Mesoscopic non-equilibrium thermodynamics of non-isothermal reaction-diffusion

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We show how the law of mass action can be derived from a thermodynamic basis, in the presence of temperature gradients, chemical potential gradients and hydrodynamic flow. The solution gives the law of mass action for the forward and the reverse contributions to the net chemical reaction. In addition we derive the fluctuation–dissipation theorem for the fluctuating contributions to the reaction rate, heat flux and mass fluxes. All these results arise without any other assumptions than those which are common in mesoscopic non-equilibrium thermodynamics; namely quasi-stationary transport across a high activation energy barrier, and local equilibrium along the reaction coordinate. Arrhenius-type behaviour of the kinetic coefficients is recovered. The thermal conductivity, Soret coefficient and diffusivity are significantly influenced by the presence of a chemical reaction. We thus demonstrate how chemical reactions can be fully reconciled with non-equilibrium thermodynamics.

1. Introduction

Non-isothermal systems, where reaction and diffusion take place, are typical in the chemical process industry,[1] and also in biological systems.[2] The chemical reaction is always central in these systems, because the rate of the reaction often will determine how fast chemicals can be produced. A high rate can be realized when the reaction is far from equilibrium. But an operation far from equilibrium is also an operation in which the energy dissipation is large. With the present interest to save valuable resources, chemical reactors should be studied also from the perspective of obtaining a more energy-efficient operation, *in addition* to maintaining the production of chemicals. In biological systems, one may expect that energy efficiency is an issue of survival, especially under harsh conditions.[3] In such cases and probably many others, a thermodynamic description will be important to understand the transport phenomena involved.[2,4] Studies of minimum energy dissipation (minimum lost work), for instance, start with an expression for the entropy production, see ref. 5–7. In other words, a description of transport processes from a thermodynamic perspective of the second law is required.

Chemical reactions are inherently non-linear processes, and are most successfully described in the field of reaction kinetics by the law of mass action.[8,9] The concentrations of a reacting mixture and the kinetic coefficients for the forward and backward reactions are then related at thermodynamic equilibrium, with the ratio of the kinetic coefficients giving the thermodynamic equilibrium constant. The driving force for the reaction at constant temperature and pressure is well described by the reaction Gibbs energy. The reaction rate is not commonly expressed as a function of the reaction Gibbs energy. This is not surprising, because classical non-equilibrium thermodynamics[10,11] assumes a linear relation between these two variables, and experimental evidence indicates that this is only correct very close to chemical equilibrium. Further development of a rate equation from non-equilibrium thermodynamics has been hampered by the difficulty of overcoming this problem.

The first to address this problem successfully was Kramers,[12] who described the reaction as a diffusion process along a reaction coordinate. This predated the introduction of mesoscopic non-equilibrium thermodynamics, which has further opened up this new possibility. This extension, to be explained in detail below, introduces new variable(s) at a level of description below the one used in macroscopic thermodynamics. The extension in the context of non-equilibrium thermodynamics was first proposed by Prigogine and Mazur,[13] see also ref. 14 and 15. By integrating over these variables to obtain the thermodynamic level, one can describe several phenomena, which are non-linear on the macroscopic level, and which retain a linear force-flux relation on the mesocopic level. This applies not only to chemical reactions,[16] but for instance also to adsorption,[17] nucleation,[18] electrode over-potentials[19] and active transport in biology.[2] The number of cases studied is now growing fast. The coupling of chemical reactions to other processes is then important.[4,16,20–23] In our analysis the chemical reaction is embedded in a system with flow. Thermodynamic coupling between the thermodynamic driving forces and their conjugate thermodynamic forces follows from the entropy production. All flows that could couple to the chemical reaction (like diffusion flows) are present in the entropy production. This coupling will been taken into account. The systems considered are isotropic and as a consequence there is no coupling in the force–flux

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relations between fluxes (flows) with a different tensorial character. Further coupling as a consequence of the balance equations will be systematically accounted for. Both types of coupling may lead to contributions to fluxes against the direction imposed by their primary driving forces.[23] In our description we follow the monograph by de Groot and Mazur,[14] to which we refer for further clarification. Coupling in the context of non-equilibrium thermodynamics means that one flux is not only related to its main driving force, but to all other driving forces with the same tensorial character. One long-range aim of the present effort is to derive corresponding results for the realistic case, when the chemical reaction is a non-linear function of its driving force. The present work lays the foundations for that, and gives the fluctuation–dissipation theorem. The analysis will be restricted to chemical reactions in a closed system. That is, there are no buffers, which add or remove components in order to keep the chemical potential of these components at a given value. Our aim is to study heat and mass transport due to a temperature gradient across such a chemically reacting system.

Non-equilibrium thermodynamics is not only a theory for transport processes, it is also a theory for fluctuations. It has been demonstrated that the fluctuating contributions to the thermodynamic fluxes in a non-equilibrium system satisfy the fluctuation–dissipation theorem just like they do in equilibrium.[24] This is what the condition of local equilibrium implies for the fluctuations. As explained in the monograph by Ortiz de Zárate and Sengers,[24] the behavior of the resulting density and temperature fluctuations is, however, very different from the equilibrium behavior. In this paper the fluctuation–dissipation theorem shall be given for fluctuations on the *mesoscopic* level, for a mixture of reacting components in a temperature gradient. A study of the nature of these fluctuations, may be important for a better understanding of coupling on the mesoscopic level, for instance in biology.[2,4] Such a coupling is not yet sufficiently understood.

The theory of non-equilibrium thermodynamics is based on the assumption of local thermodynamic equilibrium. The validity of this assumption has been established by molecular dynamics simulations in several cases.[25–27] Fluctuations and the resulting correlation functions away from equilibrium were then not considered. One of the major findings has been that although local equilibrium is valid for the description of the mean values of thermodynamic fields, it is no longer valid for the description of the fluctuations around their average non-equilibrium values.[24] In a previous paper Ortiz de Zárate *et al.*[28] analyzed this problem for a reaction-diffusion problem with a temperature gradient using a linear approximation for the description of the reaction. For the reaction-diffusion problem the assumption of local equilibrium has to be extended to be valid also along the reaction coordinate. In particular it has to be specified what this assumption implies for the fluctuating contributions. In this and a subsequent paper we shall extend the results of Ortiz de Zárate *et al.*[28] to the more realistic nonlinear description.

The paper is written in a terminology that, as far as possible, is common to chemists. We present the balance equations and the transport equations for a simple reacting mixture in a temperature gradient in section 2. The balance equations are written for the macroscopic as well as the mesoscopic level. From the entropy production we derive the flux–force relations on the mesoscopic level in sections 2.2–2.5. By integration over the reaction coordinate, we give a derivation of a generalization of the law of mass action in which the concentrations of the components are replaced by fugacities. The fluctuation–dissipation theorem on the mesoscopic level is presented in section 3. Again we are able to integrate along the reaction coordinate. The result is a realistic nonlinear description of the reaction with well-defined fluctuating contributions to the associated heat and mass fluxes.

2. Mesoscopic non-equilibrium thermodynamics of a chemically reacting fluid mixture

As a representative elementary reaction, consider a reversible association-dissociation reaction, like in a mixture of atoms and a molecule:

$$2A \rightleftharpoons A_2, \qquad (1)$$

From a macroscopic point of view, only two states are relevant, the reactant state and the product state. The reaction Gibbs energy per unit of mass results from the difference between the chemical potentials of these states

$$\Delta g = \mu_{A_2} - \mu_A. \qquad (2)$$

Here Δg is measured in units of J kg^{-1}, for reasons to be explained below. The stoichiometric coefficient of 2 in front of μ_A which follows when the unit is J mol^{-1}, disappears then in front of μ_A. Classical non-equilibrium thermodynamics postulates a linear relation between the reaction rate r and the conjugate thermodynamic force $-\Delta g/T$. This is only valid when $|\Delta g M/RT| \ll 1$, where M is the molar mass of the reaction complex (see below). We use the reaction Gibbs energy rather than the affinity, see ref. 14 for a definition.

As an alternative, reaction kinetics[9] describes the reaction from a microscopic point of view. The probability for the reactant A to collide with A and to produce A_2 is proportional to the concentration of A squared. Likewise the probability that the product A_2 splits up is proportional to the concentration of A_2. Whether 2A succeeds to make A_2 or not depends on a number of variables, like their velocities, their rotational velocity relative to each other, their interaction energy and the interparticle distance. One may envision a series of configurations in energy space on the way from reactant to product. These are so-called internal states, different from the beginning and end states in eqn (2).

In the mesoscopic formulation, the reaction path taken by the reaction over an energy barrier is considered. A distinction is made between the different states transversed, from the state of two separate atoms *via* the states during the collision all the way to the final molecule. The sequence of internal states is specified by the reaction coordinate γ, see de Groot and Mazur,[14] section X.6. We will assume that for the reaction considered, eqn (1), one single scalar γ-coordinate is sufficient. We will not consider cases where an extension of the analysis to more than one reaction coordinate is needed.[4,16,21] At any value of γ we speak of the reaction complex. For $\gamma = 0$ the

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reaction complex consists of the reactants and for $\gamma = 1$ it consists of the products. The choice of 0 and 1 as the beginning and end of the reaction coordinate can be done without loss of generality. Mass is conserved, and the reaction complex has always the molar mass of A_2. The chemical reaction is modelled as a diffusion process in γ-space over an energy barrier. Typically such energy barrier has a maximum at γ_0, which is large in the sense that the energy per kg of reaction complexes is large compared to the thermal energy RT/M. The energy at γ_0 is referred to as the transition state energy. The larger the transition state energy is, the slower is the reaction.

This picture, common in reaction kinetics since Eyring,[9] is also important in mesoscopic non-equilibrium thermodynamics. Following Kramers,[12,14] the reaction can be seen as a diffusion process along the reaction coordinate γ. Along the reaction coordinate the probability that a reaction complex is in the state γ at a position $\mathbf{r}$ and at time t is given by $c(\mathbf{r},\gamma,t)$. The integral of this probability distribution over γ is equal to one. The approach of Kramers has been extended to include fluctuating contributions by Pagonabarraga et al.[16]

