APPLICATION OF INFORMATION STATISTICAL THEORY TO THE DESCRIPTION OF THE EFFECT OF HEAT CONDUCTION ON THE CHEMICAL REACTION RATE IN GASES[*, **]

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The effect of the heat flux on the rate of chemical reaction in dilute gases is shown to be important for reactions characterized by high activation energies and in the presence of very large temperature gradients. This effect, obtained from the second-order terms in the distribution function (similar to those obtained in the Burnett approximation to the solution of the Boltzmann equation), is derived on the basis of information theory. It is shown that the analytical results describing the effect are simpler if the kinetic definition for the nonequilibrium temperature is introduced than if the thermodynamic definition is introduced. The numerical results are nearly the same for both definitions.

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1. Introduction

According to the Curie principle [1], in linear nonequilibrium thermodynamics a cross effect between the heat flux (a vector quantity) and the rate of chemical reaction (a scalar quantity) cannot exist. If nonlinear theory is developed, a coupling between these quantities can be analyzed [2,3]. For a very simple model introduced by Present [4] for the reactive cross-section, the effect of heat conduction on the rate of chemical reaction has been analyzed [5]. As shown by us recently [6], in Ref. [5] only nonlinear terms were introduced through "square" terms arising from the multiplication of two velocity distribution functions satisfying the linearized Boltzmann equation [7]. We have shown [6] that additional terms, obtained in a relatively simple way from information theory [8,9] (and similar to terms which could be obtained in a much more complicated way within the Burnett solution to the Boltzmann equation [10]) play a very important role. Looking more carefully into this problem, we could see that the way temperature is defined (possible difference between the thermodynamic and kinetic temperatures have been emphasized [9,11–13]) can play an important role. This problem is interesting not only from the point of view of the particular application considered here, but also in a much wider perspective, because phenomenological Extended Irreversible Thermodynamics (EIT) predicts that in general the heat flux is not related to the gradient of the kinetic temperature but to the gradient of the thermodynamic temperature [11,14]. This is a strong point for the measurability of the thermodynamical temperature of EIT. However, the question remains open [15–19] and it is therefore important to find out to what extent the definition of temperature affects the analysis of different nonequilibrium effects [20–23]. Therefore, we decided to analyze the same problem as in our previous paper [6], and using a similar approach, but with the introduction of the temperature in the same way as in Ref. [9] in order to see the possible differences in the forms of the analytical expressions describing the effect of the heat flux on the rate of chemical reaction and in the magnitude of this effect. As in Ref. [6], we discuss the bimolecular chemical reaction

$$A + A \rightarrow B + B \tag{1.1}$$

in its early stages, so that the concentration of product B is very small.

The paper is organized as follows: in Section 2 we introduce some fundamental definitions and the first-order approximation, in Section 3 we follow the way of derivation in Ref. [6] but with a different definition for the temperature and obtain the analytical results for the effect analyzed, in Section 4 we analyze more carefully the differences between the new predictions and the old [6] ones, and Section 5 is devoted to a discussion of the results obtained and to some concluding remarks.

2. The first-order approximation

The general expression for the rate of the bimolecular chemical reaction (1.1) in a dilute gas (in its early stages, when the products can be neglected) is [24]

$$v_{\text{ch}} = \int d\vec{c} \int d\vec{c}_1 \int d\Omega f f_1 \left| \vec{c} - \vec{c}_1 \right| \ \sigma_{\text{re}} \left(\left| \vec{c} - \vec{c}_1 \right| \right) , \qquad (2.1)$$

with $\vec{c}$ and $\vec{c}_1$ velocities of A molecules, f and f_1 their respective distribution functions, $d\Omega$ a differential of solid angle and $\sigma_{\text{re}} \left(\left| \vec{c} - \vec{c}_1 \right| \right)$ the reactive cross-section. In order to find out expressions for v_{ch} in terms of macroscopic, directly measurable quantities, it is necessary to perform the integrations in Eq. (2.1). For this one needs to have both an expression for the reactive cross-section and an expression for the distribution function. Present introduced an important expression for the reactive cross-section. His cross-section leads to results that are both analytically solvable and realistic [4,25]. It reads

$$\sigma_{\text{re}} \left(\left| \vec{c} - \vec{c}_1 \right| \right) = \begin{cases} 0 & \text{for } \varepsilon < \varepsilon^* \\ \frac{d^2}{4} \left(1 - \frac{\varepsilon^*}{\varepsilon} \right) & \text{for } \varepsilon \geq \varepsilon^* \end{cases} , \qquad (2.2)$$

where d is the collision diameter of the molecules, $\varepsilon = \frac{m}{4} \left| \vec{c} - \vec{c}_1 \right|^2$, with m the molecular mass, and ε^* is the threshold energy of the chemical reaction.

