Guldber-Waage-Onsager Dynamics: Fluctuations

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Cato Maxmilian Guldberg Peter Waage	1870	mass action law
Lars Onsager	1930	nonequilibrium thermodynamics

Mass action law

Guldberg-Waage

We consider K substances $\mathbb{A}_1, ..., \mathbb{A}_K$ undergoing s chemical reactions

$$\alpha_1^{(i)}\mathbb{A}_1 + ... + \alpha_K^{(i)}\mathbb{A}_K \rightleftarrows \beta_1^{(i)}\mathbb{A}_1 + ... + \beta_K^{(i)}\mathbb{A}_K \\ i = 1, ..., s \tag{9}$$

where $\alpha_j^{(i)}, \beta_j^{(i)}$; $i = 1, ..., s$; $j = 1, ..., K$ are stoichiometric coefficients. We also introduce $\gamma_j^{(i)} = \beta_j^{(i)} - \alpha_j^{(i)}$.

$$\dot{n}_j = \sum_{i=1}^{s} \gamma_j^{(i)} Y^{(i)} \tag{10}$$

where $Y^{(i)}$ is the flux associated with the i-th reaction; $i = 1, ..., s$. According to Guldberg and Waage [13], the constitutive relations for the chemical fluxes $\mathbf{Y} = (Y^{(1)}, ..., Y^{(s)})$ are:

$$\begin{aligned} Y^{(i)} &= \overrightarrow{k}^{(i)} \prod_{j=1}^{K} n_j^{\alpha_j^{(i)}} - \overleftarrow{k}^{(i)} \prod_{j=1}^{K} n_j^{\beta_j^{(i)}} \\ i &= 1, ..., s \end{aligned} \tag{11}$$

where $\overrightarrow{k}^{(i)}$ resp. $\overleftarrow{k}^{(i)}$ are rate coefficients of the forward resp. backward reaction.

Nonequilibrium thermodynamics

Onsager

(i) The time evolution equations are supplemented by the entropy evolution equation

(ii) The entropy production is expressed in terms of dissipative thermodynamic forces X and fluxes Y

(for isothermal systems)

$$\dot{\Phi} = -YX = -\frac{\partial \Xi}{\partial X} X \leq 0$$

$$if \;\; \Xi = \frac{1}{2} \sum_{j=1}^{s} \sum_{k=1}^{s} L^{jk} X^{(j)} X^{(k)} \; then \; \dot{\Phi} = -\sum_{j=1}^{s} \sum_{k=1}^{s} L^{jk} X^{(j)} X^{(k)}$$

Guldberg-Waage-Onsager formulation of the mass action law

Adv.Chem.Eng (2010), Physica D (2012)

$$\dot{n}_j = -\Xi_{n_j^*}$$

$$X^{(j)} = \sum_{l=1}^{K} \gamma_j^{(l)} n_j^*$$

$$n_i^* = \Phi_{n_i}$$

$\Xi(\boldsymbol{n}, \boldsymbol{n}^*)$ *is a dissipation potential*

$\Xi(\boldsymbol{n}, 0) = 0$; *minimum at* $\boldsymbol{n}^* = 0$; *convex at* 0

$$Y^{(j)} = \frac{\partial \Xi}{\partial X^{(j)}}$$

$$\dot{\Phi} = \sum_{i=1}^{K} \Phi_{n_i} \dot{n}_i = -\sum_{i=1}^{K} n_i^* \Xi_{n_i^*}$$

$$= -\sum_{i=1}^{K} \sum_{j=1}^{s} \gamma_j^{(j)} n_i^* \frac{\partial \Xi}{\partial X^{(j)}} = -\boldsymbol{X} \frac{\partial \Xi}{\partial \boldsymbol{X}} = -\boldsymbol{Y}\boldsymbol{X} \leq 0$$

$$\Xi(\boldsymbol{n}, \boldsymbol{n}^*) = \sum_{j=1}^{s} W^{(j)}(\boldsymbol{n}) \left(e^{-\frac{1}{2}X^{(j)}} + e^{\frac{1}{2}X^{(j)}} - 2 \right)$$

$$\Phi = \sum_{j=1}^{K} (n_j \ln n_j + Q_j n_j)$$

$$\overleftarrow{k}^{(i)} = \frac{1}{2} W^{(i)} e^{\frac{1}{2}\sum_{j=1}^{K}(Q_j+1)\gamma_j^{(i)}} \left(\prod_{j=1}^{K} n_j^{\beta_j^{(i)}} \prod_{j=1}^{K} n_j^{\alpha_j^{(i)}} \right)^{\frac{1}{2}}$$

$$\frac{\overleftarrow{k}^{(i)}}{\overrightarrow{k}^{(i)}} = e^{\sum_{j=1}^{K}(Q_j+1)\gamma_j^{(i)}}$$