2.1 Mesoscopic thermodynamics

Having introduced the key concept of a probability distribution $c(\mathbf{r},\gamma,t)$, the first step of mesoscopic non-equilibrium thermodynamics is to establish thermodynamics along the mesoscopic γ-coordinate. It follows from the Gibbs–Shannon entropy postulate that the specific entropy (in J K^{-1} kg^{-1}) for the probability distribution $c(\mathbf{r},\gamma,t)$ is given by:

$$s(\mathbf{r}, t) = -\frac{R}{M} \int_0^1 c(\mathbf{r}, \gamma, t) \ln c(\mathbf{r}, \gamma, t) \mathrm{d}\gamma, \qquad (3)$$

where $M = 2M_A = M_{A_2}$ is the total molar mass of the reaction complex. Along the γ-coordinate we can consider entities with different values of γ as different species in ordinary thermodynamics of multi-component systems. Then, we can define partial specific properties for each value of γ, like $s(\mathbf{r},\gamma,t)$ for the entropy, by:

$$s(\mathbf{r}, t) = \int_0^1 c(\mathbf{r}, \gamma, t) s(\mathbf{r}, \gamma, t) \mathrm{d}\gamma, \qquad (4)$$

and similarly for other extensive thermodynamic variables. From eqn (3) and (4), it immediately follows that $s(\mathbf{r},\gamma,t) = -(R/M) \ln c(\mathbf{r},\gamma,t)$. The local version of the Euler equation reads:

$$T(\mathbf{r}, t)s(\mathbf{r}, t) = h(\mathbf{r}, t) - \int_0^1 c(\mathbf{r}, \gamma, t)\mu(\mathbf{r}, \gamma, t) \mathrm{d}\gamma, \qquad (5)$$

where $h(\mathbf{r},t)$ is the specific enthalpy and where we introduced a chemical potential $\mu(\mathbf{r},\gamma,t)$ for each γ-species. At the ends of the reaction coordinate the chemical potentials are given by $\mu(\mathbf{r},0,t) = \mu_A(\mathbf{r},t)$ and $\mu(\mathbf{r},1,t) = \mu_{A_2}(\mathbf{r},t)$, which are the Gibbs energy of the reactants before the reaction starts and the Gibbs energy of the products after the reaction ends, in J kg^{-1}. From the Gibbs–Shannon postulate, eqn (3), we deduce that this chemical potential is given in terms of the temperature $T(\mathbf{r},t)$ and the probability distribution $c(\mathbf{r},\gamma,t)$ by

$$\mu(\mathbf{r}, \gamma, t) = \frac{RT(\mathbf{r}, t)}{M} \ln c(\mathbf{r}, \gamma, t) + h(\mathbf{r}, \gamma, t), \qquad (6)$$

where $h(\mathbf{r},\gamma,t)$ is the partial specific enthalpy, defined similarly to eqn (4) for the partial specific entropy. We want to stress that eqn (6) for the chemical-potential is the most general expression for the probability distribution $c(\mathbf{r},\gamma,t)$ along the γ-coordinate. It is a direct consequence of the Gibbs–Shannon postulate. Therefore, use of eqn (6) for $\mu(\mathbf{r},\gamma,t)$ does not imply any restriction in the validity of the developments presented in this paper. In particular it does not assume ideal behavior of $\mu_A(\mathbf{r},t)$ and $\mu_{A_2}(\mathbf{r},t)$, as we will explain in more detail below.

The essential property of $h(\mathbf{r},\gamma,t)$ is that there is a high barrier at some transition state γ_0 separating two flat regions. A schematic representation of such an partial specific enthalpy as a function of γ is shown in Fig. 1, where we suppress the explicit $\mathbf{r},t$ dependence for ease of notation. The maximum at the transition state γ_0 is large compared to the thermal energy RT/M. The enthalpy at γ_0 is referred to as the transition state energy. As further clarified in section 2.4, the larger the transition state energy the slower the reaction.

In equilibrium the chemical potential and the temperature will be independent of $\mathbf{r},t$ and γ and we have

$$\mu_{\mathrm{eq}} = \frac{RT_{\mathrm{eq}}}{M} \ln c_{\mathrm{eq}}(\gamma) + h_{\mathrm{eq}}(\gamma). \qquad (7)$$

For the equilibrium probability distribution this gives

$$c_{\mathrm{eq}}(\gamma) = \exp\left[\frac{M}{RT_{\mathrm{eq}}}(\mu_{\mathrm{eq}} - h_{\mathrm{eq}}(\gamma))\right]. \qquad (8)$$

Both h_{eq} and c_{eq} only depend on γ and not on $\mathbf{r},t$ in equilibrium. It follows from eqn (8) that the equilibrium probability is very small around the transition state γ_0. See in this context Fig. 2. In the Figure the non-equilibrium solid line only differs visibly from the equilibrium dashed line for γ between γ_0 and 1. The reason why the difference is small between 0 and γ_0 is on the one hand that we divide by $c_0 \equiv c(0)$, and on the other hand that the chemical potential is in good approximation constant in this region. For γ between γ_0 and 1 the chemical potential is also in good approximation constant, but it has a different value from the one between 0 and γ_0, when the system is not in equilibrium.

As mentioned in the introduction, the theory of non-equilibrium thermodynamics is based on the assumption of local thermodynamic equilibrium. For the reaction-diffusion problem local equilibrium implies that we will assume that the thermodynamic relations, given by eqn (3)–(6), are valid not only in equilibrium but also away from equilibrium.
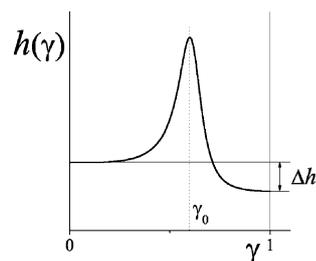

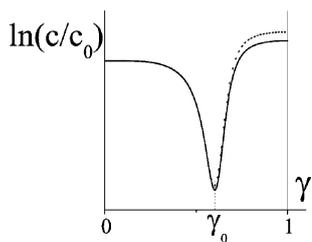**Fig. 1** The partial specific enthalpy along the reaction coordinate.

Fig. 2 The natural logarithm of the probability distribution divided by its value at $\gamma = 0$, for equilibrium (dashed line) and away from equilibrium (solid line).

2.2 Balance laws

We consider a reaction in a volume element at flow. In addition to the flow field there is a temperature and concentration variation across the system. The balance laws relevant to our problem are[14],† the balance of mass

$$\frac{\partial \rho(\mathbf{r}, \gamma, t)}{\partial t} = -\nabla \cdot (\rho(\mathbf{r}, \gamma, t)\mathbf{v}(\mathbf{r}, t) + \mathbf{J}(\mathbf{r}, \gamma, t))$$
$$- \frac{\partial r(\mathbf{r}, \gamma, t)}{\partial \gamma}, \tag{9}$$

the balance of momentum

$$\frac{\partial}{\partial t}(\rho(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)) = -\nabla p(\mathbf{r}, t) - \nabla \cdot [\rho(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)$$
$$- \mathbf{\Pi}(\mathbf{r}, t)], \tag{10}$$

When we use the comoving time derivative, $D/Dt = \partial/\partial t + \mathbf{v}(\mathbf{r}, t) \cdot \nabla$, these equations can be written as:

$$\frac{D\rho(\mathbf{r}, \gamma, t)}{Dt} = -\rho(\mathbf{r}, \gamma, t)\nabla \cdot \mathbf{v}(\mathbf{r}, t) - \nabla \cdot \mathbf{J}(\mathbf{r}, \gamma, t)$$
$$- \frac{\partial r(\mathbf{r}, \gamma, t)}{\partial \gamma}, \tag{11}$$

$$\rho(\mathbf{r}, t)\frac{D\mathbf{v}(\mathbf{r}, t)}{Dt} = -\nabla p(\mathbf{r}, t) + \nabla \cdot \mathbf{\Pi}(\mathbf{r}, t). \tag{12}$$

For the balance of energy one finds

$$\rho(\mathbf{r}, t)\frac{Du(\mathbf{r}, t)}{Dt}$$
$$= \rho(\mathbf{r}, t)T(\mathbf{r}, t)\frac{Ds(\mathbf{r}, t)}{Dt} + \frac{p(\mathbf{r}, t)}{\rho(\mathbf{r}, t)}\frac{D\rho(\mathbf{r}, t)}{Dt}$$
$$+ \rho(\mathbf{r}, t)\int_0^1 \mu(\mathbf{r}, \gamma, t)\frac{Dc(\mathbf{r}, \gamma, t)}{Dt}\mathrm{d}\gamma \tag{13}$$
$$= -\nabla \cdot \mathbf{J}_q(\mathbf{r}, t) - p(\mathbf{r}, t)\nabla \cdot \mathbf{v}(\mathbf{r}, t).$$

In eqn (9) we assume that there are no inert components so that the mass density of reaction complexes in the state γ at the location $\mathbf{r}$ at time t is given by $\rho(\mathbf{r}, \gamma, t) = \rho(\mathbf{r}, t)c(\mathbf{r}, \gamma, t)$. As $c(\mathbf{r}, \gamma, t)$ is normalized, the integral of $\rho(\mathbf{r}, \gamma, t)$ over γ gives $\rho(\mathbf{r}, t)$.

† The discussion in Chapter 2 of de Groot and Mazur carries over to the present case if one replaces the discrete index labeling the components by the continuous label γ labeling the reaction complexes. Similar to that case the momentum density and the internal energy density should not be split into separate contributions for the different reaction complexes.

It is straightforward to extent the analysis to systems where one or more components are inert. In the balance laws (10) and (13), p is the pressure, u is the specific internal energy and s is the specific entropy. Furthermore, the diffusion flux, $\mathbf{J}(\mathbf{r}, \gamma, t) = \rho(\mathbf{r}, \gamma, t)(\mathbf{v}(\mathbf{r}, \gamma, t) - \mathbf{v}(\mathbf{r}, t))$, in the balance of mass (9) is related to the difference between the velocity of the reaction complex, $\mathbf{v}(\mathbf{r}, \gamma, t)$, and the center of mass (barycentric) velocity, $\mathbf{v}(\mathbf{r}, t)$. These velocities are related by $\rho(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t) = \int_0^1 \rho(\mathbf{r}, \gamma, t)\mathbf{v}(\mathbf{r}, \gamma, t)\mathrm{d}\gamma$. When the barycentric velocity field is unequal to zero and one wants to describe flow phenomena, it is convenient to use fluxes relative to the barycentric velocity. In order to simplify the notation we will usually only specify whether a variable does or does not depend on γ. The chemical potential along the reaction coordinate is given at the end by the chemical potentials of the reactants, $\mu(\mathbf{r}, 0, t) = \mu_A$, and the product, $\mu(\mathbf{r}, 1, t) = \mu_{A_2}$. The equations above contain convection terms and are therefore fully applicable also when there is turbulence.

We readily identify on the right-hand side (RHS) of the balance laws (9)–(13) four fluxes. Two of them are vectors: the diffusion flux $\mathbf{J}(\mathbf{r}, \gamma, t)$ of the reaction complex in the state γ and the energy flux $\mathbf{J}_q(\mathbf{r}, t)$ (or total heat flux) in the barycentric frame of reference. Moreover, we have on the RHS of the mass balance (9) a scalar flux, $r(\mathbf{r}, \gamma, t)$, which is a diffusion flux along the internal γ-coordinate in mass per unit volume and unit time and unit γ. This internal diffusion flux represents the chemical reaction, as elucidated below. The last flux is the (deviatoric) stress tensor $\mathbf{\Pi}(\mathbf{r}, t)$, which appears on the RHS of the momentum balance (10) and is a second-order tensor. We note that in the balance of momentum (10), external forces (buoyancy) have been neglected, while in the balance of energy (13) we have also neglected viscous heating. Moreover, in eqn (13) we employ material time derivatives to simplify the notation. For the same reason we will from now on suppress the explicit $\mathbf{r}, t$ dependence when this is not confusing.

The diffusion fluxes are not independent, since from their definition it follows that $\int_0^1 \mathbf{J}(\gamma)\mathrm{d}\gamma = 0$.[14] Therefore, if we integrate the mass-balance law over γ, we obtain $\partial_t\rho + \nabla \cdot (\rho\mathbf{v}) = -r(1) + r(0) = 0$. In the last identity we have used that the reaction is closed so that $r(1) = r(0) = 0$. Using these constraints, we express the set of balance laws as:

$$\frac{D\rho}{Dt} + \rho\nabla \cdot \mathbf{v} = 0, \tag{14a}$$

$$\rho\frac{Dc(\gamma)}{Dt} = -\nabla \cdot \mathbf{J}(\gamma) - \frac{\partial r(\gamma)}{\partial \gamma}, \tag{14b}$$

$$\rho\frac{D\mathbf{v}}{Dt} + \nabla p = \nabla \cdot \mathbf{\Pi}, \tag{14c}$$

$$\rho c_p\frac{DT}{Dt} - \alpha T\frac{Dp}{Dt} + \rho\int_0^1 h(\gamma)\frac{Dc(\gamma)}{Dt}\mathrm{d}\gamma = -\nabla \cdot \mathbf{J}_q, \tag{14d}$$

where c_p is the isobaric specific heat capacity of the mixture, α its thermal expansion coefficient and where

$$h(\gamma) = \mu(\gamma) - T\left(\frac{\partial\mu(\gamma)}{\partial T}\right)_{p,c} = \mu(\gamma) - Ts(\gamma) \tag{15}$$

is the partial specific enthalpy along the reaction coordinate.

