

Fluctuating hydrodynamics for chemically reacting systems

I. Pagonabarraga
Univ. Barcelona

J.V. Sengers
Univ. Maryland

J.M. Ortiz de Zárate
Univ. Complutense

D. Bedeaux
S. Kjelstrup
Univ. Trondheim

J.M. Rubí
Univ. Barcelona

1. Introduction

2. Mesoscopic Non-Equilibrium Thermodynamics (MNET)

3. Fluctuating MNET

4. Reacting mixtures under temperature gradients

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1. Introduction

Nonequilibrium thermodynamics

linear relation between reaction flux and chemical potential differences



$$r = -L_r \frac{\Delta g}{T} \quad \Delta g = \mu_{A_2} - \mu_A$$

Correct for small departures from equilibrium $|\Delta g M / RT| \ll 1$ $M = 2M_A = M_{A_2}$

In general, reactions evolve according to law of mass action

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

Is it possible to derive consistently
from non-equilibrium thermodynamics formalism?

Consistent coupling to other transport processes

Include thermal fluctuations

2. Mesoscopic Non-Equilibrium Thermodynamics

Need to expand the parameter space and account for the detail of the reaction process

Reaction complex as a multicomponent mixture:

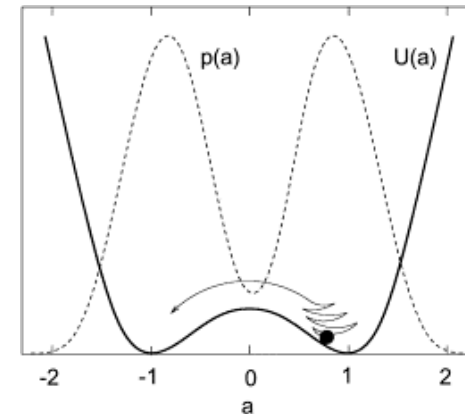
Compact variable: natural coupling to spatially dependent variables

$$\dot{\rho}(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) = \int_0^1 \dot{\rho}(\mathbf{r}, \gamma, t) \mathbf{v}(\mathbf{r}, \gamma, t) d\gamma.$$

$$\mathbf{J}(\mathbf{r}, \gamma, t) = \rho(\mathbf{r}, \gamma, t) (\mathbf{v}(\mathbf{r}, \gamma, t) - \mathbf{v}(\mathbf{r}, t)).$$

$$\int_0^1 \mathbf{J}(\gamma) d\gamma = 0.$$

$$r(1) = r(0) = 0.$$



Natural connection to Eyring/Kramers picture of a chemical reaction from thermodynamic perspective

Generalized to other kinetic models

assume separation of time scales (can be relaxed?)

2. Mesoscopic Non-Equilibrium Thermodynamics

Density along internal coordinate as a probability
connection to kinetic description: Kramers'

Apply non-equilibrium thermodynamic formalism from Gibbs entropy

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

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

Chemical potential of a mixture

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

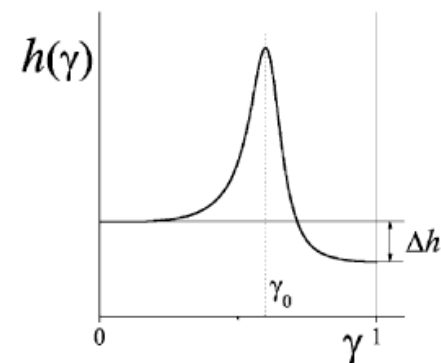
Extreme values:

connection to chemical species

$$\mu(\mathbf{r}, 0, t) = \mu_A(\mathbf{r}, t)$$

$$\mu(\mathbf{r}, 1, t) = \mu_{A_2}(\mathbf{r}, t),$$

Effective potential: reaction complex



2. Mesoscopic Non-Equilibrium Thermodynamics

Obtain balance equations:

$$\frac{D\rho(\mathbf{r}, \gamma, t)}{Dt} = -\rho(\mathbf{r}, \gamma, t) \nabla \cdot \mathbf{v}(\mathbf{r}, t) - \nabla \cdot \mathbf{J}(\mathbf{r}, \gamma, t) - \frac{\partial r(\mathbf{r}, \gamma, t)}{\partial \gamma}, \quad \frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{v} = 0.$$

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

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

Derive flux/force relations from entropy production in extended space

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

$$\mathbf{J}(\gamma) = -L_{Jq}(\gamma) \frac{\nabla T}{T^2} - L_{JJ}(\gamma) \nabla \frac{\mu(\gamma)}{T}, \quad r(\gamma) = -L_r(\gamma) \frac{1}{T} \frac{\partial \mu(\gamma)}{\partial \gamma}.$$

