dv \tag{4}
\]

\[
\mathcal{u} = \int \mathbf{v} f dv \tag{5}
\]

where \( f \) is the Boltzmann function defined by

\[
f = \bar{\tilde{f}} \tag{6}
\]

In this equation overbar(\( \bar{\quad} \)) denotes the standard ‘average’, namely ensemble average over repeated experiments, or equivalently, an average of hotwire output over a time long enough to smooth out fractals, yet short enough to resolve macroscopic unsteadiness such as periodic shedding of Kármán vortices.

We note that there are three different levels of description of the fluid velocity: Obviously expression (3) is the most exact one thinkable if \( [x^{(s)}(t), \mathbf{v}^{(s)}(t)] \) are solved from Hamiltonian mechanics of the N-particle system. Therefore it is a deterministic quantity even if the flow is turbulent.

This quantity, however, does not correspond to the fluid velocity as observed by macroscopic measurements such as hotwire anemometry. Such velocity is represented by the one in which the microscopic density \( \mathcal{f} \) is replaced with its spacial average

\[
\tilde{f} \equiv \frac{1}{\Delta X} \int_{\Delta X} dx f \tag{7}
\]

where the integration is taken over a small, yet macroscopic volume \( \Delta X = \Delta x_1 \Delta x_2 \Delta x_3 \) such that

\[
n \Delta X \gg 1 \tag{8}
\]
This is where stochastic facet of turbulence makes its appearance, therefore turbulent fluid velocity defined in terms of $\tilde{f}$ shows both stochastic and fractal behavior.

The third level of description of fluid velocity is expression (5) that is defined by the Boltzmann function, where the average is taken over a long time or a large number of repeated experiments so that both stochastic and fractal features are averaged out. The third level is what is called Reynolds-average formalism or the Boltzmann formalism, and will not be discussed here.

It is shown that equation for $f$ of the first level of description has been derived as the equation of continuity in the $\mu$-space. For the usual monatomic gases it is given in the form of Boltzmann’s equation without invoking any statistical concept [8]

$$B(f) \equiv (\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}})f - J[f,f] = 0$$

(9)

with $J$ denoting the classical Boltzmann collision integral defined by

$$J[f,f] = \int [(f(z')f(z') - f(z)f(\hat{z}))_{\mathbf{x} = \hat{\mathbf{x}}} d\hat{\mathbf{x}} d\hat{\mathbf{v}}$$

(10)

where the prime (′) denotes a phase-space point of a particle that is supposed to reach the unprimed point after collision, and integration $\int d\hat{\mathbf{x}}$ spans over the physical space of particle $\hat{z}$ supposed to collide within unit of time.

The master-Boltzmann equation (MBE), namely, Eq. (9) for the microscopic density, serves the most precise description of collective behavior of the ensemble of the $N$-particle system. It can describe thermal agitations that are not tangible to macroscopic sensors. See ref. [8] for derivation of the Landau-Lifshitz stress/heat flux density fluctuation formulae with even finer temporal resolvability than the original derivation [9].

It should be stressed that MBE holds for $f$, not for $\tilde{f}$ unless

$$\tilde{\tilde{f}} = \tilde{f}$$

a condition that lacks immediate justification is met.

3. Conservation equations as fluid moments of the master Boltzmann equation

Here we address to equations governing instantaneous fluid quantities by taking fluid moments of the MBE. A parallelism to the classical procedure by Chapman-Enskog or Grad [10] prevails also here except that the microscopic density replaces the Boltzmann function, namely that exact delta function representation replaces Hermite polynomial expansion around the Maxwellian distribution.
General expression for the moment equations of the MBE (9) takes the usual form as follows,

\[
\frac{\partial}{\partial t} \int M \, dv + \frac{\partial}{\partial x_r} \int v_r M \, dv = I(M)
\]

with

\[
I(M) \equiv \frac{1}{2} \int \langle \hat{\mathbf{x}} \, d\mathbf{x} \, d\mathbf{\hat{v}} \rangle \quad [\langle \mathbf{M} \rangle \equiv M' + \hat{M}' - M - \hat{M}]
\]

where \( M \) stands for one of the following 13 moment functions;

\[
m, mv_j, \frac{m}{2} v_k^2, m(w_j w_l - \frac{1}{3} \delta_{jl} w_k^2), \frac{m}{2} w_k^2 w_j \quad (m; \text{mass of a molecule})
\]

with

\[
w_j \equiv v_j - u_j
\]

