Rate increase in chemical reaction and its variance under turbulent equilibrium

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Abstract. As contrast to the Maxwellian distribution, equilibrium distribution of the second kind or turbulent equilibrium is shown to exist under tertiary molecular chaos hypothesis to replace the classical binary chaos by Boltzmann. It is expressed as bimodal Maxwellians each mode differing by plus/minus root-mean-squares of fluctuations in macroscopic variables. Chemical reaction rates calculated using the turbulent-equilibrium are obtained in a closed form, accounting for discrepancy between experiments and classical theory based on Arrhenius' law that underestimates the burning rate considerably. The key issue is the correct estimation of the high-energy tail of the distribution function that is minor in population, yet playing a major role for reactions with high activation energy. It is extremely sensitive to turbulence level in the temperature, causing slightly subcritical molecules to clear the potential barrier to cause reactions just like quantum particles undergoing tunnelling effect owing to the uncertainty principle. Variance of the fluctuating turbulent chemical reaction rate is also calculated, verifying that relative variance based on the turbulent equilibrium is low, whereas its classical counterpart (Arrhenius) is pathologically high. A closed set of equations governing reactive turbulent gases is presented on this sound basis.

1. Introduction — A perspective on the classical and turbulence-corrected Boltzmann formalism

It is well-known that each of the transport processes in fluids, namely, diffusion, heat transfer, momentum transfer due to shearing motion, and chemical reaction is enhanced by the presense of turbulence. The physical origin that causes such appreciable hike in those rates is the fractal nature of turbulence[1]: it is ascribed to drastic increase in net contact area of adjacent bulk of fluid, taking place through the bounding surface penetrating into each other area, thereby making it easier to transport mass,

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momentum and energy. It results in drag rise of a flat plate several times[2] the laminar counterpart, also in flame propagation velocity elevated by a few ten times[3] under internal combustion engine environment(Fig.1). Obviously the latter is a favorable facet of turbulence characteristies, whereas the former is detrimental from the viewpoint of transport vehicle technologies. In fact, the evidence that the rate increase due to turbulence is much higher for mechanism generating thrust rather than drag tempts us to imagine a midget planet where airplanes would have to install disproportionally huge engines, under the environment of *no* turbulence. Thus chemical reaction rates, among other transport processes, must be influenced by turbulence most sensitively, so is worth looking into most detail.

In general there are two aspects of approach to this problem: The one is to pursue the instantaneous value of a physical quantity $\underline{W}$ which is stochastic and fractal, using direct numerical simulation (DNS) for example. In principle, any of these quantities are described in terms of microscopic density advocated by Klimontovich[4], which we will call hereafter the K-formalism. The DNS currently being used in numerical simulation of fluid flows is the macroscopic version of the K-formalism[5]. It has been applied to problems of combustion science, enabling to compute wiggling premixed flame front with sufficient resolvability[6]. The state of the art, however, is yet to go far to be able to provide information such as turbulent flame speed for engine designers.

Another approach to turbulent combustion is based on an axiom of statistical mechanics that claims equivalence of solving for instantaneous value $\underline{W}$ of a stochastic quantity and for a set of averaged quantities

$$\{W,\ \overline{W'\widehat{W'}},\ \overline{W'\widehat{W'}\widetilde{W'}},\ \cdots\} \tag{1}$$

In the above $W = \overline{\underline{W}}$ is the average value,

$$W' = \underline{W} - W \tag{2}$$

is the instantaneous fluctuation subject to $\overline{W'} = 0$, and fluctuation correlations $\overline{W'\widehat{W'}}$ etc., refer to those between different points in the independent variable z, e.g., W = W(z), $\widehat{W} = W(\widehat{z})$, etc. The second formalism is the basis on which to found statistical mechanics for example; in fact, if one identifies $\underline{W}$ with the microscopic density, then its average W represents Boltzmann's function. So the latter may well be called B-formalism as contrast to the K-formalism as defined above.

A flow of turbulent gas is *dually* stochastic; the one is microscopic (molecular) level with the average taken with respect to the molecular velocity, whereas the other is macroscopic (fluid-dynamic) level where the average is taken over a volumelet whose size is greater than the Kolmogorov scale yet smaller than fluid-dynamic characteristic length.

If one identifies W with chemical reaction rate, there are three levels of descriptions: Following the K-formalism $\underline{W}$ is expressed as a sum of on-off step functions depending

on whether each molecular collision clears the potential barrier to effect inelastic collisions[5]. Next level is the classical B-formalism where the molecular average alone is employed. Then W is shown to be expressed as Arrhenius' law[7, 8, 9]. It is coupled with fractal analysis to estimate turbulent flame surface area to evaluate turbulent burning rate[10]. The third stage, namely, the B-formalism to be discussed here is intended to encompass both molecular and turbulent averaging procedures in its framework.

A series of earlier works along this line[11, 12, 13] has shed some light on the conflicts between the classical Arrhenius kinetics and experimental data attributable to temperature turbulence using the exact solution that represents simplified reality. In Fig.2 is shown shock-tube data of low-temperature (spotty) ignition of hydrogen oxygen premixture as compared with the classical theory ($\delta T = 0$), also with turbulence-corrected one, a primitive form[11] of the present theory. Also is shown in Fig.3 flame velocity of turbulent premixed gas[14] as compared with existing experiment and with renormalization group theory.

Although the earlier theory has thus enabled to predict some features of turbulent combustion as to their dependence on turbulent intensity without relying on any empirical parameters, no information has been provided regarding their dependence on the scale of turbulence. Revised version in the basic formalism has been proposed in ref. [15], with applications to nonreactive turbulence, where full informations on the scale of turbulence have been made available.

The objective of this paper is three-fold: The one is to show the exact solution for turbulent equilibrium still valid even without the condition of only temperature turbulence prevalent. The other is to remodel the previous theory so as to include scale of turbulence into formalism for reactive flows now at issue. The third is to show that the B-formalism, an average-oriented formalism, provides a sound description of turbulent combustion if based on turbulent equilibrium, which otherwise has been considered as out-of-date.

2. Turbulent equilibrium

In paralled with the classical kinetic theory providing molecular basis of nonturbulent fluid dynamics, molecular description of gases based on the microscopic density

$$\underline{f}(z) = \sum_{s=1}^{N} \delta(z - z_s(t)) \tag{3}$$

has given the ground for the direct numerical simulation of turbulent gases[5, 16]. In the above expression, $z = (\boldsymbol{x}, \boldsymbol{v})$ is a point in the phase space, namely, physical ($\boldsymbol{x}$) plus molecular velocity ($\boldsymbol{v}$) space, and δ denotes the (6D) delta function. This function gives, by definition, the instantaneous number density in the phase space, so is identified with unaveraged Boltzmann function. It was first applied to the plasma kinetic theory[4]

where the equation governing $\underline{f}$ is Vlasov's equation. For monatomic (neutral) ideal gases, the governing equation, derived as an equation of continuity in the phase space with precise spatial and temporal resolvability of Hamiltonian mechanics level, proves to be an unaveraged Boltzmann equation[16]

$$B(\underline{f}) \equiv \left(\frac{\partial}{\partial t} + \boldsymbol{v}\cdot\frac{\partial}{\partial \boldsymbol{x}}\right)\underline{f} - J(z;\tilde{z})[\underline{f}\,\underline{\tilde{f}}] = 0 \tag{4}$$

where J is the classical collision integral operator

$$J(z;\tilde{z})[\underline{f}\,\underline{\tilde{f}}] = \left[\int (f'\tilde{f}' - f\tilde{f})V\,d\Omega\,d\tilde{\boldsymbol{v}}\right]_{\tilde{\boldsymbol{x}}=\boldsymbol{x}} \tag{5}$$

In the above $\underline{\tilde{f}} = \underline{f}(\tilde{z})$ is the microscopic density of the collision partner molecule $\tilde{z}$, $\tilde{f}' = f(\tilde{z}')$ likewise with $\hat{z}'$ specifying the pre-collision state of the collision partner leading to $\tilde{z}$ after the collision, $V = |\tilde{\boldsymbol{v}} - \boldsymbol{v}|$, and $d\Omega$ is the differential collision-cross section of the molecular encounter.

The microscopic density, being averaged over a space with a number of unidentifiable molecules included, defines the Boltzmann function f;

$$f = \overline{\underline{f}}. \tag{6}$$

This is where the statistical concept is introduced for a quantity of deterministic mechanics. Similarly, two-point correlation function $\psi(z,\tilde{z})$ is defined using the same averaging concept as

$$\psi(z,\tilde{z}) = \overline{\underline{f}\,\underline{\tilde{f}}} - f\tilde{f} \tag{7}$$

Higher order correlations can be defined likewise.