OTHER (THERMODYNAMIC) REFORMULATIONS

1

Contact geometry

state variables : (n, n^*, ϕ) $\quad$ $contact\ one\ form:\ \ \theta = d\phi - n^* dn$

the time evolution equations:

Generating potential: $\Psi(n, n^*, \phi) = -\Xi(n, X(n^*)) + \Xi(n, X(\Phi_n))$

The time evolution:

$$\begin{aligned} \dot{n} &= \Psi_{n^*} \\ \dot{n}^* &= -\Psi_n + n^* \Psi_\phi \\ \dot{\phi} &= -\Psi + n^* \Psi_{n^*} \end{aligned}$$

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invariant manifold $\mathcal{N}$ $\quad n \hookrightarrow (n, \Phi_{nn}(n), \Phi(n))$

the time evolution on the invariant manifold $\mathcal{N}$

$$\begin{aligned} \dot{n} &= -[\Xi_{n^*}]_{n^* = \Phi_n} \\ \dot{\Phi_n} &= \Phi_{nn} \dot{n} \\ \dot{\Phi} &= -n^* \Xi_{n^*} \leq 0 \end{aligned}$$

variational formulation

thermodynamic action: $\mathcal{I} = \int dt \, (\Psi(n, n^*) - < n^*, n >)$

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note that: (i) $\delta \mathcal{I} = 0$ $\Rightarrow$ the contact geometry time evolution equations

(ii) $[\mathcal{I}]_{\mathcal{N}} =$ the free energy lost in the course of the approach
To equilibrium

Extended mass action law

state variables: $(\boldsymbol{n}, \boldsymbol{z})$

the time evolution equations:

$$\begin{pmatrix} \dot{\boldsymbol{n}} \\ \dot{\boldsymbol{z}} \end{pmatrix} = \begin{pmatrix} 0 & \gamma \\ -\gamma^T & 0 \end{pmatrix} \begin{pmatrix} \boldsymbol{n}^* \\ \boldsymbol{z}^* \end{pmatrix} - \begin{pmatrix} 0 \\ \Theta^{(chem)}_{\boldsymbol{z}^*} \end{pmatrix}$$
$$= \begin{pmatrix} \gamma \boldsymbol{z}^* \\ -\gamma^T \boldsymbol{n}^* - \Theta^{(chem)}_{\boldsymbol{z}^*} \end{pmatrix}$$

$$\Theta^{(chem)}(\boldsymbol{z}^*, \boldsymbol{n}^*) = 2\sum_{i=1}^{s} W^{(i)}(\boldsymbol{n}) \left[\sqrt{1 + (\widehat{z}^{(i)*})^2} + \widehat{z}_i^* \ln\left(\widehat{z}^{(i)*} + \sqrt{1 + (\widehat{z}^{(i)*})^2}\right)\right] + C(\boldsymbol{n}) \qquad (21)$$

where $\widehat{z}^{(i)*} = \frac{z^{(i)*}}{W^{(i)}(\boldsymbol{n})}$ and $C(\boldsymbol{n})$ is an undetermined function of $\boldsymbol{n}$.

Thermodynamic forces playing the role of independent state variables (a variant of the contact geometry formulation)

$$\frac{dn}{dt} = \gamma \Xi_{X}$$

$$\frac{dX}{dt} = \gamma^T \mathcal{S} \gamma \frac{\partial \Xi}{\partial X} = \Lambda \frac{\partial \Xi}{\partial X}$$

$$\Lambda^{(ij)} = -\sum_{k=1}^{p} \sum_{l=1}^{p} \gamma_k^{(i)} \frac{\partial^2 \Phi}{\partial n_k \partial n_l} \gamma_l^{(j)}$$

note:

$$\left[\frac{d\Xi}{dt}\right]_{n=const.} = \left(\frac{\partial \Xi}{\partial X}\right)^T \Lambda \frac{\partial \Xi}{\partial X} \leq 0$$

A lift to kinetic equations (chemical kinetics with fluctuations)

state variables:

a passage from n (or (n, n^*) or (n, z) or (n, x)) to distribution functions $f(n)$ (or $f(n, n^*)$ or $f(n, z)$ or $f(n, x)$)

Liouville equation plus some additional terms that arise due to appropriate modifications of the free energy

