Thermodynamic steady state laws for nonlinear chemical systems far from equilibrium

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Steady state laws for the chemical potential and the pressure of reaction intermediates are derived through a fluctuation relation based on an extension of the local equilibrium hypothesis for steady states. The full characterization of states appearing in the fluctuation relation and state laws was made possible by the introduction of a "disequilibrium parameter" that measures the distance of states from equilibrium. The relation of this parameter to chemical affinities and induced fluxes is discussed. Non-equilibrium effects are identified and explained in terms of the symmetry of stoichiometric coefficients.

Many recent approaches employed for the development of thermodynamics of homogeneous and isothermal systems in nonequilibrium steady states depend in different degrees on the results of stochastic analysis [1–9]. In the most direct approach [1], the probability distribution, P, of the number of intermediate species of a chemical system, determined from the solution of a Markovian birth–death master equation, has been employed to provide information about generalised potentials for steady states, U. Such potentials are obtained through a generalized Einstein fluctuation relation,

$$P \propto \exp(-U/k_B T) . \tag{1}$$

In turn, generalized chemical potentials have been defined through

$$\mu = (\partial U/\partial X)_{T,P,R} , \tag{2}$$

where X is the number of particles of the intermediate species and R the constraints that keep the system in steady states. In a compatible way, steady state thermodynamics has been developed also by Keizer [4,9] in an entropic representation. Specifically, the chemical potential has been defined through the covariant matrix of fluctuations, σ, $\partial \mu/\partial X = k_B T \sigma^{-1}$, with $\mu = T(\partial \Sigma/\partial X)_f$, where Σ is the generalized entropy and f represents certain extensive classic thermodynamic variables as well as fluxes of extensive variables that characterize the steady states of the system.

Despite the abstract development of the theory, there has been no derivation of the pressure steady state laws for a fluid phase in analogy to the state laws of equilibrium. In the following, we exploit the analytic results of stochastic theory for the case of homogeneous and isothermal one-variable nonlinear models such as

$$A + nX \underset{2}{\overset{1}{\rightleftharpoons}} (n+1)X , \quad (m+1)X \underset{4}{\overset{3}{\rightleftharpoons}} mX + B , \tag{3}$$
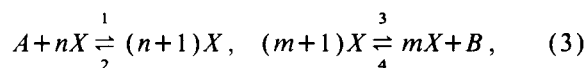
with constant A and B concentrations, in order to infer steady state laws for intensive variables such as μ and P of the intermediate X. Although this model appears to be restrictive, the following analysis is easily extendable to other chemical models as well as to more general hydrodynamic systems.

The realization of chemical systems in thermodynamic terms requires suppression of all other modes of dissipation except that of the chemical reaction [6]. This is established by requiring fast relaxation of concentration, momentum, and energy gradients compared to chemical rates. The usual chemical master equations are consistent with these considerations. As an effect, the chemical master

equations do not provide direct information about intensive variables other than the chemical potential, and thus an indirect procedure has to be employed for the determination of the pressure steady state law.

Such a procedure is provided by a generalized Gibbs–Duhem equation [4] that connects the chemical potential with the pressure. This treatment requires first an exact accounting of the state determining variables in steady state conditions. For reaction (3) taking place in a chamber of constant volume and temperature, two additional constraints, like the constancy of A and B concentrations, suffice to fix the state of the system. The controlling of these concentrations can be realized with the help of chemical baths that interact via fast transport through species selective membranes [6]. This ensures control of the chemical potentials of each of species A and B, and indirectly, assuming ideal laws, of the corresponding concentrations. Other choices of state determining parameters are possible and some are discussed below. The effect of nonequilibrium conditions on the state of the system becomes apparent through the changes they induce on state laws of the remaining intensive variables, that is, μ and P of the intermediate species.