The classical kinetic theory is founded on Eq.(4) averaged over the same space as (6) together with the Boltzmann's (binary) molecular chaos hypothesis

$$\psi = 0 \tag{8}$$

that is the Boltzmann equation in the classical sense;

$$\left(\frac{\partial}{\partial t} + \boldsymbol{v}\cdot\frac{\partial}{\partial \boldsymbol{x}}\right)f - J(z;\tilde{z})[f\tilde{f}] = 0 \tag{9}$$

Under the equilibrium condition ($\partial/\partial t = 0$, $\partial/\partial \boldsymbol{x} = 0$) the equation reduces to

$$J(z;\tilde{z})[f\tilde{f}] = 0 \tag{10}$$

whose solution is known as the Maxwellian distribution

$$\left.\begin{aligned} f = f_0 &= \frac{n}{(2\pi c^2)^{3/2}}\exp\left(-\frac{\boldsymbol{w}^2}{2c^2}\right) \\ \boldsymbol{w} &\equiv \boldsymbol{v} - \boldsymbol{u} \\ c &= (\mathcal{R}T/\mathcal{M})^{1/2} \end{aligned}\right\} \tag{11}$$

where n, $\boldsymbol{u}$, T are the number density, fluid velocity and temperature, $\mathcal{R}$ and $\mathcal{M}$ denote the universal gas constant and molar weight, respectively.

If a gas is turbulent, fluid variables exhibit (long-range) correlations, so the classical binary chaos (8) ceases to hold. Then Eq.(9) is to be replaced with

$$\overline{B(\underline{f})} = \left(\frac{\partial}{\partial t} + \boldsymbol{v}\cdot\frac{\partial}{\partial \boldsymbol{x}}\right) f - J(z;\widetilde{z})[f\widetilde{f} + \psi(z,\widetilde{z})] = 0 \tag{12}$$

Thus the equation is not closed at this level: The equation of next step to govern ψ is[15]

$$\overline{f'B(\widehat{\underline{f}}) + B(\underline{f})\widehat{f}'} = 0 \quad (f' \equiv \underline{f} - f) \tag{13}$$

which is shown to be identical with the two-particle hierarchy equation of the BBGKY theory[17]. The actual form of (13) reads

$$\begin{aligned}
\left(\frac{\partial}{\partial t} + \boldsymbol{v}\cdot\frac{\partial}{\partial \boldsymbol{x}} + \widehat{\boldsymbol{v}}\cdot\frac{\partial}{\partial \widehat{\boldsymbol{x}}}\right)&\psi(z,\widehat{z}) = J(z;\widetilde{z})[f\psi(\widehat{z},\widetilde{z}) + \widetilde{f}\psi(z,\widehat{z}) \\
&+\psi_{\mathrm{III}}(z,\widehat{z},\widetilde{z})] + J(\widehat{z};\widetilde{z})[\widehat{f}\psi(z,\widetilde{z}) + \widetilde{f}\psi(z,\widetilde{z}) + \psi_{\mathrm{III}}(z,\widehat{z},\widetilde{z})]
\end{aligned} \tag{14}$$

The simplest possible truncation of the chain of equations at this level is to put

$$\psi_{\mathrm{III}} = 0 \tag{15}$$

namely, to invoke tertiary molecular chaos to replace the classical binary chaos (8).

Eq.(14) subject to condition (15) turns out to be separable into those for respective variables in terms of the wave number $\boldsymbol{k}$,

$$\psi(z,\widehat{z}) = \mathrm{R.P.}l^3 \int \phi(z,\boldsymbol{k})\phi^*(\widehat{z},\boldsymbol{k})d\boldsymbol{k} \tag{16}$$

where symbol $*$ denotes complex conjugate, l denotes a length characteristic of the flow geometry and R.P. stands for the real part. Upon its substitution into (14) we have the equation governing ϕ as

$$\left.\begin{aligned}
i\omega(\boldsymbol{k})\phi &= \Omega_0(\phi) \\
\Omega_0(\phi) &\equiv \left(\frac{\partial}{\partial t} + \boldsymbol{v}\cdot\frac{\partial}{\partial \boldsymbol{x}}\right)\phi - J(z;\widetilde{z})[f\widetilde{\phi} + \phi\widetilde{f}]
\end{aligned}\right\} \tag{17}$$

where $\omega(\boldsymbol{k})$ is the separation constant having dimension of the frequency, and connected with the wave number through phase velocity $\boldsymbol{V}_p$ as

$$\omega = \boldsymbol{V}_p\cdot\boldsymbol{k} \tag{18}$$

¿From Eqs.(17) and (18) the following relationship is seen to hold;

$$\phi^*(\boldsymbol{k}) = \phi(-\boldsymbol{k}) \tag{19}$$

A remark should be mentioned on a renovation that has brought the scale of turbulence into formalism: In the older theory variable separation (16) is effected in the domain of frequency ω in place of wave number $\boldsymbol{k}$. Information on the scale of turbulence is missed in this form, which may be retrieved in the following way[15]: Here turbulence is characterized as a wave with frequency ω and wave number $\boldsymbol{k}$ obeying dispersion relationship (18). We may assume a plane wave

$$\phi = e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\Phi(z,\,\boldsymbol{k}) \tag{20}$$

and discuss its amplitude Φ. If further we introduce Fourier transform

$$\Phi(z,\,\boldsymbol{k}) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} e^{-i\boldsymbol{k}\cdot\boldsymbol{s}}F(z,\,\boldsymbol{s})\,d\boldsymbol{s} \tag{21}$$

to work with 'eddy' space $\boldsymbol{s}$, and employ separation rule written in terms of wave number $\boldsymbol{k}$, namely after (16), a simple formula follows:

$$\psi_{\mathrm{II}}(z,\,\widehat{z}) = \frac{1}{(2\pi l)^3}\int_{-\infty}^{\infty} F(z,\,\boldsymbol{s})F(\widehat{z},\,\boldsymbol{s}+\boldsymbol{r})\,d\boldsymbol{s} \tag{22}$$

where $\boldsymbol{r} = \widehat{\boldsymbol{x}}-\boldsymbol{x}$ is the distance between the two space points. Any informations on scale of turbulence can be obtained from this correlation formula by taking fluid moment of (22), for example, the velocity-velocity fluctuation correlation as

$$\overline{u_j'(\boldsymbol{x})u_l'(\boldsymbol{x}+\boldsymbol{r})} = (\rho\widehat{\rho})^{-1}\int w_j\widehat{w}_l\psi_{\mathrm{II}}\,d\boldsymbol{v}\,d\widehat{\boldsymbol{v}} \tag{23}$$

where $\boldsymbol{w}$ has been defined by (11).

It is a well-posed problem to seek the equilibrium solution of the new set of equations (12) and (17). It stands for a 'turbulent equilibrium' solution to substitute the local Maxwellian for nonturbulent gases. This is to solve simultaneous integral equations

$$J(z;\widetilde{z})[f\widetilde{f} + \int \phi\,\widetilde{\phi}^*\,d\boldsymbol{k}] = 0 \tag{24}$$

$$J(z;\widetilde{z})[f\widetilde{\phi} + \phi\widetilde{f}] = 0 \tag{25}$$

The exact solution under the assumption that turbulence prevails only in the temperature has been obtained in a closed form by Sagara[12] by summing an infinite series in the temperature fluctuation $\delta T = (\overline{T'^2})^{1/2}$. The same result has been reached using much simpler method[13].

We can show that the exact solution also exists for realistic turbulence where the fluctuations in number density $\delta n = (\overline{n'^2})^{1/2}$ and fluid velocity $\delta u_j = (\overline{u_j'^2})^{1/2}$ (no summation convention here) are also prevalent. Put

$$f = f^0 = \frac{1}{2}(f_0^+ + f_0^-) \tag{26}$$

$$\phi = \phi^0 = \frac{1}{2}K(\boldsymbol{k})(f_0^+ - f_0^-) \tag{27}$$

where f_0 is the local Maxwellian defined by (11), and $f_0^{\pm}$ is given as follows;

$$\left.\begin{aligned}
f_0^{\pm} &= \frac{n^{\pm}}{(2\pi c^{\pm 2})^{3/2}}\exp\left(-\frac{w_k^{\pm 2}}{2c^{\pm 2}}\right) \\
n^{\pm} &= n \pm \delta n \\
w_j^{\pm} &= v_j - u_j^{\pm} \\
u_j^{\pm} &= u_j \pm \delta u_j \\
c^{\pm 2} &= R(T \pm \delta T) \\
R &= \mathcal{R}/\mathcal{M}
\end{aligned}\right\} \tag{28}$$

It is easily confirmed that the form of (26) is designed to be consistent with definitions of the average quantity $(n, \boldsymbol{u}, T)$, and the form of (27) with that of the variance $(\delta n, \delta \boldsymbol{u}, \delta T)$ of each quantity provided that the following relationship holds;

$$\int_{-\infty}^{\infty} KK^* d\boldsymbol{k} = 1 \tag{29}$$

Direct substitution of (26) and (27) into (24) and (25) reads, respectively,

$$\left.\begin{aligned}
\frac{1}{2}J(z;\widehat{z})[f_0^+\widehat{f}_0^+ + f_0^-\widehat{f}_0^-] &= \frac{1}{2}(J^+ + J^-) \\
\frac{K}{2}J(z;\widehat{z})[f_0^+\widehat{f}_0^+ - f_0^-\widehat{f}_0^-] &= \frac{K}{2}(J^+ - J^-)
\end{aligned}\right\} \tag{30}$$

where $J^{\pm}$ has been defined as

$$J^{\pm} = J(z;\widehat{z})[f_0^{\pm}\widehat{f}_0^{\pm}] \tag{31}$$

This integral vanishes in view of the fact that $J(z;\widehat{z})[f_0\widehat{f}_0] = 0$, also that the bilinear Maxwellians in (31) consist of the same family in fluid parameters (Q.E.D.).

