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Fluctuating Hydrodynamic Equations of Mixed and of Chemically Reacting Gases

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The method of the nonlinear Langevin equation is generalized to ordinary mixed and to chemically reacting gases. The stochastic Boltzmann equations of these gases, the fluctuating hydrodynamic equations of mixed gases, and the Langevin equations for the number density of each component of a reaction–diffusion system are obtained.

KEY WORDS: Langevin equation; mixed gas; chemical reaction; Boltzmann equation; hydrodynamics; fluctuation; diffusion.

1. INTRODUCTION

Studies on fluctuations in chemically reacting systems are important for clarifying the mechanism of appearance of "dissipative structures."[1] Since chemically reacting systems are in principle described by the Boltzmann equation so long as they are dilute,[2] the fluctuations may also be described as those of the Boltzmann equation.[3] On the basis of this idea Nicolis derived a multivariate master equation that is in principle complete. However, it is so complex that no one has analyzed it. Instead, some approximate equations based on more or less phenomenological arguments, such as the nonlinear master equation,[4] have been discussed.[5]

The problem of fluctuations of the Boltzmann equation of ordinary (not chemically reacting) mixed gases has also been an important subject for study since the pioneering work of Fox and Uhlenbeck.[6,7] Clearly, the two problems are very similar. Malek-Mansour *et al.*[8] tried to apply the method of stochastic analysis developed for the problem of chemically reacting systems to the other problem. This work shows the similarity most clearly.

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The method of the nonlinear Langevin equation has recently led to some success with regard to the problem of fluctuations of ordinary gases.[9] Langevin-like equations for each of the particles that constitute a fluid are so constructed that they give the same expectation values of physical quantities as the master equation[10] gives, and then a stochastic equation of the one particle distribution is derived from them. This is just the Boltzmann equation equipped with a term of the Langevin fluctuating force. The fluctuating hydrodynamic equations of Landau and Lifshitz[11] are also derivable from this stochastic Boltzmann equation by a direct application of the Chapman–Enskog expansion.[12,13] This method may be expected to be applicable to chemically reacting systems.

This paper aims at presenting a theory of the stochastic Boltzmann equation of chemically reacting systems and a theory of hydrodynamic fluctuations in these systems. These theories include as special cases those of fluctuations in ordinary mixed gases at the kinetic and at the hydrodynamic stages.[10]

The fluctuations of the diffusion velocity, or the thermal current, are shown to be characterized by the diffusion, or the thermodiffusion, coefficients [see Eqs. (70) and (72)].

A set of Langevin equations for the number density of each component in a reaction–diffusion system is obtained [see Eqs. (114)]. The problem of the fluctuations of these systems is reduced to that of solving the set of the Langevin equations.

After this paper was submitted, the author learned of other work on hydrodynamic fluctuations associated with diffusion and chemical reactions.[14–20] In the author's opinion, those works are sufficiently different from the present work so as to make publication of this paper worthwhile.

2. MASTER EQUATION

The Boltzmann equation is derived from the master equation[10]

$$\frac{\partial}{\partial t} f(\mathbf{v}_1, \mathbf{v}_2, \ldots, \mathbf{v}_N, t) = \sum_{(ij)} \iint \{ W(\mathbf{v}_i, \mathbf{v}_j, \mathbf{v}_i', \mathbf{v}_j') f(\mathbf{v}_1, \ldots, \mathbf{v}_i', \ldots, \mathbf{v}_j', \ldots, \mathbf{v}_N, t) - W(\mathbf{v}_i', \mathbf{v}_j', \mathbf{v}_i, \mathbf{v}_j) f(\mathbf{v}_1, \ldots, \mathbf{v}_i, \ldots, \mathbf{v}_j, \ldots, \mathbf{v}_N, t)\} \, d\mathbf{v}_i' \, d\mathbf{v}_j' \tag{1}$$

When chemical reactions occur, Eq. (1) is modified. For simplicity, we consider in this section a binary reaction

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{C} + \mathrm{D} \tag{2}$$

This reaction may be considered as a collision of two particles, say i and j, in which the "state" of the ith or the jth particle changes from A to C, or B to D, respectively. Accordingly, each particle is specified not only by the velocity $\mathbf{v}$, but also by the state α. For reaction (2), this variable may take four values A, B, C, and D. Equation (1) is extended to the form

$$\begin{aligned}\frac{\partial}{\partial t} f(\mathbf{v}_1; \alpha_1,\dots, \mathbf{v}_N, \alpha_N, t) = \sum_{(ij)} \sum_{\alpha_i' \alpha_j'} \iint d\mathbf{v}_i' \, d\mathbf{v}_j' \\ \times \{W(\mathbf{v}_i, \mathbf{v}_j, \mathbf{v}_i', \mathbf{v}_j'; \alpha_i, \alpha_j, \alpha_i', \alpha_j') \\ \times f(\mathbf{v}_1, \alpha_1,\dots, \mathbf{v}_i', \alpha_i',\dots, \mathbf{v}_j', \alpha_j',\dots, \mathbf{v}_N, \alpha_N, t) \\ - W(\mathbf{v}_i', \mathbf{v}_j', \mathbf{v}_i, \mathbf{v}_j; \alpha_i', \alpha_j', \alpha_i, \alpha_j) \\ \times f(\mathbf{v}_1, \alpha_1,\dots, \mathbf{v}_i, \alpha_i,\dots, \mathbf{v}_j, \alpha_j,\dots, \mathbf{v}_N, \alpha_N, t)\} \quad (3)\end{aligned}$$

When the system is not homogeneous, the space variable $\mathbf{r}$ should be attached and we have

$$\begin{aligned}\frac{\partial}{\partial t} f(a_1, a_2,\dots, a_N, t) + \sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} f(a_1,\dots, a_N, t) \\ = \sum_{(ij)} \{W(a_i, a_j, a_i', a_j') f(a_1,\dots, a_i',\dots, a_j',\dots, a_N, t) \\ - W(a_i', a_j', a_i, a_j) f(a_1,\dots, a_i,\dots, a_j,\dots, a_N, t)\} \, da_i' \, da_j' \quad (4)\end{aligned}$$

where the following notations are used:

$$a_i = (\mathbf{r}_i, \mathbf{v}_i, \alpha_i), \qquad \int da_i = \sum_{\alpha_i} \int d\mathbf{r}_i \int d\mathbf{v}_i \quad (5)$$

So long as the system is dilute, we may consider each particle as a point and may assume that collisions are local events:

$$\begin{aligned}W(a_i, a_j, a_i', a_j') = \delta(\mathbf{r}_i - \mathbf{r}_j)\delta(\mathbf{r}_i - \mathbf{r}_i')\delta(\mathbf{r}_j - \mathbf{r}_j') \\ \times W(\mathbf{v}_i, \mathbf{v}_j, \mathbf{v}_i', \mathbf{v}_j'; \alpha_i, \alpha_j, \alpha_i', \alpha_j') \quad (6)\end{aligned}$$

The function $W = W(\mathbf{v}_i, \mathbf{v}_j, \mathbf{v}_i', \mathbf{v}_j'; \alpha_i, \alpha_j, \alpha_i', \alpha_j')$ describes all the kinds of binary collisions. Among them, we may distinguish the elastic and the inelastic collisions,

$$W = W^{\mathrm{el}} + W^{\mathrm{inel}} \quad (7)$$

$$\begin{aligned}W^{\mathrm{el}} &= \delta_{\alpha_1\alpha_1'}\delta_{\alpha_2\alpha_2'} W(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_1', \mathbf{v}_2'; \alpha_1, \alpha_2, \alpha_1', \alpha_2') \\ &= \delta_{\alpha_1\alpha_1'}\delta_{\alpha_2\alpha_2'} W_{\alpha_1\alpha_2}(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_1', \mathbf{v}_2') \quad (8)\end{aligned}$$

When the inelastic collisions are absent, Eq. (4) gives the master equation of mixed gases.