For the first three \( M \)'s that are summational invariants, \( I(M) \) is shown to vanish, and three conservation equations, same in form with the classical theory, result;

\[
\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_j)}{\partial x_j} = 0 \quad (14)
\]

\[
\frac{\partial}{\partial t} \left( \rho u_j \right) + \frac{\partial}{\partial x_r} \left( \rho u_j u_r + \delta_{jr} P + p_j r \right) = 0 \quad (15)
\]

\[
\frac{\partial}{\partial t} \left[ \rho \left( e + \frac{u^2}{2} \right) \right] + \frac{\partial}{\partial x_r} \left[ \rho u_r (h + \frac{u^2}{2}) + q_r + u_r p_{kr} \right] = 0 \quad (16)
\]

Fluid quantities to appear in these equations differ from those of Chapman-Enskog theory in that there are no statistical concepts intervening. (See, for instance, Eqs. (2) and (3), in contrast with (4) and (5).) For the rest of quantities the following definitions are employed;

\[
p \equiv \frac{m}{3} \int w_r^2 f \, dv \equiv \frac{m}{3} \sum_{1 \leq s \leq N} \left( v_r^{(s)} - u_r \right)^2 \delta(x - x^{(s)}(t)) \quad (17)
\]

\[
\frac{3}{2} kT \equiv \frac{1}{n} \int \frac{m}{2} w_r^2 f \, dv = \frac{3}{2} \frac{p}{m} \quad (k; \text{Boltzmann’s constant})
\]

\[
e = \frac{3}{2} \frac{k}{m} T
\]

\[
h = \frac{5}{2} \frac{k}{m} T
\]

\[
p_{jl} \equiv m \int w_j w_l f \, dv - \frac{\delta_{jl}}{3} P
\]

\[
= m \sum_{1 \leq s \leq N} \left[ (v_j^{(s)} - u_j)(v_l^{(s)} - u_l) - \frac{\delta_{jl}}{3} (v_k^{(s)} - u_k^{(s)})^2 \right] \delta(x - x^{(s)}) \quad (19)
\]
\[ q_j \equiv \frac{m}{2} \int w_j^2 w_j f d\mathbf{v} = \frac{m}{2} \sum_{1 \leq s \leq N} (v^{(s)}_j - \bar{u}_j)^2 (v^{(s)}_j - \bar{u}_j) \delta(\mathbf{x} - \mathbf{x}^{(s)}) \] (20)

where \( p, e, T, p_{jl} \) and \( q_j \) denote, respectively, pressure, specific internal energy and enthalpy, temperature, viscous stress tensor, and heat flux density. All of these quantities correspond to those to be computed from DNS with finest (the first) level of resolvability, much finer than those detected by any macroscopic measurements that belong to the second level of description.

4. Transport relationships for viscous stress and heat flux density

Conservation equations (14) through (16) are not closed; two more relationships that give \( p_{jl} \) and \( q_j \) in terms of other quantities are needed. Eq. (11) for

\[ M; m(w_j w_l - \frac{1}{3} \delta_{jl} w_k^2), \frac{m}{2} w_k^2 w_j \]

will provide such relationships.