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Alternatively, we can express the set of working equations in terms of the molar concentration of molecules $[A](\gamma) = \rho(\gamma)/M$, which is more customary in the chemical literature, and where we have used the fact that the total molar mass of the reaction complex $M = 2M_A = M_{A_2}$ is independent of γ along the reaction coordinate. This second approach implies modifications in eqn (14b) and (d), which have to be expressed in terms of $[A_2]$, so that eqn (14) become:

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{v} = 0, \qquad (16a)$$

$$\frac{D[A](\gamma)}{Dt} + [A](\gamma)\nabla \cdot \mathbf{v} = -\nabla \cdot \mathbf{J}'(\gamma) - \frac{\partial r'(\gamma)}{\partial \gamma}, \qquad (16b)$$

$$\rho \frac{D\mathbf{v}}{Dt} + \nabla p = \nabla \cdot \mathbf{\Pi}, \qquad (16c)$$

$$\rho c_p \frac{DT}{Dt} - \alpha T \frac{Dp}{Dt} + \int_0^1 d\gamma \, Mh(\gamma)$$
$$\times \left\{ \frac{D[A](\gamma)}{Dt} + [A](\gamma)\nabla \cdot \mathbf{v} \right\} = -\nabla \cdot \mathbf{J}_q. \qquad (16d)$$

where the term $Mh(\gamma)$ corresponds to the partial enthalpy of the reaction complex along the reaction coordinate γ in J mol^{-1}, $\mathbf{J}'(\gamma) = \mathbf{J}(\gamma)/M$ is the diffusion flux expressed in moles of the reaction complex per m^2 and s, and similarly $r'(\gamma) = r(\gamma)/M$ the internal diffusion flux expressed in terms of moles of the reaction complex produced per unit volume. The product $Mh(\gamma)$ in the RHS of eqn (16d), with the help of (15), can be expressed as:

$$Mh(\gamma) = \mu'(\gamma) - T\left(\frac{\partial \mu'(\gamma)}{\partial T}\right)_{p,c}, \qquad (17)$$

where $\mu'(\gamma) = M\mu(\gamma)$ corresponds to the chemical potential of the reaction complex $A(\gamma)$ along the reaction coordinate in J mol^{-1}. Hence, the product $Mh(\gamma)$ is closely related to the enthalpy of the chemical reaction (1), also in J mol^{-1}.

We conclude that the set of balance equations, whether formulated in terms of mass densities or in terms of molar concentrations, have a completely parallel structure. The following developments can be translated from one language to the other just by replacing $c(\gamma)$ with $[A](\gamma)$, $\rho D_t c(\gamma)$ with $D_t[A](\gamma) + [A](\gamma)\nabla \cdot \mathbf{v}$, $\mathbf{J}(\gamma)$ with $\mathbf{J}'(\gamma)$, $r(\gamma)$ with $r'(\gamma)$ and by multiplying $h(\gamma)$ everywhere by a factor M/ρ. We have chosen to use here version (14), but we emphasize that the other possibility is completely equivalent.

As usual, the RHS of the balance laws (14) or (16) contains fluxes that need be related to the physical gradients in the system. This is considered next.

2.3 The flux–force relations

The complete non-equilibrium thermodynamic formulation of the system under study requires, in addition to the balance laws (14), the consideration of the entropy production $\dot{\mathcal{S}}$ of the system as a function of the position and time. Generalizing the results in the monograph by de Groot and Mazur,[14] to which we refer for further clarification, one obtains:

$$\dot{\mathcal{S}} = -\mathbf{J}_q \cdot \frac{\nabla T}{T^2} - \int_0^1 \mathbf{J}(\gamma) \cdot \nabla \frac{\mu(\gamma)}{T} d\gamma$$
$$+ \mathbf{\Pi}^{(s)} : \frac{(\nabla \mathbf{v})^{(s)}}{T} - \int_0^1 \frac{r(\gamma)}{T} \frac{\partial \mu(\gamma)}{\partial \gamma} d\gamma, \qquad (18)$$

where the superscript (s) indicates that the viscous part of the pressure tensor is symmetric. This implies that only the symmetric part of the tensor of velocity derivatives $(\nabla \mathbf{v})^{(s)}$ contributes to $\dot{\mathcal{S}}$. The symmetric tensors can both be written as the sum of a symmetric traceless part, indicated by a superscript (st), and a contribution due to the trace

$$\mathbf{\Pi}^{(s)} = \mathbf{\Pi}^{(st)} + \Pi \mathbf{1}, \qquad (19)$$

$$(\nabla \mathbf{v})^{(s)} = (\nabla \mathbf{v})^{(st)} + \tfrac{1}{3}(\nabla \cdot \mathbf{v})\mathbf{1}, \qquad (20)$$

Here $\mathbf{1}$ is the unit tensor and $\Pi = \frac{1}{3}\mathrm{tr}\mathbf{\Pi} = \frac{1}{3}\mathrm{tr}\mathbf{\Pi}^{(s)}$. Upon substitution of eqn (19) and (20) into eqn (18) the entropy production of the system becomes

$$\dot{\mathcal{S}} = -\mathbf{J}_q \cdot \frac{\nabla T}{T^2} - \int_0^1 \mathbf{J}(\gamma) \cdot \nabla \frac{\mu(\gamma)}{T} d\gamma + \mathbf{\Pi}^{(st)} : \frac{(\nabla \mathbf{v})^{(st)}}{T}$$
$$+ \Pi \frac{\nabla \cdot \mathbf{v}}{T} - \int_0^1 \frac{r(\gamma)}{T} \frac{\partial \mu(\gamma)}{\partial \gamma} d\gamma. \qquad (21)$$

The entropy production in eqn (21) has the typical structure: it is linear in the fluxes. As is well known, the quantities multiplying each of the five fluxes in eqn (21) are the corresponding *conjugate thermodynamic forces*. The first two flux–force pairs are vectorial, the third is traceless symmetric tensorial and the last two terms are scalar.

In our analysis it has been assumed that the diffusion flux along the internal γ-coordinate, $r(\gamma)$, vanishes at both $\gamma = 0$ and $\gamma = 1$. The reaction is closed. This is appropriate for the problems we intend to consider. It is possible to consider cases for which $r(0)$ and $r(1)$ are unequal to zero. In that case there is exchange of reactants and/or products with one or more buffers. This leads to entropy fluxes at the ends of the reaction coordinate, which would have to be considered.

Next, to "close" the balance laws (14) and to obtain the equations of irreversible thermodynamics, one needs to introduce the linear phenomenological laws. Various formulations are possible and they are related to each other by a redefinition of the fluxes. The final hydrodynamic equations obtained (see eqn (60) and (61) below) for different choices of fluxes used to establish the phenomenological laws are fully equivalent. We shall use as fluxes the vectors $\mathbf{J}_q$, $\mathbf{J}(\gamma)$, the symmetric traceless tensor $\mathbf{\Pi}^{(st)}$, and the scalars Π, $r(\gamma)$. Then, taking into account that the two vectorial fluxes are coupled by virtue of the Curie principle, and assuming that the system is isotropic, one

obtains in mesoscopic non-equilibrium thermodynamics the following linear phenomenological laws:

$$\mathbf{J}_q = -L_{qq}\frac{\nabla T}{T^2} - \int_0^1 L_{qJ}(\gamma)\nabla\frac{\mu(\gamma)}{T}\,\mathrm{d}\gamma, \qquad (22a)$$

$$\mathbf{J}(\gamma) = -L_{Jq}(\gamma)\frac{\nabla T}{T^2} - L_{JJ}(\gamma)\nabla\frac{\mu(\gamma)}{T}, \qquad (22b)$$

$$\Pi_{ij}^{(\mathrm{st})} = \eta\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\nabla\cdot\mathbf{v}\right), \qquad (22c)$$

$$\Pi = \eta_v\,\nabla\cdot\mathbf{v}, \qquad (22d)$$

$$r(\gamma) = -L_r(\gamma)\frac{1}{T}\frac{\partial\mu(\gamma)}{\partial\gamma}. \qquad (22e)$$

These are the flux equations for the mesoscopic level that follow from the entropy production. We see that there is coupling between the heat and mass flux, but not between other fluxes. Even though Π and $r(\gamma)$ are both scalar, we have neglected possible coupling terms between these fluxes, because they are usually small. Such coupling terms give a so-called chemical viscosity. We refer to the monograph by Kuiken[29] pp. 133–135 for more details. The phenomenological laws, (22c) and (22d), for the two contributions to the stress tensor are expressed in the common way,[14] in terms of the shear viscosity η and the bulk viscosity η_v. The other phenomenological laws (22a)–(22e) are written in terms of Onsager coefficients L_{qq}, $L_{JJ}(\gamma)$, $L_{qJ}(\gamma)$, $L_{Jq}(\gamma)$ and $L_r(\gamma)$, that satisfy the Onsager relation $L_{qJ}(\gamma) = L_{Jq}(\gamma)$. In writing the above phenomenological laws we assumed that $\mathbf{J}(\gamma)$ and $r(\gamma)$ are true physical fluxes which only depend on their conjugate forces at the same value of γ.

In order to relate the flux equations for the mesoscopic level to measurement, we need to integrate over the internal coordinate. Because $\int_0^1 \mathbf{J}(\gamma)\mathrm{d}\gamma = 0$, it follows that the integral on the RHS of eqn (22b) over γ is zero independent of the choice of the temperature and the chemical potential gradients. This implies, by using also the Onsager relation in the first equality, that $\int_0^1 L_{Jq}(\gamma)\mathrm{d}\gamma = \int_0^1 L_{qJ}(\gamma)\,\mathrm{d}\gamma = 0$ and $\int_0^1 L_{JJ}(\gamma)\nabla[\mu(\gamma)/T]\,\mathrm{d}\gamma = 0$. We shall use these properties when we integrate below.

