# Onsager's variational principle, generalized reciprocal theorem, and their applications

**Tiezheng Qian**

*Department of Mathematics*
*Hong Kong University of Science and Technology*

昆山杜克大学
June 18, 2020

# Helpful discussions over the years

**Weizhu Bao** (NUS, Singapore)
**Wei Jiang** (Wuhan University)
**Chun Liu** (Penn State University)
**Weiqing Ren** (NUS, Singapore)
**Ping Sheng** (HKUST)
**Qi Wang** (University of South Carolina)
**Xiao-Ping Wang** (HKUST)
**Xinpeng Xu** (GTIIT)
**Wen-An Yong** (Tsinghua University)

Research supported by Hong Kong RGC

# Outline

Onsager's Reciprocal Symmetry & Variational Principle

- Diffusion equation and Stokes equation

Lorentz's Reciprocal Theorem

Reciprocal symmetry: from the local to the global

- Diffusion coupled with hydrodynamics: a phase field model

Reduced model from the variational nature of the principle

Consider a closed system whose entropy is **maximized** at equilibrium.

Close to equilibrium, the entropy can be expressed as

$$S = S_e + \Delta S(\alpha) = S_e - \frac{1}{2}\beta_{ij}\alpha_i\alpha_j$$

where $\beta_{ij}$ form a symmetric and positive definite matrix.

Spontaneous irreversible processes toward equilibrium driven by the thermodynamic forces $X_i \equiv \frac{\partial \Delta S}{\partial \alpha_i} = -\beta_{ij}\alpha_j$

In linear response regime, the kinetic equations are linear:

$$\dot{\alpha}_i = L_{ij} X_j$$

**Onsager's Reciprocal Relations:** $L_{ij} = L_{ji}$

# Linear Kinetic Equations

$$\dot{\alpha}_i = L_{ij} X_j,$$

$$X_i = R_{ij} \dot{\alpha}_j, \qquad L_{ij} R_{jk} = \delta_{ik}.$$

---

$$\dot{S}(\alpha, \dot{\alpha}) - \Phi_S(\dot{\alpha}, \dot{\alpha})$$ ***for closed systems***

to be maximized with respect to the rates $\{\dot{\alpha}_i\}$

$\dot{S} = X_i \dot{\alpha}_i$ is the rate of change of the entropy,

$\Phi_S(\dot{\alpha}, \dot{\alpha}) = R_{ij} \dot{\alpha}_i \dot{\alpha}_j / 2$ is half the rate of entropy production.

## Variational Principle

$$\mathcal{O} = \dot{S} + \dot{S}^* - \Phi_S(\dot{\alpha}, \dot{\alpha}),$$ ***for open systems***

$\dot{S}^*$ is the rate of entropy given by the system to the environment

# Isothermal systems

$$\dot{S}^* = -\dot{Q}/T = -\dot{U}/T,$$

$$\dot{F} \equiv \dot{U} - T\dot{S} = -T\left(\dot{S} + \dot{S}^*\right)$$

the dissipation function $\Phi_F(\dot{\alpha}, \dot{\alpha}) \equiv T\Phi_S(\dot{\alpha}, \dot{\alpha})$

---

$$\mathcal{R} = \dot{F}(\alpha, \dot{\alpha}) + \Phi_F(\dot{\alpha}, \dot{\alpha}),$$

to be minimized with respect to the rates $\{\dot{\alpha}_i\}$

**Lord Rayleigh's**
**Principle of the Least Dissipation of Energy**

HYDRODYNAMIC MODELS

$$\mathcal{R} = \dot{F}(\alpha, \dot{\alpha}) + \Phi_F(\dot{\alpha}, \dot{\alpha}),$$

$$\mathcal{R} = \frac{\partial F}{\partial \alpha_i}\dot{\alpha}_i + \frac{1}{2}\zeta_{ij}\dot{\alpha}_i\dot{\alpha}_j,$$

Minimization of $\mathcal{R}$ with respect to the rates gives the kinetic equations

$$-\frac{\partial F}{\partial \alpha_i} = \zeta_{ij}\dot{\alpha}_j,$$

which can be interpreted as a balance between the reversible force and the dissipative force.

$\zeta_{ij}$ forming a symmetric and positive definite matrix

**The principle of the least energy dissipation (PLED) leads to** $\dot{F} = -2\Phi_F.$

# Diffusion equation

The free energy functional arising from the entropy of the solute distribution is

$$F[c] = n_{\max} k_{\mathrm{B}} T \int c(\ln c - 1)\, d\mathbf{r}, \text{ with } 0 \le c \le 1$$

with $c$ denoting the volume fraction of the solute in the binary mixture.

$$\dot{F} = \int \mu_c \partial_t c\, d\mathbf{r} = \int \mu_c (-\nabla \cdot \mathbf{j}_c)\, d\mathbf{r} = \int \nabla \mu_c \cdot \mathbf{j}_c\, d\mathbf{r},$$

$$\delta \dot{F} = \int \nabla \mu_c \cdot \delta \mathbf{j}_c\, d\mathbf{r},$$

with the chemical potential defined by

$$\mu_c \equiv \delta F / \delta c = n_{\max} k_{\mathrm{B}} T \ln c$$

In the limit of dilute solute, the dissipation functional associated with the diffusive transport is given by

$$\Phi = \frac{1}{2}\int n_{\max} c \varsigma \mathbf{v}^2 d\mathbf{r} = \frac{1}{2}\int \frac{n_{\max}\varsigma \mathbf{j}^2}{c} d\mathbf{r}, \text{ with } \mathbf{j} = c\mathbf{v}$$

$$\delta\Phi = \int \frac{n_{\max}\varsigma \mathbf{j}\cdot\delta\mathbf{j}}{c} d\mathbf{r}$$

$$\boxed{\delta\left(\dot{F} + \Phi\right) = 0 \;\Rightarrow\; \nabla\mu_c + \frac{n_{\max}\varsigma \mathbf{j}}{c} = 0}$$

$$\boxed{\mathbf{j} = -\frac{c}{n_{\max}\varsigma}\nabla\mu_c = -\frac{k_{\mathrm{B}}T}{\varsigma}\nabla c \text{ for Fick's law of diffusion}}$$

$$\boxed{D = \frac{k_{\mathrm{B}}T}{\varsigma}: \text{ Einstein's relation for the diffusivity}}$$