The problem of the effect of temperature gradients on the rate of chemical reactions in ideal gases was tackled explicitly by Cukrowski and Popielawski twelve years ago [5], making use of Present's cross-section (2.2) and of the Chapman–Enskog kinetic theory method. In order to simplify the calculations, they considered slow reactions, so that the effect of the chemical reaction itself on the distribution function could be neglected. They found that their results agreed with those following from a more general and abstract approach based on the Grad thirteen moment method [2]. In both cases one finds the same result for the distribution function, namely

$$f = f^{(0)} \left(1 + \phi^{(1)} \right) + O(q^2) , \qquad (2.3)$$

where $f^{(0)}$ is the local Maxwell–Boltzmann distribution

$$f^{(0)} = n \left(\frac{m}{2\pi k T_{\text{K}}} \right)^{3/2} \mathrm{e}^{-\frac{mc^2}{2kT_{\text{K}}}} , \qquad (2.4)$$

$\phi^{(1)}$ is the following first-order correction in the heat flux q

$$\phi^{(1)} = \frac{m}{5nk^2 T_{\text{K}}^2} \left(\frac{mc^2}{kT_{\text{K}}} - 5 \right) \vec{q} \cdot \vec{c}, \qquad (2.5)$$

and $O(q^2)$ stands for second and higher order terms in q, which are not found out explicitly within such approximations. In the former equations, k is the Boltzmann constant, n the number density of particles, namely

$$n = \int d\vec{c} f \tag{2.6}$$

and T_K is the local kinetic temperature. Both in the Chapman–Enskog and in the Grad methods, this quantity is introduced through

$$\frac{3}{2}nkT_K \equiv \rho u = \int d\vec{c} f \, \frac{mc^2}{2}, \tag{2.7}$$

where $\rho = mn$ is the local density and u is the specific internal energy. The local phenomenological (or thermodynamical) temperature T, which is different in general from T_K [11,13], is introduced as

$$\frac{1}{T} \equiv \frac{\partial s}{\partial u}, \tag{2.8}$$

where s stands for the specific entropy. It is well-known (see, e.g., Ref. [11]) that at this level of approximation, i.e., up to first order in the heat flux $\vec{q}$ (see Eq. (2.3)), both definitions are equivalent,

$$T = T_K + O(q^2), \tag{2.9}$$

so that Cukrowski and Popielawski [5] did not have to take the problem of temperature definitions into account.

3. Temperature gradients in chemically reactive systems

After insertion of Eqs (2.2) and (2.3)–(2.5) into the general expression (2.1) and integration, one finds for v_{ch} a result which is the sum of two terms [5,6],

$$v_{ch} = v_{ch}^{(0)} + v_{ch}^{(2a)}, \tag{3.1}$$

where $v_{ch}^{(0)}$ is the rate corresponding to vanishing heat flux, i.e.

$$
\begin{aligned}
v_{ch}^{(0)} &\equiv \int d\vec{c} \int d\vec{c}_1 \int d\Omega f^{(0)} f_1^{(0)} \, |\vec{c} - \vec{c}_1| \, \sigma_{re} \left(|\vec{c} - \vec{c}_1| \right) \\
&= 4n^2 d^2 \left(\frac{\pi k T_K}{m} \right)^{1/2} e^{-\frac{\varepsilon^*}{kT_K}},
\end{aligned} \tag{3.2}
$$

and, as derived in Ref. [6],

$$v_{\text{ch}}^{(2a)} \equiv \int d\vec{c} \int d\vec{c}_1 \int d\Omega f^{(0)} f_1^{(0)} \phi^{(1)} \phi_1^{(1)} |\vec{c} - \vec{c}_1| \; \sigma_{\text{re}} \left(|\vec{c} - \vec{c}_1|\right)$$

$$= \frac{4 \, d^2 m}{75 \, k^3 T_{\text{K}}^3} \left(\frac{\pi k T_{\text{K}}}{m}\right)^{\frac{1}{2}} \vec{q} \cdot \vec{q} \, e^{-\frac{\varepsilon^*}{k T_{\text{K}}}}$$

$$\times \left(-\left[\frac{\varepsilon^*}{k T_{\text{K}}}\right]^3 + \frac{9}{2} \left[\frac{\varepsilon^*}{k T_{\text{K}}}\right]^2 - \frac{9}{4} \left[\frac{\varepsilon^*}{k T_{\text{K}}}\right] - \frac{3}{8}\right) . \qquad (3.3)$$