The deduction above claims that the state of turbulent equilibrium is represented by the Boltzmann function of the form (26), along with correlation function

$$\psi(z,\widehat{z}) = \frac{1}{4}(f_0^+ - f_0^-)(\widehat{f}_0^+ - \widehat{f}_0^-) \tag{32}$$

or the two-point distribution function

$$\begin{aligned}
f_{\mathrm{II}}(z,\widehat{z}) &\equiv f\widehat{f} + \psi(z,\widehat{z}) \\
&= \frac{1}{2}(f_0^+\widehat{f}_0^+ + f_0^-\widehat{f}_0^-)
\end{aligned} \tag{33}$$

At a glance difference between the two Boltzmann functions f_0 of (3) and f^0 of (26) looks trivial, because the difference is of the first order smallness in δ. The point at issue,

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however, is that they differ appreciably in the population of high energy molecules that play a crucial role in chemical reactions, particularly when the activation energy is high. In Fig.4 is shown the population density of molecules having absolute molecular velocity v with turbulence only in the temperature. The Maxwellian distribution ($\delta T = 0$) is seen to have lean high energy tail, namely, underestimates population of high energy molecules compared to reality of turbulence.

3. Turbulent chemical reactions

Chemical reaction rate of elementary reaction of the form

$$[a] + [b] \rightarrow [c] + [d] \quad ([\,]\,; \text{chemical symbol})$$
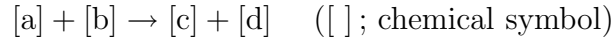
usually obeys Arrhenius' law;

$$W = An_a n_b \exp(-E/\mathcal{R}T) \tag{34}$$

where n_a and n_b denote partial number densities of reactants [a] and [b], A is the frequency factor and E is the activation energy per mol. Rate law (34) is warranted on the classical kinetic theory using a simple collision model. A most clearcut model among various ones proposed in late 40's through 50's is due to Present[9] : Let the intermolecular potential of a molecule [a] relative to a molecule [b] be repulsive, of a volcano shape having a crater with radius r_0 at altitude ϵ. Let also the locus of the [b] molecule relative to the [a] molecule written in axisymmetric polar coordinate be $[r(t), \chi(t)]$ where χ is the angle between the symmetry axis parallel to $\boldsymbol{V}_{ba} = \boldsymbol{v}_b - \boldsymbol{v}_a$ and the position vector $\boldsymbol{r} = \boldsymbol{x}_b - \boldsymbol{x}_a$ then we have

$$\left.\begin{array}{l} r^2\dot{\chi} = bV \\ (m^\dagger/2)(\dot{r}^2 + r^2\dot{\chi}^2) + \epsilon(r) = (m^\dagger/2)V^2 \end{array}\right\} \tag{35}$$

relationships representing conservation of angular momentum and of energy, where $\dot{\chi} = dx/dt$ etc., $m^\dagger = (m_a^{-1} + m_b^{-1})^{-1}$ is the reduced mass, b is the impact parameter, and $\epsilon(r)$ denotes the intermolecular potential. Since the radius of the closest approach $r = r_c$ is given by the condition $dr/d\chi = 0$, the critical collision that separates elastic from inelastic collisions is such that the closest approach occurs on the ridge line of the crater ; $r_c = r_0$. This condition determines the critical impact parameter $b_c(V)$ from (35) as

$$\frac{b_c(V)}{r_0} = \left(1 - \frac{2\epsilon}{m^\dagger V^2}\right)^{1/2} \tag{36}$$

Instantaneous reaction rates for respective species are expressed in the following form,

$$\underline{W}_a = -m_a\underline{W}, \ \underline{W}_b = -m_b\underline{W}, \ \underline{W}_c = m_c\underline{W}, \ \underline{W}_d = m_d\underline{W}$$

$$\underline{W} = \int_{\text{inel}} \underline{f}(z_a)\underline{f}(z_b)V \, d\Omega_{ab} \, dv_a \, dv_b \tag{37}$$

Utilizing the following formula

$$\int_{\text{inel}} d\Omega_{ab} = \pi b_c^2 = \pi r_0^2 \left(1 - \frac{2\epsilon}{m^\dagger V^2}\right)$$

and transforming integral variables from (v_a, v_b) to (U, V) defined by

$$\left.\begin{array}{rcl} U & = & (m_a v_a + m_b v_b)/(m_a + m_b) \\ V & = & v_b - v_a \end{array}\right\} \tag{38}$$

we have for (33)

$$\underline{W} = \pi r_0^2 \int_{V_c}^{\infty} dV \, V \left(1 - \frac{V_c^2}{V^2}\right) \int_{-\infty}^{\infty} \underline{f}(z_a)\underline{f}(z_b)dU \tag{39}$$

where

$$V_c = (2\epsilon/m^\dagger)^{1/2} \tag{40}$$

denotes the critical relative velocity for a head-on collision.

Chemical reaction rate in classical sense is obtained from (39), upon averaging and employing classical chaos (8), as

$$W = \pi r_0^2 \int_{V_c}^{\infty} dV \, V \left(1 - \frac{V_c^2}{V^2}\right) \int_{-\infty}^{\infty} f(z_a)f(z_b)dU \tag{41}$$

If the Maxwellian equilibrium (11) is employed Eq.(41) is integrated out to give

$$\left.\begin{array}{l} W_0(T, n_a, n_b) = An_a n_b e^{-\epsilon/kT} \\ A = (8kT/\pi m^\dagger)^{1/2}\pi r_0^2 \end{array}\right\} \tag{42}$$

that is nothing but Arrhenius law (34) with activation energy E and the frequency factor A written in microscopic parameters.

It should be noted that turbulence counterpart of the above deduction faces with difficulty if conducted phenomenologically, whereas it is simply straightforward if one follows the molecular approach as employed here. In fact, if one assumes that the instantaneous reaction rate is Arrhenius form (34)

$$\underline{W} = \underline{A} \, \underline{n}_a \underline{n}_b \exp(-E/\mathcal{R}\underline{T})$$

and its average given by

$$W = \overline{\underline{A} \, \underline{n}_a \underline{n}_b \exp(-E/\mathcal{R}\underline{T})} \tag{43}$$

Decomposing the r.h.s. term under average into means and fluctuations we have

$$W = A n_{\mathrm{a}} n_{\mathrm{b}} \overline{(1 + O(n'_{\mathrm{a}}, \, n'_{\mathrm{b}})) e^{-\beta + \beta^2 \tau - \beta^3 \tau^2 + \cdots}}$$

where $\beta = E/\mathcal{R}T$ is the Zel'dovich number and $\tau = \mathcal{R}T'/E$ stands for the temperature fluctuation. Leading term in the Taylor expansion of the expression under average sign gives for $\beta \gg 1$,

$$\overline{\frac{d^n W}{d\tau^n} \frac{\tau^n}{n!}} \sim \frac{\beta^n}{n!} \overline{(T')^n}$$

which implies that convergence of the series is extremely slow since the Zel'dovich number for combustion reaction is of $O(10^1)$. For example we need to take 23 terms before $\beta^n/n!$ diminishes to unity for $\beta = 10$. It also means that we need to know 22 consecutive self correlations in the temperature fluctuation. Needless to say, therefore, that the first term (Arrhenius) or a few-term approximation is far from satisfactory.