## Diffusion equation:

$$\mathbf{j} = -D\nabla c,$$

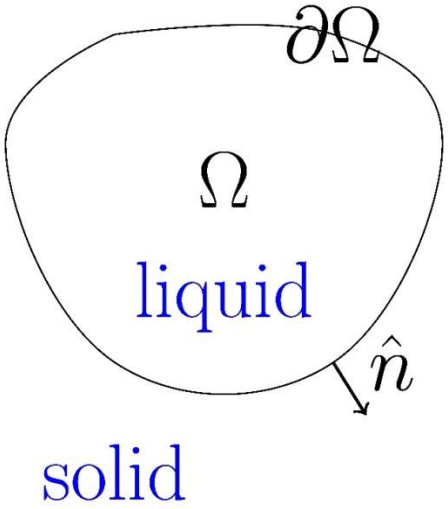
$$\partial_t c = -\nabla \cdot \mathbf{j} = D\nabla^2 c$$

## Free energy dissipation:

$$\dot{F} = -\int \frac{n_{\max}\varsigma \mathbf{j}^2}{c} d\mathbf{r}$$

# HYDRODYNAMICS

## Stokes equation from the PLED (Helmholtz)




$$\Phi_{\mathrm{v}} = \int_{\Omega} \mathrm{d}\vec{r}\ \frac{\eta}{4}\left(\partial_i v_j + \partial_j v_i\right)^2$$ **in the bulk region**

$\nabla \cdot \vec{v} = 0$ and no slip at liquid-solid interface

$R = \Phi_v$ with fluid velocity as the rate

$$-\nabla p + \nabla \cdot \left[\eta\left(\nabla\vec{v} + \nabla\vec{v}^T\right)\right] = 0$$

Stokes equation

$$\nabla \cdot \overleftrightarrow{\sigma} \equiv \nabla \cdot \left(-p\overleftrightarrow{I} + \overleftrightarrow{\sigma}^{vis}\right) = 0; \qquad \overleftrightarrow{\sigma}^{vis} \equiv \eta\left[\nabla\vec{v} + \left(\nabla\vec{v}\right)^T\right]$$

# Hydrodynamic Reciprocal Relations (HRR)

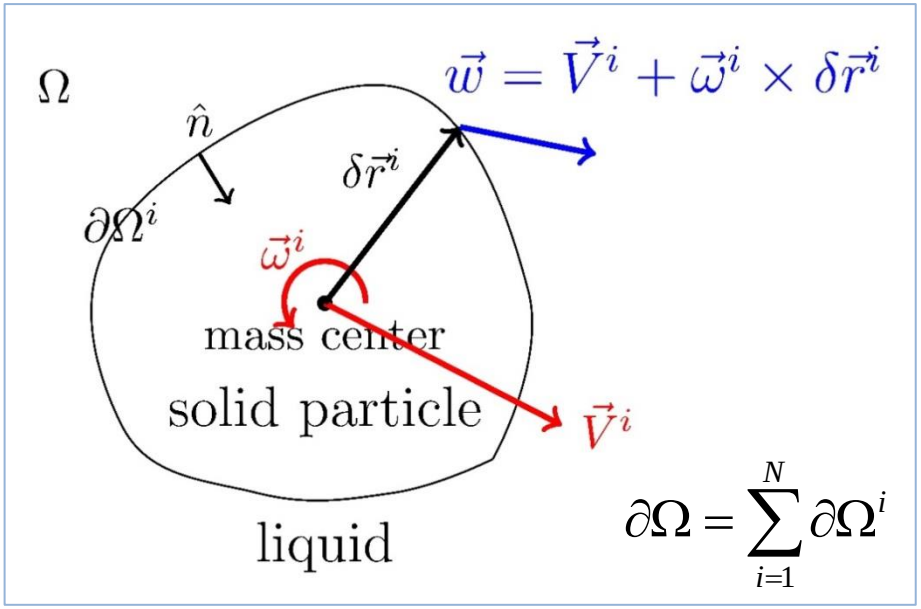
## Lorentz Reciprocal Theorem for Stokes Flows

Consider two real flows $(\vec{v}^{(1)}, \overleftrightarrow{\sigma}^{(1)})$ and $(\vec{v}^{(2)}, \overleftrightarrow{\sigma}^{(2)})$

$$\boxed{\int_{\partial\Omega} \mathrm{d}S \; \hat{n} \cdot \overleftrightarrow{\sigma}^{(1)} \cdot \vec{v}^{(2)} = \int_{\partial\Omega} \mathrm{d}S \; \hat{n} \cdot \overleftrightarrow{\sigma}^{(2)} \cdot \vec{v}^{(1)}}$$

$\partial\Omega$ can be moving.