We have introduced the superindex $^{(2a)}$ in order to stress the following very important point. If one were able to include second-order terms in f, *i.e.* if one had an expression of the form

$$f = f^{(0)} \left(1 + \phi^{(1)} + \phi^{(2)}\right) + O(q^3), \qquad (3.4)$$

which generalized Eq. (2.3), then Eq. (2.1) would not lead to Eqs (3.1)–(3.3) but to

$$v_{\text{ch}} = v_{\text{ch}}^{(0)} + v_{\text{ch}}^{(2a)} + v_{\text{ch}}^{(2b)} + O(q^3), \qquad (3.5)$$

with $v_{\text{ch}}^{(0)}$ and $v_{\text{ch}}^{(2a)}$ given by Eqs (3.2) and (3.3), respectively, and

$$v_{\text{ch}}^{(2b)} = \int d\vec{c} \int d\vec{c}_1 \int d\Omega f^{(0)} f_1^{(0)} \left(\phi^{(2)} + \phi_1^{(2)}\right) |\vec{c} - \vec{c}_1| \; \sigma_{\text{re}} \left(|\vec{c} - \vec{c}_1|\right) . \quad (3.6)$$

It should be noted that both $v_{\text{ch}}^{(2a)}$ and $v_{\text{ch}}^{(2b)}$ in Eq. (3.5) are of second order in the heat flux $\vec{q}$. This means that Eq. (3.1), which follows from (2.3), should not be expected to be a reliable result. Therefore, in contrast to Eq. (3.5), Eq. (3.1) cannot be written as $v_{\text{ch}} = v_{\text{ch}}^{(0)} + v_{\text{ch}}^{(2a)} + O(q^3)$. As it was stressed in the last part of Ref. [5], the reason why this point was not taken into account in that paper is that it is very difficult to find an explicit expression for $\phi^{(2)}$ within the kinetic theory of gases. However, this turns out to be possible making use of nonequilibrium statistical mechanics instead of kinetic theory [9,13]. The Dominguez-Jou distribution is given by Eqs (3.4), (2.4), (2.5) and the following additional terms derived in Ref. [9]

$$\phi^{(2)} = \widetilde{\phi}^{(2)} + \widetilde{\widetilde{\phi}}^{(2)}, \qquad (3.7)$$

with

$$\widetilde{\phi}^{(2)} = -\frac{m}{5 \, n^2 k^3 T_{\text{K}}^3} \left(\frac{mc^2}{k T_{\text{K}}} - 2\right) \vec{q} \cdot \vec{q}, \qquad (3.8)$$

$$\widetilde{\widetilde{\phi}}^{(2)} = \frac{m^2}{50 \, n^2 k^4 T_{\text{K}}^4} \left(\frac{mc^2}{k T_{\text{K}}} - 5\right)^2 (\vec{q} \cdot \vec{c})^2 . \qquad (3.9)$$

Here we are interested in making use of this information-theoretical result in order to find out an expression for $v_{\mathrm{ch}}^{(2b)}$ in Eq. (3.5). The method of integration is well-known (see, *e.g.*, Refs [5] or [6]) and will not be detailed again here. It is important to emphasize that we follow the method of derivation already used by us [6], but using T_{K} (which was introduced in Ref. [9]) instead of T (which was used in [6]). After use of Eqs (3.7)–(3.9), (2.4) and (2.2) into (3.6), one finally finds

$$v_{\mathrm{ch}}^{(2b)} = \widetilde{v}_{\mathrm{ch}}^{(2b)} + \widetilde{\widetilde{v}}_{\mathrm{ch}}^{(2b)}, \tag{3.10}$$

