Irreversible Thermodynamics of Chemically Reacting System Subject To Temperature Gradient

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Abstract

Irreversible thermodynamics of chemically reacting system proceeding at finite rate subjected to a small temperature gradient has been studied in this paper. Tiny but macroscopic point of view sufficiently large system has been chosen for the study.   For selected system, local equilibrium assumption (LEA) is considered valid for both chemical system and propagation of heat. The entire framework for this system has been developed using Classical and Extended Irreversible Thermodynamics (EIT). Gibbs thermodynamics space has been used for identification of rate of entropy production for chemical reaction. Entropy source strength for heat propagation due to temperature gradient has been obtained by using EIT. It is found that Classical thermodynamics and EIT can be combined together provided that the temperature gradient is sufficiently small.

KEYWORDS- Entropy, Irreversible Thermodynamics, Local Equilibrium Assumption, classical thermodynamics

1. INTRODUCTION

Nonisothermal reaction-diffusion systems are important in industry, as most chemical process plants contain units where such processes take place. These units, characterized by being out of global equilibrium, will experience hydrodynamic fluctuations. Such fluctuations arise in a Nonisothermal system because the fluctuations of the velocity parallel to the temperature or concentration gradient couple, via the temperature and concentration fluctuations.

Steady states but sufficiently close to equilibrium so that macroscopic convection or turbulence is absent. It is to be expected that fluctuations in such nonequilibrium systems are spatially long range. Long-range hydrodynamic fluctuations have not been discussed so far for these technically important systems, despite reports that stationary state operation of nonisothermal chemical reactors can be accidentally perturbed to show unstable behavior. Hence, it will be worthwhile to pursue a study of the hydrodynamic fluctuations in reactors of this kind, so as to learn about the relation between hydrodynamic fluctuations and Hopf bifurcations. This work is a first attempt in this direction, by deriving expressions entropy production for the chemical reaction in a temperature gradient.

Hydrodynamic fluctuations in nonequilibrium molecular dynamics simulations have not been discussed so far with the purpose of finding transport properties of reaction-diffusion mixtures in a temperature gradient. In order to be able to take advantage of this theory, it is first necessary to find the simulation conditions when hydrodynamic fluctuations occur. For instance, what are the system dimensions that allow their observation? Can we expect to observe such fluctuations for all densities? Another

purpose of the paper is also to discuss the theoretical results in view of recent nonequilibrium molecular dynamics simulations on a system of this type.

Insight into hydrodynamic fluctuations in nonisothermal reaction-diffusion systems may thus be valuable in an overall assessment of their importance on the macroscopic reactor scale. But, we shall see that it may also be valuable for a search to establish new methods for transport-property determinations. The paper is written in terms of a terminology that is common to chemists. We present the balance equations and the transport equations for a reversible chemical reaction with diffusion in a temperature gradient.

2. NONEQUILIBRIUM THERMODYNAMICS OF A CHEMICALLY REACTING FLUID MIXTURE

As a representative example we consider a reversible association-dissociation reaction, like in a mixture of atoms and molecules,

$$A \leftrightarrow B \tag{1}$$

Nonequilibrium thermodynamics is based on the assumption of local thermodynamic equilibrium. The nonequilibrium molecular dynamics simulations have confirmed the validity of this assumption even in the presence of a substantial temperature gradient. However, as will become evident, one of the major findings of the present paper is that, although local equilibrium is valid for the local thermodynamic quantities, it is no longer valid for the fluctuations of these quantities around their local-equilibrium values. For instance, while fluctuations in equilibrium are generally short range except near critical points, fluctuations in nonequilibrium are always long range. Moreover, their intensity is much larger than what one would expect for equilibrium fluctuations corresponding to the local temperature and concentration. Hence, nonequilibrium fluctuations differ qualitatively from those in equilibrium states.

As usual in nonequilibrium thermodynamics, we shall start by reviewing the relevant balance laws, and then discuss the phenomenological relationships required to complete the nonequilibrium thermodynamics formulation of the problem.