2.4 Transport along the reaction coordinate

In this subsection we discuss what happens along the reaction coordinate γ. At each point in space $\mathbf{r}$ at time t the state or the reaction is described by the probability distribution $c(\mathbf{r},\gamma,t)$ of the reaction complexes to be in the state γ. The time rate of change of $c(\mathbf{r},\gamma,t)$ is given by eqn (14b), and the diffusion flux along the internal γ-coordinate is given by the phenomenological eqn (22e). Substitution of eqn (6) and (22e) into eqn (14b) yields:

$$\frac{Dc(\mathbf{r},\gamma,t)}{Dt} = -\frac{1}{\rho(\mathbf{r},t)}\nabla\cdot\mathbf{J}(\mathbf{r},\gamma,t)$$
$$-\frac{\partial}{\partial\gamma}D_r\left[\frac{\partial}{\partial\gamma}c(\mathbf{r},\gamma,t) + \frac{Mc(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\frac{\partial}{\partial\gamma}h(\mathbf{r},\gamma,t)\right], \qquad (23)$$

where we introduced the following diffusion coefficient along the γ-coordinate

$$D_r(\mathbf{r},t) \equiv \frac{RL_r(\mathbf{r},\gamma,t)}{M\rho(\mathbf{r},\gamma,t)} = \frac{RL_r(\mathbf{r},\gamma,t)}{M\rho(\mathbf{r},t)c(\mathbf{r},\gamma,t)}. \qquad (24)$$

In first approximation the Onsager coefficient $L_r(\mathbf{r},\gamma,t)$ will be proportional to $c(\mathbf{r},\gamma,t)$[12] and the diffusion coefficient D_r is therefore in good approximation independent of the reaction coordinate γ. As indicated in eqn (24), the diffusion coefficient along the reaction coordinate may still depend on $\mathbf{r},t$. Upon substitution of eqn (6) and (24) into eqn (22e), one obtains

$$r(\mathbf{r},\gamma,t) = -D_r(\mathbf{r},t)\rho(\mathbf{r},t)\exp\left[-\frac{M\,h(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]$$
$$\times\frac{\partial}{\partial\gamma}\exp\left[\frac{M\mu(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]. \qquad (25)$$

The energy barrier along the γ-coordinate has a maximum at γ_0 which is large compared to RT/M. As a consequence the reaction rate r is small. A quasi-stationary state develops such that $r(\mathbf{r},\gamma,t)$ is in good approximation independent of γ along the reaction coordinate. This is illustrated for a special case in Fig. 3. Close to the ends of the γ-coordinate $r(\mathbf{r},\gamma,t)$ goes to zero. We have therefore in good approximation

$$r(\mathbf{r},\gamma,t) = r(\mathbf{r},t)\Theta(\gamma)\Theta(1-\gamma), \qquad (26)$$

where Θ is the Heaviside function, which is one for a positive argument and zero for a negative argument. Upon substitution of eqn (26) into eqn (25) we obtain

$$r(\mathbf{r},t)\Theta(\gamma)\Theta(1-\gamma) = -D_r(\mathbf{r},t)\rho(\mathbf{r},t)\exp\left[-\frac{Mh(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]$$
$$\times\frac{\partial}{\partial\gamma}\exp\left[\frac{M\mu(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]. \qquad (27)$$

It should be noted that the derivative of the reaction rate with respect to γ gives two contributions proportional to a delta function near the end of the reaction coordinate, which, as one can see in Fig. 3, are just inside the 0,1 domain. Integration of this derivative over γ therefore has $\pm r(\mathbf{r},t)$ contributions at the end of the γ-coordinate and not a half times these values.
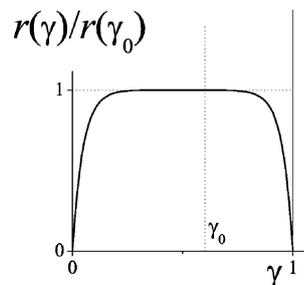

Fig. 3 Representation of a prototypical flow along the reaction coordinate for a quasi-stationary state. Note that $r(\gamma)$ vanishes at the two ends of the interval, but changes only close to these endpoints.

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If we bring the exponential factor containing h to the left in eqn (27), we can integrate this equation over γ and obtain

$$r(\mathbf{r},t) = -D_r(\mathbf{r},t)\rho(\mathbf{r},t)\left\{\frac{\exp\left[\dfrac{M\mu(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]-\exp\left[\dfrac{M\mu(\mathbf{r},0,t)}{RT(\mathbf{r},t)}\right]}{\displaystyle\int_0^\gamma \exp\left[\dfrac{M\,h(\mathbf{r},\gamma',t)}{R\,T(\mathbf{r},t)}\right]\mathrm{d}\gamma'}\right\}. \tag{28}$$

Use of eqn (6) yields

$$r(\mathbf{r},t) = -D_r(\mathbf{r},t)\rho(\mathbf{r},t)$$
$$\times\left\{\frac{c(\mathbf{r},\gamma,t)\exp\left[\dfrac{Mh(\gamma)}{RT(\mathbf{r},t)}\right]-c(\mathbf{r},0,t)\exp\left[\dfrac{Mh(0)}{RT(\mathbf{r},t)}\right]}{\displaystyle\int_0^\gamma \exp\left[\dfrac{M\,h(\mathbf{r},\gamma',t)}{R\,T(\mathbf{r},t)}\right]\mathrm{d}\gamma'}\right\}. \tag{29}$$

In the quasi-stationary state, the chemical potential is in good approximation constant in the domains between 0 and γ_0 and between γ_0 and 1. As illustrated by the example in Fig. 4, in the regions around 0 and 1, where the probability is sizeable, the chemical potential is in good approximation constant. The changeover is around $\gamma = \gamma_0$ where the probability is negligible. We have therefore

$$\mu(\mathbf{r},\gamma,t) = \mu(\mathbf{r},0,t)\Theta(\gamma_0-\gamma) + \mu(\mathbf{r},1,t)\Theta(\gamma-\gamma_0)$$
$$\equiv \mu_A(\mathbf{r},t)\Theta(\gamma_0-\gamma) + \mu_{A_2}(\mathbf{r},t)\Theta(\gamma-\gamma_0), \tag{30}$$

where we have identified the chemical potential at $\gamma = 0$ with a pair of atoms and at $\gamma = 1$ with a molecule. Combining eqn (6) and (30) we obtain for the probability distribution along the γ-coordinate

$$c(\mathbf{r},\gamma,t) = \exp\left[\frac{M}{RT(\mathbf{r},t)}(\mu_A(\mathbf{r},t)-h(\mathbf{r},\gamma,t))\right]\Theta(\gamma_0-\gamma)$$
$$+\exp\left[\frac{M}{RT(\mathbf{r},t)}(\mu_{A_2}(\mathbf{r},t)-h(\mathbf{r},\gamma,t))\right]\Theta(\gamma-\gamma_0)$$
$$= c(\mathbf{r},0,t)\exp\left[\frac{M}{RT(\mathbf{r},t)}(h(\mathbf{r},0,t)-h(\mathbf{r},\gamma,t))\right]\Theta(\gamma_0-\gamma)$$
$$+ c(\mathbf{r},1,t)\exp\left[\frac{M}{RT(\mathbf{r},t)}(h(\mathbf{r},1,t)-h(\mathbf{r},\gamma,t))\right]\Theta(\gamma-\gamma_0). \tag{31}$$
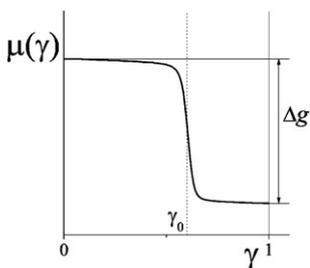

Fig. 4 The chemical-potential profile along the γ-coordinate. The data have been obtained from eqn (28) together with Fig. 1 for $h(\gamma)$ and Fig. 3 for $r(\gamma)$.

Therefore, the combination of a barrier-shape $h(\mathbf{r},\gamma,t)$ with a quasi-stationary $r(\mathbf{r},\gamma,t)$ allows us to group states along the γ-coordinate in two classes. The first class contains all states with $0 \leq \gamma < \gamma_0$ and the second class contains all states with $\gamma_0 < \gamma \leq 1$. The states in the first class are in equilibrium with the reactants, while those in the second class are in equilibrium with the products. The total probabilities to find reactants and products at the position $\mathbf{r}$ at time t are

$$c_{2A}(\mathbf{r},t) \equiv \int_0^{\gamma_0} c(\mathbf{r},\gamma,t)\mathrm{d}\gamma$$
$$= c(\mathbf{r},0,t)\int_0^{\gamma_0}\exp\left[\frac{M}{RT(\mathbf{r},t)}(h(0)-h(\gamma))\right]\mathrm{d}\gamma,$$

$$c_{A_2}(\mathbf{r},t) \equiv \int_{\gamma_0}^1 c(\mathbf{r},\gamma,t)\mathrm{d}\gamma$$
$$= c(\mathbf{r},1,t)\int_{\gamma_0}^1\exp\left[\frac{M}{RT(\mathbf{r},t)}(h(1)-h(\gamma))\right]\mathrm{d}\gamma. \tag{32}$$

We define $c_{A_2}(\mathbf{r},t) \equiv c(\mathbf{r},t)$ and $c_{2A}(\mathbf{r},t) \equiv 1 - c(\mathbf{r},t)$. Given that there is a single product of the reaction A_2 with a stochiometric coefficient 1, $c_{A_2}(\mathbf{r},t) \equiv c(\mathbf{r},t)$ is equal to the concentration of A_2 at the position $\mathbf{r}$ at time t. The reactants have a stoichiometric coefficient 2 and as a consequence $c_{2A}(\mathbf{r},t) = c_A^2(\mathbf{r},t)$, where $c_A(\mathbf{r},t)$ is the concentration of A at the position $\mathbf{r}$ at time t, see Pagonabarraga *et al.*[16] Substituting these relations into eqn (29) for the diffusion flux along the internal γ-coordinate we obtain

$$r(\mathbf{r},t) = \frac{D_r(\mathbf{r},t)\rho(\mathbf{r},t)}{\displaystyle\int_0^1\exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]\mathrm{d}\gamma}$$
$$\times\left\{\frac{c_{2A}(\mathbf{r},t)}{\displaystyle\int_0^{\gamma_0}\exp\left[-\dfrac{Mh(\gamma)}{RT(\mathbf{r},t)}\right]\mathrm{d}\gamma}-\frac{c_{A_2}(\mathbf{r},t)}{\displaystyle\int_{\gamma_0}^1\exp\left[-\dfrac{Mh(\gamma)}{RT(\mathbf{r},t)}\right]\mathrm{d}\gamma}\right\}. \tag{33}$$

This can be written as

$$r(\mathbf{r},t) = k_+(\mathbf{r},t)\,c_{2A}(\mathbf{r},t) - k_-(\mathbf{r},t)c_{A_2}(\mathbf{r},t)$$
$$= k_+(\mathbf{r},t)\,c_A^2(\mathbf{r},t) - k_-(\mathbf{r},t)c_{A_2}(\mathbf{r},t), \tag{34}$$

where the rate coefficients are:

$$k_+(\mathbf{r},t) = \frac{D_r(\mathbf{r},t)\rho(\mathbf{r},t)}{\displaystyle\int_0^1\exp\left[\dfrac{Mh(\gamma)}{RT(\mathbf{r},t)}\right]\mathrm{d}\gamma\int_0^{\gamma_0}\exp\left[-\dfrac{Mh(\gamma)}{RT(\mathbf{r},t)}\right]\mathrm{d}\gamma},$$

$$k_-(\mathbf{r},t) = \frac{D_r(\mathbf{r},t)\rho(\mathbf{r},t)}{\displaystyle\int_0^1\exp\left[\dfrac{Mh(\gamma)}{RT(\mathbf{r},t)}\right]\mathrm{d}\gamma\int_{\gamma_0}^1\exp\left[-\dfrac{Mh(\gamma)}{RT(\mathbf{r},t)}\right]\mathrm{d}\gamma}. \tag{35}$$

Eqn (34) is the law of mass action of Guldberg and Waage.[8] Thus, unlike classical non-equilibrium thermodynamics, the mesoscopic extension of the theory reproduces the law of mass action. It is also clear from the thermodynamic derivation that the kinetic coefficients are Arrhenius-like.