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

$$\int_0^1 L_{Jq}(\gamma) d\gamma = \int_0^1 L_{qJ}(\gamma) d\gamma = 0$$

$$\int_0^1 L_{JJ}(\gamma) \nabla [\mu(\gamma)/T] d\gamma = 0.$$

chemical viscosity neglected

Active process at an interface: additional flux/force couplings

2. Mesoscopic Non-Equilibrium Thermodynamics

Reaction along internal coordinate

transformation reactants \rightarrow products

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

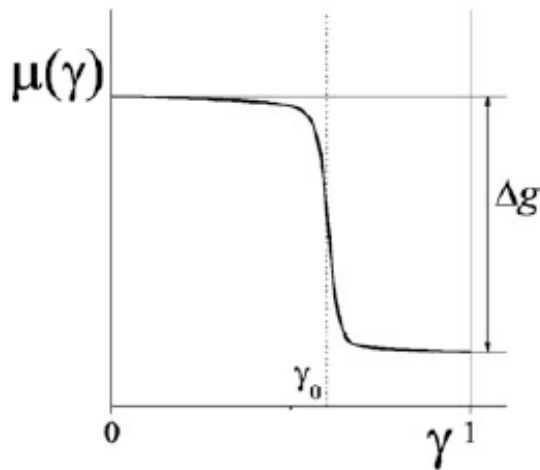
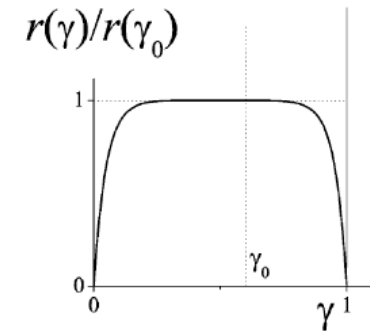
Diffusion in terms of Onsager coefficient

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

Quasi steady state assumption

high energy barrier reaction complex

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



$$\begin{aligned} \mu(\mathbf{r}, \gamma, t) &= \mu(\mathbf{r}, 0, t)\Theta(\gamma_0 - \gamma) + \mu(\mathbf{r}, 1, t)\Theta(\gamma - \gamma_0) \\ &\equiv \mu_A(\mathbf{r}, t)\Theta(\gamma_0 - \gamma) + \mu_{A_2}(\mathbf{r}, t)\Theta(\gamma - \gamma_0). \end{aligned}$$

Identify reactants and products in two basins

$$c_{2A}(\mathbf{r}, t) \equiv \int_0^{\gamma_0} c(\mathbf{r}, \gamma, t) d\gamma \quad c_{A_2}(\mathbf{r}, t) \equiv \int_{\gamma_0}^1 c(\mathbf{r}, \gamma, t) d\gamma$$

2. Mesoscopic Non-Equilibrium Thermodynamics

Identify local reaction flux

$$r(\mathbf{r}, t) = -D_r(\mathbf{r}, t)\rho(\mathbf{r}, t) \left\{ \frac{c(\mathbf{r}, \gamma, t) \exp\left[\frac{Mh(\gamma)}{RT(\mathbf{r}, t)}\right] - c(\mathbf{r}, 0, t) \exp\left[\frac{Mh(0)}{RT(\mathbf{r}, t)}\right]}{\int_0^\gamma \exp\left[\frac{Mh(\mathbf{r}, \gamma', t)}{RT(\mathbf{r}, t)}\right] d\gamma'} \right\}$$

Compatible with law of mass action

Gulberg-Waage

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

Thermodynamic expressions for reaction constants

2. Mesoscopic Non-Equilibrium Thermodynamics

Connection kinetic/NET expressions/concepts

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

Connection kinetic/NET expressions/concepts

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

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

Identifies fugacities as relevant quantities in law of mass action $f_i = \exp(\tilde{M}_i\mu_i/RT)$

2. Mesoscopic Non-Equilibrium Thermodynamics

Transport coefficients in the presence of a chemical reactions:
 integrating over internal variable

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

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

Effective kinetic coefficients in terms of average over internal coordinates

$$L_{qJ} = \int_{\gamma_0}^1 L_{qJ}(\gamma) d\gamma = - \int_0^{\gamma_0} L_{qJ}(\gamma) d\gamma, \quad 2L_{JJ} = \int_{\gamma_0}^1 L_{JJ}(\gamma) d\gamma.$$

