

非線形輸送現象が気相化学反応に及ぼす効果

京都大学 大学院理学研究科

金賢得、早川尚男

Graduate School of Science, Kyoto University

Kim Hyeon-Deuk and Hisao Hayakawa

I. CHEMICALLY REACTING GAS

In the early stage of a chemical reaction between monatomic molecules:



the rate of chemical reaction is not affected by the existence of products. From the viewpoint of kinetic collision theory[1], the rate of chemical reaction (1) can be described as

$$R = \int d\mathbf{v} \int d\mathbf{v}_1 \int d\mathbf{k} \int f f_1 g \sigma(g), \quad (2)$$

where $\mathbf{v}$ and $\mathbf{v}_1$ are the velocities of the molecules, $g = |\mathbf{v} - \mathbf{v}_1|$ their relative speed, $\mathbf{k}$ the solid angle, $f = f(\mathbf{r}, \mathbf{v})$ and $f_1 = f(\mathbf{r}, \mathbf{v}_1)$ are the distributions of $\mathbf{v}$ and $\mathbf{v}_1$ at $\mathbf{r}$, respectively.

The line-of-centers model proposed by Present has been accepted as a standard model to describe the chemical reaction in gases.[1] It assumes the chemical cross-section as

$$\sigma(g) = \begin{cases} 0 & g < \sqrt{\frac{4E^*}{m}} \\ \frac{d^2}{4} \left(1 - \frac{4E^*}{mg^2}\right) & g \geq \sqrt{\frac{4E^*}{m}} \end{cases}, \quad (3)$$

with m mass of the molecules and E^* the threshold energy of the chemical reaction. d is regarded as a distance between centers of monatomic molecules at contact.

II. NONEQUILIBRIUM EFFECT ON THE RATE OF CHEMICAL REACTION

In order to calculate the rate of chemical reaction (2), we expand the velocity distribution function f to second order as

$$f = f^{(0)} + f^{(1)} + f^{(2)} = f^{(0)}(1 + \phi^{(1)} + \phi^{(2)}), \quad (4)$$

around the local Maxwellian, $f^{(0)} = n(m/2\pi\kappa T)^{3/2} \exp[-m\mathbf{v}^2/2\kappa T]$, with n the density of molecules, κ the Boltzmann constant and T the temperature defined from the kinetic energy. Substitution of eq.(4) into eq.(2) leads to

$$R = R^{(0)} + R^{(1)} + R^{(2)}, \quad (5)$$

up to second order. The zeroth-order term of R , the rate of chemical reaction of the equilibrium theory, becomes $R^{(0)} = \int d\mathbf{v} \int d\mathbf{v}_1 \int d\mathbf{k} \int f^{(0)} f_1^{(0)} g \sigma(g) = 4n^2 \sigma^2 \left(\frac{\pi\kappa T}{m}\right)^{1/2} e^{-\frac{E^*}{\kappa T}}$. The first-order term of R , i.e. $R^{(1)}$, does not appear because $\phi^{(1)}$ is an odd functions of $\mathbf{c}$. The second-order term of R , i.e. $R^{(2)}$, is divided into

$$R^{(2,A)} = \int d\mathbf{v} \int d\mathbf{v}_1 \int d\mathbf{k} \int f^{(0)} f_1^{(0)} \phi^{(1)} \phi_1^{(1)} g \sigma(g), \quad (6)$$

and

$$R^{(2,B)} = \int d\mathbf{v} \int d\mathbf{v}_1 \int d\mathbf{k} \int f^{(0)} f_1^{(0)} [\phi^{(2)} + \phi_1^{(2)}] g \sigma(g). \quad (7)$$

Since the integrations (6) and (7) have the cutoff from eq.(3), the explicit forms of $\phi^{(1)}$ and $\phi^{(2)}$ of the steady-state Boltzmann equation for hard-sphere molecules are required to calculate $R^{(2,A)}$ and $R^{(2,B)}$, respectively. Because Burnett had not derived the explicit second-order velocity distribution function of the Boltzmann equation[2], none has succeeded to obtain the correct reaction rate of Present's model except for Fort and Cukrowski who adopted information theory[4] as the nonequilibrium velocity distribution function to second order.[5] We have recently derived the explicit velocity distribution function of the steady-state Boltzmann equation for hard-core molecules to second order in density and the temperature gradient.[3] This enables us to calculate the effect of steady heat flux on the rate of chemical reaction based on the line-of-centers model.[6]