In the further analysis it is convenient to write eqn (28) in the form

$$r(\mathbf{r}, t) = -\frac{D_r(\mathbf{r}, t)\rho(\mathbf{r}, t)}{\int_0^1 \exp\left[\dfrac{Mh(\mathbf{r}, \gamma, t)}{RT(\mathbf{r}, t)}\right]\mathrm{d}\gamma}$$

$$\times \left\{\exp\left[\frac{M\mu_{A_2}(\mathbf{r}, t)}{RT(\mathbf{r}, t)}\right] - \exp\left[\frac{M\mu_A(\mathbf{r}, t)}{RT(\mathbf{r}, t)}\right]\right\}$$

$$= -\frac{L_r(\mathbf{r}, t)R}{M}\left\{1 - \exp\left[-\frac{M(\mu_{A_2}(\mathbf{r}, t) - \mu_A(\mathbf{r}, t))}{RT(\mathbf{r}, t)}\right]\right\}$$

$$= -\frac{L_r(\mathbf{r}, t)R}{M}\left\{1 - \exp\left[-\frac{M\Delta g(\mathbf{r}, t)}{RT(\mathbf{r}, t)}\right]\right\}, \quad (36)$$

where

$$L_r(\mathbf{r}, t) = \frac{MD_r(\mathbf{r}, t)\rho(\mathbf{r}, 1, t)}{R\int_0^1 \exp\left[\dfrac{M(h(\mathbf{r}, \gamma, t) - h(\mathbf{r}, 0, t))}{RT(\mathbf{r}, t)}\right]\mathrm{d}\gamma}$$

$$= \frac{MD_r(\mathbf{r}, t)\rho_{A_2}(\mathbf{r}, t)}{R\int_0^1 \exp\left[\dfrac{Mh(\mathbf{r}, \gamma, t)}{RT(\mathbf{r}, t)}\right]\mathrm{d}\gamma \int_{\gamma_0}^1 \exp\left[-\dfrac{Mh(\mathbf{r}, \gamma, t)}{RT(\mathbf{r}, t)}\right]\mathrm{d}\gamma}$$

$$= \frac{M}{R}k_-(\mathbf{r}, t)\rho_{A_2}(\mathbf{r}, t), \quad (37)$$

and where the Gibbs energy of the reaction is $\Delta g(\mathbf{r}, t) = \mu_{A_2}(\mathbf{r}, t) - \mu_A(\mathbf{r}, t)$. Eqn (36) is the thermodynamic form of the law of mass action. It contains activities of the reactants and products rather than concentrations, and can thus be said to be more general than the formulation which uses the ideality assumption. While the law of mass action (34) uses the probabilities for the forward and backward reactions, mesoscopic non-equilibrium thermodynamics shows that one should use the fugacities $f_i = \exp(M\mu_i/RT)$ rather than the densities ρ_i. This gives a different physical understanding. Eqn (36) is the most appropriate form to be used in entropy production minimization, see e.g., ref. 5,7 or in descriptions of chemical reactions in general. Eqn (37) gives a useful relation between the rate coefficients L_r and k_-, which in many cases is known from experiments. We propose to calculate the thermodynamic rate coefficient L_r from experimental data in this manner. Many data are then readily available for a thermodynamic analysis.[6,7,30]

Using the expression for the concentration of A_2 which follows from eqn (32) one obtains from eqn (14b) by integrating from γ_0 to 1:

$$\rho(\mathbf{r}, t)\frac{Dc(\mathbf{r}, t)}{Dt} = -\nabla \cdot \mathbf{J}(\mathbf{r}, t) + r(\mathbf{r}, t), \quad (38)$$

where

$$\mathbf{J}(\mathbf{r}, t) \equiv \int_{\gamma_0}^1 \mathbf{J}(\mathbf{r}, \gamma, t)\mathrm{d}\gamma = -\int_0^{\gamma_0} \mathbf{J}(\mathbf{r}, \gamma, t)\mathrm{d}\gamma, \quad (39)$$

To obtain the last term in eqn (38) we used that the diffusion flux along the internal γ-coordinate is such that $\partial r(\mathbf{r}, \gamma, t)/\partial \gamma$

has a contribution $r(\mathbf{r}, t)\delta(1 - \gamma)$ which is just inside the integration domain; see the explanation under eqn (26) and (27) to clarify why there is no factor of 1/2. This term gives the slow conversion of reactants to products, which is equal to the reaction rate.

From eqn (15) and (30) it follows that

$$h(\mathbf{r}, \gamma, t) = h(\mathbf{r}, 0, t)\Theta(\gamma_0 - \gamma) + h(\mathbf{r}, 1, t)\Theta(\gamma - \gamma_0)$$

$$\equiv h_A(\mathbf{r}, t)\Theta(\gamma_0 - \gamma) + h_{A_2}(\mathbf{r}, t)\Theta(\gamma - \gamma_0). \quad (40)$$

Substitution of this expression into the integral containing $h(\mathbf{r}, \gamma, t)$ in eqn (14d) and use of the definition of $c(\mathbf{r}, t)$ given below eqn (32) yields

$$\int_0^1 h(\mathbf{r}, \gamma, t)\frac{Dc(\gamma, t)}{Dt}\mathrm{d}\gamma = [h_A(\mathbf{r}, t) - h_{A_2}(\mathbf{r}, t)]\frac{Dc(\mathbf{r}, t)}{Dt}$$

$$= -\Delta h(\mathbf{r}, t)\frac{Dc(\mathbf{r}, t)}{Dt}, \quad (41)$$

where Δh is the enthalpy of the reaction, see Fig. 1.

2.5 Transport coefficients in the presence of a chemical reaction

Substitution of eqn (30) for the chemical potential into eqn (22a) for the heat flux yields

$$\mathbf{J}_q = -L_{qq}\frac{\nabla T}{T^2} - L_{qJ}\nabla\frac{\mu_{A_2} - \mu_A}{T}$$

$$= -L_{qq}\frac{\nabla T}{T^2} - L_{qJ}\nabla\frac{\Delta g}{T}, \quad (42)$$

where the coupling coefficient is given by

$$L_{qJ} = \int_{\gamma_0}^1 L_{qJ}(\gamma)\mathrm{d}\gamma = -\int_0^{\gamma_0} L_{qJ}(\gamma)\mathrm{d}\gamma. \quad (43)$$

Integrating eqn (22b) from γ_0 to 1 one obtains

$$\mathbf{J} = -L_{Jq}\frac{\nabla T}{T^2} - L_{JJ}\nabla\frac{\mu_{A_2} - \mu_A}{T}$$

$$= -L_{Jq}\frac{\nabla T}{T^2} - L_{JJ}\nabla\frac{\Delta g}{T}, \quad (44)$$

where

$$2L_{JJ} = \int_{\gamma_0}^1 L_{JJ}(\gamma)\mathrm{d}\gamma. \quad (45)$$

In the derivation of eqn (44) we have used that the integral of $\mathbf{J}(\gamma)$ over γ is equal to zero, so that:

$$\int_0^1 L_{JJ}(\gamma)\nabla\frac{\mu(\gamma)}{T}\mathrm{d}\gamma = \int_{\gamma_0}^1 L_{JJ}(\gamma)\mathrm{d}\gamma\nabla\frac{\mu_{A_2}}{T}$$

$$(46)$$

$$+ \int_0^{\gamma_0} L_{JJ}(\gamma)\mathrm{d}\gamma\nabla\frac{\mu_A}{T} = 0$$

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By using eqn (34), (42) and (44) the phenomenological eqn (22c)–22(e) become

$$\mathbf{J}_q = -L_{qq}\frac{\nabla T}{T^2} - L_{qJ}\nabla\frac{\Delta g}{T}, \tag{47}$$

$$\mathbf{J} = -L_{Jq}\frac{\nabla T}{T^2} - L_{JJ}\nabla\frac{\Delta g}{T}, \tag{48}$$

$$\Pi_{ij} = \eta\left(\frac{\partial \mathbf{v}_i}{\partial x_j} + \frac{\partial \mathbf{v}_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\nabla\cdot\mathbf{v}\right), \tag{49}$$

$$\Pi = \eta_v\,\nabla\cdot\mathbf{v} \tag{50}$$

$$r = \frac{L_r R}{M}\left[1 - \exp\left(\frac{M\Delta g}{RT}\right)\right]. \tag{51}$$

As we explained between eqn (34) and (37), eqn (51) is consistent with the law of mass action given in eqn (34). As we showed in the previous subsection, the coefficient L_r associated with the chemical reaction, can be related to the rate constant k_-, see eqn (37). We prefer to give the reaction rate with the Onsager coefficient L_r, to underline its thermodynamic basis. Finally we see that linear phenomenological laws of traditional non-equilibrium thermodynamics are recovered for small deviations, $M\Delta g \ll RT$, from chemical equilibrium.[14]

In order to be able to compare with experiments, we relate the phenomenological coefficients to the well-known transport coefficients. In the case of the coupled equations for $\mathbf{J}$ and $\mathbf{J}_q$, this is achieved by expressing first the gradient in the reaction Gibbs energy in eqn (48) in terms of pressure, temperature and concentration gradients. This procedure yields:

$$\mathbf{J}_q = -\left[L_{qq} - \frac{L_{Jq}^2}{L_{JJ}}\right]\frac{\nabla T}{T^2} + \frac{L_{qJ}}{L_{JJ}}\mathbf{J}, \tag{52}$$

$$\mathbf{J} = -\{L_{qJ} - L_{JJ}\Delta h\}\frac{\nabla T}{T^2} \\ - \frac{L_{JJ}}{T}\left(\frac{\partial\Delta g}{\partial p}\right)_{T,c}\nabla p - \frac{L_{JJ}}{T}\left(\frac{\partial\Delta g}{\partial c}\right)_{p,T}\nabla c. \tag{53}$$

On comparing this with the phenomenological equations for binary systems[31]

$$\mathbf{J}_q = -\lambda\nabla T + \left\{\Delta h + k_T\left(\frac{\partial\Delta g}{\partial c}\right)_{p,T}\right\}\mathbf{J}, \tag{54}$$

$$\mathbf{J} = -\rho D\left\{\nabla c + \frac{k_T}{T}\nabla T + \frac{k_p}{p}\nabla p\right\}, \tag{55}$$

we can express the Onsager coefficients in terms of the usual transport coefficients: thermal conductivity λ, mutual diffusion coefficient D, dimensionless thermal diffusion ratio k_T

and dimensionless barodiffusion ratio k_p. The resulting expressions are:

$$D = \frac{L_{JJ}}{\rho T}\left(\frac{\partial\Delta g}{\partial c}\right)_{p,T}, \quad \lambda = \frac{1}{T^2}\left[L_{qq} - \frac{L_{qJ}^2}{L_{JJ}}\right], \\ \rho DTk_T = L_{qJ} - L_{JJ}\Delta h, \quad k_p = p\left(\frac{\partial\Delta g}{\partial p}\right)_{T,c}\left(\frac{\partial\Delta g}{\partial c}\right)_{p,T}^{-1}. \tag{56}$$

The expressions show that the coefficients differ significantly from the corresponding coefficients without a chemical reaction. The value of D has a contribution from the concentration variation in Δg, which can be substantial. The coupling coefficient $L_{qJ} = L_{Jq}$ can be large, because Δh can be of appreciable magnitude. This can be seen more clearly by defining the heat of transfer

$$q^* = \left(\frac{\mathbf{J}_q}{\mathbf{J}}\right)_T = \frac{L_{qJ}}{L_{JJ}} = \Delta h + k_T\left(\frac{\partial\Delta g}{\partial c}\right)_{p,T}. \tag{57}$$

The sign of the coefficient may also vary. The barodiffusion ratio is independent of the Onsager coefficients; it is an equilibrium property and not related to a dissipative process. Barodiffusion seems to be important only in geological problems, and is negligibly small for ordinary fluid mixtures. Hence, we neglect barodiffusion here, which means that we neglect the dependence of the specific Gibbs energy difference on pressure in eqn (53), so that $\Delta g = \Delta g(T, c)$ only.