2.1 Balance laws

The balance laws relevant to our problem are

2.1.1   balance of mass

$$\frac{\partial \rho_A}{\partial t} = -\nabla \cdot \left(\rho_A v + J_A \right) - \xi, \qquad \frac{\partial \rho_B}{\partial t} = -\nabla \cdot \left(\rho_B v + J_A \right) - \xi \tag{2}$$

2.1.2   balance of momentum

$$\frac{\partial (\rho v)}{\partial t} = -\nabla p - \nabla \cdot \left[(\rho v) v - \Pi \right] \tag{3}$$

balance of energy

$$\rho \frac{\partial u}{\partial t} = -\nabla \cdot Q - p\nabla \cdot v = \rho T \frac{\partial s}{\partial t} + \frac{p}{\rho} \frac{\partial \rho}{\partial t} + \rho \mu_A \frac{\partial C_A}{\partial t} + \rho \mu_B \frac{\partial C_B}{\partial t} \tag{4}$$

In the balance laws, p is the pressure, and the mass density ρ of the mixture is obtained by adding the partial densities in mass per unit volume: $\rho = \rho_A + \rho_B$. The center of mass velocity is given by $\rho v = \rho_A v_A + \rho_B v_B$. The symbols μ_A and μ_B represent the chemical potentials per unit mass of each component, u is the specific internal energy, and s is the specific entropy, while $C_A = \rho_A / \rho$ and $C_B = \rho_B / \rho$ represent the mass fractions of the two components of the mixture. Furthermore, the diffusion fluxes, $\mathbf{J}_A$ and $\mathbf{J}_B$ in the balance of mass equation, are related to the difference between the velocity of the component and the center of mass velocity; thus $J_A = \rho_A (v_A - v)$ and similarly for the diffusion of molecules.

Because we are considering a binary system, the two diffusion fluxes are not independent, since from their definition it follows that $J_A + J_B = 0$. Therefore, if we add the two mass balance laws, we obtain $\partial_t \rho_A + \partial_t \rho_A = -\nabla \cdot (\rho v)$. Using these constraints, we express the set of balance laws in terms of the mass fraction of B and temperature T as

$$\frac{\partial \rho}{\partial t} + v \cdot \nabla \rho + \rho \nabla \cdot v = 0 \tag{5}$$

$$\rho \left[\frac{\partial c}{\partial t} + v \cdot \nabla c \right] = -\nabla \cdot J + \xi \tag{6}$$

$$\rho \left[\frac{\partial v}{\partial t} + (v \cdot \nabla) v \right] + \nabla p = \nabla \cdot \Pi \tag{7}$$

$$\rho c_p \left[\frac{\partial T}{\partial t} + v \cdot \nabla T \right] - \alpha T \left[\frac{\partial p}{\partial t} + v \cdot \nabla p \right] + \rho \nabla h \left[\frac{\partial c}{\partial t} + v \cdot \nabla c \right] = -\nabla \cdot Q \tag{8}$$

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

$$\nabla h = \mu_B - T \left(\frac{\partial \mu_B}{\partial T} \right) - \mu_A + T \left(\frac{\partial \mu_A}{\partial T} \right) = \Delta \mu - T \left(\frac{\partial \Delta \mu}{\partial T} \right) \tag{9}$$

is the difference in specific enthalpy of the reaction, i.e., the difference in specific enthalpy between the two components of the mixture, with $\Delta \mu = \mu_B - \mu_A$ being the difference in specific Gibbs energy between the two components. Above equations represent the balance laws expressed in terms of a single diffusion flux $J = J_B = -J_A$, and have to be complemented with two equations of state, namely $\rho = \rho(T, p, c)$ and $\Delta \mu = \Delta \mu(T, p, c)$.