Equation (4) is the fundamental assumption of this paper. The relation of Eq. (4) to the Boltzmann equation is simple. On the assumption of molecular chaos

$$f(a_1, a_2, \ldots, a_N, t) = \prod_i f_{\alpha_i}^{(1)}(\mathbf{r}_i, \mathbf{v}_i, t) \tag{9}$$

Eq. (4) gives

$$\begin{aligned} &\frac{\partial}{\partial t} f_\alpha^{(1)}(\mathbf{r}, \mathbf{v}, t) + \mathbf{v}\frac{\partial}{\partial \mathbf{r}} f_\alpha^{(1)}(\mathbf{r}, \mathbf{v}, t) \\ &\quad = \mathscr{I}_\alpha(\{f_\alpha^{(1)}\}) \equiv \sum_{\alpha'\alpha_1\alpha_1'} \iiint d\mathbf{v}'\, d\mathbf{v}_1\, d\mathbf{v}_1' \\ &\quad \times \{W(\mathbf{v}, \mathbf{v}_1, \mathbf{v}'\mathbf{v}_1'; \alpha, \alpha_1, \alpha', \alpha_1') f_{\alpha'}^{(1)}(\mathbf{r}, \mathbf{v}', t) f_{\alpha_1'}^{(1)}(\mathbf{r}, \mathbf{v}_1', t) \\ &\quad - W(\mathbf{v}', \mathbf{v}_1'; \mathbf{v}, \mathbf{v}_1; \alpha', \alpha_1', \alpha, \alpha_1) f_\alpha^{(1)}(\mathbf{r}, \mathbf{v}, t) f_{\alpha_1}^{(1)}(\mathbf{r}, \mathbf{v}_1, t)\} \end{aligned} \tag{10}$$

Equation (10) reduces to the Boltzmann equation of Ross and Mazur[2] when the system is homogeneous.

3. STOCHASTIC BOLTZMANN EQUATION

The stochastic process that is described by the Fokker–Planck equation may also be described by the Langevin equation (see, e.g., Ref. 21). This theorem is formally extended in previous papers[9] to the case of the master equation

$$\frac{\partial}{\partial t} f(a) = \int \{W(a, a')f(a') - W(a', a)f(a)\}\, da' \tag{11}$$

We may construct the Langevin equations

$$\frac{d}{dt} a(t) = \alpha_1(a(t)) + R(t) \tag{12}$$

$$\frac{d}{dt} a^n(t) = \sum_{k=1}^{n} \binom{n}{k} a^{n-k}(t)\alpha_k(a(t)) + R_n(t), \qquad n = 2, 3, \ldots \tag{13}$$

that are stochastically equivalent to Eq. (11). In Eq. (13), $\alpha_k(a)$ is the kth derivate moment of the transition probability and $R_n(t)$ is a random force.[9] Further, when the distribution

$$g(x, t) = \delta(x - a(t)) \tag{14}$$

is introduced, Eqs. (12) and (13) may be simply expressed by

$$\frac{\partial}{\partial t} g(x, t) = \int k(x, x')g(x', t)\, dx' + r(x, t) \tag{15}$$

where

$$k(x, x') = W(x, x') - \delta(x - x') \int W(x'', x)\, dx'' \tag{16}$$

through the relations

$$a^n(t) = \int x^n g(x, t)\, dx, \qquad R_n(t) = \int x^n r(x, t)\, dx, \qquad R(t) = R_1(t) \tag{17}$$

The expectation values of the random force are given as follows:

$$\overline{r(x, t)} = 0 \tag{18}$$

$$\begin{aligned} \overline{r(x, t)r(y, s)} = \delta(t - s) \iint dz_1\, dz_2\, [\delta(x - z_1) - \delta(x - z_2)] \\ \times [\delta(y - z_1) - \delta(y - z_2)] W(z_1, z_2) g(z_2, t) \end{aligned} \tag{19}$$

The higher order correlation functions of $r(x, t)$ have similar expressions to Eq. (19), since $r(x, t)$ is a Poisson-like process. When Eq. (11) is multivariate, $a = \{a_1, a_2, \dots, a_N\}$, the following replacements should be done:

$$\begin{aligned} &g(x, t) \to g(x_1, x_2, \dots, x_N, t) = \prod_{i=1}^{N} \delta(x_i - a_i(t)) \\ &\delta(x - y) \to \prod_{i=1}^{N} \delta(x_i - y_i), \qquad \int da \to \int \cdots \int da_1\, da_2 \cdots da_N, \quad \text{etc.} \end{aligned} \tag{20}$$

[Detailed derivations of Eqs. (12)–(20) are given in Ref. 9.]

Now, we may apply this theorem to Eq. (4). We have

$$\begin{aligned} \frac{\partial}{\partial t} g(x_1, \dots, x_N, t) + \sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} g(x_1, \dots, x_N, t) \\ = \int \cdots \int dx_1' \cdots dx_N'\, k(x_1, \dots, x_N, x_1', \dots, x_N') \\ \times g(x_1', \dots, x_N') + r(x_1, \dots, x_N, t) \end{aligned} \tag{21}$$

where

$$k(x_1,\ldots,x_N,x_1',\ldots,x_N')$$

$$=\sum_{(ij)}\Omega(x_i,x_j,x_i',x_j')\prod_{k\neq i,j}\delta(x_k-x_k')$$

$$\equiv\sum_{(ij)}\{W(x_i,x_j,x_i',x_j')-\delta(x_i-x_i')\delta(x_j-x_j')$$

$$\times\iint dx_i''\,dx_j''\,W(x_i'',x_j'',x_i,x_j)\}\sum_{k\neq i,j}\delta(x_k-x_k') \tag{22}$$

Because of the factorization property of Eq. (20), we may reduce Eq. (21) to

$$\frac{\partial}{\partial t}g_i(x,t)+\mathbf{v}\frac{\partial}{\partial\mathbf{r}}g_i(x,t)=\sum_j\iiint\Omega(x,x_1,x',x_1')g_i(x',t)$$

$$\times g_j(x_1',t)\,dx_1\,dx'\,dx_1'+r_i(x,t) \tag{23}$$

where

$$g_i(x,t)=\delta(x-a_i(t)) \tag{24}$$

$$r_i(x,t)=\int\cdots\int dx_1\cdots dx_N\,\delta(x-x_i)r(x_1,\ldots,x_N,t) \tag{25}$$