1. The system is derived from Onsager's variational principle.
2. The system is linear.




$$F_k^{(1)} \dot{x}_k^{(2)} = F_k^{(2)} \dot{x}_k^{(1)}$$

$\dot{x}_k$ Generalized velocities of the solid objects

$F_k = \zeta_{kl} \dot{x}_l$ Conjugate forces in linear response regime

**HRR:** $\zeta_{kl} = \zeta_{lk}$

$$\int_{\partial\Omega} \mathrm{d}S \hat{n} \cdot \overleftrightarrow{\sigma}^{(1)} \cdot \vec{W}^{(2)}$$

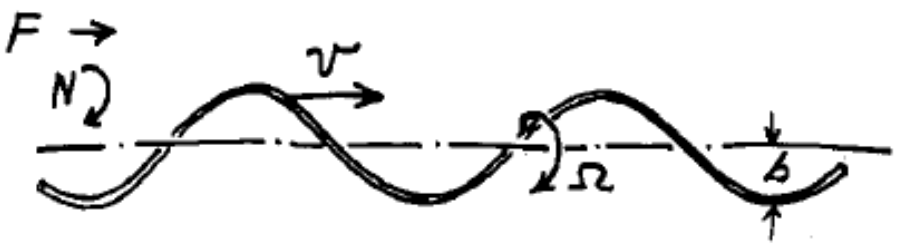
$$= \sum_{i=1}^{N} \left( \int_{\partial\Omega^i} \mathrm{d}S \hat{n} \cdot \overleftrightarrow{\sigma}^{(1)} \right) \cdot \vec{V}^{i(2)} + \sum_{i=1}^{N} \left[ \int_{\partial\Omega^i} \mathrm{d}S \delta\vec{r}^i \times \left( \hat{n} \cdot \overleftrightarrow{\sigma}^{(1)} \right) \right] \cdot \vec{\omega}^{i(2)}$$

**Force by the solid particle on the fluid** **Torque by the solid particle on the fluid**

# Bacterial Motility and HRR

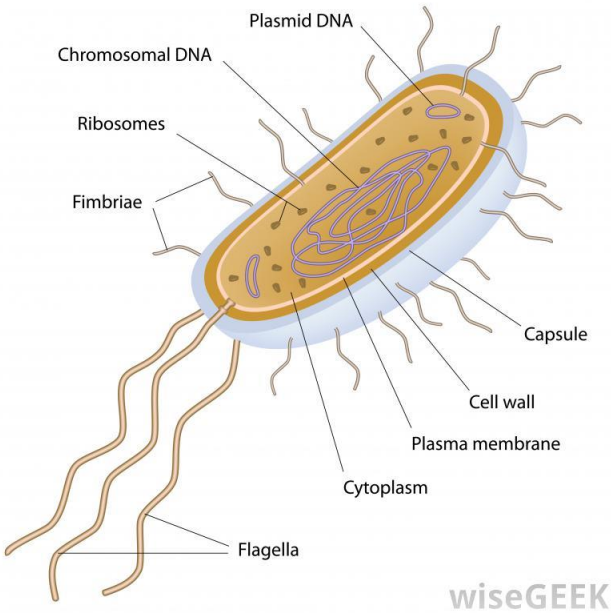
**Life at low Reynolds number**

E. M. Purcell
*Lyman Laboratory, Harvard University, Cambridge, Massachusetts 02138*
(Received 12 June 1976)




(force) $F = Av + B\Omega$

(torque) $N = Cv + D\Omega$



# Diffusion coupled with hydrodynamics: a phase field model

Consider a system enclosed by a solid boundary where $\partial_n \phi = 0$.

The free energy functional $F\left[\phi(\mathbf{r})\right]$ takes the Cahn-Hilliard form

No fluid-solid interaction

Rate of change of the free energy

$$\dot{F} = \int \mu \frac{\partial \phi}{\partial t}\, d\mathbf{r} = \int \mu\left(-\nabla \cdot \mathbf{J}\right)\, d\mathbf{r} = \int \nabla \mu \cdot \mathbf{J}\, d\mathbf{r} = \int \nabla \mu \cdot \left(\phi \mathbf{v} + \mathbf{j}\right)\, d\mathbf{r}$$

in which

$$\mu = \frac{\delta F}{\delta \phi} = -K\nabla^2 \phi + \frac{d}{d\phi} f\left(\phi\right), \quad \frac{\partial \phi}{\partial t} = -\nabla \cdot \mathbf{J}, \quad \mathbf{J} = \phi \mathbf{v} + \mathbf{j}.$$

Dissipation functional

$$\Phi = \int \frac{\eta}{4}\left[\nabla \mathbf{v} + \left(\nabla \mathbf{v}\right)^T\right]^2 d\mathbf{r} + \int \frac{\mathbf{j}^2}{2M}\, d\mathbf{r}$$

with $\eta = \eta\left(\phi\right)$ & $M = M\left(\phi\right)$.

## Application of Onsager's variational principle using the action

$$R = \dot{F} + \Phi$$

Momentum equation

$$-\nabla p - \phi \nabla \mu + \nabla \cdot \boldsymbol{\sigma}_{\text{visc}} = 0,$$

$$\text{with } \boldsymbol{\sigma}_{\text{visc}} = \eta \left[ \nabla \mathbf{v} + \left( \nabla \mathbf{v} \right)^T \right] \text{ and } p \text{ due to } \nabla \cdot \mathbf{v} = 0$$

Diffusive current density $\mathbf{j} = -M \nabla \mu$

Boundary conditions: $\partial_n \phi = 0 \ \& \ \mathbf{v}_\tau = 0$ **(dynamic BCs)**

$j_n = 0 \ \& \ v_n = 0$ **(kinematic BCs)**

Consider a system with solid wall (where $\partial_n \phi = 0$ is applied) and **inlets/outlets**.

