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## Nonisothermal diffusion–reaction with nonlinear Kramers kinetics

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## ABSTRACT

Recently, we have started to develop mesoscopic nonequilibrium thermodynamics for a reaction far from equilibrium in the presence of a temperature gradient, so that the interplay between the chemical reaction, diffusion and thermal diffusion can be described within the same theoretical framework. In this article we show that the spatial symmetry properties of the deterministic solution, which were so characteristic for conditions close to equilibrium, are no longer valid far from equilibrium. This is expected to have some conceptual consequences for the spatial spectrum of the fluctuations of temperature and concentrations around their local equilibrium values.

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## 1. Introduction

Although isothermal reaction–diffusion problems have been thoroughly studied in the scientific literature with many papers and even dedicated monographs, reaction–diffusion in the presence of temperature gradients has received, comparatively, much less attention. This situation is a bit awkward because a chemical reaction very seldom takes place in a truly isothermal environment. For instance, temperature gradients in reacting mixtures greatly affect the transport properties of such mixtures, and the importance of thermal diffusion (Soret effect) has been increasingly appreciated during the past decade [1]. Part of the problem is that different levels of description are usually adopted for thermal diffusion and for chemical reactions. Indeed, the Soret effect is usually described in the phenomenological context of nonequilibrium thermodynamics. Good microscopic theories are lacking, except for the case of dilute gases. Chemical reactions, on the other hand, are usually described by microscopic kinetic models, the current consensus being that thermodynamic descriptions are only valid for chemical reactions at, or extremely close to, equilibrium. In our opinion the lack of studies of nonisothermal reaction–diffusion can only be overcome when a common theoretical basis is established for both thermal diffusion and chemical reactions.

So far, most theoretical studies on nonisothermal reaction–diffusion have been developed in the context of nonequilibrium thermodynamics. Pioneering papers by Meixner and Prigogine have been reviewed in the classic monograph of de Groot and Mazur [2], where temperature and concentration profiles in the presence of (mass) diffusion, thermal diffusion and a chemical reaction are discussed. In these exploratory works so-called linear kinetics was employed for the chemical reactions, such that

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$$r = -L_r \frac{\Delta g}{T} \quad (1)$$

where  $r$  is the chemical reaction rate,  $L_r$  a proportionality constant,  $T$  the local temperature, and  $\Delta g$  denotes the local value of the Gibbs energy of the reaction, i.e., the chemical potential of the products minus that of the reactants. Combining Eq. (1) with the well-known linear phenomenological laws for thermal conduction, (mass) diffusion and thermal diffusion, yields (given an equation of state for  $\Delta g$  as a function of the temperature  $T$  and the concentration  $c$ ) nonlinear profiles for diffusion flux (including the Soret effect), temperature and concentration, as documented in §X1.8 of de Groot and Mazur [2]. Recently, some of us [3] have also elucidated the long-range characteristic nature of thermal fluctuations around these classical solutions. For the purpose of the present paper it is important to emphasize that, in the case of a reacting fluid layer bounded by two planes maintained at different temperatures, the deterministic diffusion–flux profiles obtained from linear kinetics, Eq. (1), are *symmetric* with respect to the midplane of the layer.

Unfortunately, Eq. (1) is not compatible with the kinetic law of mass action, a building block of chemical kinetics. This is a very well-known flaw of nonequilibrium thermodynamics, that has historically led people to even question the usefulness of nonequilibrium thermodynamics for systems with chemical reactions [4]. In spite of this evident shortcoming, linear kinetics like in Eq. (1) continue to be used until today, particularly in the physics literature [5].

However, this does not appear to be the end of the story. Since the original study of Kramers [6] dealing with a Brownian particle diffusing over a (potential) energy barrier, it has become evident that a similar approach can be used to apply nonequilibrium thermodynamics to chemical reactions. The basic idea is that one can imagine a chemical reaction as a diffusion along some “internal” coordinate,  $\gamma$ , from a reactant state to a product state. Internal diffusion has to proceed over some barrier (in this case an enthalpy barrier). As shown in a previous publication [7], a modified nonequilibrium thermodynamics approach following the original Kramers steps for Brownian motion [2,6,8] leads to a nonlinear relationship between the local value of the chemical reaction rate  $r$  and the Gibbs energy of the reaction  $\Delta g$ , namely:

$$r = -\frac{L_r R}{M} \left[ 1 - \exp\left(-\frac{M \Delta g}{RT}\right) \right] \quad (2)$$

where  $M$  is the molar mass of the “reaction complex” (total molar mass of the reactants, which is equal to the total molar mass of the products) and  $R$  the universal molar gas constant. Eq. (2) has enormous advantages over Eq. (1), the most important being its compatibility with the kinetic law of mass action. Furthermore, we have demonstrated that Eq. (2) is compatible with nonequilibrium thermodynamics, since it can be obtained by postulating a linear phenomenological relation between the diffusion flux in  $\gamma$ -space and the corresponding thermodynamic force [7]. When the dimensionless Gibbs energy of the reaction  $\Delta \hat{g} \equiv M \Delta g / RT$  is small ( $\Delta \hat{g} \ll 1$ ), Eq. (2) reduces to Eq. (1).

These two features, compatibility both with the kinetic law of mass action and with nonequilibrium thermodynamics, were already implicit in the original work of Kramers [6], as also reviewed by de Groot and Mazur in §X.6 of their book [2].

Lately, there has been a renewed interest in the thermodynamics of fluids with internal degrees of freedom. Authors have followed the path pioneered by Kramers for chemical reactions [6], and developed a systematic way of incorporating internal variables into the general formalism of nonequilibrium thermodynamics. Establishing linear phenomenological laws in terms of  $\gamma$ -coordinates and, later, integrating over these to obtain a (nonlinear) thermodynamic formalism in terms of the observable variables only. This scheme has been applied not only to include fluctuations in the chemical reactions [7], but also to diffusion problems [8], biological problems [9], etc., yielding a new branch of nonequilibrium thermodynamics for which the name *mesoscopic nonequilibrium thermodynamics* [10] has been adopted.

A mesoscopic nonequilibrium thermodynamics approach for dealing with chemical reactions has also been considered by some previous investigators. Specifically, we may mention the work of Pagonabarraga et al. [11], who show how from this thermodynamic scheme a chemical Langevin equation can be obtained, where the statistical properties of the chemical noise are exactly the same as the traditional ones, and a more involved approach, that includes a chemical master equation, a Kramers–Moyal approximation and a van Kampen system-size expansion [12,13].

All these studies of chemical reactions are limited to the isothermal case. Recently we have started to develop mesoscopic nonequilibrium thermodynamics for reacting fluids in the presence of a temperature gradient [7], so that the interplay between the chemical reaction, diffusion and thermal diffusion can be described within a single theoretical framework, in the spirit mentioned at the beginning of this introduction.

The current paper is a continuation of this work. In the previous publication [7] we established the general theory and here we use it to consider a particular case: a reacting fluid mixture bounded between two plane parallel plates maintained at different temperatures. In Sections 2 and 3 we shall discuss how the stationary profiles of the diffusion flux (including the role of thermal diffusion), the temperature and the Gibbs energy of the reaction are modified when one uses nonlinear Kramers kinetics, Eq. (2). We are going to find that the profiles no longer have the spatial symmetry properties which were characteristic in the linear approximation. Concluding remarks are presented in the last section.

## 2. Stationary solution for a chemical reaction in the presence of a temperature gradient

Our problem here is a binary reacting mixture enclosed between two rigid impervious walls, located at  $x = 0$  and  $x = L$ , that are maintained at two different temperatures,  $T_0$  and  $T_L$ , respectively. The analytic steady-state solution of this problem

for the case of linear kinetics, Eq. (1), has been discussed by de Groot and Mazur [2], and reviewed in a more recent paper by some of us [3]. Our goal here is to study the case of nonlinear Kramers kinetics, Eq. (2), for which the general theoretical framework, compatible with nonequilibrium thermodynamics, was established in our previous publication [7]. In particular, the starting point to solve our problem here are Eqs. (58) in that paper [7]. An examination of these equations shows that there exists a quiescent ( $\mathbf{v} = 0$ ,  $p$  constant) stationary solution that is translationally invariant in the  $yz$ -plane (i.e., that depends only on the  $x$ -coordinate). Specifically, the temperature and the Gibbs energy satisfy the following equations:

$$0 = -L_{qJ} \frac{d^2}{dx^2} \left( \frac{1}{T} \right) + L_{JJ} \frac{d^2}{dx^2} \left( \frac{\Delta g}{T} \right) - \frac{L_r R}{M} \left[ 1 - \exp \left( -\frac{M \Delta g}{RT} \right) \right] \tag{3}$$

$$0 = -L_{qq} \frac{d^2}{dx^2} \left( \frac{1}{T} \right) + L_{Jq} \frac{d^2}{dx^2} \left( \frac{\Delta g}{T} \right) \tag{4}$$

where  $L_{JJ}$ ,  $L_{qq}$ ,  $L_{Jq}$  and  $L_{qJ}$  represent the various appropriate Onsager transport coefficients. According to the Onsager symmetry relations we have  $L_{Jq} = L_{qJ}$ . For the relationships between these Onsager coefficients and the conventional transport coefficients, namely, the thermal conductivity  $\lambda$ , diffusion coefficient  $D$ , and thermal diffusion ratio  $k_T$ , we refer to our previous paper [7]. In the analysis here we shall work in terms of the Onsager transport coefficients, which are assumed to be independent of temperature and concentration in the actual ranges under consideration. Consequently, the only nonlinearity we are considering in this paper is in the chemical reaction kinetics.

Integrating first Eq. (4), we obtain

$$\left( \frac{1}{T} \right) = \frac{L_{Jq}}{L_{qq}} \left( \frac{\Delta g}{T} \right) + C_0 + C_1 \frac{x}{L} \tag{5}$$

where  $C_0$  and  $C_1$  are integration constants. Next, by substituting Eq. (5) into Eq. (3), we obtain a closed ordinary nonlinear differential equation for  $\Delta g/T$ , namely:

$$\frac{d^2}{dx^2} \left( \frac{M \Delta g}{RT} \right) = \frac{1}{d^2} \left[ 1 - \exp \left( -\frac{M \Delta g}{RT} \right) \right] \tag{6}$$

where, similarly to the linear case [2,3], we have introduced a penetration depth  $d$  (units of length) defined by  $1/d^2 = L_r L_{qq} / (L_{JJ} L_{qq} - L_{Jq} L_{qJ})$ . The differential equation (6) can be integrated once by standard techniques, giving:

$$\frac{d}{dx} \Delta \hat{g} = \frac{1}{\sqrt{2}d} \sqrt{C_2 + \Delta \hat{g} + \exp(-\Delta \hat{g})} \tag{7}$$

in terms of the dimensionless Gibbs energy  $\Delta \hat{g} = M \Delta g / RT$ .  $C_2$  is a new integration constant. Eq. (7) must be integrated numerically to obtain the solution for  $\Delta \hat{g}$ .

Impermeable walls require that the diffusion flux  $J$  vanishes at both  $x = 0$  and  $x = L$ . From Eq. (42) in the previous paper [7] it follows that:

$$J = L_{Jq} \frac{d}{dx} \left( \frac{1}{T} \right) - L_{JJ} \frac{d}{dx} \left( \frac{\Delta g}{T} \right) = \frac{-R}{\sqrt{2}Md} \left( L_{JJ} - \frac{L_{Jq}^2}{L_{qq}} \right) \sqrt{C_2 + \Delta \hat{g} + \exp(-\Delta \hat{g})} + L_{Jq} \frac{C_1}{L} \tag{8}$$

where we have used Eqs. (5) and (7) for the gradients of the thermal properties in our particular problem. Eq. (8) represents an analytic relationship between the local values of the diffusion flux  $J(x)$  and of the dimensionless Gibbs energy  $\Delta \hat{g}(x)$ . The boundary condition  $J(0) = 0$  gives a relationship between two of the integration constants, namely:

$$C_1 = \frac{L}{L_{Jq}} \frac{RL_r d}{\sqrt{2}M} \sqrt{C_2 + \Delta \hat{g}(0) + \exp(-\Delta \hat{g}(0))} \tag{9}$$