For this purpose somewhat tedious calculations of

\[ I_{jl} \equiv I[m(w_j w_l - \frac{1}{3} \delta_{jl} w_k^2)] \] (21)

\[ I_{j} \equiv I[\frac{m}{2} w_k^2 w_j] \] (22)

will be carried out. Substituting (11) into (11) we have

\[ I(M) = \frac{1}{2} \int [[M]] \sum_{s, \hat{s}} \delta(\mathbf{x} - \mathbf{x}^{(s)}) \delta(\hat{x} - \mathbf{x}^{(\hat{s})}) \delta(\mathbf{v} - \mathbf{v}^{(s)}) \delta(\hat{v} - \mathbf{v}^{(\hat{s})}) d\hat{x} d\mathbf{v} d\hat{v} d\mathbf{v} \] (23)

It is more convenient to transform velocity variables to relative and center-of-gravity ones as

\[ \mathbf{V} = \hat{v} - \mathbf{v}, \quad U = \frac{1}{2}(\mathbf{v} + \hat{v}) \]

\[ \frac{\partial(U, \mathbf{V})}{\partial(\mathbf{v}, \hat{v})} = 1 \] (24)

Note also that

\[ \int d\hat{x} = \int V d\Omega \] (25)

where \( d\Omega = d\Omega(s, \hat{s}) \) is the differential cross-section for a molecular encounter of a pair of particles \( (s, \hat{s}) \) such that

\[ V d\Omega = V bdbde = B(V, \theta) d\theta de \] (26)
with $b, \epsilon$ and $\theta$ denoting impact parameter, azimuthal angle, and bisect angle in the physical space between approaching and leaving asymptote loci of $\hat{s}$ relative to $s$. For ‘hard’ repulsive intermolecular force $F = aR^{-n} (n \geq 3)$, elementary calculation of two-body mechanics gives

$$B(\theta, V) = \left( \frac{2a}{m} \right)^{\frac{2}{n-1}} V^{\frac{n-3}{2}} \beta d\beta \frac{d\theta}{\theta}$$

(27)

where $\beta$ is a scaled impact parameter

$$\beta \equiv \left( \frac{m}{2a} \right)^{\frac{2}{n-1}} V^{\frac{2}{n-1}} b$$

introduced to eliminate $V$-dependence of $\theta(\beta)$;

$$\theta(\beta) = \int_0^{\tau_0} \frac{d\tau}{[1 - \tau^2 - \frac{2}{n-1}(\beta \tau)^{n-1}]}$$

$$1 - \tau_0^2 - \frac{2}{n-1}(\tau_0 \beta)^{n-1} = 0$$

(28)

In what follows, unless stated otherwise, we will employ Maxwellian molecules ($n = 5$). This is the particular case in which $B(\theta, V)$ is independent of $V$, yet representing a realistic model for usual neutral gas molecules. (See for example ref.[10].)

With this specification for the molecular property, calculation of $I(M)$ proceeds as follows:

$$I(M) = \int B d\theta d\epsilon \sum_{s, \hat{s}} \delta(x - x^{(s)}) \delta(x - x^{(\hat{s})})$$

$$\times \int \frac{1}{2} [[M]] \delta(U - \frac{w^{(s)} + w^{(\hat{s})}}{2}) \delta(V - w^{(s)} + w^{(\hat{s})}) dU dV$$

$$= \sum_{s, \hat{s}} \delta(x - x^{(s)}) \delta(x - x^{(\hat{s})}) \int_0^{2\pi} d\epsilon \int_0^{\pi/2} d\theta B(\theta)$$

$$\times K(\frac{w^{(s)} + w^{(\hat{s})}}{2}, w^{(s)} - w^{(\hat{s})}, \theta, \epsilon)$$

(29)

where we have defined

$$K(U, V, \theta, \epsilon) \equiv \frac{1}{2} [[M]]$$

(30)

The actual forms of $K$ together with the integrals above for $M = mw_j w_l$ and $mw_j \frac{w^2}{2}$ have been given by Grad [10], yielding

$$\int K(U, V, \theta, \epsilon) B(\theta) d\theta d\epsilon = \begin{cases} -3mB_1(V_j V_l - \frac{\delta_{jl} V^2}{3}) \\ \frac{3}{2} mB_1(V_j V_k U_k - \frac{V^2}{3} U_j) \end{cases}$$