2.6 Hydrodynamic equations

Next, we substitute the phenomenological eqn (47)–(50) into the set of balance laws, eqn (14a), (14c), (38), (14d), and use eqn (41) in eqn (14d), so as to obtain the set of differential equations from which the spatiotemporal evolution of the velocity, the temperature and the concentration of the mixture can be evaluated. If we neglect the dependence of the Onsager coefficients on pressure, concentration or temperature, the hydrodynamic equations can be written as:

$$\frac{D\rho}{Dt} + \rho\nabla\cdot\mathbf{v} = 0,$$

$$\rho\frac{D\mathbf{v}}{Dt} = -\nabla p + \eta\nabla^2\mathbf{v} + \left(\frac{1}{3}\eta + \eta_v\right)\nabla\nabla\cdot\mathbf{v},$$

$$\rho\frac{Dc}{Dt} = -L_{qJ}\nabla^2\left(\frac{1}{T}\right) + L_{JJ}\nabla^2\left(\frac{\Delta g}{T}\right) \\ - \frac{L_r R}{M}\left[1 - \exp\left(-\frac{M\Delta g}{RT}\right)\right],$$

$$\rho c_p\frac{DT}{Dt} - \alpha T\frac{Dp}{Dt} + \rho\Delta h\frac{Dc}{Dt} = -L_{qq}\nabla^2\left(\frac{1}{T}\right) + L_{Jq}\nabla^2\left(\frac{\Delta g}{T}\right), \tag{58}$$

which, combined with the equations of state $p = p(\rho, T, c)$ and $\Delta g = \Delta g(p, T, c) \simeq \Delta g(T, c)$ constitute the hydrodynamic equations of the chemically reacting mixture under consideration. We have used the fact that the chemical potential along the

internal coordinate is constant separately for reactants and products and have used the enthalpy of the chemical reaction, $\Delta h = h_{A_2} - h_A$. As discussed in Section 2.2, these equations can be expressed in terms of the molar concentration, $[A_2]$, multiplying by the corresponding factors involving the molar mass, M_{A_2}. For example, the molar enthalpies of the chemical reaction is obtained multiplying Δh by the factor M_{A_2}.

Again, it is usually advantageous to express the second pair of the hydrodynamic eqn (58) in terms of the ordinary transport coefficients: λ, D, k_T, instead of the Onsager coefficients L_{JJ}, etc. This can be achieved by inverting eqn (56) and substituting the result into eqn (58). Furthermore, it can be assumed that:

$$\nabla^2\left(\frac{1}{T}\right) \simeq -\frac{1}{T^2}\nabla^2 T,$$

$$\nabla^2\left(\frac{\Delta g}{T}\right) \simeq -\frac{\Delta g}{T^2}\nabla^2 T + \frac{1}{T}\nabla^2(\Delta g)$$

$$\simeq -\frac{1}{T^2}\left[\Delta g - T\left(\frac{\partial \Delta g}{\partial T}\right)_c\right]\nabla^2 T + \frac{1}{T}\left(\frac{\partial \Delta g}{\partial c}\right)_T\nabla^2 c, \tag{59}$$

where terms proportional to the square of gradients, like $(\nabla T)^2$, $(\nabla \mu)^2$ etc., have been neglected, since they are second order in the fluxes as can be immediately seen by inverting the phenomenological relations (47)–(50). In addition, we recall that we may neglect barodiffusion and, consequently, the dependence of the reaction Gibbs energy on the pressure, see eqn (56). Then, substitution of eqn (59) into the second pair of eqn (58), and use of the well-known transport coefficients, give the hydrodynamic equations in their more classical form, namely:

$$\frac{Dc}{Dt} = D\left\{\nabla^2 c + \frac{k_T}{T}\nabla^2 T\right\} - \frac{L_r R}{\rho M}\left\{1 - \exp\left[-\frac{M\Delta g}{RT}\right]\right\}, \tag{60}$$

$$\frac{DT}{Dt} = [a + D\epsilon_D]\nabla^2 T + \frac{DT}{k_T}\epsilon_D\nabla^2 c + \frac{L_r RT}{\rho M}\Delta\hat{h}\left\{1 - \exp\left[-\frac{M\Delta g}{RT}\right]\right\}, \tag{61}$$

where in the energy eqn (61) we have introduced a thermal diffusivity

$$a = \frac{\lambda}{\rho c_p - \alpha T(\partial p/\partial T)_{\rho,c}}, \tag{62}$$

a dimensionless Dufour effect ratio

$$\epsilon_D = \frac{\rho k_T^2}{T(\rho c_p - \alpha T(\partial p/\partial T)_{\rho,c})}\left(\frac{\partial \Delta g}{\partial c}\right)_{p,T}, \tag{63}$$

which measures the importance of the Dufour effect, and a dimensionless specific enthalpy of reaction:

$$\Delta\hat{h} = \frac{(\rho\Delta h - \alpha T(\partial p/\partial c)_{\rho,T})}{(\rho c_p - \alpha T(\partial p/\partial T)_{\rho,c})T}. \tag{64}$$

This dimensionless specific enthalpy of reaction $\Delta\hat{h}$ shows up multiplying the last term in the energy balance eqn (61); it thus causes a heating due to the chemical reaction. This term is important and cannot be neglected.

3. Fluctuations in a chemically reacting mixture

In this section we discuss the theory of thermodynamic fluctuations for a chemically reacting system. In particular we will combine the description of fluctuations along the reaction coordinate with the fluctuations in the stress tensor, the heat flux and the diffusion of the reaction complex through space. We will first discuss the fluctuation source terms in the fluxes and then give the generic formulation in terms of the fluctuation–dissipation theorem.

3.1 Fluctuating hydrodynamics

Following the general guidelines of fluctuating hydrodynamics[24] we formulate the stochastic version of the hydrodynamic eqn (58) for the mesoscopic level by the following three-step procedure: This has been done before, but for simpler cases where there are either no internal variables[31–35] or for chemical reactions using the mesoscopic description.[16]

1. The fluxes (in our case $\mathbf{J}_q$, $\mathbf{J}(\gamma)$, $\mathbf{\Pi}^{(st)}$, Π and $r(\gamma)$) reflect the random nature of molecular motion, so they must be considered as stochastic variables with a probability distribution to be specified below. As a consequence, both the temperature and the concentration also become stochastic variables whose spatiotemporal evolutions depend on the stochastic fluxes through the balance laws (14), as the balance laws (14) continue to hold even in the presence of fluctuations.

2. Because of stochastic phenomena, the phenomenological relationships (22a)–(22e) are only valid on "average". This means that when fluctuations are present, eqn (22a)–(22e) must be replaced by:

$$\mathbf{J}_q = -L_{qq}\frac{\nabla T}{T^2} - \int_0^1 L_{qJ}(\gamma)\nabla\frac{\mu(\gamma)}{T}d\gamma + \delta\mathbf{J}_q, \tag{65}$$

$$\mathbf{J}(\gamma) = -L_{Jq}(\gamma)\frac{\nabla T}{T^2} - L_{JJ}(\gamma)\nabla\frac{\mu(\gamma)}{T} + \delta\mathbf{J}(\gamma), \tag{66}$$

$$\Pi_{ij}^{(st)} = \eta\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\nabla\cdot\mathbf{v}\right) + \delta\Pi_{ij}^{(st)}, \tag{67}$$

$$\Pi = \eta_v\nabla\cdot\mathbf{v} + \delta\Pi \tag{68}$$

$$r(\gamma) = -L_r(\gamma)\frac{1}{T}\frac{\partial\mu(\gamma)}{\partial\gamma} + \delta r(\gamma), \tag{69}$$

where $\delta\mathbf{J}_q(\mathbf{r},t)$, $\delta\mathbf{J}(\mathbf{r}, \gamma, t)$, $\delta\Pi_{ij}^{(st)}(\mathbf{r},t)$, $\delta\Pi(\mathbf{r},t)$, $\delta r(\mathbf{r}, \gamma, t)$ are the random contributions to $\mathbf{J}_q(\mathbf{r},t)$, $\mathbf{J}(\mathbf{r}, \gamma, t)$, $\Pi_{ij}^{(st)}(\mathbf{r},t)$, $\Pi(\mathbf{r},t)$, $r(\mathbf{r}, \gamma, t)$. We will refer to the other terms on the right-hand side as the deterministic contributions. For ease of notation we do not indicate the $\mathbf{r}$ and t dependence explicitly.

3. To completely specify the probability distribution of the random fluxes ($\delta\mathbf{J}_q(\mathbf{r},t)$ and the like), we need not only the first moment, but all the other moments of their probability distributions. When the system is in a global equilibrium state,

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the probability distributions of the random fluxes are generated by a set of Gaussian stochastic processes. Hence, only the first and second moments are required to specify them completely. The first moments are:

$$\langle \delta \mathbf{J}_q(\mathbf{r},t) \rangle = \langle \delta \mathbf{J}(\mathbf{r}, \gamma, t) \rangle = \langle \delta \mathbf{\Pi}^{(st)}(\mathbf{r},t) \rangle$$
$$= \langle \delta \Pi(\mathbf{r},t) \rangle = \langle \delta r(\mathbf{r}, \gamma, t) \rangle = 0. \quad (70)$$

Here $\langle \ldots \rangle$ is the average over the functional probability distribution. The second moments are given by:

$$\langle \delta J_{q,k}^*(\mathbf{r}, t) \cdot \delta J_{q,l}(\mathbf{r}', t') \rangle = 2k_B L_{qq,0}(\mathbf{r},t)\delta_{kl}\delta(t - t')\delta(\mathbf{r} - \mathbf{r}'), \quad (71)$$

$$\langle \delta J_k^*(\mathbf{r}, \gamma, t) \cdot \delta J_l(\mathbf{r}', \gamma', t') \rangle = k_B L_{JJ,0}(\mathbf{r}, \gamma, t)\delta_{kl}\, \delta(t - t') \times \delta(\mathbf{r} - \mathbf{r}')\delta(\gamma - \gamma'), \quad (72)$$

$$\langle \delta J_k^*(\mathbf{r}, \gamma, t) \cdot \delta J_{q,l}(\mathbf{r}', t') \rangle = 2k_B L_{Jq,0}(\mathbf{r}, \gamma, t)\, \delta_{kl} \times \delta(t - t')\, \delta(\mathbf{r} - \mathbf{r}'), \quad (73)$$

$$\langle \delta \Pi_{ij}^*(\mathbf{r}, t) \cdot \delta \Pi_{kl}(\mathbf{r}', t') \rangle$$
$$= 2k_B(T\eta)_0(\mathbf{r}, t)\left[\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl}\right]\delta(t - t')\delta(\mathbf{r} - \mathbf{r}'), \quad (74)$$

$$\langle \delta \Pi^*(\mathbf{r},t) \cdot \delta \Pi(\mathbf{r}', t') \rangle = 2k_B(T\eta_v)_0(\mathbf{r},t)\, \delta(t - t')\, \delta(\mathbf{r} - \mathbf{r}'), \quad (75)$$

$$\langle \delta r^*(\mathbf{r}, \gamma, t) \cdot \delta r(\mathbf{r}', \gamma', t') \rangle = 2k_B L_{r,0}(\mathbf{r}, \gamma, t)\, \delta(t - t') \times \delta(\mathbf{r} - \mathbf{r}')\delta(\gamma - \gamma'). \quad (76)$$

where k_B is the Boltzmann constant. These equations are a generalization of the *Fluctuation–Dissipation Theorem*, which gives the stochastic properties of the fluxes when the system is in a global equilibrium state,[31] to the case under consideration. New is the use of the mesoscopic description along the reaction coordinate in the context of other transport processes. For the description of fluctuations along the reaction coordinate alone, we refer to Pagonabarraga *et al.*[16] Fluctuations around equilibrium are described with the equilibrium values of the Onsager coefficients in eqn (71)–(76). We recall that the Onsager coefficients for the stress tensor are proportional to $T\eta$ and $T\eta_v$, and note that the fluctuation–dissipation theorem for the random stress, written as in eqn (74), clearly shows the symmetry under permutation of indices: *i* by *j*, or *k* by *l*. When the mixture is not in global equilibrium, the assumption of local equilibrium remains valid, also for the fluctuations in the above equations.[24] All Onsager coefficients on the right-hand side of eqn (71)–(76) are then evaluated at the pressure $p_0(\mathbf{r},t)$, temperature $T_0(\mathbf{r},t)$ and probability distribution $c_0(\mathbf{r}, \gamma, t)$ of the deterministic solution found when the random contributions to the fluxes are neglected. In the fluctuation–dissipation theorem the Onsager coefficients therefore have a subscript zero. The reason why there should be no factor 2 in front of $k_B L_{JJ,0}$ will become clear below. As explained in the

monograph by Ortiz de Zárate and Sengers[24] for a number of cases, the correlation functions of the temperature and the concentrations do not satisfy local equilibrium when the mixture is not in global equilibrium. Long-range correlations develop also in a chemically reacting mixture, which will be considered in a subsequent publication.