Since the diffusion flux is also zero at  $x = L$ , one has

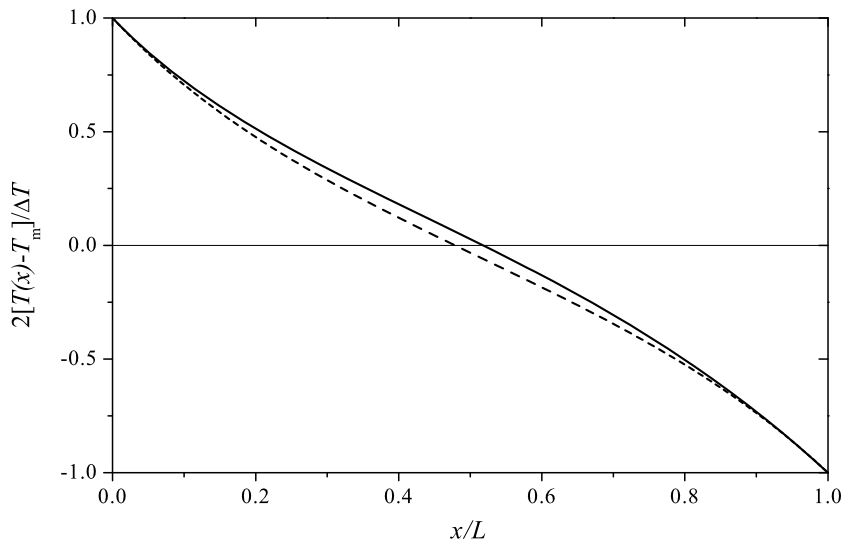
$$\Delta \hat{g}(L) + \exp(-\Delta \hat{g}(L)) = \Delta \hat{g}(0) + \exp(-\Delta \hat{g}(0)) \tag{10}$$

One should not use the trivial solution  $\Delta \hat{g}(L) = \Delta \hat{g}(0)$ .

To finalize the specification of the steady-state solution, we need to impose the boundary conditions for the (inverse) temperature. From Eq. (5) we readily obtain:

$$C_0 = \frac{1}{T_0} - \frac{RL_{Jq}}{ML_{qq}} \Delta \hat{g}(0), \quad C_1 = \frac{1}{T_L} - \frac{1}{T_0} - \frac{RL_{Jq}}{ML_{qq}} (\Delta \hat{g}(L) - \Delta \hat{g}(0)) \tag{11}$$

While in the case of linear kinetics it is possible to obtain explicit analytic solutions for the profiles, in the case of nonlinear kinetics the solutions of Eqs. (5) and (8) can only be obtained numerically.



**Fig. 1.** Temperature profiles for nonlinear (solid) and linear (dotted) chemical kinetics. Parameters are the same for both cases:  $\phi = L/d = 7.64$  and positive  $RL_{Jq}/ML_{qq}$  (positive Soret effect).  $T_m$  represents the average temperature and  $\Delta T = T(L) - T(0)$  the temperature difference.

### 3. Properties of the stationary solution

In this section we discuss some relevant features of the steady-state solution obtained from the equations presented in the previous section. In particular, we present a detailed comparison with the solutions of the same problem that are obtained with linear kinetics [2,3].

The linear-kinetics solution [2,3] for the diffusion flux is symmetric with respect to the mid-layer,  $x = L/2$ . It therefore has its maximum (in absolute value) at this point. The inverse temperature and the Gibbs energy of the reaction for the linear-kinetics solution are both anti-symmetric with respect to the mid-layer,  $x = L/2$ . At mid-layer the inverse temperature is in this approximation the average of the inverse hot and cold temperatures, while the Gibbs energy of the reaction is zero,  $\Delta \hat{g}(x = L/2) = 0$ .