***An open system***

$$\dot{F} = \int \mu \frac{\partial \phi}{\partial t}\, d\mathbf{r} = \int \mu \left(-\nabla \cdot \mathbf{J}\right)\, d\mathbf{r} = \int \mu \left[-\nabla \cdot \left(\phi \mathbf{v} + \mathbf{j}\right)\right]\, d\mathbf{r}$$

There is still a surface integral at inlets/outlets, which actually vanishes in stationary states.

becomes

$$\dot{F} = \underbrace{\int -\mu J_n\, dS}_{\boxed{1}} + \underbrace{\int \mathbf{n} \cdot \boldsymbol{\sigma} \cdot \mathbf{v}\, dS}_{\boxed{2}} + \underbrace{\int \nabla \mu \cdot \mathbf{j}\, d\mathbf{r}}_{\boxed{3}} + \underbrace{\int -\boldsymbol{\sigma} : \nabla \mathbf{v}\, d\mathbf{r}}_{\boxed{4}}$$

as it should be.

1. **Free energy pumped into the system**
2. **Work done onto the system with** $\boldsymbol{\sigma} = -p\mathbf{I} + \boldsymbol{\sigma}_{\text{visc}}$
3. **Diffusive dissipation** $\int \nabla \mu \cdot \mathbf{j}\, d\mathbf{r} = \int -\frac{\mathbf{j}^2}{M}\, d\mathbf{r}$
4. **Viscous dissipation** $\int -\boldsymbol{\sigma} : \nabla \mathbf{v}\, d\mathbf{r} = \int -\boldsymbol{\sigma}_{\text{visc}} : \nabla \mathbf{v}\, d\mathbf{r} = \int -\frac{\eta}{2}\left[\nabla \mathbf{v} + \left(\nabla \mathbf{v}\right)^T\right]^2\, d\mathbf{r}$

Rate of change of the free energy can be expressed as

$$\dot{F} = \int -\mu J_n \, dS + \int \mathbf{n} \cdot \boldsymbol{\sigma} \cdot \mathbf{v} \, dS + \underbrace{\int -\frac{\mathbf{j}^2}{M} \, d\mathbf{r} + \int -\frac{\eta}{2}\left[\nabla \mathbf{v} + (\nabla \mathbf{v})^T\right]^2 \, d\mathbf{r}}_{-2\Phi}$$

Below we consider stationary states with

$$\dot{F} = 0, \quad \frac{\partial \phi}{\partial t} = -\nabla \cdot \mathbf{J} = 0, \quad \nabla \cdot \mathbf{v} = 0.$$

Note that without inlet/outlet, the two $\int \cdots \, dS$ would vanish, and the stationary states become the global equilibrium state.

At equilibrium state, we have

$$\mathbf{j}_{\mathrm{eq}} = 0, \quad \mu_{\mathrm{eq}} = \mathrm{const.}, \quad \mathbf{v}_{\mathrm{eq}} = 0, \quad p_{\mathrm{eq}} = \mathrm{const.}, \quad \boldsymbol{\sigma}_{\mathrm{eq}} = -p_{\mathrm{eq}}\mathbf{I}$$

$$\int J_n \, dS = 0 \quad \& \quad \int v_n \, dS = 0$$

---

$\dot{F} = 0$: ***Boundary contributions fully dissipated***

$$\int -\mu J_n \, dS + \int \mathbf{n} \cdot \boldsymbol{\sigma} \cdot \mathbf{v} \, dS = \int \frac{\mathbf{j}^2}{M} \, d\mathbf{r} + \int \frac{\eta}{2} \left[ \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right]^2 \, d\mathbf{r}$$

becomes

$$\int -(\mu - \mu_{\mathrm{eq}}) J_n \, dS + \int \mathbf{n} \cdot (\boldsymbol{\sigma} + p_{\mathrm{eq}}\mathbf{I}) \cdot \mathbf{v} \, dS = \int \frac{\mathbf{j}^2}{M} \, d\mathbf{r} + \int \frac{\eta}{2} \left[ \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right]^2 \, d\mathbf{r}$$

$$\tilde{\mu} = \mu - \mu_{\mathrm{eq}} \quad \& \quad \tilde{\boldsymbol{\sigma}} = \boldsymbol{\sigma} + p_{\mathrm{eq}}\mathbf{I}$$

**Net forces due to deviation from global equilibrium state**

$$\int -\tilde{\mu} J_n \, dS + \int \mathbf{n} \cdot \tilde{\boldsymbol{\sigma}} \cdot \mathbf{v} \, dS = \int \frac{\mathbf{j}^2}{M} \, d\mathbf{r} + \int \frac{\eta}{2} \left[ \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right]^2 \, d\mathbf{r}$$

$$\int -\tilde{\mu} J_n \, dS + \int \mathbf{n} \cdot \tilde{\boldsymbol{\sigma}} \cdot \mathbf{v} \, dS = \int \frac{\mathbf{j}^2}{M} \, d\mathbf{r} + \int \frac{\eta}{2} \left[ \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right]^2 \, d\mathbf{r}$$

It can be expressed as $\sum_{\alpha} F_\alpha I_\alpha = \sum_{m,n} j_m \varsigma_{mn} j_n$

$F_\alpha$ & $I_\alpha$ forces and fluxes at the boundary

$j_m$ fluxes in the bulk region

If the system is very close to the global equilibrium state, then it can be linearized around the equilibrium state.

$$F_\alpha = A_{\alpha m} j_m, \quad I_\alpha = B_{\alpha m} j_m$$

Note that matrices *A* and *B* are <u>independent</u> of the dynamic state.
**They are properties of the equilibrium state.**

$$F^T I = j^T \varsigma j, \quad F = Aj, \quad I = Bj \quad \mapsto \quad A^T B = \varsigma$$

Note that $\varsigma$ is not only symmetric but also independent of the dynamic state.