On the other hand, if one adopts microscopic approach, namely, starts with the averaged version of (39) insted of (43);

$$W = \pi r_0^2 \int_{V_c}^{\infty} d\boldsymbol{V} V \left(1 - \frac{V_c^2}{V^2}\right) \int_{-\infty}^{\infty} \overline{f_{\mathrm{a}} f_{\mathrm{b}}} d\boldsymbol{U} \tag{44}$$

and employs turbulent equilibrium (33) for $\overline{f_{\mathrm{a}} f_{\mathrm{b}}} \equiv f_{\mathrm{II}}$, a simple calculation leads immediately to the final expression

$$W^0 = \frac{1}{2}(W_0^+ + W_0^-) \tag{45}$$

with

$$W_0^{\pm} \equiv W_0(T \pm \delta T, \, n_{\mathrm{a}} \pm \delta n_{\mathrm{a}}, \, n_{\mathrm{b}} \pm \delta n_{\mathrm{b}}) \tag{46}$$

where W_0 has been defined by (42). Formula (45) for the turbulent reaction rate turns out to be a bimodal Arrhenius: It allows us to draw a intuitive picture that a half of the chemical reaction takes place under temperature elevated and population of reactant molecules denser by their root-mean-square turbulent intensity, and another half under those quantities lowered by the same amount.

The bimodal Arrhenius low (45) is the full turbulence version derived on the basis of exact solution of Eqs. (24) and (25), supplementing the previous one[11, 12, 13], where turbulence prevails only in the temperature. As already sketched it is obvious that anomalous increase in the reaction rate is overwhelmingly due to the temperature turbulence that feeds extra high energy molecules capable of reaction (see Fig.4). The first term of (45) looks as if the potential barrier is lowered by the factor of $(1 + \delta T/T)^{-1}$; a macroscopic equivalent of tunnelling effect of quantum mechanics where the potential barrier is lowered by a factor of Planck's constant due to the uncertainty principle.

On the other hand, fluctuation in the reactant number density does not have such effects on the reaction rate beyond the first order smallness. However, when coupled

with the temperature effect, it leaves with a possible account for below-critical lean combustion that actually occurs in the operation of the direct injection engines (GDI).

Rate law (45) also tells us that turbulence in the fluid velocity has no influence on the reaction rate (as it should not). In fact, the collision integral for a pair of molecules about to collide are not influenced by the fluctuation in the fluid velocity, because they are aboard on the 'same boat' in the turbulent ocean. Its effects on turbulent flame velocity are exclusively via other transport processes, namely, turbulent diffusion and turbulent heat transfer. (See Table 1, next section).

4.   Reaction rate variance

It is an experimental evidence that instantaneous chemical reaction rate $\underline{W} = W + W'$ at a fixed point undergoes fluctuation over a wide range, therefore, quality of a statistical theory employing any average concepts hinges crucially on reliable estimate for its variance around the average W.

This issue again is beyond the reach of phenomenologies and we have to address to statistical approach as developed in the preceding section. To be remarked at this point is that what appear in the governing equations are not the variance itself, but the fluctuation correlations $\overline{Z'W'}$ where Z stands for fluid variables such as velocity, temperature, etc..

The equation governing W' is obtained from (39) by separating it into mean and fluctuating parts. We have, then,

$$W' = I_{\text{inel}} \left[f'(z_{\text{a}})f(z_{\text{b}}) + f(z_{\text{a}})f'(z_{\text{b}}) + f'(z_{\text{a}})f'(z_{\text{b}}) - \overline{f'(z_{\text{a}})f'(z_{\text{b}})} \right] \quad (47)$$

where we have defined

$$I_{\text{inel}}[\Phi(z_{\text{a}},\, z_{\text{b}})] \equiv \pi r_0^2 \int_{V_c}^{\infty} d\boldsymbol{V} V \left(1 - \frac{V_c^2}{V^2} \right) \int_{-\infty}^{\infty} \Phi(z_{\text{a}},\, z_{\text{b}}) d\boldsymbol{U}$$

Since, in general, fluid variable fluctuation is expressed as a moment of fluctuation of the Boltzmann function in the velocity space as

$$Z' = \int_{-\infty}^{\infty} \zeta(z_\alpha) f'(z_\alpha) d\boldsymbol{v}_\alpha \quad (48)$$

we have, from (43) and (44),

$$\int_{-\infty}^{\infty} \zeta d\boldsymbol{v}_\alpha \left\{ \overline{W' f'_\alpha} - I_{\text{inel}} \left[\overline{f'_{\text{a}} f'_\alpha} f_{\text{b}} + f_{\text{a}} \overline{f'_\alpha f'_{\text{b}}} + \overline{f'_{\text{a}} f'_\alpha f'_{\text{b}}} \right] \right\} = 0 \quad (49)$$

Let the variable separation be invoked after (16) as

$$\overline{W' f'_\alpha} = \text{R.P.} l^3 \int_{-\infty}^{\infty} g_W(\boldsymbol{k}) \phi_\alpha^*(\boldsymbol{k}) d\boldsymbol{k} \quad (50)$$

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and

$$\overline{f_a' f_\alpha' f_b'} = \text{R.P.}l^9 \int \phi_a(\boldsymbol{k}_a)\phi_\alpha(\boldsymbol{k}_\alpha)\phi_b(\boldsymbol{k}_b)\delta(\boldsymbol{k}_a + \boldsymbol{k}_\alpha + \boldsymbol{k}_b)d\boldsymbol{k}_a\,d\boldsymbol{k}_\alpha\,d\boldsymbol{k}_b$$

$$= \text{R.P.}l^6 \int \phi_\alpha^*(\boldsymbol{k})\phi_a(\widetilde{\boldsymbol{k}})\phi_b(\boldsymbol{k} - \widetilde{\boldsymbol{k}})d\boldsymbol{k}\,d\widetilde{\boldsymbol{k}}$$

where, in the last row, $-\boldsymbol{k}_\alpha$ is replaced with $\boldsymbol{k}$, also $\boldsymbol{k}_a$ with $\widetilde{\boldsymbol{k}}$, and condition (19) has been made use of. Then Eq.(49) leads to

$$\int_{-\infty}^{\infty} d\boldsymbol{k}\phi_\alpha^*(\boldsymbol{k})\Big\{ g_W(\boldsymbol{k}) - I_{\text{inel}}[\phi_a(\boldsymbol{k})f_b + f_a\phi_b(\boldsymbol{k})$$
$$+\text{R.P.}l^3 \int_{-\infty}^{\infty} d\widetilde{\boldsymbol{k}}\phi_a(\boldsymbol{k} - \widetilde{\boldsymbol{k}})\phi_b(\widetilde{\boldsymbol{k}})d\widetilde{\boldsymbol{k}}]\Big\} = 0 \tag{51}$$

If one decomposes g_W and ϕ into a plane wave after (20)

$$\left.\begin{array}{rcl} g_W &=& e^{i\boldsymbol{k}\cdot\boldsymbol{x}}G_W \\ \phi &=& e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\Phi \end{array}\right\} \tag{52}$$

and deals with its amplitude G_W and Φ, or its Fourier-transform version

$$\left.\begin{array}{rcl} G_W(\boldsymbol{x},\,\boldsymbol{k}) &=& \dfrac{1}{(2\pi l)^3}\displaystyle\int_{-\infty}^{\infty} d\boldsymbol{s}\,e^{-i\boldsymbol{k}\cdot\boldsymbol{s}}q_W(\boldsymbol{x},\,\boldsymbol{s}) \\[3mm] \Phi(\boldsymbol{x},\,\boldsymbol{k}) &=& \dfrac{1}{(2\pi l)^3}\displaystyle\int_{-\infty}^{\infty} d\boldsymbol{s}\,e^{-i\boldsymbol{k}\cdot\boldsymbol{s}}F(\boldsymbol{x},\,\boldsymbol{s}) \end{array}\right\} \tag{53}$$

we have two alternatives for the reaction rate fluctuation from (51),

$$G_W(\boldsymbol{x},\,\boldsymbol{k}) = I_{\text{inel}}\left[\Phi_a f_b + f_a\Phi_b + \text{R.P.}l^3 \int_{-\infty}^{\infty} d\widetilde{\boldsymbol{k}}\Phi_a(\boldsymbol{k} - \widetilde{\boldsymbol{k}})\Phi_b(\widetilde{\boldsymbol{k}})d\widetilde{\boldsymbol{k}}\right] \tag{54}$$

$$q_W(\boldsymbol{x},\,\boldsymbol{s}) = I_{\text{inel}}[F_a f_b + f_a F_b + F_a F_b] \tag{55}$$

depending on which of the wave number ($\boldsymbol{k}$) or the eddy ($\boldsymbol{s}$) spaces is more convenient to work with.