(31)

respectively, where $B_1$ is a constant defined by the following integral

$$B_1 = \pi \int_0^{\pi/2} B(\theta) \sin^2 \theta \cos^2 \theta d\theta$$

(32)
Eq. (31) substituted into (29) with \((U, V)\) replaced by \((\frac{1}{2}(w^{(s)} + w^{(s)}), w^{(s)} - w^{(s)})\) leads to

\[
I_{jl} = -3mB_1 \sum_{s,s'} \delta(x - x^{(s)}) \delta(x - x^{(s')}) \\
\times [(w^{(s)}_j - w^{(s)}_j)(w^{(s')}_i - w^{(s')}_i) - \frac{\delta_{jl}}{3}(w^{(s)}_k - w^{(s')}_k)^2]
\]

\[
= -3mB_1 \sum_s \delta(x - x^{(s)}) \sum_{s'} \delta(x - x^{(s')})(w^{(s)}_j w^{(s')}_i - \frac{\delta_{jl}}{3} w^{(s)}_k^2)
\]

\[
+ \sum_{s'} \delta(x - x^{(s')}) \sum_s \delta(x - x^{(s)})(w^{(s)}_j w^{(s')}_i) - \frac{2}{3} \delta_{jl}(w^{(s)}_k)^2)
\]

\[
+ \frac{2}{3} \delta_{jl} \sum_s \delta(x - x^{(s)}) w^{(s)}_k \sum_{s'} \delta(x - x^{(s')}) w^{(s')}_k]
\]

\[
= -6B_1 w_{jl}
\]

(33)

\[
I_j = -2mB_1 \sum_{s,s'} \delta(x - x^{(s)}) \delta(x - x^{(s')})[\frac{1}{2}(w^{(s)}_j w^{(s')}_k + w^{(s')}_j w^{(s)}_k)]
\]

\[
- (w^{(s')}_j w^{(s)}_k)^2 + w^{(s')}_j w^{(s)}_k + \frac{1}{2}(w^{(s)}_k w^{(s')}_j w^{(s)}_k + w^{(s)}_k w^{(s)}_k w^{(s)}_k)]
\]

\[
= -4B_1 n_{jl}
\]

(34)

where definitions (33) for \(w_j\) and (19), (20) for \(p_{jl}\) and \(q_j\), respectively, have been made use of. Lines of lengthy deduction of algebra have been suppressed in deriving (34).

The lefthand side of the moment equation (11) for the stress tensor and the heat flux density are calculated using only fluid quantities as defined here, namely, those with no statistical average involved, yet leading to the same expression as the 13-moment method (Eq. (17), (18)) as;

\[
p \left( \frac{\partial u_j}{\partial x_l} + \frac{\partial u_l}{\partial x_j} - \frac{2}{3} \delta_{jl} \frac{\partial u_k}{\partial x_k} \right) + O(p_{jl}, q_j)
\]

(35)

and

\[
\frac{5}{2} \frac{k}{m} \frac{\partial T}{\partial x_i} + O(q_i, p_{il})
\]

(36)

respectively. Equating expressions (33) and (35) we have

\[
p_{jl} = -\mu \left( \frac{\partial u_j}{\partial x_l} + \frac{\partial u_l}{\partial x_j} - \frac{2}{3} \delta_{jl} \frac{\partial u_k}{\partial x_k} \right)
\]

with

\[
\mu = \frac{kT}{6B_1} \text{ (viscosity coefficient)}
\]

(37)
likewise, from (34) and (36)

\[ q_{j} = -\lambda \frac{\partial T}{\partial x_{j}} \]

with

\[ \lambda = \frac{5(k/m)}{8B_{1}} kT \]  

(heat conductivity coefficient)

both exact to the first order smallness of \( p_{jl} \) and \( q_{j} \).

Formulae (37) and (38) are nothing but the Navier-Stokes and the Fourier laws for fluctuating fluid quantities and viscosity/heat conductivity coefficients that also fluctuate with temperature.

It is rather surprising that these transport relationships that have been derived originally as the first-order deviation from the equilibrium (Maxwellian) distribution prove to be correct even without any statistical concept. In fact, formulae (37) and (38) are written in terms of collective coordinates of N-particle Hamiltonian mechanics alone. Their validity is subject to the only assumption that both \( p_{jl} \) and \( q_{j} \) are of the first order smallness compared with those quantities representing first terms of (35) and (36), respectively.