where

$$\begin{aligned}
\widetilde{v}_{\mathrm{ch}}^{(2b)} &= \int d\vec{c} \int d\vec{c}_1 \int d\Omega f^{(0)} f_1^{(0)} \left(\widetilde{\phi}^{(2)} + \widetilde{\phi}_1^{(2)} \right) |\vec{c} - \vec{c}_1| \ \sigma_{\mathrm{re}} \left(|\vec{c} - \vec{c}_1| \right) \\
&= -\frac{4 \, d^2 m}{5 \, k^3 T_{\mathrm{K}}^3} \left(\frac{\pi k T_{\mathrm{K}}}{m} \right)^{1/2} \vec{q} \cdot \vec{q} \, \mathrm{e}^{-\frac{\varepsilon^*}{k T_{\mathrm{K}}}} \left(2 \left[\frac{\varepsilon^*}{k T_{\mathrm{K}}} \right] + 3 \right).
\end{aligned} \tag{3.11}$$

and

$$\begin{aligned}
\widetilde{\widetilde{v}}_{\mathrm{ch}}^{(2b)} &= \int d\vec{c} \int d\vec{c}_1 \int d\Omega f^{(0)} f_1^{(0)} \left(\widetilde{\widetilde{\phi}}^{(2)} + \widetilde{\widetilde{\phi}}_1^{(2)} \right) |\vec{c} - \vec{c}_1| \ \sigma_{\mathrm{re}} \left(|\vec{c} - \vec{c}_1| \right) \\
&= \frac{4 \, d^2 m}{75 \, k^3 T_{\mathrm{K}}^3} \left(\frac{\pi k T_{\mathrm{K}}}{m} \right)^{1/2} \vec{q} \cdot \vec{q} \, \mathrm{e}^{-\frac{\varepsilon^*}{k T_{\mathrm{K}}}} \\
&\quad \times \left(\left[\frac{\varepsilon^*}{k T_{\mathrm{K}}} \right]^3 + \frac{13}{2} \left[\frac{\varepsilon^*}{k T_{\mathrm{K}}} \right]^2 + \frac{85}{4} \left[\frac{\varepsilon^*}{k T_{\mathrm{K}}} \right] + \frac{341}{8} \right).
\end{aligned} \tag{3.12}$$

From these results and Eq. (3.3) we find

$$\begin{aligned}
v_{\mathrm{ch}}^{(2)} &\equiv v_{\mathrm{ch}}^{(2a)} + v_{\mathrm{ch}}^{(2b)} \\
&= \frac{44 \, d^2 m}{75 \, k^3 T_{\mathrm{K}}^3} \left(\frac{\pi k T_{\mathrm{K}}}{m} \right)^{1/2} \vec{q} \cdot \vec{q} \, \mathrm{e}^{-\frac{\varepsilon^*}{k T_{\mathrm{K}}}} \left(\left[\frac{\varepsilon^*}{k T_{\mathrm{K}}} \right]^2 - \left[\frac{\varepsilon^*}{k T_{\mathrm{K}}} \right] - \frac{1}{4} \right).
\end{aligned} \tag{3.13}$$

We may introduce the correction, arising from the heat flux and relative to the equilibrium reaction rate, as follows

$$r \equiv \frac{v_{\mathrm{ch}}^{(2)}}{v_{\mathrm{ch}}^{(0)}} + O(q^3). \tag{3.14}$$

Insertion of Eqs (3.13) and (3.2) into (3.14) gives the predicted effect in terms of macroscopic quantities,

$$r = \frac{11 \, m}{75 \, n^2 k^3 T_{\mathrm{K}}^3} \vec{q} \cdot \vec{q} \left(\left[\frac{\varepsilon^*}{k T_{\mathrm{K}}} \right]^2 - \left[\frac{\varepsilon^*}{k T_{\mathrm{K}}} \right] - \frac{1}{4} \right) + O(q^3). \tag{3.15}$$

However, two important problems arise: First, it is usually easier to measure the temperature gradient rather than the heat flux. Second, it is not clear whether T_K is the quantity measured by a thermometer or not. This second problem will be tackled in the next section. In order to write down r in terms of the gradient of T_K instead of the heat flux, one may easily generalize the usual moment method [11, 26] by insertion of the distribution (3.4) (instead of (2.3)) into the Boltzmann equation. Making use also of Eqs (2.4), (2.5) and (3.7)–(3.9), and assuming for simplicity a constant and uniform heat flux, this procedure yields

$$\vec{q} = -\lambda \vec{\nabla} T_K + O(q^2), \tag{3.16}$$

with λ the thermal conductivity, which for hard spheres is given by [10, 26]