The actual form of q_W associated with turbulent equilibrium (26) and (27) is straightforward. In fact, in view of (52) and (53), we have

$$F_\alpha^0(z,\,\boldsymbol{s}) = S(\boldsymbol{x},\,\boldsymbol{s})\frac{f_{0\alpha}^+ - f_{0\alpha}^-}{2} \tag{56}$$

with

$$S(\boldsymbol{x},\,\boldsymbol{s}) = (2\pi l)^{3/2}\frac{q_0}{\left(\displaystyle\int_{-\infty}^{\infty} q_0^2\,d\boldsymbol{s}\right)^{1/2}} \tag{57}$$

where q_0 is related to variance of the density fluctuation by

$$(\delta\rho)^2 = \frac{1}{(2\pi l)^3}\int_{-\infty}^{\infty} q_0^2\,d\boldsymbol{s} \tag{58}$$

Utilizing (56) in (55) we have

$$q_W(\boldsymbol{x},\,\boldsymbol{k}) = \frac{S}{2}\left[W_0^+ - W_0^- + \frac{S}{2}(W_0^+ + W_0^- - W_0^{+-})\right] \tag{59}$$

where

$$\begin{aligned} W_0^{+-} = A\Big\{& (n_\mathrm{a} + \delta n_\mathrm{a})(n_\mathrm{b} - \delta n_\mathrm{b})\exp\left[-E/\mathcal{R}\left(T + \frac{m_\mathrm{a} - m_\mathrm{b}}{m_\mathrm{a} + m_\mathrm{b}}\delta T\right)\right] \\ &+ (n_\mathrm{a} - \delta n_\mathrm{a})(n_\mathrm{b} + \delta n_\mathrm{b})\exp\left[-E/\mathcal{R}\left(T - \frac{m_\mathrm{a} - m_\mathrm{b}}{m_\mathrm{a} + m_\mathrm{b}}\delta T\right)\right]\Big\} \end{aligned} \tag{60}$$

Once we have obtained explicit expression for q_W variance of the reaction rate can be calculated from (see Eq.(50))

$$\begin{aligned} \overline{W'^2} &= \mathrm{R.P.}l^3\int_{-\infty}^{\infty} g_W g_W^*\,d\boldsymbol{k} \\ &= \frac{1}{(2\pi l)^3}\int_{-\infty}^{\infty} q_W^2\,d\boldsymbol{s} \end{aligned} \tag{61}$$

where (52), (53) have been taken into account. In Fig.5a is shown the relative variance $(\overline{W'^2})^{1/2}/W_0$ of reaction rate around classical Arrhenius, which amounts to quantities exceeding $O(1)$ by far, indicating extraordinary fluctuation intensity to be observed by a fixed-point measurement. Also is shown in Fig.5b the same ratio for turbulent reaction rate (41). In this case the relative variance stays within sound realm, and approaches unity with increase in turbulence in the temperature and with Zel'dovich number. This is a sign of stochastic signals characteristic of on-off type.

5. Phenomenology-coupled Boltzmann formalism on turbulent equilibrium

Statistical description of stochastic phenomena where relative variance far exceeds unity is pathological. It is for this reason that a formalism using the averaged Arrhenius law fails in describing turbulent combustion. However, as asserted in the preceding section, such formalism using the bimodal law as the averaged reaction rate deserves reconsideration. For this purpose it is advisable to follow the recipe prepared for nonreactive turbulence[15]: We start with phenomenological equations generalized to reactive gases written in instantaneous quantities:

$$\underline{\Lambda}_0 \equiv \frac{\partial\underline{\rho}}{\partial t} + \frac{\partial\underline{m}_r}{\partial x_r} = 0 \tag{62}$$

$$\underline{m}_r \equiv \underline{\rho}\,\underline{u}_r \tag{63}$$

$$\underline{\Lambda}_j \equiv \frac{\partial m_j}{\partial t} + \frac{\partial}{\partial x_r}\left(\frac{\underline{m}_j\underline{m}_r}{\underline{\rho}} + \underline{p}\delta_{jr} + \underline{p}_{jr}\right) = 0 \tag{64}$$

$$p_{jr} \equiv -\mu \left[\frac{\partial}{\partial x_j} \left(\frac{m_r}{\rho} \right) + \frac{\partial}{\partial x_r} \left(\frac{m_j}{\rho} \right) - \frac{2}{3} \delta_{jr} \frac{\partial}{\partial x_k} \left(\frac{m_k}{\rho} \right) \right] \tag{65}$$

$$\left. \begin{aligned} \Lambda_4 &\equiv \frac{\partial E}{\partial t} + \frac{\partial}{\partial x_r} \left(m_r H + Q_r \right) + \sum e_\alpha^0 W_\alpha = 0 \\ E &\equiv \rho e + \frac{m_k^2}{2\rho}, \quad H \equiv E + p \end{aligned} \right\} \tag{66}$$

$$Q_r \equiv -\lambda \frac{\partial}{\partial x_r} \left(\frac{p}{\rho R} \right) \tag{67}$$

$$\left. \begin{aligned} \Lambda_a &\equiv \frac{\partial \rho_a}{\partial t} + \frac{\partial}{\partial x_r} \left(\rho_a u_r + M_{a,r} \right) - W_a = 0 \\ Y_a &\equiv \rho_a / \rho \end{aligned} \right\} \tag{68}$$

$$M_{a,r} \equiv -\rho D_a \frac{\partial Y_a}{\partial x_r} \tag{69}$$

In the above, ρ, m_j, p and e denote density, massflux density, pressure and specific internal energy (thermal part only), p_{jr}, Q_r and M_{ar} are viscous stress, heat flux density and diffusion mass flux density for species a, and ρ_a, Y_a and e_a^0 are partial density, mass fraction and zero-point enthalpy of species a, respectively. Also, μ, λ and D_a are coefficients of viscosity, thermal conductivity and diffusion for species a, respectively. Note that all the equations have the form in accordance with a rule (rule I) that they are written in terms of quantities proportional to the density. This is to use mass-flux density instead of fluid velocity, pressure instead of temperature, and internal energy per unit of volume instead of specific internal energy.

A few words must be mentioned about modified Fick's law (69) that is not exact consequence of the kinetic theory of gases as distinct from other molecular transport relationships. The 'effective' diffusion coefficient D_a is expressed in terms of binary diffusion coefficient for each pair of constituents as [18]

$$\begin{aligned} D_a &= (1 - Y_a) / \sum_b D_{ab}^{-1} Y_b \\ &= 1 / \sum_b D_{ab}^{-1} Y_b' \end{aligned} \tag{70}$$

where $Y_b' = Y_b / (1 - Y_a)$ is mass fraction of species b of the mixture with species a excepted. The approximate formula (69) with (70) warrants validity for practical use except a minor flaw that condition $\sum_a M_{a,r} = 0$ is not exactly met.

Equations for the average are provided by

$$\Lambda_\alpha \equiv \overline{\underline{\Lambda}}_\alpha = 0 \quad (\alpha\,;\, 0,\, j,\, 4,\, a,\, b,\, \cdots) \tag{71}$$

whose actual forms are given as follows:

$$\Lambda_0 = \frac{\partial \rho}{\partial t} + \frac{\partial m_r}{\partial x_r} = 0 \tag{72}$$

$$\Lambda_j = \frac{\partial m_j}{\partial t} + \frac{\partial}{\partial x_r}\left(\frac{m_j m_r}{\rho} + p\delta_{jr} + p_{jr} \right) = 0 \tag{73}$$

$$p_{jr} \equiv (\overline{\underline{p}}_{jr})_{\mathrm{NS}} + \rho\overline{u'_j u'_r} \tag{74}$$

$$\Lambda_4 = \frac{\partial E}{\partial t} + \frac{\partial}{\partial x_r}\left(\frac{m_r}{\rho}H + Q_r \right) + \sum_{\mathrm{a,\,b,\,\cdots}} e^0_{\mathrm{a}} W_{\mathrm{a}} = 0 \tag{75}$$

$$Q_r \equiv (\overline{\underline{Q}}_r)_{\mathrm{Fourier}} + \rho\overline{u'_r h'} \tag{76}$$

$$\Lambda_{\mathrm{a}} = \frac{\partial \rho_{\mathrm{a}}}{\partial t} + \frac{\partial}{\partial x_r}\left(\frac{m_r}{\rho}\rho_{\mathrm{a}} + M_{\mathrm{a},\,r} \right) - W_{\mathrm{a}} = 0 \tag{77}$$

$$M_{\mathrm{a},\,r} \equiv (\overline{\underline{M}}_{\mathrm{a},\,r})_{\mathrm{Fick}} + \rho\overline{u'_r Y'_{\mathrm{a}}} \tag{78}$$

$$W_{\mathrm{a}} = \frac{1}{2}(W^+_{\mathrm{0a}} + W^-_{\mathrm{0a}}) \tag{79}$$

where p_{jr}, Q_r, $M_{\mathrm{a},\,r}$ and W_{a} are average transports of momentum, thermal energy, species mass due to diffusion and chemical reactions, viewed from the center of gravity frame of reference, respectively. Of the four transport processes three but chemical reactions have a structure such that molecular and turbulent transports are additive, whereas these are tightly coupled and built in a single exponential form for chemical reactions (Table 1). A few remarks are in order in deriving Eqs.(72) through (78) from (71): They are exact to $O(Z'^2)$ if Mach number is small enough. Single term turbulence corrections as derived here would not be available unless one followed rule I plus the following one (rule II) that fluctuation of each density-proportional quantity be written in density-independent quantities except fluctuation in density itself, for example, $\overline{m}_j = m_j + \rho u'_j + \rho' u_j + \rho' u'_j - \overline{\rho' u'_j}$. It is remarkable that turbulence correction to each of Navier-Stokes, Fourier and Fick laws is represented by such a

simple expression[19] without employing the so-called mass average concept. Note also that artifice of this kind is not necessary to reach the same result if phenomenologies are discarded and the whole deduction to fluid equations starts from the B-formalism in the phase space, which, unfortunately, is practicable only to nonreactive monatomic gases.