All the quantities on the r.h.s. of (37) and (38) correspond to hotwire or thermocouple outputs that are stochastic and fractal. Seeming difficulty of partial differential representations of such fractal (therefore not differentiable) quantities are remedied by the experimental evidence that the fractal structure does not persist to infinitesimal region, but ceases to operate at Kolmogorov length [11]. Real difficulties arise when the differentials are replaced with finite differences for computational purposes, in which case a step size be chosen smaller than the Kolmogorov length (the high Reynolds number difficulty).

5. **Chemical reaction rate**

Chemical reactions of the following type

\[ A + B \rightarrow C + D \]

that are caused by inelastic binary collisions have reaction rates obeying Arrhenius’ low

\[ W \sim e^{-E/RT} \]  

(39)

Present [4] has derived this rate law using a simple collision model, where the activation energy \( E \) is expressed in terms of molecular parameters, namely, threshold potential \( \epsilon \) for inelastic collisions and reduced mass \( m_{AB} \) as

\[ E = \frac{\epsilon}{2m_{AB}} \]  

(40)
It is an open question that how the rate law (39) is modified if microscopic density is used instead of the Maxwellian distribution in calculating the reaction rate;

\[ W = \int_{\text{inel.}} f_A f_B d\mathbf{v}_A d\mathbf{v}_B V d\Omega_{AB} \]  

(41)

First we note that the following relationship holds independently of the intermolecular force law

\[ \int_{\text{inel.}} d\Omega_{AB} = \int_0^{2\pi} d\epsilon \int_0^{b^\dagger} b db = \pi b^{\dagger 2} \]  

(42)

where \( b^\dagger \) denotes the maximum impact parameter for a reactive collision to occur. The value of \( b^\dagger \) can be obtained from the conservation laws of angular momentum and energy of two-body mechanics,

\[
\begin{align*}
R^2 \dot{\theta} &= bV : \text{const} \\
\left( \frac{m_{AB}}{2} \right) (R^2 + R^2 \dot{\theta}^2) + \Omega(R) &= \left( \frac{m_{AB}}{2} \right) V^2 : \text{const}
\end{align*}
\]

where \((R(t), \theta(t))\) is the relative particle trajectory, \(\Omega(R)\) is the intermolecular potential as depicted in Fig.1.

Eliminating \( \dot{\theta} \) and solving for the critical impact parameter \( b = b^\dagger \) corresponding to the trajectory of the closest elastic encounter that is tangential to the ridge line \((dR/d\theta = 0\) at \(R = r_0\), \(\Omega(r_0) = \epsilon)\) of the potential ‘crater’, we have

\[ \frac{b^\dagger}{r_0} = \left(1 - \frac{2\epsilon}{m_{AB} V^2}\right)^{\frac{1}{2}} \]  

(43)

Substitution of Eqs.(42) and (43) into (41) gives

\[
W = \pi r_0^2 \int_{V > V_{cr}} dVV (1 - \frac{V^2_{cr}}{V^2}) \int f_A f_B dU \]  

\[
V_{cr} \equiv \left( \frac{2\epsilon}{m_{AB}} \right)^{\frac{1}{2}} = [2E(M_A^{-1} + M_B^{-1})]^\frac{1}{2}, \ (M; \text{molarweight})
\]  

(44)

valid for any force laws governing elastic part of collisions. Employing definition (I) for the microscopic density, rate of reaction (44) is written in an alternative form

\[
W = \pi r_0^2 \sum_{s,s} \delta(\mathbf{x} - \mathbf{x}_A^{(s)}) \delta(\mathbf{x} - \mathbf{x}_B^{(s)}) \int_{V > V_{cr}} \delta(\mathbf{V} - \mathbf{v}_B^{(s)} + \mathbf{v}_A^{(s)}) V (1 - \frac{V^2_{cr}}{V^2}) d\mathbf{V}
\]  

(45)