Effect of chemical reactions on transport coefficients

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

Nonlinear effects of reaction may
 lead to relevant couplings

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

3. Fluctuating MNET

Generalize the formalism to account for hydrodynamic fluctuations

Express including variations along internal coordinate

Exploit the standard formalism from NET

$$\mathbf{J}_q = -L_{qq} \frac{\nabla T}{T^2} - \int_{\gamma}^1 L_{qJ}(\gamma) \nabla \frac{\mu(\gamma)}{T} d\gamma + \delta \mathbf{J}_q \quad \mathbf{J}(\gamma) = -L_{Jq}(\gamma) \frac{\nabla T}{T^2} - L_{JJ}(\gamma) \nabla \frac{\mu(\gamma)}{T} + \delta \mathbf{J}(\gamma)$$

$$\Pi_{ij}^{(st)} = \eta \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \nabla \cdot \mathbf{v} \right) + \delta \Pi_{ij}^{(st)} \quad r(\gamma) = -L_r(\gamma) \frac{1}{T} \frac{\partial \mu(\gamma)}{\partial \gamma} + \delta r(\gamma)$$

Gaussian fluctuating fluxes that satisfy detailed balance in extended space

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

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

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

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

3. Fluctuating MNET

How do we derive the properties of the random fluxes in real space?

Need to integrate over internal coordinate

$$r(\mathbf{r}, t) = -D_r(\mathbf{r}, t)\rho(\mathbf{r}, t) \exp\left[-\frac{Mh(\mathbf{r}, \gamma, t)}{RT(\mathbf{r}, t)}\right] \frac{\partial}{\partial \gamma} \exp\left[\frac{M\mu(\mathbf{r}, \gamma, t)}{RT(\mathbf{r}, t)}\right] + \delta r(\mathbf{r}, \gamma, t)$$

In quasisteady regime: total fluctuating reaction flux uniform

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

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

3. Fluctuating MNET

Integrated fluctuating fluxes retain its Gaussian character

$$\langle \delta r(\mathbf{r}, t) \rangle = 0.$$

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

$$= 2D_{r,0}(\mathbf{r}, t) m_{A_2} \rho_0(\mathbf{r}, t) \left\{ \int_0^1 \exp \left[\frac{Mh(\mathbf{r}, \gamma, t)}{RT_0(\mathbf{r}, t)} \right] d\gamma \right\}^{-2} \int_0^1 \exp \left[\frac{2Mh(\mathbf{r}, \gamma, t)}{RT_0(\mathbf{r}, t)} \right] c_0(\mathbf{r}, \gamma, t) d\gamma \delta(t - t') \delta(\mathbf{r} - \mathbf{r}')$$

If reaction controlled by the reaction complex

$$\begin{aligned} \langle \delta r^*(\mathbf{r}, t) \delta r(\mathbf{r}', t') \rangle &= m_{A_2} [k_{+,0}(\mathbf{r}, t) c_{2A,0}(\mathbf{r}, t) + k_{-,0}(\mathbf{r}, t) c_{A_2,0}(\mathbf{r}, t)] \delta(t - t') \delta(\mathbf{r} - \mathbf{r}') \\ &= -k_B L_{r,0}(\mathbf{r}, t) \left\{ 1 - \exp \left[-\frac{M\Delta g_0(\mathbf{r}, t)}{RT_0(\mathbf{r}, t)} \right] \right\} \delta(t - t') \delta(\mathbf{r} - \mathbf{r}') \end{aligned}$$

Consistent with law of mass action

Second moment has a clear thermodynamic interpretation

3. Fluctuating MNET

The same procedure can be applied to all fluctuating fluxes to derive the corresponding second moments in real space

$$\begin{aligned}\langle \delta J_{q,k}^*(\mathbf{r}, t) \cdot \delta J_l(\mathbf{r}', t') \rangle &= \left\langle \delta J_{q,k}^*(\mathbf{r}, t) \cdot \int_{\gamma_0}^1 \delta J_l(\mathbf{r}', \gamma, t') d\gamma \right\rangle \\ &= 2k_B L_{Jq,0}(\mathbf{r}, t) \delta_{kl} \delta(t - t') \delta(\mathbf{r} - \mathbf{r}')\end{aligned}$$

4. Reacting mixture under a thermal gradient

Effect of non-linear kinetics in correlation outside equilibrium?