Equations governing turbulent transports to close the system emerge from the following equations[15]

$$\overline{Z'_\alpha \widehat{\Lambda}'_\beta + \Lambda'_\alpha \widehat{Z}'_\beta} = 0, \quad ((\alpha,\, \beta)\,;\, (0,\, j,\, 4,\, a,\, b,\, \cdots)) \tag{80}$$

where $\Lambda'_\alpha = \underline{\Lambda}_\alpha - \Lambda_\alpha$, and Z'_α denotes fluctuation of fluid variable Z_α. Regardless of the fact that those equations are nonlinear, they are again separable exactly in the form of (22) and (23), resulting in the following set of equations (see Appendix for its derivation);

$$Dq_0 + \partial_r q_r = 0 \tag{81}$$

$$\left.\begin{aligned}
&Dq_j + \partial_r(u_r^\dagger q_j + q_{40}\delta_{rj} + q_{rj}) + q_r \partial u_j^\dagger/\partial x_r - \rho^{-1}(\partial p/\partial x_j)q_0 = 0\\
&q_{jr} = -\mu[\partial_j(\rho^{-1}q_r) + \partial_r(\rho^{-1}q_j) - (2/3)\delta_{jr}\partial_k(\rho^{-1}q_k)]\\
&\qquad -[\partial u_r^\dagger/\partial x_j + \partial u_j^\dagger/\partial x_r - (2/3)\delta_{jr}\partial u_k^\dagger/\partial x_k]\frac{q_4}{\rho R}\frac{d\mu}{dT}\\
&\qquad +\rho^{-1}[q_j q_r - (\delta_{jr}/3)q_k^2]
\end{aligned}\right\} \tag{82}$$

$$\left.\begin{aligned}
&\frac{1}{\gamma-1}Dq_{40} + \partial_r\left(\frac{\gamma}{\gamma-1}q_{40}u_r^\dagger + q_{rkk}\right) + \sum_a e_a^0 q_{aW} = 0\\
&q_{rkk} = -(\lambda/R)[\partial_r(\rho^{-1}q_4) + p^{-1}q_4\frac{d\lambda}{dT}\partial RT/\partial x_r]\\
&\qquad +[\gamma/(\gamma-1)](RT q_r + \rho^{-1}q_r q_4)
\end{aligned}\right\} \tag{83}$$

$$\left.\begin{aligned}
&Dq_a + \partial_r(u_r^\dagger q_a + q_{a,r}) + q_r\partial Y_a/\partial x_r - q_{Wa} + \rho^{-1}q_0 W_a = 0\\
&q_{a,r} = -\rho D_a \partial_r(\rho^{-1}q_a) - \frac{d(\rho D_a)}{dT}\frac{q_4}{\rho R}\frac{\partial Y_a}{\partial x_r} + \rho^{-1}q_a q_r\\
&q_{Wa} = \pm m_a q_W \qquad (\pm\,;\, \text{species [a] produced/disappeared})\\
&q_W = \frac{S}{2}\left[W_0^+ - W_0^- + \frac{S}{2}(W_0^+ + W_0^- - W_0^{+-})\right]
\end{aligned}\right\} \tag{84}$$

$$q_{40} = q_4 + \rho R q_0 \tag{85}$$

where

$$\partial_j \equiv \partial/\partial x_j + \partial/\partial s_j$$

$$Dq_\alpha \equiv \partial q_\alpha/\partial t - V_{pr}\partial q_\alpha/\partial s_r$$

Of these equations terms of fluctuations in transport processes are listed in Table 2.

Turbulent transports having appeared in equations for the average are written in terms of q's as

$$\left. \begin{aligned} \rho\overline{u_j'u_r'} &= \frac{1}{\rho(2\pi)^3} \int_{-\infty}^{\infty} q_j q_r \, d\boldsymbol{s} \\ \rho\overline{h'u_r'} &= \frac{1}{\rho(2\pi)^3} \frac{\gamma}{\gamma-1} \int_{-\infty}^{\infty} q_4 q_r \, d\boldsymbol{s} \\ \rho\overline{Y_a'u_r'} &= \frac{1}{\rho(2\pi)^3} \int_{-\infty}^{\infty} q_a q_r \, d\boldsymbol{s} \\ (\overline{T'^2})^{1/2} &= \frac{1}{\rho R} \left(\int_{-\infty}^{\infty} q_4^2 \, d\boldsymbol{s} \right)^{1/2} \end{aligned} \right\}$$

(86)

Thus the two sets of equations for the average (Eqs.(71)) and separated equations for fluctuation-correlations (Eqs.(80)) are coupled through those quantities. They have to be solved simultaneously subject to homogeneous boundary conditions for q's as

$$\left. \begin{aligned} q_\alpha(\boldsymbol{x}_b, \boldsymbol{s}) &= 0 \quad (\alpha \neq 40) \\ (\partial q_{40}/\partial x_n)_{\boldsymbol{x}=\boldsymbol{x}_b} &= 0 \end{aligned} \right\}$$

(87)

at solid boundaries and at laminar-turbulent flow boundaries $\boldsymbol{x} = \boldsymbol{x}_b$, also

$$q_\alpha(\boldsymbol{x}, \pm\infty) = 0$$

(88)

a necessary condition to secure convergence of the integral in the $\boldsymbol{s}$-space.

6. Concluding remarks

So far the 'Reynolds average' concept is considered not to be applicable to turbulent combustion gasdynamics. This negative view has its origin in poor predictivity for one of the four average turbulent transports, namely, the chemical reaction rate. It is concluded that if one employs bimodal Arrhenius law to replace the classical one, sound 'average' description of turbulent combustion may well be expected despite its on-off structure of signals to be observed at the reaction front, a sign of marginal variance amplitude allowed for statistical description.

The bimodal law as the average turbulent reaction rate and its variance are derived on the basis of the turbulent equilibrium, an exact solution of non-equilibrium statistical mechanics. It is only through the microscopic approach that the correct estimate for population of high energy (reactive) molecules is possible, and thereby high reactivity under turbulent environment is elucidated.

Also proposed are Reynolds averaged gasdynamic equations for turbulent combustion with those renovations incorporated. They are coupled with another set

governing turbulent fluctuations through the turbulent transport processes to constitute a closed system.

Appendix. Equations governing turbulent fluctuation-correlations

The actual expression for Λ'_α of Eq.(80) subject to rules I and II are

$$\left.\begin{aligned}
\Lambda'_0 &\equiv \partial\rho'/\partial t + (\partial/\partial x_r)(\rho u'_r + \rho' u_r^\dagger + \rho' u'_r - \overline{\rho' u'_r}) = 0 \\
u_r^\dagger &= m_r/\rho = (\rho u_r + \overline{\rho' u'_r})/\rho
\end{aligned}\right\} \tag{A1}$$

$$\left.\begin{aligned}
\Lambda'_j &\equiv \frac{\partial}{\partial t}(\rho' u_j^\dagger + \rho u'_j) + \frac{\partial}{\partial x_r}[\rho u_r^\dagger u'_j + \rho u_j^\dagger u'_r \\
&\quad + \rho' u_j^\dagger u_r^\dagger + \rho u'_j u'_r - \rho\overline{u'_j u'_r} + p'\delta_{jr} + (p'_{jr})_{\text{NS}}] = 0 \\
(p'_{jr})_{\text{NS}} &= -\mu[\partial u'_r/\partial x_j + \partial u'_j/\partial x_r - (2\delta_{jr}/3)\partial u'_k/\partial x_k] \\
&\quad -(d\mu/dT)T'[\partial u_r^\dagger/\partial x_j + \partial u_j^\dagger/\partial x_r - (2\delta_{jr}/3)\partial u_k^\dagger/\partial x_k]
\end{aligned}\right\} \tag{A2}$$