For the one-particle distribution

$$\tilde{g}(x,t)=\sum_i g_i(x,t) \tag{26}$$

we have

$$\frac{\partial}{\partial t}\tilde{g}(x,t)+\mathbf{v}\frac{\partial}{\partial\mathbf{r}}\tilde{g}(x,t)$$

$$=\int\cdots\int\Omega(x,x_1,x',x_1')\tilde{g}(x',t)\tilde{g}(x_1',t)+\tilde{r}(x,t) \tag{27}$$

where

$$\tilde{r}(x,t)=\sum_i r_i(x,t) \tag{28}$$

Going back to the concrete notation,

$$\tilde{g}(x,t)=g(\mathbf{r},\mathbf{v},t)$$

we may rewrite Eq. (27) as

$$\mathscr{D}[g_\alpha(\mathbf{r}, \mathbf{v}, t)] \equiv \left(\frac{\partial}{\partial t} + \mathbf{v}\frac{\partial}{\partial \mathbf{r}}\right)g_\alpha(\mathbf{r}, \mathbf{v}, t) = \mathscr{J}_\alpha(\{g_\alpha\}) + r_\alpha(\mathbf{r}, \mathbf{v}, t) \tag{29}$$

that is, the stochastic Boltzmann equation. By this reduction of variables, Eq. (19) reduces to

$$\overline{r_\alpha(\mathbf{r}, \mathbf{v}, t)r_\beta(\mathbf{r}', \mathbf{v}', t')} = 2n^2\delta(t - t')\delta(\mathbf{r} - \mathbf{r}')[\delta_{\mathbf{v}\alpha}, \delta_{\mathbf{v}'\beta}] \tag{30}$$

where $n = n(\mathbf{r})$ is the total number density of the gas,

$$\delta_{\mathbf{v}\alpha} = \delta_{\mathbf{v}\alpha}(\mathbf{v}_1, \alpha_1) = \delta(\mathbf{v} - \mathbf{v}_1)\delta_{\alpha\alpha_1}$$

and the inner product of two functions is defined as follows:

$$[\Phi, \Psi] = (1/4n^2) \sum_{\alpha_1\alpha_2\alpha_1'\alpha_2'} \int \cdots \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{v}_1'\, d\mathbf{v}_2'\, \Delta[\Phi]\Delta[\Psi]$$
$$\times W(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_1', \mathbf{v}_2'; \alpha_1, \alpha_2, \alpha_1', \alpha_2')g_{\alpha_1'}(\mathbf{r}, \mathbf{v}_1', t)g_{\alpha_2'}(\mathbf{r}, \mathbf{v}_2', t) \tag{31}$$

$$\Delta[\Phi] = \Phi(\mathbf{v}_1, \alpha_1) + \Phi(\mathbf{v}_2, \alpha_2) - \Phi(\mathbf{v}_1', \alpha_1') - \Phi(\mathbf{v}_2', \alpha_2') \tag{32}$$

Equations (29) and (30) are the conclusions of this section. Equation (29) is similar in form to Eq. (10), but is free from the assumption of molecular chaos. It is stochastically equivalent to the master equation.

4. FLUCTUATIONS IN MIXED GASES

We are going to analyze the stochastic Boltzmann equation [Eq. (29)]. In this section, we consider the case in which chemical reactions are absent. The transition probability is given by Eq. (8).

The arbitrary one-particle quantity

$$\Psi_t \equiv \sum_i \Psi(\mathbf{r}_i(t), \mathbf{v}_i(t), \alpha_i(t)) = \sum_\alpha \iint d\mathbf{r}\, d\mathbf{v}\, \Psi(\mathbf{r}, \mathbf{v}, \alpha)g_\alpha(\mathbf{r}, \mathbf{v}, t) \tag{33}$$

obeys

$$\mathscr{D}[\Psi] = \sum_{\alpha\beta} \int \cdots \int d\mathbf{r}\, d\mathbf{v}\, d\mathbf{v}_1\, d\mathbf{v}'\, d\mathbf{v}_1'\, \Psi(\mathbf{r}, \mathbf{v}, \alpha)$$
$$\times \{W_{\alpha\beta}(\mathbf{v}, \mathbf{v}_1, \mathbf{v}', \mathbf{v}_1')g_\alpha(\mathbf{r}, \mathbf{v}', t)g_\beta(\mathbf{r}, \mathbf{v}_1', t)$$
$$- W_{\alpha\beta}(\mathbf{v}', \mathbf{v}_1', \mathbf{v}, \mathbf{v}_1)g_\alpha(\mathbf{r}, \mathbf{v}, t)g_\beta(\mathbf{r}, \mathbf{v}_1, t)\} + R_\Psi(t) \tag{34}$$

where

$$R_\Psi(t) = \sum_\alpha \iint d\mathbf{r}\, d\mathbf{v}\, \Psi(\mathbf{r}, \mathbf{v}, \alpha)r_\alpha(\mathbf{r}, \mathbf{v}, t) \tag{35}$$

By the method of change of variables, $(\mathbf{v}, \alpha) \leftrightarrow (\mathbf{v}_1, \beta)$, Eq. (34) changes to

$$\mathscr{D}[\Psi] = \frac{1}{2} \sum_{\alpha_1\alpha_2\alpha_1'\alpha_2'} \int \cdots \int d\mathbf{r}\, d\mathbf{v}\, d\mathbf{v}_1\, d\mathbf{v}'\, d\mathbf{v}_1'\, \Delta[\Psi] \delta_{\alpha_1\alpha_1'} \delta_{\alpha_2\alpha_2'} \times W_{\alpha_1\alpha_2}(\mathbf{v}, \mathbf{v}_1, \mathbf{v}', \mathbf{v}_1') g_{\alpha_1}(\mathbf{r}, \mathbf{v}', t) g_{\alpha_2}(\mathbf{r}, \mathbf{v}_1', t) + R_\Psi(t) \tag{36}$$

where $\Delta[\Psi]$ is defined by Eq. (32).

Accordingly, both the collision and the random force terms vanish for conserved quantities Ψ because of the identity

$$\Psi_{\alpha_1}(\mathbf{v}_1) + \Psi_{\alpha_2}(\mathbf{v}_2) - \Psi_{\alpha_1}(\mathbf{v}_1') - \Psi_{\alpha_2}(\mathbf{v}_2') = 0 \tag{37}$$

We may say that the random force term vanishes when its correlation functions vanish. Then, the local equilibrium distribution

$$F_\alpha(\mathbf{r}, \mathbf{C}, t) = n_\alpha(\mathbf{r})(\beta_\alpha/\pi)^{3/2} \exp(-\beta_\alpha C^2) \tag{38}$$

where

$$\beta_\alpha = m_\alpha/2kT, \qquad \mathbf{C} = \mathbf{v} - \mathbf{u}(\mathbf{r}) \tag{39}$$

is a stationary solution of Eq. (34). We may follow the theory of the Chapman–Enskog expansion. We use the notations of Waldmann[13] in the following.