$$\lambda = \frac{75}{64} \frac{k}{d^2} \sqrt{\frac{kT_K}{\pi m}}. \tag{3.17}$$

Therefore, Eq. (3.15) may also be written

$$r = \frac{825 \, \pi}{2048} \left(\frac{1}{T_K/l} \vec{\nabla} T_K \right)^2 \left(\left[\frac{\varepsilon^*}{kT_K} \right]^2 - \left[\frac{\varepsilon^*}{kT_K} \right] - \frac{1}{4} \right) + O(q^3), \tag{3.18}$$

with $l = \left(\sqrt{2} \, \pi n d^2 \right)^{-1}$ the mean free path [10]. We will refer to $\frac{1}{T_K/l} \vec{\nabla} T_K$ as the reduced temperature gradient.

For the following typical values: $T_K = 300$ K, $n = 2.687 \cdot 10^{25}$ molecules/m^3 and $d = 10^{-10}$ m, Eq. (3.18) yields an effect of 8.9% for $\left| \vec{\nabla} T_K \right| = 10^7$ K/m and $\frac{\varepsilon^*}{kT_K} = 10$. The predicted effect increases the slower the considered reaction is: for example, for $\frac{\varepsilon^*}{kT_K} = 100$ the equilibrium rate of reaction is lower (see Eq. (3.2)) and the effect (3.18) is of 9.8% already for $\left| \vec{\nabla} T_K \right| = 10^6$ K/m. It is interesting to compare Eq. (3.18) with some previous results. Because the first term inside the parenthesis in Eq. (3.18) is positive and dominates over the others, this equation predicts an *increase* of the rate of chemical reaction in presence of a heat flux, whereas the result (3.3), which was obtained in Ref. [5] (see also Ref. [6]) by taking into account only the first-order correction to the Maxwell–Boltzmann distribution function (see Eq. (2.3)) predicted a completely different effect, which was a *decrease* of the rate of reaction, namely

$$\frac{v_{ch}^{(2a)}}{v_{ch}^{(0)}} = \frac{75 \, \pi}{2048} \left(\frac{1}{T_K/l} \vec{\nabla} T_K \right)^2 \left(- \left[\frac{\varepsilon^*}{kT_K} \right]^3 + \frac{9}{2} \left[\frac{\varepsilon^*}{kT_K} \right]^2 - \frac{9}{4} \left[\frac{\varepsilon^*}{kT_K} \right] - \frac{3}{8} \right). \tag{3.19}$$

We would like to emphasize that such different results are due to the fact that this equation does not take all second-order terms into account. The difference between both predictions is illustrated in Fig. 1 for a specific value of the reduced temperature gradient, as a function of the reduced threshold energy (which characterizes the chemical reaction considered). In
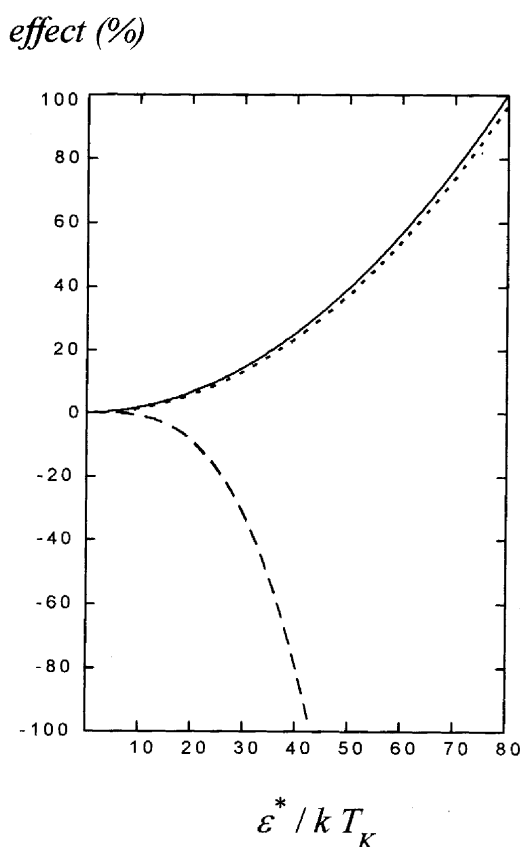
effect (%)