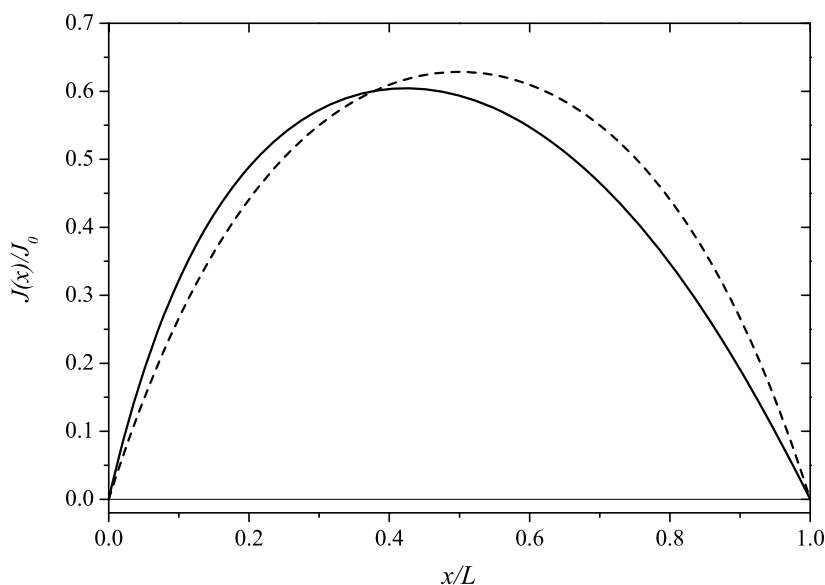
For the nonlinear solution the location of maximum diffusion flux is no longer at mid-layer. Indeed, by differentiating Eq. (8) it can be easily verified that the maximum diffusion flux corresponds to the point where  $\Delta \hat{g} = 0$  (a feature shared with the linear-kinetics model). However, the spatial location, where  $\Delta \hat{g} = 0$ , is no longer at the middle of the layer. It can be demonstrated that the position of maximum diffusion flux is closer to the hot or the cold wall depending on the sign of the ratio of Onsager's coefficients  $L_{Jq}/L_{qq}$ . The sign of this ratio is, in terms of transport coefficients, determined by the sign of the quantity  $k_T + \Delta h(\frac{\partial \Delta \hat{g}}{\partial c})^{-1}$ , that is essentially the sign of the thermal diffusion factor. Then, if the Soret effect is positive the point of maximum diffusion flux (and of  $\Delta \hat{g} = 0$ ) is located closer to the hot plane; while if the Soret effect is negative, the point of maximum diffusion flux (and of  $\Delta \hat{g} = 0$ ) is located closer to the cold plane.

While Eq. (5) for the profile of the inverse temperature is the same in the linear and in the nonlinear case, the actual nonlinear inverse-temperature profile is no longer anti-symmetric due to the lack of symmetry of the solution of Eq. (6) for  $\Delta \hat{g}$ . As happens with the diffusion flux, the spatial point where the inverse temperature equals the average of the inverse plate temperatures will be closer to the hot or to the cold plate depending on the sign of the Soret coefficient.

To show the differences in the temperature and in the diffusion-flux profiles we give plots for both linear and nonlinear (Kramers) chemical kinetics in Figs. 1 and 2. The adopted parameter values are the same in the linear and in the nonlinear case in both figures. Namely,  $\phi = L/d = 7.64$  (corresponding to a diffusion-dominated chemical reaction) and a positive ratio  $RL_{Jq}/ML_{qq}$  (corresponding to a positive Soret effect). The hot plate is located at  $x = 0$ :  $T_0 > T_L$ . For the case of linear kinetics (dotted curve) the maximum flux (see Fig. 2) is exactly located at  $x = L/2$ . The asymmetry in the flux profile in the case of nonlinear kinetics is obvious, and the maximum flux is closer to the hot plate, as mentioned above for the case of positive Soret effect.

### 4. Conclusions

Nonisothermal chemical reactions can now be fully treated within the framework of nonequilibrium thermodynamics. Mesoscopic nonequilibrium thermodynamics yields some novel perspectives for describing nonisothermal reacting fluid mixtures. The primary conclusion from the present paper is that nonlinear Kramers kinetics causes a breaking of the spatial symmetries of the various property profiles in a reacting system in the presence of a temperature gradient. This is a very important difference with the case of linear kinetics and is expected to lead to some conceptual differences in the spatial



**Fig. 2.** Comparison of diffusion flux profiles for nonlinear (solid) and linear (dotted) chemical kinetics. Parameters are the same as in Fig. 1, i.e.,  $\phi = L/d = 7.64$  and positive  $RL_{jq}/ML_{qq}$  (positive Soret effect).  $J_0$  represents the constant prefactor in Eq. (8).

spectrum of the nonequilibrium fluctuations of temperature and concentration around their local equilibrium values [3,14]. We intend to study the latter issue in a subsequent publication.

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