Together with the balance laws (14), the properties of the fluctuating contributions to the thermodynamic fluxes given above completely specify the mesoscopic description of the reaction-diffusion in a temperature gradient. They not only specify the behavior along the reaction coordinate, but also embed this in the background of the diffusion problem for heat and mass. This will enable us to not only study properties like how heat conduction is modified by the reaction but also how long-range correlations develop under non-equilibrium conditions for systems where the reaction kinetics has a realistic nonlinear behavior.

3.2 Fluctuations along the reaction coordinate

Before we proceed we first discuss what happens along the reaction coordinate. At each point in space $\mathbf{r}$ the state or the reaction is described by the probability distribution $c(\mathbf{r}, \gamma, t)$. The time rate of change of this quantity is given by (14b):

$$\rho(\mathbf{r},t)\frac{Dc(\mathbf{r},\gamma,t)}{Dt} = -\nabla \cdot \mathbf{J}(\mathbf{r},\gamma,t) + \frac{\partial r(\mathbf{r},\gamma,t)}{\partial \gamma}. \quad (77)$$

The reaction rate along the reaction coordinate is now given by

$$r(\mathbf{r},\gamma,t) = -L_r(\mathbf{r},\gamma,t)\frac{1}{T(\mathbf{r},t)}\frac{\partial \mu(\mathbf{r},\gamma,t)}{\partial \gamma} + \delta r(\mathbf{r},\gamma,t). \quad (78)$$

For the chemical potential we can use eqn (6). Substituting eqn (78) and (6) into eqn (77) we obtain:

$$\rho(\mathbf{r},t)\frac{Dc(\mathbf{r},\gamma,t)}{Dt} = -\nabla \cdot \mathbf{J}(\mathbf{r},\gamma,t) - \rho(\mathbf{r},t)\frac{\partial}{\partial \gamma}D_r(\mathbf{r},t)$$
$$\times \left[\frac{\partial}{\partial \gamma}c(\mathbf{r},\gamma,t) + \frac{Mc(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\frac{\partial}{\partial \gamma}h(\mathbf{r},\gamma,t)\right]$$
$$+ \frac{\partial \delta r(\mathbf{r},\gamma,t)}{\partial \gamma}, \quad (79)$$

where $\mathbf{J}(\mathbf{r}, \gamma, t)$ is given by eqn (66) and contains the fluctuating part $\delta \mathbf{J}(\mathbf{r}, \gamma, t)$. Furthermore we used that the diffusion coefficient along the γ-coordinate defined in eqn (24) is constant. The energy barrier along the γ-coordinate has a maximum at γ_0 which is high compared to RT/M. As a consequence the total reaction rate r is small. A quasi-stationary state develops such that the *total* reaction rate is independent of γ.

Using eqn (6) and (24) one obtains for the total reaction rate

$$r(\mathbf{r},t) = -D_r(\mathbf{r},t)\rho(\mathbf{r},t)\exp\left[-\frac{Mh(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]$$
$$\times \frac{\partial}{\partial \gamma}\exp\left[\frac{M\mu(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right] + \delta r(\mathbf{r},\gamma,t) \text{ for } 0 < \gamma < 1. \quad (80)$$

An important aspect of this equation is that the deterministic and the random contribution to the reaction rate separately

are functions of γ. It is only their sum, which is independent of γ. Multiplying this equation with the exponential factor containing ϕ we can integrate this equation and we obtain

$$r(\mathbf{r},t) = -D_r(\mathbf{r},t)\rho(\mathbf{r},t)\left\{\frac{\exp\left[\dfrac{M\mu(\mathbf{r},1,t)}{RT(\mathbf{r},t)}\right]-\exp\left[\dfrac{M\mu(\mathbf{r},0,t)}{RT(\mathbf{r},t)}\right]}{\displaystyle\int_0^1 \exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]d\gamma}\right\}$$

$$+ \delta r(\mathbf{r},t) = -D_r(\mathbf{r},t)\rho(\mathbf{r},t)$$

$$\times\left\{\frac{c(\mathbf{r},1,t)\exp\left[\dfrac{Mh(\mathbf{r},1,t)}{RT(\mathbf{r},t)}\right]-c(\mathbf{r},0,t)\exp\left[\dfrac{Mh(\mathbf{r},0,t)}{RT(\mathbf{r},t)}\right]}{\displaystyle\int_0^1 \exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]d\gamma}\right\}$$

$$+ \delta r(\mathbf{r},t), \tag{81}$$

where

$$\delta r(\mathbf{r},t) \equiv \frac{\displaystyle\int_0^1 \exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]\delta r(\mathbf{r},\gamma,t)d\gamma}{\displaystyle\int_0^1 \exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT(\mathbf{r},t)}\right]d\gamma}. \tag{82}$$

The random contribution to the reaction rate $\delta r(\mathbf{r},t)$ is therefore a weighted average of the random reaction rate along the reaction coordinate γ. It shows that the contribution in the neighborhood of the transition state is dominating its behavior. In order to assure that $\delta r(\mathbf{r},t)$ is again Gaussian we replace $T(\mathbf{r},t)$ by $T_0(\mathbf{r},t)$ in eqn (82), thereby assuming non-Gaussian contributions due to possible correlations between $\delta T(\mathbf{r},t) = T(\mathbf{r},t) - T_0(\mathbf{r},t)$ and $\delta r(\mathbf{r},\gamma,t)$ to be negligible.

The properties of $\delta r(\mathbf{r},t)$ follow from those of $\delta r(\mathbf{r},\gamma,t)$ by integration. Thus $\delta r(\mathbf{r},t)$ is again Gaussian white noise with $\langle \delta r(\mathbf{r},t)\rangle = 0$. For the second moment we find

$$\langle \delta r^*(\mathbf{r},t)\delta r(\mathbf{r}',t')\rangle$$

$$= \left\{\int_0^1 \exp\left[\frac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma\right\}^{-2}$$

$$\times \int_0^1\int_0^1 \exp\left[\frac{M}{R}\left(\frac{h(\mathbf{r},\gamma,t)}{T_0(\mathbf{r},t)}+\frac{h(\mathbf{r}',\gamma',t)}{T_0(\mathbf{r}',t')}\right)\right]$$

$$\times \langle \delta r^*(\mathbf{r},\gamma,t)\delta r(\mathbf{r}',\gamma',t')\rangle d\gamma d\gamma'$$

$$= 2k_B\left\{\int_0^1 \exp\left[\frac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma\right\}^{-2}$$

$$\times \int_0^1 \exp\left[\frac{2Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]L_{r,0}(\mathbf{r},\gamma,t)d\gamma\,\delta(t-t')\,\delta(\mathbf{r}-\mathbf{r}')$$

$$= 2D_{r,0}(\mathbf{r},t)m_{A_2}\rho_0(\mathbf{r},t)\left\{\int_0^1 \exp\left[\frac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma\right\}^{-2}$$

$$\times \int_0^1 \exp\left[\frac{2Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]c_0(\mathbf{r},\gamma,t)d\gamma\,\delta(t-t')\,\delta(\mathbf{r}-\mathbf{r}'), \tag{83}$$

where $m_{A_2} = M/N_{Av}$ is the mass of an A_2 molecule. N_{Av} is Avogadro's number. We can use a combination of eqn (31) and (32) for the density profile along the reaction coordinate in the absence of fluctuations. This gives

$$c_0(\mathbf{r},\gamma,t) = c_{2A,0}(\mathbf{r},t)\frac{\exp\left[-\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]}{\displaystyle\int_0^{\gamma_0} \exp\left[-\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma}\Theta\,(\gamma_0-\gamma)$$

$$+ c_{A_2,0}(\mathbf{r},t)\frac{\exp\left[-\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]}{\displaystyle\int_{\gamma_0}^1 \exp\left[-\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma}\Theta(\gamma-\gamma_0). \tag{84}$$

Substituting this expression into eqn (83) one obtains

$$\langle \delta r^*(\mathbf{r},t)\delta r(\mathbf{r}',t')\rangle = 2D_{r,0}(\mathbf{r},t)m_{A_2}\rho_0(\mathbf{r},t)$$

$$\times \left\{\int_0^1 \exp\left[\frac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma\right\}^{-2}$$

$$\times \left\{c_{2A,0}(\mathbf{r},t)\frac{\displaystyle\int_0^{\gamma_0} \exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma}{\displaystyle\int_0^{\gamma_0} \exp\left[-\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma}\right.$$

$$\left.+ c_{A_2,0}(\mathbf{r},t)\frac{\displaystyle\int_{\gamma_0}^1 \exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma}{\displaystyle\int_{\gamma_0}^1 \exp\left[-\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma}\right\}$$

$$\times \delta(t-t')\,\delta(\mathbf{r}-\mathbf{r}'). \tag{85}$$

With the rate coefficients given in eqn (35) this can be written as:

$$\langle \delta r^*(\mathbf{r},t)\delta r(\mathbf{r}',t')\rangle$$

$$= 2m_{A_2}\left\{k_{+,0}(\mathbf{r},t)c_{2A,0}(\mathbf{r},t)\frac{\displaystyle\int_0^{\gamma_0} \exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma}{\displaystyle\int_0^1 \exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma}\right.$$

$$\left.+ k_{-,0}(\mathbf{r},t)c_{A_2,0}(\mathbf{r},t)\frac{\displaystyle\int_{\gamma_0}^1 \exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma}{\displaystyle\int_0^1 \exp\left[\dfrac{Mh(\mathbf{r},\gamma,t)}{RT_0(\mathbf{r},t)}\right]d\gamma}\right\}$$

$$\times \delta(t-t')\delta(\mathbf{r}-\mathbf{r}'). \tag{86}$$

When the energy barrier is high the dominant contribution to the integrals in eqn (86) occurs around γ_0. One then obtains

$$\langle \delta r^*(\mathbf{r},t)\delta r(\mathbf{r}',t')\rangle = m_{A_2}[k_{+,0}(\mathbf{r},t)c_{2A,0}(\mathbf{r},t)$$

$$+ k_{-,0}(\mathbf{r},t)c_{A_2,0}(\mathbf{r},t)]\,\delta(t-t')\,\delta(\mathbf{r}-\mathbf{r}'). \tag{87}$$

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With the help of eqn (34) and (36) this can alternatively be written as

$$\langle \delta r^*(\mathbf{r}, t)\delta t(\mathbf{r}', t')\rangle$$

$$= -k_B L_{r,0}(\mathbf{r}, t)\left\{1 - \exp\left[-\frac{M\Delta g_0(\mathbf{r}, t)}{RT_0(\mathbf{r}, t)}\right]\right\}\delta(t - t')\delta(\mathbf{r} - \mathbf{r}').$$

$$(88)$$

For the case that fugacities should be used rather that mass fractions in the law of mass action, the correct expressions follow from eqn (88). As pointed out in 16 eqn (87) and (88) are equivalent to a corresponding expression given by Keizer.[36]