Alternatively, we can express the set of working equations in terms of the molar concentration of molecules $B = \rho_B / M_B$, which is more customary in the chemical literature. This second approach implies modifications in Eqs. (5)-(8), which have to be expressed in terms of B, so that

$$\frac{\partial [B]}{\partial t} + v \cdot \nabla [B] + [B] \nabla \cdot v = -\nabla \cdot J^{'} + \xi^{'} \tag{10}$$

$$\rho C_p \frac{\partial T}{\partial t} - \alpha T \frac{\partial p}{\partial t} + \nabla h M_B \left\{ \frac{\partial B}{\partial t} - \frac{B}{\rho} \frac{\partial \rho}{\partial t} \right\} = -\nabla \cdot Q \tag{11}$$

where the term $\nabla h M_B$ is the reaction enthalpy expressed in J/mol, $J' = J/M_B$ is the diffusion flux expressed in moles of molecules per m^2 and second, and similarly $\xi^{'} = \xi/M_B$ thechemical reaction rate expressed in terms of moles produced per unit volume.

2.2. Phenomenological relationships

The complete nonequilibrium thermodynamic formulation of the system under study requires the consideration, in addition to the balance laws Eqs. (5)-(8), of the entropy production rate $S^{\cdot}$ of the system. This has been also evaluated by de Groot and Mazur with the result

$$\sigma = Q \cdot \frac{\nabla T}{T^2} + \Pi : \frac{(\nabla v)^s}{T} - J_A \cdot \nabla \left[\frac{\mu_A}{T} \right] - J_B \cdot \nabla \left[\frac{\mu_B}{T} \right] - \xi \frac{\Delta \mu}{T} \tag{12}$$

where the superscript 's' indicates that only the symmetric part of the tensor of velocity derivatives contributes to σ .The entropy-production rate in Eq.(12) has the typical structure linear in the dissipative fluxes. As is well known, the quantities multiplying each of the five fluxes in Eq.(12) are the corresponding *conjugate thermodynamic forces*. To set up the linear phenomenological laws and to facilitate the application to simulations, it is necessary to rewrite Eq. (12) in terms of independent fluxes,

$$\sigma = Q \cdot \frac{\nabla T}{T^2} + \Pi : \frac{(\nabla v)}{T} - J \cdot \nabla \left[\frac{\Delta \mu}{T} \right] - \xi \frac{\Delta \mu}{T} \tag{13}$$

where we have introduced the notation $\Delta \mu = \mu_B - \mu_A$, for the reaction Gibbs energy of the chemical reaction Eq.(1). Next, to obtain the equations of irreversible thermodynamics from the balance laws Eq. (5)-(8) one needs to introduce the linear phenomenological laws relating the fluxes to the gradients in terms of the appropriate Onsager coefficients or corresponding transport coefficients. Various formulations are possible and they are related to each other by a redefinition of the fluxes. The final hydrodynamic equations do not depend on the choice of dissipative fluxes used to establish the phenomenological laws. We shall use as fluxes the tensor Π, the vectors **Q**, **J**, and the scalar ξ. Then, taking into account that the two vectorial heat and diffusive mass fluxes are coupled by virtue of the Curie principle, and assuming that the system is isotropic, one obtains for the linear phenomenological law

$$\Pi_{ij} = \eta \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \tag{14}$$

$$Q = -L_{QQ} \frac{\nabla T}{T^2} - L_{Qj} \nabla \left[\frac{\Delta \mu}{T} \right] \tag{15}$$

$$J = -L_{jQ}\frac{\nabla T}{T^2} - L_{jj}\nabla\left[\frac{\Delta\mu}{T}\right] \tag{16}$$

$$\xi = -L_r\frac{\Delta\mu}{T} \tag{17}$$

Notice that in the phenomenological law Eq.(14) for the stress tensor we have already introduced the assumption of a divergence-free (incompressible) fluid and expressed it in the

common way, in terms of the shear viscosity η. As usual, we are assuming that due to their different tensorial character there is no coupling between the chemical-reaction rate and