Putting

$$g_\alpha(\mathbf{r}, \mathbf{v}, t) = F_\alpha(\mathbf{r}, \mathbf{C}, t)\{1 + \Phi_\alpha(\mathbf{r}, \mathbf{C}, t)\} \tag{40}$$

we obtain

$$\mathscr{D}[F_\alpha] = -\sum_\beta n_\alpha n_\beta \mathscr{I}_{\alpha\beta}[\Phi] + r_\alpha(\mathbf{r}, \mathbf{v}, t) \tag{41}$$

where

$$n_\alpha n_\beta \mathscr{I}_{\alpha\beta}[\Phi] = \int \cdots \int d\mathbf{v}_1\, d\mathbf{v}'\, d\mathbf{v}_1' \times \{\Phi_\alpha(\mathbf{r}, \mathbf{v}, t) + \Phi_\beta(\mathbf{r}, \mathbf{v}_1, t) - \Phi_\alpha(\mathbf{r}, \mathbf{v}', t) - \Phi_\beta(\mathbf{r}, \mathbf{v}_1', t)\} \times W_{\alpha\beta}(\mathbf{v}, \mathbf{v}_1, \mathbf{v}', \mathbf{v}_1') F_\alpha(\mathbf{r}, \mathbf{v}', t) F_\beta(\mathbf{r}, \mathbf{v}_1', t) \tag{42}$$

In this approximation Eq. (30) reduces to

$$\begin{aligned}
&\overline{r_\alpha(\mathbf{r}, \mathbf{v}, t) r_\beta(\mathbf{r}', \mathbf{v}', t')} \\
&= 2\delta(t - t')\delta(\mathbf{r} - \mathbf{r}')n^2[\delta_{\mathbf{v}\alpha}, \delta_{\mathbf{v}'\beta}]_F \equiv 2\delta(t - t')\delta(r - r') \\
&\times \sum_{\alpha_1\alpha_2} \iint d\mathbf{v}\, d\mathbf{v}_1\, \delta(\mathbf{v} - \mathbf{v}_1)\delta_{\alpha\alpha_1} n_{\alpha_1} n_{\alpha_2} \mathscr{I}\, [\delta_{v'\beta}]
\end{aligned} \tag{43}$$

Notice that our definition of the inner product $[\cdot, \cdot]_F$ is identical to that of Waldmann.[15]

The solvability condition of Eq. (41) gives the hydrodynamical equations of the number density n, the fractional number density $\gamma_\alpha = n_\alpha/n$, the temperature T, etc.:

$$\frac{\partial}{\partial t} n + \frac{\partial}{\partial x_\mu} n w_\mu = 0 \tag{44}$$

$$\rho \frac{\partial u_\mu}{\partial t} + \rho u_\nu \frac{\partial u_\mu}{\partial x_\nu} = -\frac{\partial p_{\mu\nu}}{\partial x_\nu} \tag{45}$$

$$\left(\frac{d\gamma_\alpha}{dt}\right)_{\mathrm{w}} = -\frac{1}{n}\frac{\partial}{\partial x_\mu} n_\alpha W_{\mu\alpha} \tag{46}$$

$$\frac{5}{2} kT \left(\frac{dT}{dt}\right)_{\mathrm{w}} = \frac{dp}{dt} - \frac{\partial}{\partial x_\mu} q_\mu^{(\mathrm{w})} - (p_{\mu\nu} - p\delta_{\mu\nu}) \frac{\partial u_\mu}{\partial x_\nu} \tag{47}$$

where

$$w_\mu = u_\mu + \frac{1}{n} \int C_\mu \sum_\alpha F_\alpha(\mathbf{r}, \mathbf{C}, t)\, d\mathbf{C} \tag{48}$$

$$\left(\frac{df}{dt}\right)_{\mathrm{w}} \equiv \frac{\partial f}{\partial t} + w_\mu \frac{\partial f}{\partial x_\mu} \tag{49}$$

The pressure tensor $p_{\mu\nu}$, the diffusion velocity $W_{\mu\alpha}$, *and the heat current* $q_\mu^{(\mathrm{w})}$ are given as follows:

$$p_{\mu\nu} = \sum_\alpha m_\alpha \int C_\mu C_\nu F_\alpha \Phi_\alpha\, d\mathbf{C} \tag{50}$$

$$W_{\mu\alpha} = \int C_\mu \left(\frac{F_\alpha}{n_\alpha} \Phi_\alpha - \frac{1}{n} \sum_l F_l \Phi_l\right) d\mathbf{C} \tag{51}$$

$$q_\mu^{(\mathrm{w})} = \sum_\alpha \int \left(\frac{m_\alpha}{2} C^2 - \frac{5}{2} kT\right) C_\mu F_\alpha \Phi_\alpha\, d\mathbf{C} \tag{52}$$

Because the collision operator is linear, the solution of Eq. (41) is given by

$$\Phi_\alpha = \Phi_\alpha' + \Phi_\alpha'' \tag{53}$$

where

$$\mathscr{D}[F_\alpha] = -\sum_\beta n_\alpha n_\beta \mathscr{I}_{\alpha\beta}[\Phi'] \tag{54}$$

$$-\sum_\beta n_\alpha n_\beta \mathscr{I}_{\alpha\beta}[\Phi''] + r_\alpha(\mathbf{r}, \mathbf{v}, t) = 0 \tag{55}$$

Corresponding to the decomposition of Eq. (53), we have

$$p_{\mu\nu} = p'_{\mu\nu} + p''_{\mu\nu}, \qquad W_{\mu\alpha} = W'_{\mu\alpha} + W''_{\mu\alpha}, \qquad q_\mu^{(\mathrm{w})} = q_\mu'^{(\mathrm{w})} + q_\mu''^{(\mathrm{w})} \tag{56}$$

The solution of Eq. (54) and the resulting expressions for the hydrodynamical variables are well known,[13]

$$\begin{aligned} p'_{\mu\nu} &= p\delta_{\mu\nu} - 2\eta\langle \partial u_\mu/\partial x_\nu\rangle \\ W'_{\mu\alpha} &= -\sum_\beta D_{\alpha\beta} d_{\mu\beta} - D_{T\alpha}(\partial T/T\,\partial x_\mu) \\ q_\mu'^{(\mathrm{w})} &= -p\sum_\alpha D_{T\alpha} d_{\mu\alpha} - \lambda'\,\partial T/\partial x_\mu \end{aligned} \tag{57}$$

where

$$d_{\mu\alpha} = \partial\gamma_\alpha/\partial x_\mu + (\gamma_\alpha - \rho_\alpha/\rho)(\partial p/p\,\partial x_\mu)$$

The transport coefficients are given[13] by

$$\eta = (kT/10)[B\beta\langle C_\mu C_\nu\rangle, B\beta\langle C_\mu C_\nu\rangle]_F \tag{58}$$

$$D_{\alpha\beta} = (1/3n)[A^{(\alpha)}C_\mu, A^{(\beta)}C_\mu]_F \tag{59}$$

$$D_{T\alpha} = (1/3n)[AC_\mu, A^{(\alpha)}C_\mu]_F \tag{60}$$

$$\lambda' = \tfrac{1}{3}k[AC_\mu, AC_\mu]_F \tag{61}$$

The functions A, $A^{(\cdot)}$, B are defined as the solutions of the following integral equations:

$$\sum_j \gamma_j \mathscr{I}_{ij}\left[\left(A^{(k)} - \sum_l \gamma_l \mathbf{A}^{(l)}\right)C_\mu\right] = \frac{F_i}{n_i}\left(\frac{\delta_{ik}}{\gamma_i} - 1\right) \tag{62}$$

$$\sum_j \gamma_j \mathscr{I}_{ij}[AC_\mu] = \frac{F_i}{n_i}(\beta_i C^2 - \tfrac{5}{2})C_\mu \tag{63}$$

$$\sum_j \gamma_j \mathscr{I}_{ij}[B\beta\langle C_\mu C_\nu\rangle] = 2\frac{F_i}{n_i}\beta_i\langle C_\mu C_\nu\rangle \tag{64}$$