The chemical potential can be determined from "generalized availabilities", which are deduced from probability densities, as discussed above. Specifically, for reaction scheme (3) the transition probability density from state r of a master equation in the "continuum limit" [10] acquires the general form

$$P \propto \exp\left(\int_r \ln(j^-/j^+)\,\mathrm{d}X\right),\qquad (4)$$

where j represents the forward and backward total reaction rates of the intermediate X. The corresponding reaction equation reads

$$\dot{x}=j_1+j_4-j_2-j_3=j^+-j^-.\qquad (5)$$

By treating the fluctuation relation in a local steady state approach, we can identify the exponent of the transition probability as a generalized availability, which around equilibrium is equal to the chemical work needed to shift the system from an initial state

r to a final state s, in analogy to equilibrium fluctuation theory [11],

$$A=\int_r^s (\mu^s-\mu^r)\,\mathrm{d}X=k_\mathrm{B}T\int_r^s \ln(j^-/j^+)\,\mathrm{d}X.\qquad (6)$$

Different approaches have been employed in the past for the extraction of a meaningful chemical potential from this availability, not always with complete success. In one of them, the steady state condition, $j^+=j^-$, was interpreted as "equilibrium condition" of a one-step reaction [12]. This approach lacks exact identification of the steady state of the system, since one variable in addition to X is needed to specify such a state. In the theory of Ross and coworkers [6], chemical potentials have been obtained by treating the above equation in a local equilibrium approach that does not require explicit specification of all steady state determining variables. Contrary to this, an indeterminacy appears in state laws that have been based on fluctuation theory [1] and the relation $\partial\mu/\partial X=k_\mathrm{B}T\sigma^{-1}$. The integration of such a relation requires the knowledge of the dependence of σ on a state determining variable in addition to X. This inefficiency though, does not appear in the work of Keizer [2,9,13] in which a sufficient number of state determining variables has been considered. Here, we determine chemical potentials, using an alternative procedure through eq. (6), and proceed further to calculate pressure laws in a pure fluid phase.

The difficulty in the implementation of eq. (6) arises because the term on the r.h.s. of eq. (6) depends on A^r and B^r parameters of the initial state and only on one variable, X^s, of the final state. It is thus required to specify one more variable, in order to fix the final state of the system. In general, as was mentioned above, the knowledge of A^s and B^s would serve the purpose. However, there are many other choices, such as X^s and B^s or A^s and X^s or X^s and any other general variable that is related monotonically to A^s and B^s. In the following, we use the latter choice, in order to make vivid the characterization of the state, while we are working with μ and X variables. The second needed variable is selected in such a way as allows the construction of a chemical potential scale independent of the state chosen to be the reference one. In addition, the scale should re-

duce to the equilibrium scale close to equilibrium. It is easily verified, as it will be shown below through a specific example that the above requirements are met whenever the parameters A^s and B^s of the final state are taken proportional to A^r and B^r, that is $A^s/B^s = A^r/B^r$. The ratio $\eta = A^s/B^s$ provides the second variable needed to characterize the final state of the system. The value of η in equilibrium states depends only on reaction rate constants and is determined through the microscopic reversibility conditions of equilibrium, $j_1 = j_2$ and $j_3 = j_4$. However, in the case of nonequilibrium steady states, this variable attains a range of values since it is not fixed from a single steady state condition, $j_1 + j_4 = j_2 + j_3$. According to the above assertion, states that appear in fluctuation relation (1) with a probability density derived from a usual master equation [10], are characterized by the same value of η. This consideration could also be seen as a supplement to the local steady state hypothesis employed in deriving eq. (6). Since this analysis is restricted to states of any but the same value of η, we can identify such a variable with a parameter. We term it "disequilibrium parameter" because it provides a measure of the distance of steady states from equilibrium. This parameter is also related to other variables that measure the distance of states from equilibrium. Specifically, since $\ln \eta = \ln(A/B) \propto \mu^A - \mu^B$, the parameter η relates monotonically to the total chemical affinity. Further, in the case where a linear relation between the generalized force, $\mu^A - \mu^B$, and the induced flux through the reactive system, f, is legitimate, we obtain $\ln \eta \propto f$. This relation brings the current approach into conformity with Keizer's considerations, where the fluxes are treated as state variables.

We can now define the chemical potential of steady state s through

$$\mu^s = \mu^r + k_B T \ln(j^-/j^+) \tag{7}$$

having in mind that states s and r are characterized by the same parameter η. Further, an activity coefficient, α, that measures nonidealities relative to the reference state is also introduced through

$$\alpha X = j^-/j^+ . \tag{8}$$

It is easily verified that $\alpha = 1$ when equilibrium states are considered. Similarly, ideality holds also for linear and isoautocatalytic models in steady states [7].

However, in the case of nonlinear models in steady states, this coefficient reflects the effect of non-Poissonian deformations of probability distributions on the chemical potential [14]. These deformations depend on the exact mechanism of the chemical reactions and are due to the nonsymmetric stoichiometry of the forward and backward reaction steps. The nonidealities are also present in the pressure steady state laws, which we determine in the following.