1. Near equilibrium dynamics:

The thermodynamic forces X are small and consequently the dissipation potential Is replace by

$$\Xi^{(neq)}(n, X) = \sum_{l=1}^{q} X^{(l)} \frac{1}{2} W^{(l)}(n) X^{(l)}$$

The mass-action-law dynamics becomes

$$\frac{dn}{dt} = -\lambda \nabla \Phi(n)$$

$$\lambda = \gamma W^T \gamma^T$$

Lift to kinetic theory

state variables: $n \;\to\; f(n)$

time evolution equations: $\frac{dn}{dt} = -\left[\Xi^{(neq)}_{n^*}\right]_{n^*=\Phi_n} \;\to\; \frac{\partial f(n)}{\partial t} = -\left[\Xi^{(neqfl)}_{f^*(n)}\right]_{f^*(n)=\Phi^{(fl)}_{f(n)}}$

free energy: $\Phi(n) \;\to\; \Phi^{(fl)}(f) = \int dn\, f(n)\,(\Phi(n) + \ln f(n))$

thermodynamic forces: $\mathcal{X} = \gamma^T \Phi_n \;\to\; \mathcal{X}^{(fl)} = \gamma^T \frac{\partial}{\partial n}\Phi^{(fl)}_{f(n)}$

dissipation potential: $\Xi^{(neq)}(n, \mathcal{X}) = \mathcal{X}^T W \mathcal{X} \;\to\; \Xi^{(neqfl)} = \int dn\, f(n) \left(\mathcal{X}^{(fl)}\right)^T W \mathcal{X}^{(fl)}$

Explicit form of the kinetic equation:

$$\frac{\partial f(\boldsymbol{n})}{\partial t} = -\sum_{i=1}^{p}\sum_{j=1}^{p}\frac{\partial}{\partial n_i}\left(f(\boldsymbol{n})\lambda_{ij}\frac{\partial}{\partial n_j}\left(\frac{\partial \Phi^{(fl)}(f)}{\partial f(\boldsymbol{n})}\right)\right)$$
$$= -\sum_{i=1}^{p}\sum_{j=1}^{p}\frac{\partial}{\partial n_i}\left(\lambda_{ij} f(\boldsymbol{n})\frac{\partial \Phi(\boldsymbol{n})}{\partial n_j} + \lambda_{ij} f(\boldsymbol{n})\frac{\partial (ln f(\boldsymbol{n}))}{\partial n_j}\right)$$

Approach to equilibrium:

$$\frac{d\Phi^{(fl)}}{dt} = \int d\boldsymbol{n}\frac{\partial \Phi^{(fl)}(f)}{\partial f(\boldsymbol{n})}\frac{\partial f(\boldsymbol{n})}{\partial t}$$
$$= -\sum_{i=1}^{p}\sum_{j=1}^{p}\int d\boldsymbol{n}\frac{\partial \phi(\boldsymbol{n})}{\partial n_i} f(\boldsymbol{n})\lambda_{ij}\frac{\partial \phi(\boldsymbol{n})}{\partial n_j} \leq 0$$

2. Fast dynamics of thermodynamic forces

$$\left(\frac{\partial f(\boldsymbol{x})}{\partial t}\right)_{fast} = \mu^{-1}\sum_{i=1}^{q}\sum_{j=1}^{q}\frac{\partial}{\partial x^{(i)}}\left(f(\boldsymbol{x})\Lambda^{(ij)}\frac{\partial}{\partial x^{(j)}}\left(\frac{\partial \Xi^{(fl)}(f,\boldsymbol{Y}(\boldsymbol{n}))}{\partial f(\boldsymbol{x})}\right)\right)$$

$$= \mu^{-1}\sum_{i=1}^{q}\sum_{j=1}^{q}\frac{\partial}{\partial x^{(i)}}\left(\Lambda^{(ij)}f(\boldsymbol{x})\frac{\partial \widehat{\Xi}(\boldsymbol{x},\boldsymbol{Y}(\boldsymbol{n}))}{\partial x^{(j)}}\right.$$

$$\left.+\Lambda^{(ij)}f(\boldsymbol{x})\frac{\partial(ln f(\boldsymbol{x}))}{\partial x^{(j)}}\right)$$

$$\left(\frac{d\Xi^{(fl)}}{dt}\right)_{fast} = \int d\boldsymbol{x}\frac{\partial \Xi^{(fl)}(f,\boldsymbol{Y}(\boldsymbol{n}))}{\partial f(\boldsymbol{x})}\frac{\partial f(\boldsymbol{x})}{\partial t}$$

$$= \mu^{-1}\sum_{i=1}^{q}\sum_{j=1}^{q}\int d\boldsymbol{y}\frac{\partial \psi(\boldsymbol{x},\boldsymbol{Y}(\boldsymbol{n}))}{\partial x^{(i)}}f(\boldsymbol{x})\Lambda^{(ij)}\frac{\partial \psi(\boldsymbol{x},\boldsymbol{Y}(\boldsymbol{n}))}{\partial x^{(j)}} \leq 0$$