In calculating the integral, we make use of the following formula

\[
\int_{V > V_{cr}} F(V) \delta(\mathbf{V} - \mathbf{V}) d\mathbf{V} = F(\mathbf{V}) \int_{V > V_{cr}} \delta(\mathbf{V} - \mathbf{V}) d\mathbf{V}
\]
\[= F(\bar{V}) \int dV_x dV_y \delta(V_x - \bar{V}_x) \delta(V_y - \bar{V}_y) S(\bar{V}_z; \sqrt{V_{cr}^2 - V_x^2 - V_y^2})\]

\[= F(\bar{V}) S(\bar{V}_z; \sqrt{V_{cr}^2 - V_x^2 - V_y^2})\]

\[= F(\bar{V}) S(\bar{V}; V_{cr})\]  \hspace{1cm} (46)

where \(S\) is the step function defined by

\[S(X; Y) = \begin{cases} 1, & \text{if } X > Y \\ 0, & \text{otherwise} \end{cases}\]  \hspace{1cm} (47)

Then Eq. (45) reads

\[
\tilde{W} = \pi r_0^2 \sum_{s,s'} \delta(x - x_A^{(s)}) \delta(x - x_B^{(s)}) S(V_{AB}; V_{cr}) V_{AB} (1 - \frac{V_x^2}{V_{AB}^2})
\]

with

\[V_{AB} \equiv v_B^{(s)} - v_A^{(s)}\]  \hspace{1cm} (48)

This expression is the ultimate form of the instantaneous reaction rate after the Klimontovich formalism; further deduction is not possible unless any assumption is made on \(V_{AB}\); its average \(\tilde{V}_{AB} = (8kT/\pi m_{AB})^{1/2}\) for instance. Then we have

\[
\tilde{W} = \alpha \begin{cases} 1 - \frac{\pi}{4} \left(\frac{\epsilon}{kT}\right), & \text{for } kT > \left(\frac{\pi}{4}\right)\epsilon \\ 0, & \text{otherwise} \end{cases}
\]  \hspace{1cm} (49)

where

\[\alpha \equiv \pi r_0^2 n_A n_B \left(\frac{8kT}{\pi m_{AB}}\right)^\frac{3}{2}\]

is the frequency factor.

Another model to make formula (48) tractable would be to take the average of the following type;

\[
\tilde{W} = \int W F(V_{AB}) dV_{AB}
\]  \hspace{1cm} (50)

where

\[F(V_{AB}) \equiv \frac{1}{(2\pi c_{AB}^2)^{3/2}} \exp\left(-\frac{V_{AB}^2}{2c_{AB}^2}\right), \quad (c_{AB}^2 = \frac{kT}{m_{AB}})\]

is the probability density of the relative velocity distribution in statistical equilibrium. Then the classical Arrhenius rate law written in terms of the average temperature

\[
\tilde{W} = \alpha e^{-\epsilon/kT}
\]  \hspace{1cm} (51)

is recovered as it should be.

In Fig.2 is shown the comparison of the two average reaction rates (49) and (51) plotted against the inverse Zeldovich number \((\epsilon/kT)^{-1}\). The former which might be called the ignition temperature model predicts the ignition temperature \(T_i\) as

\[kT_i = \left(\frac{\pi}{4}\right)\epsilon\]
in somewhat overestimating manner of reality.

6. Conclusions

The open question of whether the fluid equations as used for the direct numerical simulation of turbulence, namely, those written in terms of fluctuating variables have ‘first principle’ basis is looked into by the molecular approach using the microscopic density. On this Klimontovich formalism as contrast to the Boltzmann formalism of the classical statistical mechanics, three conservation equations, the Navier-Stokes viscous-stress law and the Fourier heat conduction law prove to be valid with much finer spatial resolvability, and without any concepts of averaging or statistical equilibrium.

For reactive gases, however, the parallelism breaks down in that the Arrhenius reaction rate law depends crucially on these concepts, therefore that this rate law written by the fluctuating temperature is not justified.

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Figure captions

Fig.1 The intermolecular potential with threshold $\epsilon$ for reactive collisions
Fig.2 Arrhenius-and ignition-temperature models