The second part of the right-hand side of Eq. (56) is now given as follows:

$$\begin{aligned} p''_{\mu\nu} &= \sum_\alpha m_\alpha \int C_\mu C_\nu F_\alpha \Phi_\alpha'' \, d\mathbf{v} \\ &= \frac{kT}{n}\sum_{ij}\int n_i n_j \mathscr{I}_{ij}[B\beta\langle C_\mu C_\nu\rangle]\Phi_i'' \, d\mathbf{v} \\ &= \frac{kT}{n}\sum_{ij}\int n_i n_j \mathscr{I}_{ij}[\Phi'']B_i\beta_i\langle C_\mu C_\nu\rangle \, d\mathbf{v} \\ &= -\frac{kT}{n}\sum_i \int B_i\beta_i\langle C_\mu C_\nu\rangle r_i(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{v} \end{aligned} \tag{65}$$

where Eqs. (50), (53), and (64) have been used. Similarly, we have

$$W''_{\mu\alpha} = -\frac{1}{n^2}\sum_i \int A_i^{(\alpha)} C_\mu r_i(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{v} \tag{66}$$

$$q_\mu''^{(\mathrm{w})} = -\frac{kT}{n}\sum_\alpha \int A_\alpha C_\mu r_\alpha(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{v} \tag{67}$$

Since Eqs. (65)–(67) are linear functionals of $\{r_\alpha(\mathbf{r}, \mathbf{v}, t)\}$, Eq. (17) yields

$$\overline{p''_{\mu\nu}} = \overline{W''_{\mu\alpha}} = \overline{q_\mu''^{(\mathrm{w})}} = 0 \tag{68}$$

Finally, with the aid of Eqs. (43), (58)–(61), and (65)–(68), we obtain the following results:

$$\overline{p''_{\mu\nu}(\mathbf{r}, t)p''_{\mu'\nu'}(\mathbf{r}', t')} = 2\eta kT\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \times (\delta_{\mu\mu'}\delta_{\nu\nu'} + \delta_{\mu\nu'}\delta_{\nu\mu'} - \tfrac{2}{3}\delta_{\mu\nu}\delta_{\mu'\nu'}) \tag{69}$$

$$\overline{W''_{\mu\alpha}(\mathbf{r}, t)W''_{\mu'\alpha'}(\mathbf{r}', t')} = (2/n)D_{\alpha\alpha'}\delta_{\mu\mu'}\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \tag{70}$$

$$\overline{q_\mu''^{(\mathrm{w})}(\mathbf{r}, t)q_{\mu'}''^{(\mathrm{w})}(\mathbf{r}', t')} = 2\lambda' kT^2\delta_{\mu\mu'}\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \tag{71}$$

$$\overline{W''_{\mu\alpha}(\mathbf{r}, t)q_{\mu'}''^{(\mathrm{w})}(\mathbf{r}, t')} = 2D_{T\alpha}kT\delta_{\mu\mu'}\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \tag{72}$$

Equations (69)–(72), together with Eqs. (56) and (68), are the conclusions of this section. Equation (69) is the well-known expression of Landau and Lifshitz[12] and Eqs. (70)–(72) are the generalizations to multicomponent fluids.

5. CHEMICALLY REACTING FLUIDS

Now we consider Eq. (29) in the case of chemical reactions

$$\mathscr{D}[g_\alpha(\mathbf{r}, \mathbf{v}, t)] = \mathscr{I}_\alpha^{\text{el}}(\{g_\beta\}) + \mathscr{I}_\alpha^{\text{inel}}(\{g_\beta\}) + r_\alpha(\mathbf{r}, \mathbf{v}, t) \tag{73}$$

Even in this case, almost all the collisions are elastic. Inelastic collisions occur seldomly. Accordingly, the zeroth-order approximate solution of Eq. (73) is the local equilibrium distribution as before, and the first-order solution is also given by Eq. (40). Because of the inelastic collisions, Eq. (41) is to be modified as

$$\mathscr{D}[F_\alpha] = -\sum_\beta n_\alpha n_\beta \mathscr{I}_{\alpha\beta}[\Phi] + \mathscr{I}_\alpha^{\text{inel}}(\{F_\beta\}) + r_\alpha(\mathbf{r}, \mathbf{v}, t) \tag{74}$$

The solvability condition of Eq. (74)

$$\sum_\alpha \int d\mathbf{v}\, \psi_\alpha(\mathbf{v})\{\mathscr{D}[F_\alpha] - \mathscr{I}_\alpha^{\text{inel}}(\{F_\beta\}) - r_\alpha(\mathbf{r}, \mathbf{v}, t)\} = 0 \tag{75}$$

for

$$\psi_\alpha(\mathbf{v}) = \delta_{\alpha\beta}, \qquad m_\alpha v_{\alpha\mu} \quad (\mu = x, y, z), \qquad \text{and} \qquad \tfrac{1}{2} m_\alpha v_\alpha{}^2 \tag{76}$$

gives the set of hydrodynamic equations. The first one of (76) with Eq. (75) gives

$$\left(\frac{\partial n_\alpha}{\partial t}\right)_{\text{inel}} = \sum_{\beta\alpha'\beta'} (n_{\alpha'} n_{\beta'} K_{\alpha\beta\alpha'\beta'} - n_\alpha n_\beta K_{\alpha'\beta'\alpha\beta}) + R_\alpha(\mathbf{r}, t) \tag{77}$$

where

$$K_{\alpha\beta\alpha'\beta'} = \int \cdots \int W^{\text{inel}}(\mathbf{v}, \mathbf{v}_1, \mathbf{v}', \mathbf{v}_1{}'; \alpha, \beta, \alpha', \beta') \times F_{\alpha'}(\mathbf{v}') F_{\beta'}(\mathbf{v}_1{}')\, d\mathbf{v}_1\, d\mathbf{v}'\, d\mathbf{v}_1{}'/n_{\alpha'} n_{\beta'} \tag{78}$$

$$R_\alpha(\mathbf{r}, t) = \int r_\alpha(\mathbf{r}, \mathbf{v}, t) d\mathbf{v} \tag{79}$$

The correlation function of the random force is calculated with the use of Eq. (30) as

$$\overline{R_\alpha(\mathbf{r}, t) R_\beta(\mathbf{r}', t')} = \tfrac{1}{2}\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \times \sum_{\alpha_1\alpha_2\alpha_1'\alpha_2'} K_{\alpha_1\alpha_2\alpha_1'\alpha_2'} n_{\alpha_1'} n_{\alpha_2'} \bar{\Delta}(\delta_\alpha)\bar{\Delta}(\delta_\beta) \tag{80}$$

where

$$\overline{\Delta}(\delta_\alpha) = \delta_{\alpha\alpha_1} + \delta_{\alpha\alpha_2} - \delta_{\alpha\alpha'_1} - \delta_{\alpha\alpha'_2} \tag{81}$$

Combined with the contribution of the elastic collisions, Eq. (77) gives

$$\left(\frac{\partial \gamma_\alpha}{\partial t}\right)_{\text{w}} = -\frac{1}{n}\frac{\partial}{\partial x_\mu} n_\alpha W_{\mu\alpha} + \frac{1}{n}\left(\frac{\partial n_\alpha}{\partial t}\right)_{\text{inel}} \tag{77'}$$