$$\left.\begin{aligned}
\Lambda'_4 &= \frac{1}{\gamma-1}\frac{\partial p'}{\partial t} + \frac{\partial}{\partial x_r}\left[\frac{\gamma}{\gamma-1}(p' u_r^\dagger + p u'_r + p' u'_r - \overline{p' u'_r})\right. \\
&\quad \left. + (Q'_r)_{\text{Fourier}}\right] + \sum_{\text{a}} e_{\text{a}}^0 W'_{\text{a}} = 0 \\
(Q'_r)_{\text{Fourier}} &= -\lambda \partial T'/\partial x_r - (d\lambda/dT)T'\partial T/\partial x_r
\end{aligned}\right\} \tag{A3}$$

$$\left.\begin{aligned}
\Lambda'_{\text{a}} &= \frac{\partial\rho Y'_{\text{a}}}{\partial t} + \frac{\partial}{\partial x_r}\left[\rho u_r^\dagger Y'_{\text{a}} + \rho Y'_{\text{a}} u'_r - \rho\overline{Y'_{\text{a}} u'_r} + (M'_{\text{a}r})_{\text{Fick}}\right] \\
&\quad + \rho u'_r\frac{\partial Y_{\text{a}}}{\partial x_r} - W'_{\text{a}} + \frac{\rho'}{\rho}W_{\text{a}} = 0 \\
(M'_{\text{a}r})_{\text{Fick}} &= -\rho D_{\text{a}}\frac{\partial Y'_{\text{a}}}{\partial x_r} - \frac{d(\rho D_{\text{a}})}{dT}T'\frac{\partial Y_{\text{a}}}{\partial x_r}
\end{aligned}\right\} \tag{A4}$$

Eqs.(80) are again separable into respective independent variables $\boldsymbol{x}$ and $\widehat{\boldsymbol{x}}$ with full nonlinear terms retained when subjected to the following separation rules:

$$\left.\begin{aligned}
\overline{Z'_\alpha \widehat{Z}'_\beta} &= \text{R.P.}l^3 \int_{-\infty}^{\infty} d\boldsymbol{k}\, g_\alpha(\boldsymbol{k})\, \widehat{g}^*_\beta(\boldsymbol{k}) \\
\overline{Z'_\alpha \widehat{Z}'_\beta Z'_\gamma} &= \text{R.P.}l^6 \int_{-\infty}^{\infty} d\boldsymbol{k}\, \widehat{g}^*_\beta(\boldsymbol{k}) \int_{-\infty}^{\infty} d\widehat{\boldsymbol{k}}\, g_\alpha(\boldsymbol{k}-\widehat{\boldsymbol{k}})\, g_\gamma(\widehat{\boldsymbol{k}}) \\
\overline{Z'_\alpha \widehat{Z}'_\beta \widehat{Z}'_\gamma} &= \text{R.P.}l^6 \int_{-\infty}^{\infty} d\boldsymbol{k}\, g_\alpha(\boldsymbol{k}) \int_{-\infty}^{\infty} d\widehat{\boldsymbol{k}}\, \widehat{g}^*_\beta(\boldsymbol{k}-\widehat{\boldsymbol{k}})\, \widehat{g}^*_\gamma(\widehat{\boldsymbol{k}})
\end{aligned}\right\} \tag{A5}$$

This separation rule preserves the property that periodic part in g's be separated out after (52), namely,

$$g_\alpha(\boldsymbol{x},\, \boldsymbol{k}) = e^{i\boldsymbol{k}\cdot\boldsymbol{x}} G_\alpha(\boldsymbol{x},\, \boldsymbol{k})$$

which converts Eqs.(78) in 6D space $(\boldsymbol{x}, \widehat{\boldsymbol{x}})$ into those in another 6D space $(\boldsymbol{x}, \boldsymbol{k})$ as

$$D(\boldsymbol{k})G_0 + \partial_r(\boldsymbol{k})G_r = 0 \tag{A6}$$

$$\left.\begin{array}{l} D(\boldsymbol{k})G_j + \partial_r(\boldsymbol{k})(u_r^\dagger G_j + G_{40}\delta_{rj} + G_{rj}) \\ \qquad + (\partial u_j^\dagger/\partial x_r)G_r - \rho^{-1}(\partial p/\partial x_j)G_0 = 0 \\ G_{rj} = -\mu[\partial_j(\boldsymbol{k})(\rho^{-1}G_r) + \partial_r(\boldsymbol{k})(\rho^{-1}G_j) - (2/3)\delta_{jr}\partial_k(\boldsymbol{k})(\rho^{-1}G_k)] \\ \qquad - [\partial u_r^\dagger/\partial x_j + \partial u_j^\dagger/\partial x_r - (2/3)\delta_{jr}\partial u_k^\dagger/\partial x_k]\dfrac{G_4}{\rho R}\dfrac{d\mu}{dT} \\ \qquad + (1/\rho)[\Gamma(G_jG_r) - (\delta_{jr}/3)\Gamma(G_kG_k)] \end{array}\right\} \tag{A7}$$

$$\left.\begin{array}{l} \dfrac{1}{\gamma-1}D(\boldsymbol{k})G_{40} + \partial_r(\boldsymbol{k})\left(\dfrac{\gamma}{\gamma-1}G_{40}u_r^\dagger + G_{rkk}\right) + \displaystyle\sum_a e_a^0 G_{aW} = 0 \\ G_{rkk} = -(\lambda/R)[\partial_r(\boldsymbol{k})(\rho^{-1}G_4) + p^{-1}G_4\dfrac{d\lambda}{dT}\partial RT/\partial x_r] \\ \qquad + [\gamma/(\gamma-1)][RTG_r + \rho^{-1}\Gamma(G_rG_4)] \end{array}\right\} \tag{A8}$$

$$\left.\begin{array}{l} D(\boldsymbol{k})G_a + \partial_r(\boldsymbol{k})(u_r^\dagger G_a + G_{a,r}) + G_r\partial Y_a/\partial x_r - G_{Wa} + \dfrac{G_0}{\rho}W_a = 0 \\ G_{a,r} = -\rho D_a\partial_r(\boldsymbol{k})(\rho^{-1}G_a) - \dfrac{d(\rho D_a)}{dT}\dfrac{G_4}{\rho R}\dfrac{\partial Y_a}{\partial x_r} + \rho^{-1}\Gamma(G_aG_r) \end{array}\right\} \tag{A9}$$

where we have defined the following quantities,

$$D(\boldsymbol{k})G \equiv \partial G/\partial t - i\boldsymbol{k}\cdot\boldsymbol{V}_pG \tag{A10}$$

$$\partial_r(\boldsymbol{k}) \equiv \partial/\partial x_r + ik_r \tag{A11}$$

$$\Gamma(G_\alpha G_\beta) \equiv \int_{-\infty}^{\infty} G_\alpha(\boldsymbol{k} - \boldsymbol{k}')G_\beta(\boldsymbol{k}')d\boldsymbol{k}' \tag{A12}$$

$$G_{40} = G_4 + RTG_0 \tag{A13}$$

Eqs.(A4) through (A7) govern the 'wave' functions G_0, G_j, $G_4(G_{40})$ and G_a, G_b, $\cdots$ from which turbulent correlations $\overline{Z_\alpha'\widehat{Z}_\beta'}$ are calculated. Relationships between the two groups of variables are the following;

$$Z_\alpha' = \begin{pmatrix} \rho' \\ \rho u_j' \\ \rho RT' \\ p' \\ \rho Y_a' \\ W_a' \end{pmatrix} \qquad G_\alpha = \begin{pmatrix} G_0 \\ G_j \\ G_4 \\ G_{40} \\ G_a \\ G_{Wa} \end{pmatrix} \tag{A14}$$

Turbulent transports that appear in the equations for the average are

$$
\begin{aligned}
\rho\overline{u_j' u_r'} &= \frac{1}{\rho}\text{R.P.}l^3 \int_{-\infty}^{\infty} G_j G_r^* d\boldsymbol{k}, \quad \text{(Reynolds stress)} \\
\rho\overline{h' u_r'} &= \frac{1}{\rho}\frac{\gamma}{\gamma-1}\text{R.P.}l^3 \int_{-\infty}^{\infty} G_4 G_r^* d\boldsymbol{k}, \quad \text{(turbulent heat flux density)} \\
\rho\overline{Y_a' u_r'} &= \frac{1}{\rho}\text{R.P.}l^3 \int_{-\infty}^{\infty} G_a G_r^* d\boldsymbol{k}, \quad \text{(turbulent diffusion)} \\
(\overline{T'^2})^{1/2} &= \frac{1}{\rho R}\left(l^3 \int_{-\infty}^{\infty} G_4 G_4^* d\boldsymbol{k}\right)^{1/2}, \quad \text{(turbulent chemical reaction)}
\end{aligned}
\right\} \quad \text{(A15)}
$$