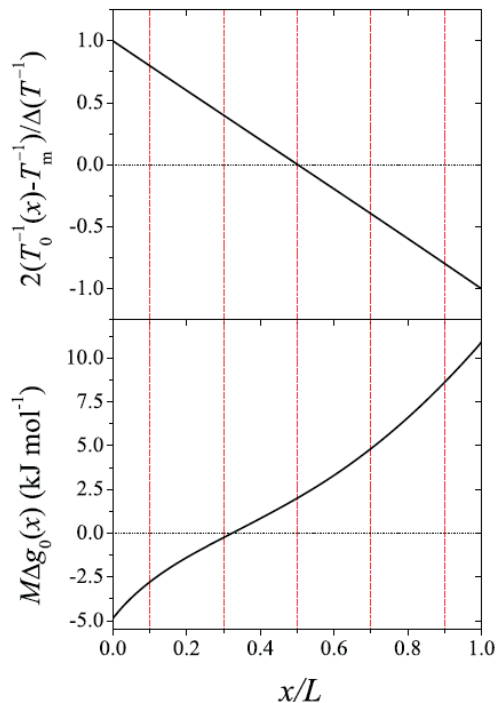
Consider a fluid mixture reacting under a thermally imposed gradient

What is the reference steady state?

Assume a conducting configuration

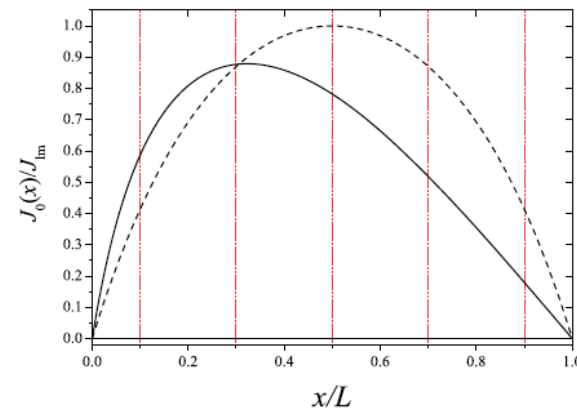
$$0 = -L_{qJ} \frac{d^2}{dx^2} \left(\frac{1}{T_0} \right) + L_{JJ} \frac{d^2}{dx^2} \left(\frac{\Delta g_0}{T_0} \right)$$

$$0 = -L_{qJ} \frac{d^2}{dx^2} \left(\frac{1}{T_0} \right) + L_{JJ} \frac{d^2}{dx^2} \left(\frac{\Delta g_0}{T_0} \right)$$



$$\frac{1}{d^2} = \frac{L_r L_{qq}}{(L_{JJ} L_{qq} - L_{Jq} L_{qJ})} \quad \text{reaction penetration depth}$$

$$= \frac{L_r}{\rho D T} \left(\frac{\partial \Delta g}{\partial c} \right)_T \left[1 + \frac{(\epsilon_D + k_T \Delta \tilde{h})^2}{Le \epsilon_D} \right]$$



4. Reacting mixture under a thermal gradient

Linearize around maximum flux

neglect details of boundary conditions

neglect dependence transport coefficients on temperature

gravity longest length scale

assume large Lewis number

$$a_T = \lambda / \rho c_p$$

$$Le = a_T / D$$

$$0 = \nu_0 \nabla^4 \delta v_x + \frac{1}{\rho_0} \{ \nabla \times \nabla \times (\nabla \cdot \delta \Pi^{(st)}) \}_x$$

$$\frac{\partial}{\partial t} \delta c + \delta v_x \nabla c_0 = D_0 \nabla^2 \delta c - \frac{L_{r,0}}{\rho_0 T_0} \exp\left(-\frac{M \Delta g_0}{RT_0}\right) \left(\frac{\partial \Delta g_0}{\partial c_0}\right)_{p,T} \delta c - \frac{1}{\rho_0} \nabla \cdot \delta \mathbf{J} + \frac{1}{\rho_0} \delta r$$

Analyze correlations of concentration fluctuations

$$\langle \delta c^*(\omega, \mathbf{q}) \delta c(\omega', \mathbf{q}') \rangle$$

4. Reacting mixture under a thermal gradient

Mode-coupling

$$S_{cc,0}(\omega, \omega', \mathbf{q}, \mathbf{q}') = S_{cc,0}(\omega, q)(2\pi)^4 \delta(\omega - \omega') \delta(\mathbf{q} - \mathbf{q}')$$

Non-linear concentration profile

$$S_{cc,1}(\omega, \omega', \mathbf{q}, \mathbf{q}') = S_{cc,1}(\omega, \mathbf{q}_{\parallel}, q_x, q'_x)(2\pi)^4 \delta(\omega - \omega') \delta(\mathbf{q}_{\parallel} - \mathbf{q}'_{\parallel}) \frac{\partial}{\partial q_x} \delta(q_x - q'_x)$$

$$S_{cc,2}(\omega, \omega', \mathbf{q}, \mathbf{q}') = S_{cc,2}(\omega, \mathbf{q}_{\parallel}, q_x, q'_x)(2\pi)^4 \delta(\omega - \omega') \delta(\mathbf{q}_{\parallel} - \mathbf{q}'_{\parallel}) \frac{\partial}{\partial q_x} \delta(q_x - q'_x)$$