When the thermodiffusion coefficients $D_{T\alpha}$ are negligibly small, Eqs. (77′) and (57) form a set of closed equations, which we may rewrite as one equation,

$$\begin{aligned}\left(\frac{\partial \gamma_\alpha}{\partial t}\right)_{\text{w}} &= \frac{1}{n}\sum_{\beta\mu} \frac{\partial}{\partial x_\mu} n_\alpha D_{\alpha\beta} \frac{\partial}{\partial x_\mu} \gamma_\beta \\ &\quad + n \sum_{\beta\beta'\alpha'} (\gamma_{\alpha'}\gamma_{\beta'} K_{\alpha\beta\alpha'\beta'} - \gamma_\alpha \gamma_\beta K_{\alpha'\beta'\alpha\beta}) \\ &\quad + R_\alpha(\mathbf{r}, t) - \frac{1}{n}\sum_\mu \frac{\partial}{\partial x_\mu} n_\alpha W''_{\mu\alpha}\end{aligned} \tag{82}$$

Equation (82) is a simple result. The last two terms are random forces and the other terms give just the deterministic equation of the reaction–diffusion system. The two contributions of the total random force are mututally independent

$$\overline{R_\alpha(\mathbf{r}, t) W''_{\mu\beta}(\mathbf{r}', t')} = 0 \tag{83}$$

since random forces due to different mechanisms are independent in general,[2] as we can see from Eq. (18).

6. TRIMOLECULAR AND UNIMOLECULAR REACTIONS

From the viewpoint of the formation of dissipative structure, trimolecular reactions of the form

$$2X + Y \rightleftarrows 3X$$

are important.[1,5,21] We must generalize Eq. (3) so that it includes processes of three-particle scattering.

[2] If the transision probability is composed of contributions of different mechanisms $W(x, y) = \sum_i W^{(i)}(x, y)$, we may write

$$r(x, t) = \sum_i r^{(i)}(x, t)$$

$$\begin{aligned}\overline{r^{(i)}(x, t) r^{(j)}(y, s)} &= \delta(t - s)\delta_{ij} \iint dz_1\, dz_2\, [\delta(x - z_1) - \delta(x - z_2)] \\ &\quad \times [\delta(y - z_1) - \delta(y - z_2)] W^{(i)}(z_1, z_2) g(z_2, t)\end{aligned}$$

since this set of equations reproduces Eq. (18).

These processes are characterized by the form of transition probability

$$W(\mathbf{v}_i, \mathbf{v}_j, \mathbf{v}_k, \mathbf{v}_i', \mathbf{v}_j', \mathbf{v}_k'; \alpha_i, \alpha_j, \alpha_k, \alpha_i', \alpha_j', \alpha_k') \tag{84}$$

We may easily generalize the formulation of Section 3 to this case by only replacing Eq. (22) by

$$k(x_1, x_2, \ldots, x_N') = \sum_{(ijk)} \Omega(x_i, x_j, x_k, x_i', x_j', x_k') \prod_{l \neq i,j,k} \delta(x_l - x_l') \tag{85}$$

Then, the contribution of the three-particle processes to the stochastic Boltzmann equation is found to be

$$\begin{aligned}\left[\frac{\partial}{\partial t} g_\alpha(\mathbf{r}, \mathbf{v}, t)\right]_{\text{tri}} = \frac{1}{2} \sum_{\alpha_2\alpha_3\alpha'\alpha_2'\alpha_3'} & \int \cdots \int d\mathbf{v}_2\, d\mathbf{v}_3\, d\mathbf{v}'\, d\mathbf{v}_2'\, d\mathbf{v}_3' \\ & \times \{W(\mathbf{v}, \mathbf{v}_2, \mathbf{v}_3, \mathbf{v}', \mathbf{v}_2', \mathbf{v}_3'; \alpha, \alpha_2, \alpha_3, \alpha', \alpha_2', \alpha_3') \\ & \times g_{\alpha'}(\mathbf{r}, \mathbf{v}', t) g_{\alpha_2'}(\mathbf{r}, \mathbf{v}_2', t) g_{\alpha_3'}(\mathbf{r}, \mathbf{v}_3', t) \\ & - W(\mathbf{v}', \mathbf{v}_2', \mathbf{v}_3', \mathbf{v}, \mathbf{v}_2, \mathbf{v}_3; \alpha', \alpha_2', \alpha_3', \alpha, \alpha_2, \alpha_3) \\ & \times g_\alpha(\mathbf{r}, \mathbf{v}, t) g_{\alpha_2}(\mathbf{r}, \mathbf{v}_2, t) g_{\alpha_3}(\mathbf{r}, \mathbf{v}_3, t)\} + r_\alpha(\mathbf{r}, \mathbf{v}, t)\end{aligned} \tag{86}$$

A rather complicated calculation similar to the derivation of Eq. (30) yields

$$\begin{aligned}&\overline{r_\alpha(\mathbf{r}, \mathbf{v}, t) r_{\alpha'}(\mathbf{r}', \mathbf{v}', t')} \\ &\quad = \tfrac{1}{6}\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \\ &\quad \times \sum_{\alpha_1\alpha_2\alpha_3\alpha_1'\alpha_2'\alpha_3'} \int \cdots \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{v}_3\, d\mathbf{v}_1'\, d\mathbf{v}_2'\, d\mathbf{v}_3'\, \Delta_3[\delta_{\mathbf{v}\alpha}]\Delta_3[\delta_{\mathbf{v}'\alpha'}] \\ &\quad \times W(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3, \mathbf{v}_1', \mathbf{v}_2', \mathbf{v}_3'; \alpha_1, \alpha_2, \alpha_3, \alpha_1', \alpha_2', \alpha_3') \\ &\quad \times g_{\alpha_1'}(\mathbf{r}, \mathbf{v}_1', t) g_{\alpha_2'}(\mathbf{r}, \mathbf{v}_2', t) g_{\alpha_3'}(\mathbf{r}, \mathbf{v}_3', t)\end{aligned} \tag{87}$$

where

$$\begin{aligned}\Delta_3[\delta_{\mathbf{v}\alpha}] = {} & \delta(\mathbf{v} - \mathbf{v}_1)\delta_{\alpha\alpha_1} + \delta(\mathbf{v} - \mathbf{v}_2)\delta_{\alpha\alpha_2} + \delta(\mathbf{v} - \mathbf{v}_3)\delta_{\alpha\alpha_3} \\ & - \delta(\mathbf{v} - \mathbf{v}_1')\delta_{\alpha\alpha_1'} - \delta(\mathbf{v} - \mathbf{v}_2')\delta_{\alpha\alpha_2'} - \delta(\mathbf{v} - \mathbf{v}_3')\delta_{\alpha\alpha_3'}\end{aligned} \tag{88}$$