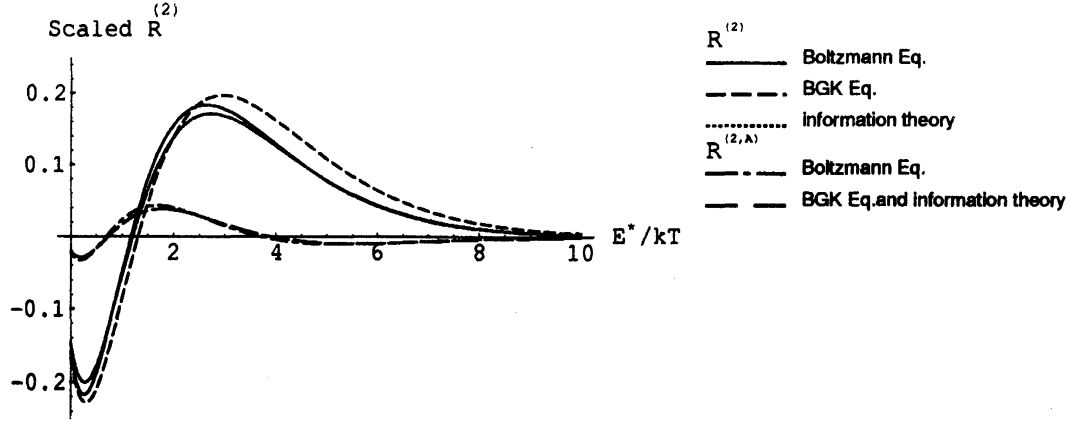


FIG. 1: Both of $R^{(2)}$ and $R^{(2,A)}$ are scaled by $\pi^{1/2} d^2 m^{1/2} J_s^2 / \kappa^{5/2} T^{5/2}$. Here J_s means a steady heat flux.

III. RESULTS AND DISCUSSION

We show only the graphical results of $R^{(2)}$ compared with those of $R^{(2,A)}$ in Fig.1.

We have found that $R^{(2,B)}$ plays an essential role for the evaluation of $R^{(2)}$, and that there are no qualitative differences in $R^{(2)}$ of the steady-state Boltzmann equation, the steady-state Bhatnagar-Gross-Krook (BGK) equation and information theory. It should be mentioned that, however, we have found qualitative differences among these theories in pressure tensor and the kinetic temperature.[3] We have also found that the steady-state BGK equation belongs to the same universality class as Maxwell molecules, and that information theory is inconsistent with the steady-state Boltzmann equation.[7]

The nonequilibrium effect on the rate of chemical reaction will substantiate significance of the second-order coefficients in the solution of the steady-state Boltzmann equation, although their importance has been demonstrated only for descriptions of shock wave profiles and sound propagation phenomena. This indicates the significance of the second-order coefficients as terms which reflect the local nonequilibrium effect.

We also propose a *thermometer* of a monatomic dilute gas system under a steady heat flux.[6] We mean that we can measure the temperature T around a heat bath at T_0 in the nonequilibrium steady-state system indirectly with the aid of the nonequilibrium effect on the rate of chemical reaction. The nonequilibrium effect in the early stage of chemical reaction around the heat bath can be measured experimentally. Thus, one can compare the experimental result with the theoretical result by setting $T = T_0$. The difference between the former and the latter will indicate that the temperature T around the heat bath is not identical with T_0 , but $T = T_0 + \Delta$ where Δ depends upon the steady heat flux in general.

Finally, we mention that we have performed calculations for the two-dimensional case in our recent paper.[8]

-
- [1] R. D. Present, *Kinetic Theory of Gases*, (Mcgraw-Hill, New York, 1958).
 - [2] D. Burnett, *Proc. Lond. Math. Soc.* **40**, 382-435 (1935).
 - [3] Kim. H.-D. and H. Hayakawa, *J. Phys. Soc. Jpn.* **72**, 1904-1916 (2003); *J. Phys. Soc. Jpn.* Vol.73 No.6 p.1609 (2004).
 - [4] D. Jou, J. Casas-Vázquez and G. Lebon: *Extended Irreversible Thermodynamics*, (Springer, Berlin, 2001).
 - [5] J. Fort and A. S. Cukrowski, *Chem. Phys.* **222**, 59-69 (1997).
 - [6] Kim. H.-D. and H. Hayakawa, *Chem. Phys. Lett.* **372**, 314-319 (2003).
 - [7] Kim. H.-D. and H. Hayakawa, *J. Phys. Soc. Jpn.* **72**, 2473-2476 (2003).
 - [8] Kim. H.-D., *Phys. Rev. E*, **71**, 041203 (2005).