4. Reacting mixture under a thermal gradient

Main contribution

$$S_{cc,0}(\omega, q) = S_{cc}^{(E)}(\omega, q) \left\{ 1 + \frac{q_{\parallel}^2 \left(\frac{\partial \Delta g}{\partial c} \right)_{T,m} (\nabla c)_m^2}{\nu_0 q^4 \left[D_0 q^2 + \frac{L_{r,0}}{\rho_0 T_m} \left(\frac{\partial \Delta g}{\partial c} \right)_{T,m} \right]} \right\}$$

$$S_{cc}^{(E)}(\omega, q) = \frac{k_B T_m}{\rho_0} \left(\frac{\partial \Delta g}{\partial c} \right)_{T,m}^{-1} \frac{2 \left[D_0 q^2 + \frac{L_{r,0}}{\rho_0 T_m} \left(\frac{\partial \Delta g}{\partial c} \right)_{T,m} \right]}{\omega^2 + \left[D_0 q^2 + \frac{L_{r,0}}{\rho_0 T_m} \left(\frac{\partial \Delta g}{\partial c} \right)_{T,m} \right]^2}$$

$$S_{cc}^{(E)} = \frac{k_B T_m}{\rho_0} \left(\frac{\partial \Delta g}{\partial c} \right)_{T,m}^{-1}$$

4. Reacting mixture under a thermal gradient

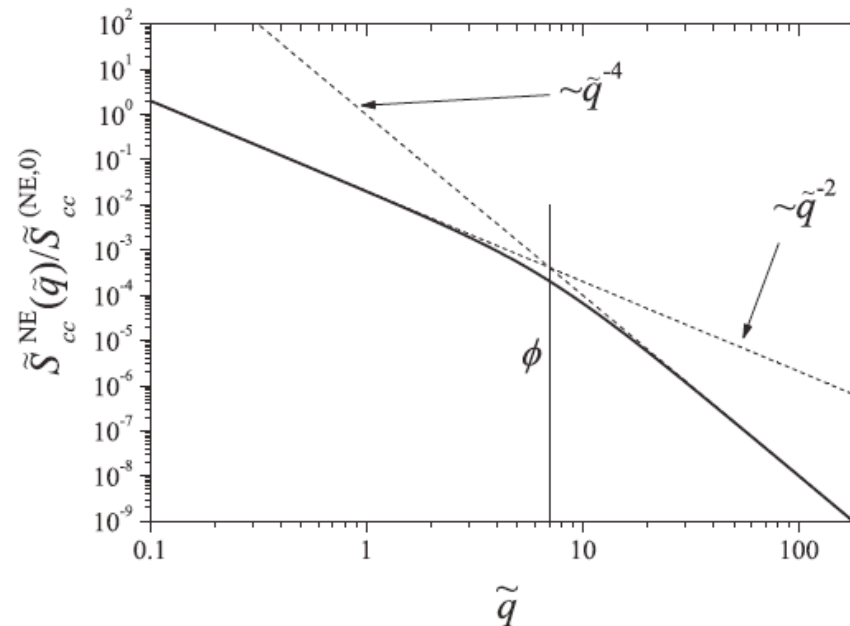
Correlations in static correlation

$$S_{cc,0}(\mathbf{q}) = S_{cc}^{(E)} \left\{ 1 + \tilde{S}_{cc}^{(NE)} \frac{\tilde{q}_{\parallel}^2}{\tilde{q}^4 \left[\tilde{q}^2 + \frac{L^2}{d^2} \right]} \right\}$$

$$\tilde{S}_{cc}^{(NE)} = \frac{(\nabla c)_m^2 L^4}{\nu_0 D_0} \left(\frac{\partial \Delta g}{\partial c} \right)_{T,m}$$

Amplitude quadratic in gradients

Crossover at penetration length



5. Conclusions

MNET consistent framework to account for kinetic processes in a thermodynamic description

Law of mass action comes out naturally

Connection with thermodynamic quantities

Internal variables

Identify fluctuating fluxes

generalized to coupled reactions

Fluctuating MNET

Effect of law of mass action on non-equilibrium correlations

Enhancement of correlations

dependence on penetration depth