Equations (86) and (87) give the general expressions for the three-particle processes. We may suppose that almost all the collisions are two-particle elastic collisions as before, and that three-particle collisions are inelastic and seldom. Accordingly, we may substitute the local equilibrium distribution into g_α of Eq. (86) and obtain

$$\left(\frac{\partial n_\alpha}{\partial t}\right)_{\text{tri}} = \sum_{\alpha_2,\alpha_3,\alpha',\alpha_2',\alpha_3'} (K_{\alpha\alpha_2\alpha_3\alpha'\alpha_2'\alpha_3'} n_{\alpha'} n_{\alpha_2'} n_{\alpha_3'} - K_{\alpha'\alpha_2'\alpha_3'\alpha\alpha_2\alpha_3} n_\alpha n_{\alpha_2} n_{\alpha_3}) + R_\alpha(\mathbf{r}, t) \tag{89}$$

$$\overline{R_\alpha(\mathbf{r}, t) R_\beta(\mathbf{r}', t')} = \tfrac{1}{3}\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \times \sum_{\alpha_1 \cdots \alpha_3'} \bar{\Delta}_3(\delta_\alpha)\bar{\Delta}_3(\delta_\beta) K_{\alpha_1\alpha_2\alpha_3\alpha_1'\alpha_2'\alpha_3'} n_{\alpha_1'} n_{\alpha_2'} n_{\alpha_3'} \tag{90}$$

where

$$\Delta_3(\delta_\alpha) = \delta_{\alpha\alpha_1} + \delta_{\alpha\alpha_2} + \delta_{\alpha\alpha_3} - \delta_{\alpha\alpha_1'} - \delta_{\alpha\alpha_2'} - \delta_{\alpha\alpha_3'} \tag{91}$$

$$K_{\alpha_1\alpha_2\alpha_3\alpha_1'\alpha_2'\alpha_3'} = \frac{1}{2}\int \cdots \int d\mathbf{v}_1 \cdots d\mathbf{v}_3' \; W(\mathbf{v}_1, \ldots, \mathbf{v}_3'; \alpha_1, \ldots, \alpha_3') \times F_{\alpha_1'}(\mathbf{r}, \mathbf{v}_1', t) F_{\alpha_2'}(\mathbf{r}, \mathbf{v}_2', t) F_{\alpha_3'}(\mathbf{r}, \mathbf{v}_3', t)/n_{\alpha_1'} n_{\alpha_2'} n_{\alpha_3'} \tag{92}$$

Equation (89) gives the correction of Eq. (77) due to three-particle processes.

The reaction of the form

$$\text{A} \rightleftarrows \text{X} \tag{93}$$

is a unimolecular process. It is characterized by another form of the transition probability

$$W(\mathbf{v}_i, \mathbf{v}_i'; \alpha_i, \alpha_i')$$

The contribution of this process to the stochastic Boltzmann equation is found to be

$$\left[\frac{\partial}{\partial t} g_\alpha(\mathbf{r}, \mathbf{v}, t)\right]_{\text{uni}} = \sum_{\alpha'} \int d\mathbf{v}' \, [W(\mathbf{v}, \mathbf{v}'; \alpha, \alpha') g_{\alpha'}(\mathbf{r}, \mathbf{v}', t) - W(\mathbf{v}', \mathbf{v}; \alpha', \alpha) g_\alpha(\mathbf{r}, \mathbf{v}, t)] + \mathbf{r}_\alpha(\mathbf{r}, \mathbf{v}, t) \tag{94}$$

where

$$\overline{r_\alpha(\mathbf{r}, \mathbf{v}, t) r_\beta(\mathbf{r}', \mathbf{v}', t')} = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \sum_{\alpha_1\alpha_1'} \iint d\mathbf{v}_1 \, d\mathbf{v}_1' \times [\delta(\mathbf{v} - \mathbf{v}_1)\delta_{\alpha\alpha_1} - \delta(\mathbf{v} - \mathbf{v}_1')\delta_{\alpha\alpha_1'}] \times [\delta(\mathbf{v}' - \mathbf{v}_1')\delta_{\beta\alpha_1} - \delta(\mathbf{v}' - \mathbf{v}_1')\delta_{\beta\alpha_1'}] \times W(\mathbf{v}_1, \mathbf{v}_1'; \alpha_1, \alpha_1') g_{\alpha_1'}(\mathbf{r}, \mathbf{v}_{1'}, t) \tag{95}$$

By substituting the local equilibrium distribution into Eq. (94), we obtain the following results

$$\left(\frac{\partial n_\alpha}{\partial t}\right)_{\text{uni}} = \sum_\beta (K_{\alpha\beta} n_\beta - K_{\beta\alpha} n_\alpha) + R_\alpha(\mathbf{r}, t) \tag{96}$$

$$\overline{R_\alpha(\mathbf{r}, t) R_\beta(\mathbf{r}', t')} = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \times \sum_{\alpha_1 \alpha_1'} (\delta_{\alpha\alpha_1} - \delta_{\alpha\alpha_1'})(\delta_{\alpha\alpha_1} - \delta_{\alpha\alpha_1'}) K_{\alpha_1\alpha_1'} n_{\alpha_1'} \tag{97}$$

$$K_{\alpha_1\alpha_1'} = \iint d\mathbf{v}_1\, d\mathbf{v}_1'\; W(\mathbf{v}_1, \mathbf{v}_1'; \alpha_1, \alpha_1') F_{\alpha_1'}(\mathbf{r}, \mathbf{v}_1', t)/n_{\alpha_1'} \tag{98}$$

7. EXAMPLE

We consider now the fluctuations of the Brusselator,[1,4]

$$\begin{array}{llll} \mathrm{A} \rightarrow \mathrm{X} & \text{(a)}, & 2\mathrm{X} + \mathrm{Y} \rightarrow 3\mathrm{X} & \text{(b)} \\ \mathrm{B} + \mathrm{X} \rightarrow \mathrm{Y} + \mathrm{D} & \text{(c)}, & \mathrm{X} \rightarrow \mathrm{E} & \text{(d)} \end{array} \tag{99}$$

The transition probability of this system is composed of the contributions of the four kinds of reactions and of the elastic collisions. The number densities of the spaces A, B, D, and E are assumed homogeneous and time independent and only $X = n_{\mathrm{X}}$ and $Y = n_{\mathrm{Y}}$ are the variables of this system.

For each kind of reaction, we may apply the results of the preceding sections separately. We obtain the following results:

$$K_{\alpha\beta}^{(a)} = k_1 \qquad \text{only if} \quad \alpha = \mathrm{X}, \quad \beta = \mathrm{A} \tag{100}$$

$$\overline{R_{\mathrm{X}}^{(a)}(\mathbf{r}, t) R_{\mathrm{X}}^{(a)}(\mathbf{r}', t')} = k_1 A \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \tag{101}$$

$$K_{\alpha_1\alpha_2\alpha_3\beta_1\beta_2\beta_3}^{(b)} = k_2 \qquad \text{only if } \alpha_1 = \alpha_2 = \alpha_3 = \mathrm{X}, \quad \beta_1 = \beta_2 = \mathrm{X}, \quad \beta_3 = \mathrm{Y} \tag{102}$$

$$\overline{R_{\mathrm{X}}^{(b)}(\mathbf{r}, t) R_{\mathrm{X}}^{(b)}(\mathbf{r}', t')} = \overline{R_{\mathrm{Y}}^{(b)}(\mathbf{r}, t) R_{\mathrm{Y}}^{(b)}(\mathbf{r}', t')} = -\overline{R_{\mathrm{X}}^{(b)}(\mathbf{r}, t) R_{\mathrm{Y}}^{(b)}(\mathbf{r}', t')} = k_2 X^2 Y \delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \tag{103}$$