These equations as derived above in the $\boldsymbol{k}$-space are integro-differential equations having nonlinear integrals Γ. These integral expressions are of convolution type, so are eliminated by Fourier transform

$$
G_\alpha(\boldsymbol{x},\,\boldsymbol{k}) = \frac{1}{(2\pi l)^3}\int_{-\infty}^{\infty} d\boldsymbol{s}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{s}} q_\alpha(\boldsymbol{x},\,\boldsymbol{s}) \tag{A16}
$$

leading to an equivalent set of equations in eddy ($\boldsymbol{s}$) space simply through a transformation rule posted in Table A. Their actual forms are:

$$
Dq_0 + \partial_r q_r = 0 \tag{A17}
$$

$$
\begin{aligned}
&Dq_j + \partial_r(u_r^\dagger q_j + q_{40}\delta_{rj} + q_{rj}) + q_r \partial u_j^\dagger/\partial x_r - \rho^{-1}(\partial p/\partial x_j)q_0 = 0 \\
&q_{jr} = -\mu[\partial_j(\rho^{-1}q_r) + \partial_r(\rho^{-1}q_j) - (2/3)\delta_{jr}\partial_k(\rho^{-1}q_k)] \\
&\qquad -[\partial u_r^\dagger/\partial x_j + \partial u_j^\dagger/\partial x_r - (2/3)\delta_{jr}\partial u_k^\dagger/\partial x_k]\frac{q_4}{\rho R}\frac{d\mu}{dT} \\
&\qquad +\rho^{-1}[q_j q_r - (\delta_{jr}/3)q_k^2]
\end{aligned}
\right\} \quad \text{(A18)}
$$

$$
\begin{aligned}
&\frac{1}{\gamma-1}Dq_{40} + \partial_r\left(\frac{\gamma}{\gamma-1}q_{40}u_r^\dagger + q_{rkk}\right) + \sum_a e_a^0 q_{aW} = 0 \\
&q_{rkk} = -(\lambda/R)[\partial_r(\rho^{-1}q_4) + p^{-1}q_4\frac{d\lambda}{dT}\partial RT/\partial x_r] \\
&\qquad +[\gamma/(\gamma-1)](RT q_r + \rho^{-1}q_r q_4)
\end{aligned}
\right\} \quad \text{(A19)}
$$

$$
\begin{aligned}
&Dq_a + \partial_r(u_r^\dagger q_a + q_{a,r}) + q_r\partial Y_a/\partial x_r - q_{Wa} + \rho^{-1}q_0 W_a = 0 \\
&q_{a,r} = -\rho D_a \partial_r(\rho^{-1}q_a) - \frac{d(\rho D_a)}{dT}\frac{q_4}{\rho R}\frac{\partial Y_a}{\partial x_r} + \rho^{-1}q_a q_r \\
&q_{Wa} = \pm m_a q_W \qquad (\pm\,;\text{ species [a] produced/disappeared}) \\
&q_W = \frac{S}{2}\left[W_0^+ - W_0^- + \frac{S}{2}(W_0^+ + W_0^- - W_0^{+-})\right]
\end{aligned}
\right\} \quad \text{(A20)}
$$

$$
q_{40} = q_4 + \rho R q_0 \tag{A21}
$$

22

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Figure captions

Fig.1 Dependence of flame velocity u_T/u_L on turbulent intensity u'/u_L of methane-air premixture in elevated pressure environments. Kobayashi et al (1996)[3].

Fig.2 Failure of the classical theory $(\delta T = 0)$ in predicting ignition time τ at low-temperatures $(T < 1000°K)$, as corrected by turbulent reaction rate formula $(\delta T > 0)$[11].

Fig.3 Turbulent flame velocity u_T/u_L as dependent on turbulent intensity u'/u_L of 9.0 percent H_2-air premixture due to a predecessor theory[14] of the current one as compared with existing experiments, also with Arrhenius law equivalent and renormalization group theory.

Fig.4 Maxwellian equilibrium f_0 $(\delta T = 0)$ and Turbulent equilibrium f^0 $(\delta T > 0)$ distribution function plotted against absolute molecular velocity, revealing appreciable difference in the population of high-energy molecules eligible for chemical reactions.

Fig.5 Relative variance of reaction rates under turbulence around (a) averaged Arrhenius reaction rate and (b) turbulent (bimodal) reaction rate.

Table captions

Table 1 Molecular and turbulent transport processes

Table 2 Fluctuations in transport processes

Table A Conversion rules from wave-number space ($\boldsymbol{k}$) to eddy space ($\boldsymbol{s}$)

momentum (shear) flux density	$p_{jl} = -\mu \left(\dfrac{\partial u_j^\dagger}{\partial x_l} + \dfrac{\partial u_l^\dagger}{\partial x_j} - \dfrac{2}{3}\delta_{jl}\dfrac{\partial u_k^\dagger}{\partial x_k} \right) + \rho\overline{u_j' u_l'}$ $\qquad$ (Navier-Stokes' law) $\qquad$ (Reynolds stress) $(u_j^\dagger = m_j/\rho)$
heatflux density	$q_j = -\lambda\dfrac{\partial T^\dagger}{\partial x_j} \qquad\qquad + \rho\overline{u_j' h'}$ $\qquad$ (Fourier's law) $\qquad$ (turbulent heatflux density) $(T^\dagger = p/\rho R)$
partial mass flux density	$= -\rho D\dfrac{\partial Y_a^\dagger}{\partial x_j} \qquad\quad + \rho\overline{u_j' Y_a'}$ $\qquad$ (Fick's law) $\qquad$ (turbulent diffusion) $(Y_a^\dagger = \rho_a/\rho)$
chemical reaction rate	$W = \dfrac{1}{2}\left[A(n_a + \delta n_a)(n_b + \delta n_b)\exp\left(-\dfrac{E}{\mathcal{R}(T + \delta T)} \right) \right.$ $\qquad\qquad \left. + A(n_a - \delta n_a)(n_b - \delta n_b)\exp\left(-\dfrac{E}{\mathcal{R}(T - \delta T)} \right) \right]$ $\qquad$ (turbulence-corrected Arrhenius law)

Table 1

fluctuations in	molecular	turbulent
momentum (shear) flux density	$-\mu[\partial_j(\rho^{-1}q_r) + \partial_r(\rho^{-1}q_j)$ $-(2/3)\delta_{jr}\partial_k(\rho^{-1}q_k)]$ $-[\partial u_r^\dagger/\partial x_j + \partial u_j^\dagger/\partial x_r$ $-(2/3)\delta_{jr}\partial u_k^\dagger/\partial x_k]\dfrac{q_4}{\rho R}\dfrac{d\mu}{dT}$	$+\rho^{-1}[q_j q_r - (\delta_{jr}/3)q_k^2]$
heatflux density	$-(\lambda/R)[\partial_r(\rho^{-1}q_4)$ $+p^{-1}q_4\dfrac{d\lambda}{dT}\partial RT/\partial x_r]$	$+[\gamma/(\gamma-1)](RTq_j + \rho^{-1}q_j q_4)$
partial mass flux density	$-\rho D_a \partial_r(\rho^{-1}q_a)$ $-\dfrac{d(\rho D_a)}{dT}\dfrac{q_4}{\rho R}\dfrac{\partial Y_a}{\partial x_r}$	$+\rho^{-1}q_a q_r$
chemical reaction rate	$\dfrac{S}{2}\left[W_0^+ - W_0^- + \dfrac{S}{2}(W_0^+ + W_0^- - W_0^{+-})\right]$	

Table 2

wave number ($\boldsymbol{k}$) space	$\rightarrow$	eddy ($\boldsymbol{s}$) space
$G_\alpha(\boldsymbol{x},\,\boldsymbol{k})$	$\rightarrow$	$q_\alpha(\boldsymbol{x},\,\boldsymbol{s})$
ik_j	$\rightarrow$	$\partial/\partial s_j$
$\partial_j(\boldsymbol{k}) = \partial/\partial x_j + ik_j$	$\rightarrow$	$\partial_j = \partial/\partial x_j + \partial/\partial s_j$
$D(\boldsymbol{k})G_\alpha = \partial G_\alpha/\partial t - i\boldsymbol{k}\cdot\boldsymbol{V}_pG_\alpha$	$\rightarrow$	$Dq_\alpha = \partial q_\alpha/\partial t - V_{pr}\partial q_\alpha/\partial s_r$
$l^3\displaystyle\int_{-\infty}^{\infty} G_\alpha(\boldsymbol{k}')G_\beta(\boldsymbol{k}-\boldsymbol{k}')d\boldsymbol{k}'$	$\rightarrow$	$q_\alpha q_\beta$

Table A

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