For a certain value of the irreversibility parameter the pressure is determined through the integration of a generalized Gibbs–Duhem equation [1,4],

$$\int_r^s V \, dP = \int_r^s X \, d\mu . \tag{9}$$

By substituting the chemical potential from eq. (7) in the above equation we obtain

$$(P^s - P^r) V = k_B T \int_r^s X \frac{\partial}{\partial X} \ln(j^-/j^+) \, dX$$

$$= k_B T \int_r^s X(j^{-\prime}/j^- - j^{+\prime}/j^+) \, dX , \tag{10}$$

where the primes indicate differentiation with respect to X.

Another way to derive approximate state laws for small deviations from equilibrium, useful in the case of complex systems, is through an iterative solution of the Gibbs–Duhem equation in differential form for the density,

$$V/X = d\mu/dP . \tag{11}$$

By substituting in the expression for the chemical potential the number of species X from the ideal state law, $X = PV/RT$, we obtain a first approximation for the pressure,

$$V/X = k_B T(j^{-\prime}/j^- - j^{+\prime}/j^+)_{X = PV/k_B T} . \tag{12}$$

Further iterations, by using the derived expression as input in eq. (11), can provide more accurate limiting laws. Other forms of limiting laws can be derived directly from eq. (10) by expanding the expression of the chemical potential around X^r, or equilibrium where $j^-/j^+ \simeq 1$.

As an example, we consider the nonlinear model

(3) with $n=1$ and $m=0$, where the forward and backward reaction rates are given by

$$j^+ = k_1 AX + k_4 B, \quad j^- = k_2 X^2 + k_3 X. \tag{13}$$

The chemical potential of state $(X^s, \eta^s = A^s/B^s)$ with respect to a reference state (X^r, η^r) is given by eq. (7) with $\eta^r = \eta^s$. It is easily checked that the scale of μ for states of the same parameter η is independent of the reference state. Alternatively, it can be tested that the relation $\mu^a - \mu^b = (\mu^a - \mu^c) + (\mu^c - \mu^b)$ becomes an identity, when the chemical potential differences are substituted from eq. (7). In general, this property holds for nonlinear reaction schemes, only when compared states are characterized by the same parameter η.

By introducing these rates in eq. (10) we obtain a state law for the pressure,

$$\frac{(P^s - P^r)V}{RT} = X^s - X^r + \frac{k_4 B^r}{k_1 A^r} \ln \frac{k_1 A^r X^s + k_4 B^r}{k_1 A^r X^r + k_4 B^r}$$

$$- \frac{k_3}{k_2} \ln \frac{k_2 X^s + k_3}{k_2 X^r + k_3}, \tag{14}$$

where hereafter X, A and B are measured in moles and the k's are considered consistently modified. When η takes its equilibrium value $(\eta = k_2 k_4 / k_1 k_3)$, or the model is assumed linear $(n = m = 0)$, the relation turns into the ideal gas law. This ensures the legitimacy of the procedure in providing pressure steady state laws.

An approximate law for small deviations from equilibrium is also derived from eq. (12),

$$\frac{P^s V}{XRT} = 1 - \frac{P^s(k_1 k_3 A^r - k_2 k_4 B^r)}{(k_2 P^s + k_3)(k_1 A^r P^s + k_4 B^r)}. \tag{15}$$

By expanding the denominator of the r.h.s. of the above equation, the law takes the form of a virial equation,

$$PV/X = RT - B_1 \omega + B_2 \omega^2 - B_3 \omega^3 + ..., \tag{16}$$

with "dynamic virial coefficients" given by

$$B_n = RT \frac{k_3 k_4}{P} \left(\frac{P}{k_4(k_2 P + k_3)} \right)^{n+1}, \tag{17}$$

where $\omega = k_1 k_3 \eta - k_2 k_4$ is a measure of the distance of the compared states from equilibrium $(\omega = 0)$.

We thus conclude that steady state laws for homogeneous and isothermal nonlinear systems can be derived in analogy to equilibrium thermodynamics, provided that supplementary relations of steady state thermodynamics, like the Gibbs–Duhem equation, are employed. The crucial step is the identification of steady state determining variables, such as the concentration of intermediate species X and the disequilibrium parameter η. Although the employed chemical model has a single steady state in the parameter space of A and B, the above analysis can be extended easily to systems of multiple stable states.

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