Notice that in Eq. (102) "only if . . ." means "if . . . , or the sets $\{\alpha_i\}$ and $\{\beta_i\}$ are permutations of . . . and zero otherwise."

$$K_{\alpha_1\alpha_2\beta_1\beta_2}^{(c)} = k_3 \qquad \text{only if} \quad \alpha_1 = \mathrm{Y}, \quad \alpha_2 = \mathrm{D}, \quad \beta_1 = \mathrm{B}, \quad \beta_2 = \mathrm{X} \tag{104}$$

$$\overline{R_X^{(c)}(\mathbf{r}, t)R_X^{(c)}(\mathbf{r}', t')} = \overline{R_Y^{(c)}(\mathbf{r}, t)R_Y^{(c)}(\mathbf{r}', t')} = -\overline{R_X^{(c)}(\mathbf{r}, t)R_Y^{(c)}(\mathbf{r}', t')}$$
$$= k_3BX\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \quad (105)$$

$$k_{\alpha\beta}{}^{(d)} = k_4 \qquad \text{only if} \quad \alpha = \mathrm{E}, \quad \beta = \mathrm{X} \quad (106)$$

$$\overline{R_X^{(d)}(\mathbf{r}, t)R_X^{(d)}(\mathbf{r}', t')} = k_4X\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \quad (107)$$

The elastic collisions cause diffusion. Among the many diffusion coefficients $D_{\alpha\beta}$, only the three D_{XX}, D_{YY}, and $D_{XY} = D_{YX}$ appear explicitly in the diffusion equations. We may introduce another set of coefficients

$$D = -D_{XY}, \qquad D_1 = \gamma_X(D_{XX} - D_{XY}), \qquad D_2 = \gamma_Y(D_{YY} - D_{XY}) \quad (108)$$

and for simplicity assume them to be constants. If the mutual diffusions between the X (or Y) and the A (or B, D, E) components are negligible, the system may be considered as a two-component system, for which a simple relation

$$D = D_1 = D_2 \quad (109)$$

holds.

On the condition that the total number density n is a constant and there is no net flow of masses ($\mathbf{w} = 0$), Eq. (46) reduces to

$$\frac{\partial}{\partial t} X = D_1 \nabla^2 X + R_X^{(e)}(\mathbf{r}, t) \quad (110)$$

$$\frac{\partial}{\partial t} Y = D_2 \nabla^2 Y + R_Y^{(e)}(\mathbf{r}, t) \quad (111)$$

where

$$R_\alpha^{(e)}(\mathbf{r}, t) = -\sum_\mu \frac{\partial}{\partial x_\mu} n_\alpha W''_{\mu\alpha}, \qquad \alpha = \mathrm{X}, \mathrm{Y} \quad (112)$$

Then, Eq. (70) gives

$$\overline{R_\alpha^{(e)}(\mathbf{r}, t)R_\beta^{(e)}(\mathbf{r}', t')} = \frac{2}{n} D_{\alpha\beta} \sum_\mu \frac{\partial}{\partial x_\mu} \frac{\partial}{\partial x_\mu{}'} n_\alpha(\mathbf{r}, t)n_\beta(\mathbf{r}', t')\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \quad (113)$$

When all the contributions in the above are taken into account, Eq. (82) yields

$$\begin{aligned} \frac{\partial}{\partial t} X &= k_1A + k_2X^2Y - k_3BX - k_4X + D_1 \nabla^2 X + R_X \\ \frac{\partial}{\partial t} Y &= k_3BX - k_2X^2Y + D_2 \nabla^2 Y + R_Y \end{aligned} \quad (114)$$

where

$$\overline{R_X(\mathbf{r}, t)R_X(\mathbf{r}', t')} = [k_1A + k_4X + k_2X^2Y + k_3BX + 2D\,\nabla\nabla' XY/n + 2(D_1 - D)\,\nabla\nabla' X]\delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$$
$$\overline{R_Y(\mathbf{r}, t)R_Y(\mathbf{r}', t')} = [k_2X^2Y + k_3BX + 2D\,\nabla\nabla' XY/n + 2(D_2 - D)\,\nabla\nabla' Y]\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \quad (115)$$
$$\overline{R_X(\mathbf{r}, t)R_Y(\mathbf{r}', t')} = -[k_2X^2Y + k_3BX + 2D\,\nabla\nabla' XY/n]\delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$$

Since the random forces in the hydrodynamical approximation are Gaussian,[9] we may write them as sums of the white noise fields $\{\xi_i(\mathbf{r}, t); i = 1,..., n\}$. We assume

$$\overline{\xi_i(\mathbf{r}, t)\xi_j(\mathbf{r}', t')} = \delta_{ij}\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \quad (116)$$

and

$$R_\alpha(\mathbf{r}, t) = \sum_i \sigma_{\alpha i}\xi_i(\mathbf{r}, t) \quad (117)$$

and determine the coefficients $\sigma_{\alpha i}$ so that Eq. (117) is consistent with Eqs. (115). The results are as follows

$$\sigma_{X1} = \sigma_{Y1} = (k_2X^2Y + k_3BX)^{1/2}$$
$$\sigma_{X2} = (k_1A + k_4X)^{1/2}, \qquad \sigma_{Y2} = 0$$
$$\sigma_{X3\mu} = -\sigma_{Y3\mu} = (\partial/\partial x_\mu)(2DXY/n)^{1/2} \quad (118)$$
$$\sigma_{X4\mu} = (\partial/\partial x_\mu)[2(D_1 - D)X/n]^{1/2}, \qquad \sigma_{Y4\mu} = 0$$
$$\sigma_{X5\mu} = 0, \qquad \sigma_{Y5\mu} = (\partial/\partial x_\mu)[2(D_2 - D)Y/n]^{1/2}, \qquad \mu = x, y, z; \; n = 11$$

Equations (114) together with Eqs. (118) are the final results of this section. The set (114) has a simple structure: Its deterministic part is just the kinetic equation of the Prigogine school.[1,4] The Langevin fluctuating forces characterized by Eqs. (118) describe the fluctuations of the Brusselator.

In the course of the derivation of Eqs. (114) and (118), no approximations have been used except for the hydrodynamical one of Eq. (40). This approximation is usually valid, since chemical reactions are phenomena near local equilibrium,[3] even if they are far from absolute equilibrium.

8. CONCLUDING REMARKS

The main results of this paper are the fluctuating hydrodynamic equations of mixed gases in Section 4 and the Langevin equations of chemically reacting fluids, an example of which is given in Eqs. (114). This is still a rather complicated set of equations: Besides the nonlinearity of the deterministic part, the correlation function of the random force depends on the variables, as Eqs. (118) show. Yet, Eqs. (114) enable us to analyze the fluctuations in a way parallel to the analyses of the deterministic part. For example, small fluctuations from a steady state (X_0, Y_0) may be studied by putting $X = X_0 + x$, $Y = Y_0 + y$ in Eqs. (114), and $X = X_0$, $Y = Y_0$ in Eqs. (118). The resulting linear Langevin equation may be easily solved with the aid of the linear stability theory.[1,4]

Hydrodynamic fluctuations are also important in many other phenomena. They are studied in the case of convection instability.[1,23,24] Of the various methods developed in that case, the method of Graham[24] based on the Landau–Lifshitz equation seems directly applicable to the case of Eqs. (114). A detailed analysis of Eqs. (114) will be given elsewhere.

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