$$\varepsilon^* / k\, T_K$$

Fig. 1. Predictions of the effect of a temperature gradient on the chemical rate of reaction in dilute gases. The dotted line is the prediction (3.18), which has been calculated in the present paper including all second-order terms and corresponds to the hypothesis that T_K is the measurable temperature. The dashed line corresponds to the calculations in Ref. [5]. The full line includes all second-order terms but corresponds to the assumption that T is the measurable temperature [6] (see Eq. (4.2)), so that in this case the horizontal axis is ε^*/kT. The reduced temperature gradient is 0.011, corresponding to a temperature gradient of $3.46 \cdot 10^6$ K/m (assuming that the temperature is 300 K, $n = 2.687 \cdot 10^{25}$ molecules/m^3 and $d = 10^{-10}$ m).

this figure, the dotted curve has been obtained from Eq. (3.18) and shows that this equation predicts an *increase* of the reaction rate, which is more important the slower the chemical reaction is. The solid curve corresponds to results similar to those from Eq. (3.18) but derived with the use of the thermodynamic temperature definition (see Eq. (4.2) in the next section). The dashed curve in Fig. 1 has been obtained from Eq. (3.19) and shows that this equation corresponds to a *decrease* of the reaction rate in the presence of a temperature gradient.

4. Temperature definitions in chemically reactive systems

As discussed in Sec. 2, the difference between T_K and T, defined by Eqs (2.7) and (2.8), respectively, is negligible up to the first-order approximation (which corresponds to Eq. (2.3)). However, Extended Irreversible Thermodynamics (EIT) is a phenomenological theory that generalizes the usual first-order, linear theory (namely, local-equilibrium thermodynamics [1]) and predicts that the difference between T_K and T is not negligible in the second-order approximation (Eq. (3.4)). Indeed, microscopic approaches based on the kinetic theory of gases [11] and on information theory [9] yield the same result for the relationship between both temperature-like variables, namely

$$\frac{1}{T} = \frac{1}{T_\mathrm{K}} + \frac{2m}{5n^2 k^3 T_\mathrm{K}^4} q^2 + O(q^3) \,. \tag{4.1}$$

Therefore, the problem arises to compare the effect predicted under the assumption that T_K is the measurable temperature with that resulting from the assumption that T is the quantity measured by a thermometer outside equilibrium. In our previous paper [6], the second-order distribution function was written in terms of T instead of T_K (simply by using Eq. (4.1) into Eqs (3.4), (2.4), (2.5) and (3.7)–(3.9), and neglecting third- and higher-order terms). This lead to an expression for the effect in terms of T and its gradient, instead of T_K and its gradient, namely, as derived in Ref. [6],

$$r_T = \frac{75\,\pi}{2048} \left(\frac{1}{T/l} \vec{\nabla} T \right)^2 \left(11 \left[\frac{\varepsilon^*}{kT} \right]^2 + 19 \left[\frac{\varepsilon^*}{kT} \right] + \frac{49}{4} \right) + O(q^3) \,. \tag{4.2}$$

Since the right-hand side of this equation is not the same function of T and its gradient as that of Eq. (3.18) is of T_K and its gradient, we have two different predictions for the effect considered in this paper. For a given value of the quantity measured by a thermometer, if we assume that this value corresponds to T_K, then the effect is given by Eq. (3.18), with T_K the value read by the thermometer. However, if one assumed that the value measured by a thermometer were T, then the predicted effect would be that obtained

by making use of Eq. (4.2), with T the value obtained from the experimental reading of the thermometer.

In Fig. 1 it is shown that although the analytical results corresponding to the assumptions that T is the measurable temperature (Eq. (4.2)) and that T_K is the measurable temperature (Eq. (3.18)) are different, the numerical results are nearly the same.

5. Discussion and concluding remarks

Since the full and dotted curves in Fig. 1 differ only by a few percent, it is clear from this figure that the question of which temperature is the measurable one does not substantially change the predicted effect. Therefore, the question of the measurable temperature does not pose a quantitatively relevant problem for this particular application. This is not a trivial result, since the opposite conclusion is reached in the information-theoretical analysis of the modification of the Planck spectral law due to a radiative heat flux [23].