local reciprocal symmetry linearity

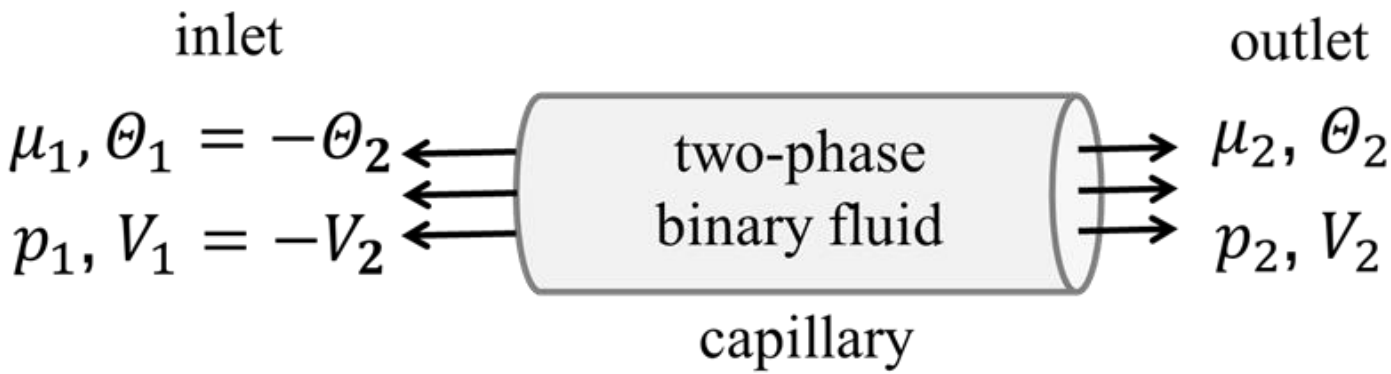
Consider two dynamic states labelled by superscripts (1) and (2)

$$\left[F^{(1)}\right]^T I^{(2)} = \left[j^{(1)}\right]^T \varsigma j^{(2)} = \left[j^{(2)}\right]^T \varsigma j^{(1)} = \left[F^{(2)}\right]^T I^{(1)}$$

Linear response: $F_\alpha = L_{\alpha\beta} I_\beta$

$$L_{\alpha\beta} = L_{\beta\alpha}$$

Reciprocal symmetry for forces and fluxes at the boundary



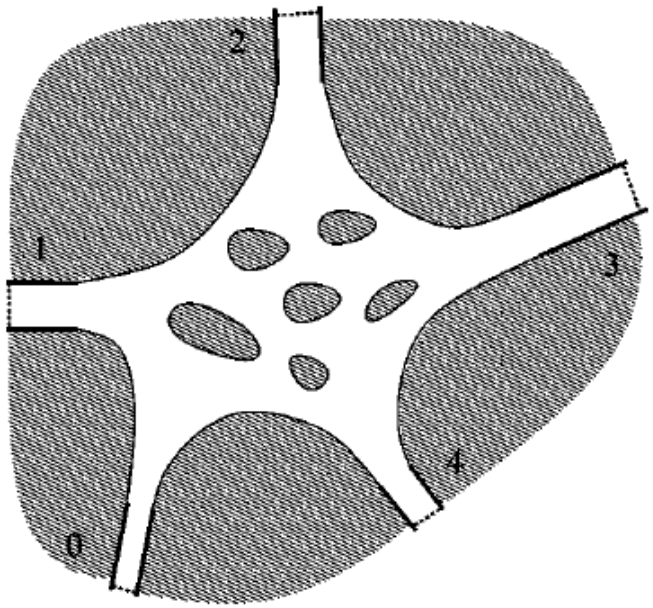

The two ends of the capillary are connected to two reservoirs, respectively, where the chemical potentials ( $\mu_1$ and $\mu_2$ ) and pressures ( $p_1$ and $p_2$ ) are prescribed. The integrated outward flux of the solute volume is denoted by $\Theta_i$ and the integrated outward flux of the fluid volume is denoted by $V_i$ .

$$\sum_\beta F_\beta I_\beta = \Delta\mu\Theta_2 + \Delta p V_2$$

$$\left.\begin{aligned} \Delta\mu &\equiv \mu_1 - \mu_2 \\ \Delta p &\equiv p_1 - p_2 \end{aligned}\right\} \text{Driving forces}$$

$$\begin{bmatrix} \Delta\mu \\ \Delta p \end{bmatrix} = \begin{bmatrix} R_{\phi\phi} & R_{\phi v} \\ R_{v\phi} & R_{vv} \end{bmatrix} \begin{bmatrix} \Theta_2 \\ V_2 \end{bmatrix} \quad \text{with} \quad R_{\phi v} = R_{v\phi}$$

# Systems with Inlets & Outlets

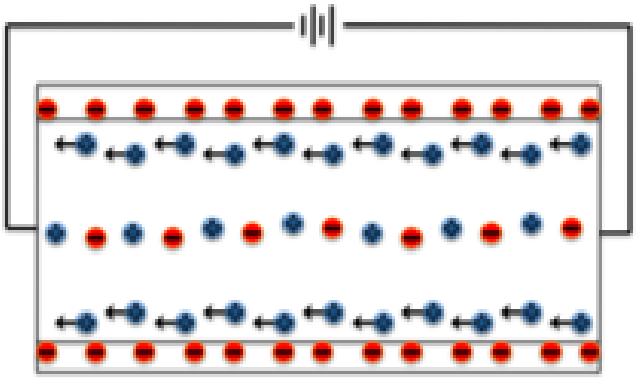



Reciprocal theorem for ***forces*** and ***fluxes*** at open boundaries, which are directly related to the operation of the "device".