3.3 Integrated phenomenological relationships with fluctuations

Using eqn (65)–(68) we have

$$\mathbf{J}_q(\mathbf{r}, t) = -L_{qq}(\mathbf{r}, t)\frac{\nabla T(\mathbf{r}, t)}{T^2(\mathbf{r}, t)} - \int_0^1 L_{qJ}(\mathbf{r}, \gamma, t)\nabla\frac{\mu(\mathbf{r}, \gamma, t)}{T(\mathbf{r}, t)}\mathrm{d}\gamma$$

$$+ \delta\mathbf{J}_q(\mathbf{r}, t),$$

$$\mathbf{J}(\mathbf{r}, t) = -\int_{\gamma_0}^1 L_{Jq}(\mathbf{r}, \gamma, t)\frac{\nabla T(\mathbf{r}, t)}{T^2(\mathbf{r}, t)}\mathrm{d}\gamma$$

$$- \int_{\gamma_0}^1 L_{JJ}(\mathbf{r}, \gamma, t)\nabla\frac{\mu(\mathbf{r}, \gamma, t)}{T(\mathbf{r}, t)}\mathrm{d}\gamma$$

$$+ \int_{\gamma_0}^1 \delta\mathbf{J}(\mathbf{r}, \gamma, t)\mathrm{d}\gamma.$$

$$(89)$$

Similarly to the derivation of eqn (42) and (44) we find

$$\mathbf{J}_q(\mathbf{r}, t) = -L_{qq}(\mathbf{r}, t)\frac{\nabla T(\mathbf{r}, t)}{T^2(\mathbf{r}, t)} - L_{qJ}(\mathbf{r}, t)\nabla\frac{\Delta g(\mathbf{r}, t)}{T(\mathbf{r}, t)} + \delta\mathbf{J}_q(\mathbf{r}, t),$$

$$\mathbf{J}(\mathbf{r}, t) = -L_{Jq}(\mathbf{r}, t)\frac{\nabla T(\mathbf{r}, t)}{T^2(\mathbf{r}, t)} - L_{JJ}(\mathbf{r}, t)\nabla\frac{\Delta g(\mathbf{r}, t)}{T(\mathbf{r}, t)} + \delta\mathbf{J}(\mathbf{r}, t),$$

$$(90)$$

where the coupling coefficient is given by eqn (44) and (45). Furthermore

$$\delta\mathbf{J}(\mathbf{r}, t) \equiv \int_{\gamma_0}^1 \delta\mathbf{J}(r, \gamma, t)\mathrm{d}\gamma. \quad (91)$$

It follows from eqn (70) through (73) that the random heat flux and the integrated random mass flux are Gaussian white noise with zero averages

$$\langle \delta\mathbf{J}q(\mathbf{r}, t)\rangle = 0 \text{ and } \langle \delta\mathbf{J}(\mathbf{r}, t)\rangle = 0. \quad (92)$$

The fluctuation–dissipation theorem for $\delta\mathbf{J}_q(\mathbf{r}, t)$ is given by eqn (71). For the correlations of $\delta\mathbf{J}_q(\mathbf{r}, t)$ and $\delta\mathbf{J}(\mathbf{r}', t')$ we have

$$\langle \delta J_{q,k}^*(\mathbf{r}, t) \cdot \delta J_l(\mathbf{r}', t')\rangle$$

$$= \left\langle \delta J_{q,k}^*(\mathbf{r}, t) \cdot \int_{\gamma_0}^1 \delta J_l(\mathbf{r}', \gamma, t')\mathrm{d}\gamma\right\rangle$$

$$(93)$$

$$= 2k_B \int_{\gamma_0}^1 L_{Jq,0}(\mathbf{r}, \gamma, t)\mathrm{d}\gamma\delta_{kl}\delta(t - t')\delta(\mathbf{r} - \mathbf{r}')$$

$$= 2k_B L_{Jq,0}(\mathbf{r}, t)\delta_{kl}\delta(t - t')\delta(\mathbf{r} - \mathbf{r}').$$

For the correlations of $\delta\mathbf{J}(\mathbf{r}, t)$ and $\delta\mathbf{J}(\mathbf{r}', t')$ we have

$$\langle \delta J_k^*(\mathbf{r}, t) \cdot \delta J_l(\mathbf{r}', t')\rangle$$

$$= \left\langle \int_{\gamma_0}^1 \delta J_k^*(\mathbf{r}, t)\mathrm{d}\gamma \cdot \int_{\gamma_0}^1 \delta J_l(\mathbf{r}', \gamma', t')\mathrm{d}\gamma'\right\rangle$$

$$(94)$$

$$= k_B \int_{\gamma_0}^1 L_{JJ,0}(\mathbf{r}, \gamma, t)\mathrm{d}\gamma\delta_{kl}\delta(t - t')\delta(\mathbf{r} - \mathbf{r}')$$

$$= 2k_B L_{JJ,0}(\mathbf{r}, t)\delta_{kl}\delta(t - t')\delta(\mathbf{r} - \mathbf{r}'),$$

where we used eqn (45). It should be noted that one now has the usual factor 2 on the right-hand side of this equation. This was the reason why this factor should not be used in eqn (73).

The phenomenological coefficients can be related again to the well-known transport coefficients. This can be achieved by inverting eqn (56) and substituting the result into the above equations. Using the equations given above it is now possible to study both the deterministic behavior and the fluctuations in a reaction diffusion system with flow. In a subsequent paper we will in particular analyse how the correlation functions of the temperature and the mass densities are modified in a non-equilibrium stationary state.

4. Discussion and conclusions

In this paper we have obtained two important results. The first is that we give a general theory for the description of reaction-diffusion in a temperature gradient using mesoscopic non-equilibrium thermodynamics. This description not only yields the balance equations and the flux–force relations to be used in a deterministic description, but was also extended to include random contributions to the thermodynamic fluxes for which a fluctuation–dissipation theorem was presented. In view of the large value of the transition state energy barrier along the reaction coordinate, we were able to obtain both the deterministic equations along the reaction coordinate and the fluctuating equations.

Integration over the reaction coordinate then lead to our second important result, which is a realistic nonlinear description of the reaction (the law of mass action) and the inclusion of fluctuating source terms with well-defined properties. In all cases, these properties were found embedded in the diffusion problem for heat and mass with the corresponding fluctuating contributions. The second result puts us in a position to analyze many important properties for the system.

In this paper we have given the general theory for the description of reaction-diffusion in non-isothermal systems using mesoscopic non-equilibrium thermodynamics. The reaction was described using as internal variable the probability distribution of the reaction complex along the reaction coordinate. Using the large value of the transition state energy compared to the thermal energy, it was then possible to integrate along the reaction coordinate to obtain the law of mass action, together with well defined fluctuating contributions. As far as we know this is the first time such results were derived for a description which incorporates the law of mass action.

Mesoscopic non-equilibrium thermodynamics is a theory that also gives a systematic treatment of the fluctuations. We used this to formulate the fluctuation–dissipation theorem for the random contributions to the thermodynamic fluxes for *non-equilibrium states*.

In a subsequent paper we will analyze how the long-range contributions to the correlation functions of the temperature and the mass densities are modified by these nonlinear contributions in the presence of a stationary temperature gradient.

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References

1 G. F. Froment and K. B. Bischoff, *Chemical Reactor Analysis and Design*, Wiley, New York, 2nd edn, 1990.
2 S. Kjelstrup, J. M. Rubi and D. Bedeaux, *Phys. Chem. Chem. Phys.*, 2005, **7**, 4009.
3 A. S. Blix, *Arctic Animals*, Tapir Academic Publishers, Trondheim, Norway, 2001.
4 D. Bedeaux and S. Kjelstrup, *Phys. Chem. Chem. Phys.*, 2008, **10**, 7304.
5 E. Johannessen and S. Kjelstrup, *Chem. Eng. Sci.*, 2005, **60**, 1491.
6 S. Kjelstrup, D. Bedeaux and E. Johannessen, *Elements of Irreversible Thermodynamics for Engineers*, Tapir Academic Publishers, Trondheim, Norway, 2007.
7 L. van der Ham, J. Gross, A. Verkooijen and S. Kjelstrup, *Ind. Eng. Chem. Res.*, 2009, **48**, 8500.
8 C. M. Guldberg and P. Waage, *Forhandlinger: Videnskabs-Selskabet i Christiania*, 1864, 35.
9 H. Eyring and E. Eyring, *Modern Chemical Kinetics*, Chapman & Hall, London, 1965.
10 L. Onsager, *Phys. Rev.*, 1931, **37**, 405.
11 L. Onsager, *Phys. Rev.*, 1931, **38**, 2265.
12 H. A. Kramers, *Physica*, 1940, **7**, 284.
13 I. Prigogine and P. Mazur, *Physica*, 1953, **19**, 241.
14 S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam, 1962, Dover edition, 1984.
15 D. Reguera, J. M. Rubi and J. M. G. Vilar, *J. Phys. Chem. B*, 2005, **109**, 21502.
16 I. Pagonabarraga, A. Pérez-Madrid and J. M. Rubi, *Phys. A*, 1997, **237**, 205.
17 I. Pagonabarraga and J. M. Rubi, *Phys. A*, 1992, **188**, 553.
18 D. Reguera and J. M. Rubi, *J. Chem. Phys.*, 2001, **115**, 7100.
19 J. M. Rubi and S. Kjelstrup, *J. Phys. Chem. B*, 2003, **107**, 13471.
20 Y. Demirel and S. I. Sandler, *Int. J. Heat Mass Transfer*, 2002, **45**, 75.
21 S. Kjelstrup and D. Bedeaux, in *Applied Non-equilibrium Thermodynamics, in Applied Thermodynamics*, ed. A. H. Goodwin, J. V. Sengers and C. J. Peters, IUPAC Chemical Data Series No. XX, Royal Society of Chemistry, London, 2010, ch. 14, in press.
22 Y. Demirel, *Chem. Eng. Sci.*, 2006, **61**, 3379.
23 Y. Demirel, *Chem. Eng. J.*, 2008, **139**, 106.
24 J. M. Ortiz de Zárate and J. V. Sengers, *Hydrodynamic Fluctuations in Fluids and Fluid Mixtures*, Elsevier, Amsterdam, 2006.
25 B. Hafskjold and S. Kjelstrup Ratkje, *J. Stat. Phys.*, 1995, **78**, 463.
26 J. Xu, S. Kjelstrup, D. Bedeaux and J.-M. Simon, *Phys. Chem. Chem. Phys.*, 2007, **9**, 969.
27 J. Xu, S. Kjelstrup and D. Bedeaux, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2017.
28 J. M. Ortiz de Zárate, J. V. Sengers, D. Bedeaux and S. Kjelstrup, *J. Chem. Phys.*, 2007, **127**, 034501.
29 G. D. C. Kuiken, *Thermodynamics for Irreversible Processes*, John Wiley & Sons, Chichester, England, 1994.
30 E. Johannessen and S. Kjelstrup, *Chem. Eng. Sci.*, 2005, **60**, 3347.
31 L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, Pergamon, London, 1959, 2nd revised edition, 1987.
32 L. D. Landau and E. M. Lifshitz, *Statistical Mechanics, Part I*, Pergamon, London, 1958.
33 R. F. Fox and G. E. Uhlenbeck, *Phys. Fluids*, 1970, **13**, 2881.
34 R. Schmitz and E. G. D. Cohen, *J. Stat. Phys.*, 1985, **39**, 285.
35 R. Schmitz and E. G. D. Cohen, *J. Stat. Phys.*, 1985, **40**, 431.
36 J. Keizer, *Statistical Thermodynamics of Nonequilibrium Processes*, Springer, Berlin, Germany, 1987.