We have seen that, independently of the definition of the temperature, the predicted effect would only be measurable for large temperature gradients (*i.e.*, of the order 10^6 K/m or higher, which correspond to heat fluxes of the order 10^5 W/m^2 or higher). It is very interesting that this agrees with recent results found out by Nettleton by a different method [27], and that such high temperature gradients are currently found experimentally in shock waves [28, 29] and ultrasound chemistry [30]. However, the following question on the validity of the second-order approximation arises. It is well-known, both from theory [31] and from experiment [11, 28, 32], that if one makes use of the traditional methods from the kinetic theory of gases in order to deal with an expression for the distribution-function including second-order terms (see Eq. (3.4)), the resulting hydrodynamic equations (the Burnett equations) need not be valid. This means that subsequent terms in such kinetic-theoretical expansions are not negligible in general. The expansion (3.4), (2.4), (2.5), (3.7)–(3.9) was not derived on the basis of kinetic theory. It was derived by means of information theory, which is a statistical-mechanical method [9], making use of a Taylor expansion on the heat flux. Although the hydrodynamical consequences of this expansion have to be analyzed yet, and its validity is therefore and open question [33], we should ask ourselves whether such an expansion is consistent or not. After all, we have obtained a detectable effect only for very large values of the heat flux (or temperature gradient). Therefore, in Figs 2.(a)–2.(f) we plot this distribution function $f^{(2)}$ (Eqs (3.4), (2.4), (2.5) and (3.7)–(3.9)), together with the zeroth-order (or local Maxwellian) approximation $f^{(0)}$ (Eq. (2.4)) and the first-order one $f^{(1)}$ (Eqs (2.3), (2.4) and (2.5)), for several values

of the heat flux, (with increasing q from (a) to (f)) and for molecules that travel in the direction of the heat flux ($\vec{q} \cdot \vec{c} > 0$, with $c > 0$) and in the opposite direction ($\vec{q} \cdot \vec{c} > 0$, with $c < 0$). As stressed in Section 2, $f^{(1)}$ is the same result as that obtained from either the Chapman–Enskog or the Grad thirteen moment methods. However, $f^{(2)}$ generalizes $f^{(1)}$ and has been derived by means of statistical mechanics. The fact that the areas under the different curves in each one of the Figs 2.(a)–2.(f) are different is not surprising since the distribution function depends on the three components of the velocity $\vec{c}$, and it is easy to check that integration of any of the three functions times $d^3c = c^2 d\Omega$ over all possible values of $\vec{c}$ yields the same result, namely n, as it should. Similarly, there is no problem with the fact that the maxima appear for $c < 0$ in spite of the fact that we have considered values of the heat flux such that $q > 0$: integration of any of the three functions times $\frac{mc^2}{2}\vec{c}d^3c$ over all possible values of $\vec{c}$ yields $\vec{q}$, also as it should. The fact that in Fig. 2.(a) the three approximations are not distinguishable from each other leads us to expect that they are a good approximation to the distribution function f in the case $q = 10^5$ W/m^2. However, on the contrary, if the heat flux approaches a value of the order of 10^8 W/m^2 the second-order nonequilibrium correction becomes almost as important as the first one, which casts doubts on its validity: in this situation, third- and higher-order terms in the Maclaurin expansion (3.4) should not be expected to be negligible. For such an extremely large heat flux, the validity of $f^{(2)}$ is lost for sure in the case depicted in Fig. 2.f ($q = 10^8$ W/m^2), where we also observe clearly a negative-probability region for $f^{(1)}$ and $f^{(2)}$. However, in the present paper we have concluded that, independently of the considered temperature definition, the predicted nonequilibrium correction to the reaction rate is measurable already for temperature gradients of the order of 10^6 K/m (see the discussion under Eq. (3.18) and Fig. 1). For typical dilute gases, this corresponds to a heat flux of the order of $q \sim 10^5$ W/m^2. Thus the qualitative impression transmitted by Fig. 2 is that it seems reasonable to trust on the validity of the Taylor expansion that has been derived in Ref. [9] and led to the estimations in the present paper.