## ***F*** versus ***I***

$$F_\alpha = L_{\alpha\beta} I_\beta$$

$$L_{\alpha\beta} = L_{\beta\alpha}$$



Electro-osmotic flows

(from Wikipedia)

# Remarks

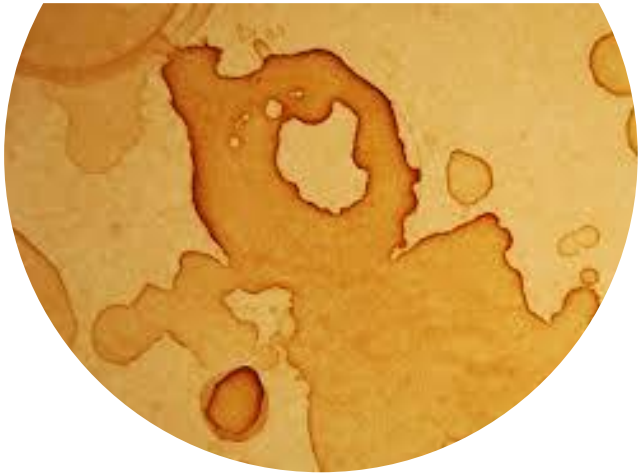
1. The system is derived from Onsager's variational principle.

2. The system is in the immediate proximity of global equilibrium.

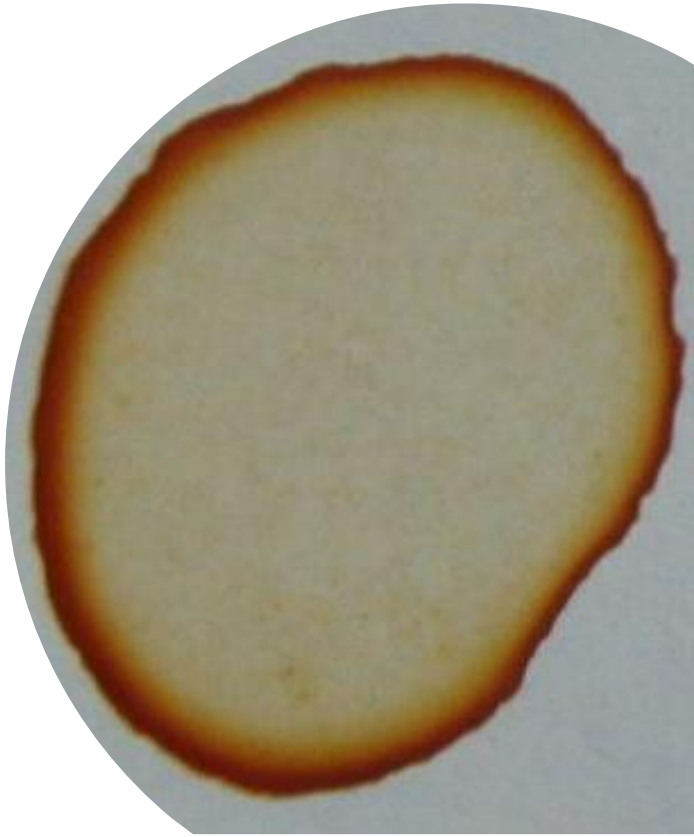
3. Open or moving boundary for non-equilibrium stationary states.

Electro-osmotic flows
Micropolar fluids
Non-isothermal situation (thermal diffusion)

Xinpeng Xu and **T. Qian**, Generalized Lorentz reciprocal theorem in complex fluids and in non-isothermal systems, Journal of Physics: Condensed Matter 31, 475101 (2019).

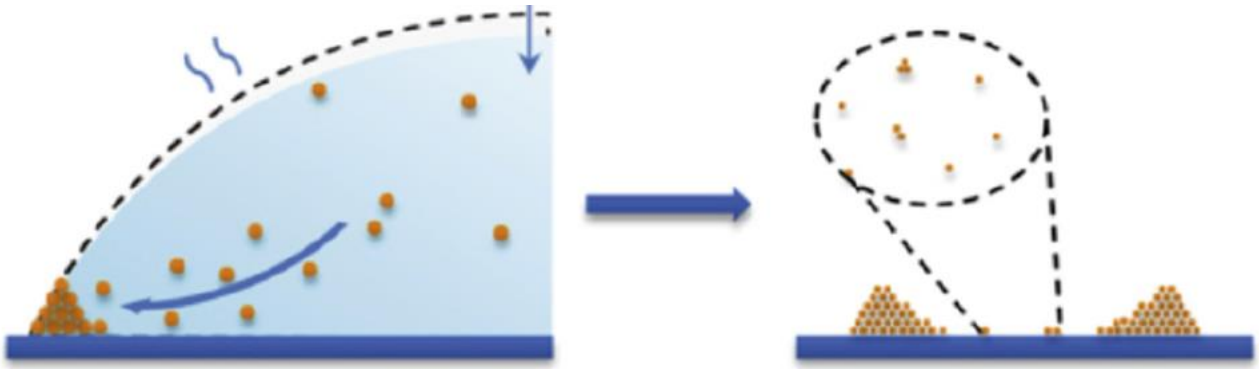


# The coffee-ring effect seen in daily life



# The underlying mechanism for the deposition pattern of evaporating droplets

Coffee-ring effect



As the contact line is **pinned**, a compensating flow is needed to keep the contact line fixed.

Advances in Colloid and Interface Science 252 (2018) 38–54

Pinning of the contact line of the drying drop ensures that liquid evaporating from the edge is **replenished by liquid from the interior**.

Deegan R D *et al*. 1997 Capillary flow as the cause of ring stains from dried liquid drops *Nature* **389** 827

# How to model this phenomenon?

What are involved?