the heat and mass fluxes. The phenomenological laws Eqs.(15)-(16) are written in terms of Onsager coefficients $L_{QQ}, L_{jj}, L_{Qj}, L_{jQ}$, and L_r which satisfy the Onsager relations microscopic reversibility. For practical use, it is convenient to relate the Onsager coefficients to the well-known transport coefficients. In the case of the coupled phenomenological laws for **J** and **Q**, this is achieved first by expressing the gradient in the reaction Gibbs energy in Eq(15) in terms of the diffusion flux **J**, and then using the equation of state $\Delta\mu = \Delta\mu(p,T,c)$ in Eq.(16) to write it explicitly in terms of pressure, temperature, and concentration gradients. This procedure yields

$$Q = -\left[L_{QQ} - \frac{L_{Qj}^2}{L_{jj}}\right]\frac{\nabla T}{T^2} + \frac{L_{Qj}}{L_{jj}}J \tag{18}$$

$$J = -\left(L_{jQ} - L_{jj}\Delta h\right)\frac{\nabla T}{T^2} - \frac{L_{jj}}{T}\left[\frac{\partial\Delta\mu}{\partial p}\right]_{T,C}\nabla p - \frac{L_{jj}}{T}\left[\frac{\partial\Delta\mu}{\partial C}\right]_{p,T}\nabla C \tag{19}$$

which, on comparing with the phenomenological equations for binary systems,

$$Q = -\lambda\nabla T + \left[\Delta h + k_r\left(\frac{\partial\Delta\mu}{\partial C}\right)_{p,T}\right]J \tag{20}$$

$$J = -\rho D\left[\nabla c + \frac{k_T}{T}\nabla T + \frac{k_p}{p}\nabla p\right] \tag{21}$$

allows us to express the Onsager coefficients in terms of the usual transport coefficients: a thermal conductivity λ, a mutual diffusion coefficient D, a dimensionless thermal diffusion ratio k_T, and a dimensionless baro-diffusion ratio k_p. The resulting expressions are

$$D = \frac{L_{jj}}{\rho T}\left(\frac{\partial\Delta\mu}{\partial C}\right) \tag{22}$$

$$\lambda = \frac{1}{T^2}\left(L_{QQ} - \frac{L_{Qj}^2}{L_{jj}}\right) \tag{23}$$

$$k_p = p \left(\frac{\partial \Delta \mu}{\partial p} \right)_{T,C} \left(\frac{\partial \Delta \mu}{\partial C} \right)_{p,T} \tag{24}$$

$$k_T = \frac{1}{\rho D T} \left(L_{Qj} - L_{jj} \Delta h \right) \tag{25}$$

3. CONCLUSION

The phenomenological coefficients calculated above for the energy and diffusion fluxes are related to the practical transport coefficients D, λ, and k_T, the coefficient L_r associated with the chemical reaction can be related to the rate constants used in chemical kinetics. But, this relationship is not as straightforward as for the other transport coefficients, since several complications in chemical kinetics need to be accounted for (concentrations units, distinction between reactions proceeding at constant volume or not, possibility of intermediate reaction steps, etc.). Hence, we prefer to use the Onsager coefficient L_r. In addition, we should note that the linear phenomenological law Eq.(17) is only valid for small deviations from chemical equilibrium, actually so small that many authors doubt the practical usefulness of Eq.(17) itself. In this respect we mention that, although this criticism may be valid, recent developments have shown that by introducing an internal *mesoscopic* variable to describe the advancement of a chemical reaction, a linear phenomenological law similar to Eq.(17) can be formulated in terms of that mesoscopic variable, thereby extending the validity of linear nonequilibrium thermodynamics (and its associated theory of fluctuating hydrodynamics). Therefore, in this paper we continue to assume the validity of Eq.(17), keeping in mind that a mesoscopic extension may be necessary. *Such an extension* is beyond our present scope here.

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