It is also interesting that the factor $\left(\left[\frac{\varepsilon^*}{kT_{\mathrm{K}}} \right]^2 - \left[\frac{\varepsilon^*}{kT_{\mathrm{K}}} \right] - \frac{1}{4} \right)$, which we have got in the information-theoretical result (3.13) or (3.18), appears in papers analyzing various nonequilibrium effects with the use of the reactive cross-section of Present. Already in the analysis of nonequilibrium effects associated with the proceeding of a chemical reaction [4], in the final formula the square of this factor appears. It also appears in the analysis of the effect of coupling of the shear viscosity and a chemical reaction [5], as well as in the similar coupling between diffusion and a chemical reaction [34, 35]. It is worthwhile to emphasize that in all cases mentioned above, an approximate
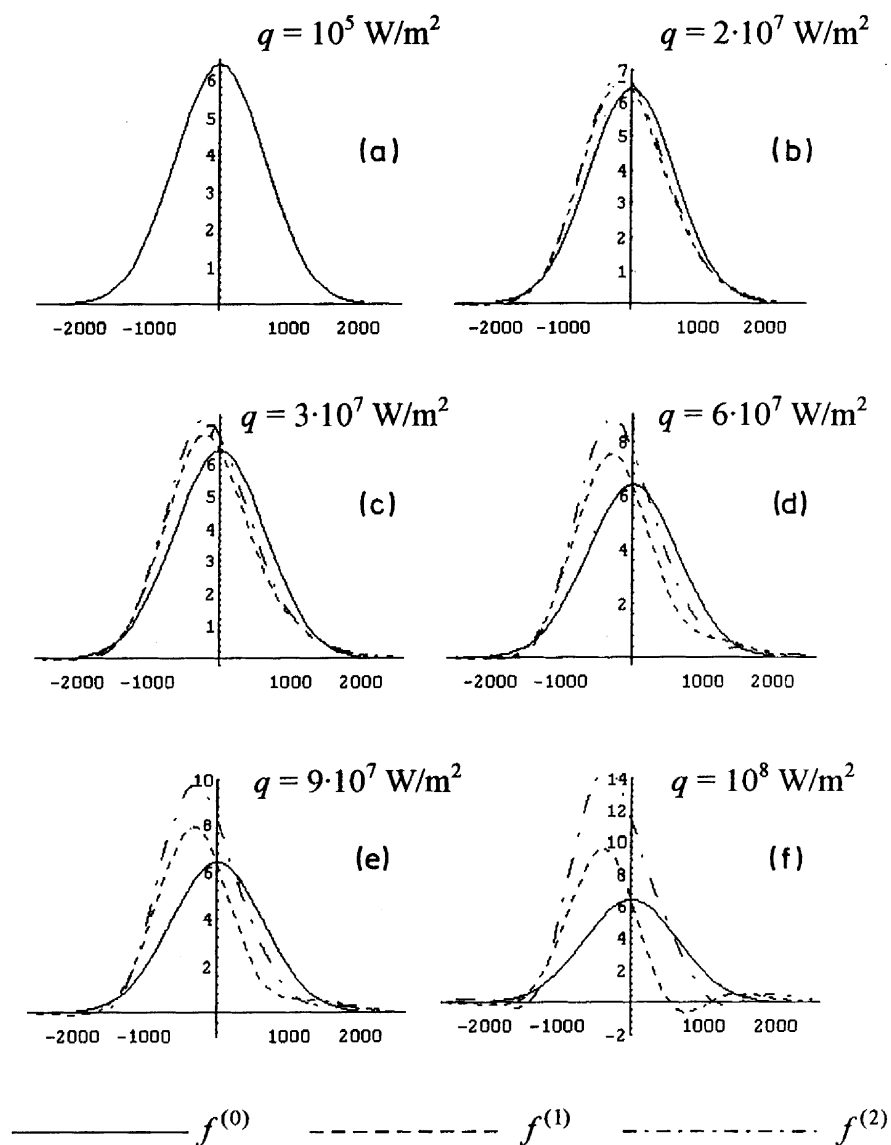
Fig. 2. Zeroth-, first- and second-order approximations (full, dotted and dashed-dotted curves, respectively) to the distribution function, as a function of c, for several values of the heat flux and molecules traveling in the same ($c > 0$) and opposite direction ($c < 0$) to that of the heat flux. It has been assumed that $m = 10^{-26}$ Kg, $n = 2.687 \cdot 10^{25}$ molecules/m^3 and $T_{\mathrm{K}} = 300$ K.

solution to the Boltzmann equation was used without application of the information-theory approach. Because of that reason, it is clear that use of T_K leads to more familiar expressions than the use of T.

Just to summarize, we have shown that the large effect of the heat flux on the rate of chemical reaction (predicted in Ref. [6] with the use of the thermodynamic temperature T) is nearly the same (numerically) if the kinetic temperature T_K is introduced. Although the numerical results are nearly the same, in the second case the analytical form of the final expressions is even simpler.

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