An evaporating droplet of colloidal suspension on a solid surface
Capillary flow
Contact line pinning

***The physics principle to be applied***

***Onsager's variational principle to model the non-equilibrium processes in the linear response regime***

***Linear irreversible thermodynamics ： Slow hydrodynamics***

Contact line pinning/contact angle hysteresis ？ ？ ？

Onsager's variational principle has been shown to be useful in deriving many evolution equations in soft matter physics.

***PDE systems***

**The variational nature of the principle allows its application as a tool for approximation.**

Consider a dissipative system that can be approximately described by a finite set of state variables. If we express its total free energy F and dissipation function $\Phi$ in terms of these state variables and their time derivatives, then application of Onsager's variational principle yields a system of ordinary differential equations that describe the time evolution of the state variables, i.e., the time evolution of the system.

***An ansatz for the solution to the evolution partial differential equations***

**Classical works:**

- **L. Onsager, Phys. Rev. 37, 405 (1931).**
- **L. Onsager, Phys. Rev. 38, 2265 (1931).**

## Variational modeling based on Onsager's principle → *PDE models*

- **T. Qian**, X.-P. Wang, & P. Sheng, J. Fluid Mech. 564, 333 (2006). (moving contact line)
- M. Doi, J. Phys. Condens. Matter 23, 284118 (2011). (overview)
- X. Xu, U. Thiele, & **T. Qian**, J. Phys. Condens. Matter 27, 085005 (2015). (thin film dynamics)
- Yang, X., Li, J., Forest, M., & Wang, Q. (2016). Entropy 18(6), 202. (active nematics)

## The variational principle as a tool for approximation → *ODE models*

- M. Doi, *Onsager principle as a tool for approximation*, Chin. Phys. B 24, 1674 (2015).
- X. Man & M. Doi, Phys. Rev. Lett. 116, 066101 (2016). (evaporative droplet on solid surface)
- X. Xu, Y. Di, & M. Doi, Physics of Fluids, 28(8), 087101 (2016). (moving droplet on solid surface)
- H. Wang, D. Yan, & **T. Qian**, J. Phys.: Condens. Matter 30, 435001 (2018). (evaporative droplet on solid surface)
- W. Jiang, Q. Zhao, **T. Qian**, D. Srolovitz, & W. Bao, Acta Materialia, 163, 154 (2019). (solid-state surface diffusion)

## Thin film hydrodynamics: $h = h(x,t)$ in 1D space

**Evolution equation derived from Onsager's variational principle**

Free energy functional $F[h] = \int \mathrm{d}x \left\{ \gamma \left[ 1 + \frac{1}{2}(\partial_x h)^2 \right] + f(h) \right\}$

Dissipation functional $\Phi_v = \int \mathrm{d}x \int_0^h \mathrm{d}z \left[ \frac{\eta}{2}(\partial_z u)^2 \right]$

Constraint due to incompressibility $C = \int \mathrm{d}x \int_0^h \mathrm{d}z \left[ -p(\partial_x u + \partial_z w) \right]$

$$\delta \mathcal{A} = \delta \dot{F} + \delta \Phi_v + \delta C = 0 \text{ w.r.t. } u, w, \partial_t h$$

**Thin film evolution equation** $\partial_t h = -\partial_x \left\{ \frac{h^3}{3\eta} \partial_x \left[ \gamma \partial_x^2 h - f'(h) \right] \right\}$

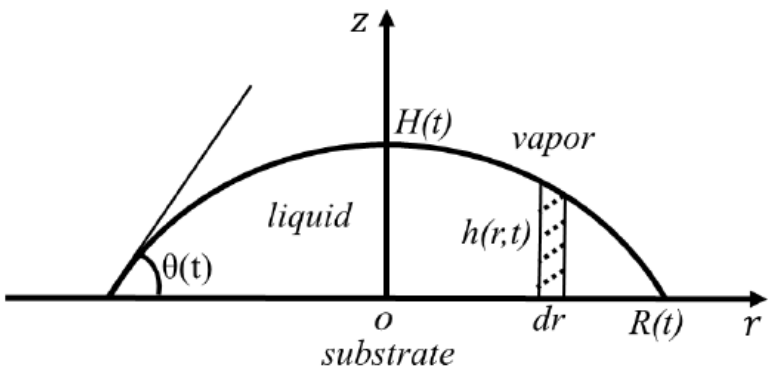
X. Xu, U. Thiele, and **T. Qian**, J. Phys. Condens. Matter 27, 085005 (2015).

- There is a complete model for immiscible two-phase flows, which can be derived from Onsager's variational principle.

- On the one hand, the thin film evolution equation is an approximate description of thin film hydrodynamics based on the lubrication approximation.

- On the other hand, it can be further simplified if the capillary number $\mathrm{Ca} = \eta U/\gamma$ is small enough.

An evaporating droplet




A parabolic film profile with uniform curvature:

Slow contact line motion leads to $Ca = \eta U/\gamma \to 0$.

An ODE for $R(t)$ is to be derived by applying the variational principle, with $H(t)$ determined from $V(t)$ and $R(t)$.

X. Man and M. Doi, Phys. Rev. Lett. 116, 066101 (2016).
H. Wang, D. Yan, and T. Qian, J. Phys.: Condens. Matter **30**, 435001 (2018).

## Modeling components:

Free energy function, dissipation function, and continuity equation, supplemented with a phenomenological description of contact line pinning

Parabolic film profile, contact angle, and the volume of the droplet

$$h(r,t) = H(t)\left[1 - \frac{r^2}{R^2(t)}\right], \qquad \theta(t) \simeq \tan(\theta) = -\left.\frac{\partial h}{\partial r}\right|_{r=R} = \frac{2H(t)}{R(t)}. \ll 1 \text{ for thin film}$$

$$V(t) = \int_0^R 2\pi r h(r,t)\mathrm{d}r = \frac{\pi}{2}HR^2.$$

Free energy

$$F = (\gamma_{\mathrm{ls}} - \gamma_{\mathrm{sv}})\pi R^2 + \gamma_{\mathrm{lv}}\int_0^R 2\pi r\sqrt{1 + h'(r)^2}\mathrm{d}r$$
$$= (\gamma_{\mathrm{ls}} - \gamma_{\mathrm{sv}})\pi R^2 + \gamma_{\mathrm{lv}}\pi(R^2 + H^2)$$

$$F = \gamma_{\mathrm{lv}}\left(\frac{\theta_e^2}{2}\pi R^2 + \pi H^2\right) = \gamma_{\mathrm{lv}}\left(\frac{\theta_e^2}{2}\pi R^2 + \frac{4V^2}{\pi R^4}\right), \qquad \dot{F} = \gamma_{\mathrm{lv}}\left[\pi R\left(\theta_e^2 - \theta^2\right)\dot{R} + \frac{8V\dot{V}}{\pi R^4}\right].$$

$$\boxed{\gamma_{\mathrm{ls}} + \gamma_{\mathrm{lv}}\cos\theta_e = \gamma_{\mathrm{sv}}}$$

*Unbalanced Young stress at contact line*

Dissipation function based on lubrication approximation $\frac{\partial p}{\partial z} = 0,\ \eta \frac{\partial^2 u}{\partial z^2} - \frac{\partial p}{\partial x} = 0.$

$$\Phi_{\mathrm{F}} = \frac{1}{2}\int_0^R 2\pi r \frac{3\eta}{h} v_{\mathrm{f}}^2 \mathrm{d}r + \xi_{\mathrm{cl}} \pi R \dot{R}^2.$$

Here $v_f(r)$ is the *z*-averaged liquid velocity and $\xi_{cl}$ is associated with contact line dissipation.

Mass conservation of the evaporating droplet:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_0^r 2\pi s h(s,t)\mathrm{d}s = -\int_0^r 2\pi s J(s,t)\mathrm{d}s - 2\pi r h(r,t) v_{\mathrm{f}}(r,t)$$

via evaporation via outgoing liquid flow

$$v_{\mathrm{f}}(r,t) = r\left(\frac{\dot{R}}{2R} - \frac{\dot{H}}{4H}\right) = r\left(\frac{\dot{R}}{R} - \frac{\dot{V}}{4V}\right) \propto r \Rightarrow \Phi_F$$

$$\Phi_{\mathrm{F}} = \frac{1}{2}\int_0^{R-\epsilon} 2\pi r \frac{3\eta}{h} v_{\mathrm{f}}^2 \mathrm{d}r + \xi_{\mathrm{cl}} \pi R \dot{R}^2$$

A cut-off length $\epsilon$ is needed in the integral.

$$= \frac{3\eta\pi^2 R^4}{4V}\left(\dot{R} - \frac{R\dot{V}}{4V}\right)^2 \left[\ln\left(\frac{R}{2\epsilon}\right) - 1\right] + \xi_{\mathrm{cl}} \pi R \dot{R}^2.$$

Variational derivation of the governing equation for $R(t)$:
Minimizing $\dot{F} + \Phi_F$ with respect to $\dot{R}$ leads to a force balance equation

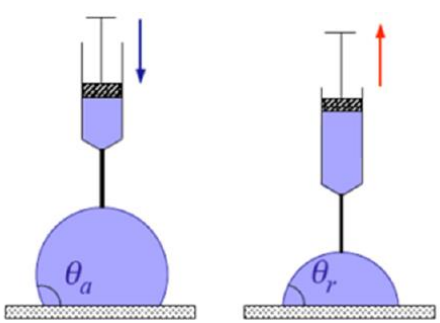
$$\frac{\partial(\dot{F} + \Phi_{\mathrm{F}})}{\partial \dot{R}} = 0.$$

$$\gamma_{\mathrm{lv}}(\cos\theta - \cos\theta_e) = \gamma_{\mathrm{lv}}\left(\frac{\theta_e^2}{2} - \frac{\theta^2}{2}\right) = -\frac{3\eta C}{\theta}\dot{R} - \xi_{\mathrm{cl}}\dot{R} + \frac{3\eta C}{\theta}\frac{R\dot{V}}{4V}$$

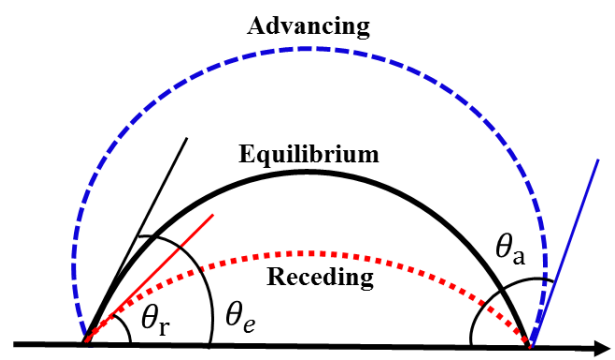
with $C = \ln(R/2\epsilon) - 1.$

***R(t) solved, liquid flow obtained, particle motion traced, ring formation predicted.***

The dissipative force at the contact line, $-\xi_{cl}\dot{R}$, is linear in $\dot{R}$.
The contact angle hysteresis (CAH), which is commonly observed for evaporative droplets, can be incorporated.




Contact line pinning on rough surfaces



*A minimal model reported*

*Thank you for your attention!*