2012/01/17 Symposium on Mathematics for Various Disciplines 5

Onsager's Variational Principle in Soft Matter Physics

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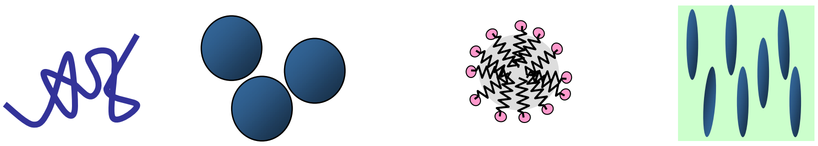
Aim of my talk

Soft Matter

Polymer Colloids Surfactants Liquid crystals



Consisting of very large unit
- Strongly perturbed from equilibrium state by weak force
- Relaxation to equilibrium is very slow

⇩

Strongly non-linear and non-equilibrium

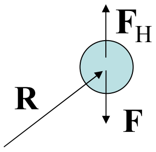
The PDEs which describe the non-linear dynamics of soft matter can be conveniently derived by the Onsager's variational principle.

Outline

1. Variational principle in Stokesian hydrodynamics
2. Onsager’s variational principle in irrevesible thermodynamics
3. Applications
   1. Diffusion in colloidal solutions
   2. Liquid crystals (Leslie-Ericksen theory)
4. Summary

Variational Principle in Stokesian Hydrodynamics

Sedimentation of a Particle in a Viscous Fluid



$$\mathbf{F} = m\mathbf{g} = -\frac{\partial U}{\partial \mathbf{R}}$$ potential force

$$\mathbf{F}_H = -\zeta\dot{\mathbf{R}}$$ frictional force

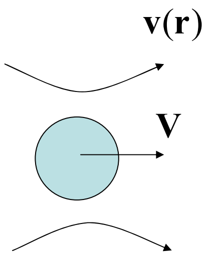
In a steady state

minimize

$$\zeta\dot{\mathbf{R}} = -\frac{\partial U}{\partial \mathbf{R}} \quad \Longleftrightarrow \quad R = \underbrace{\frac{1}{2}\zeta\dot{\mathbf{R}}^2}_{\text{dissipation function}} + \underbrace{\frac{\partial U}{\partial \mathbf{R}} \bullet \dot{\mathbf{R}}}_{\dot{U}}$$

The principle of the least dissipation of energy

Friction Constant for a Sphere



$$\mathbf{F}_H = -\zeta\dot{\mathbf{R}}$$

$$\eta\nabla^2\mathbf{v} = \nabla p$$

$$\nabla \bullet \mathbf{v} = 0$$

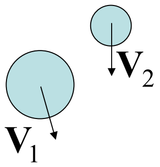
$$\mathbf{v} = \mathbf{V}$$ at the surface

$$\mathbf{v} = 0$$ at inifinity

$$\mathbf{F}_H = \int dS\, \boldsymbol{\sigma} \bullet n = -\zeta\mathbf{V}$$

$$\zeta = 6\pi\eta a$$

Sedimentation of Two Interacting Particles in a Viscous Fluid



$$U = m\mathbf{g}\bullet\mathbf{R}_1 + m\mathbf{g}\bullet\mathbf{R}_2 + U_{int}(\mathbf{R}_1,\mathbf{R}_2)$$

$$\zeta_{11}\dot{\mathbf{R}}_1 + \zeta_{12}\dot{\mathbf{R}}_2 = -\frac{\partial U}{\partial \mathbf{R}_1}$$

$$\zeta_{21}\dot{\mathbf{R}}_1 + \zeta_{22}\dot{\mathbf{R}}_2 = -\frac{\partial U}{\partial \mathbf{R}_2}$$

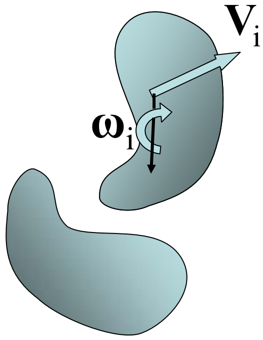
$$\zeta_{ij} = \zeta_{ij}(\mathbf{R}_1,\mathbf{R}_2)$$

$\zeta_{ij} = (\zeta_{ji})^t$ Helmholtz’s reciprocal relation

$$\boxed{R = \frac{1}{2}\sum \zeta_{ij} : \dot{\mathbf{R}}_i\dot{\mathbf{R}}_j + \sum \frac{\partial U}{\partial \mathbf{R}_i}\bullet\dot{\mathbf{R}}_i}$$

Variational Principle for Particle Dynamics in Viscous Fluids

Interacting particle moving in a viscous fluid



$x_i \ (i = 1,2,...f)$ Generalized coordinate (position, orientation)

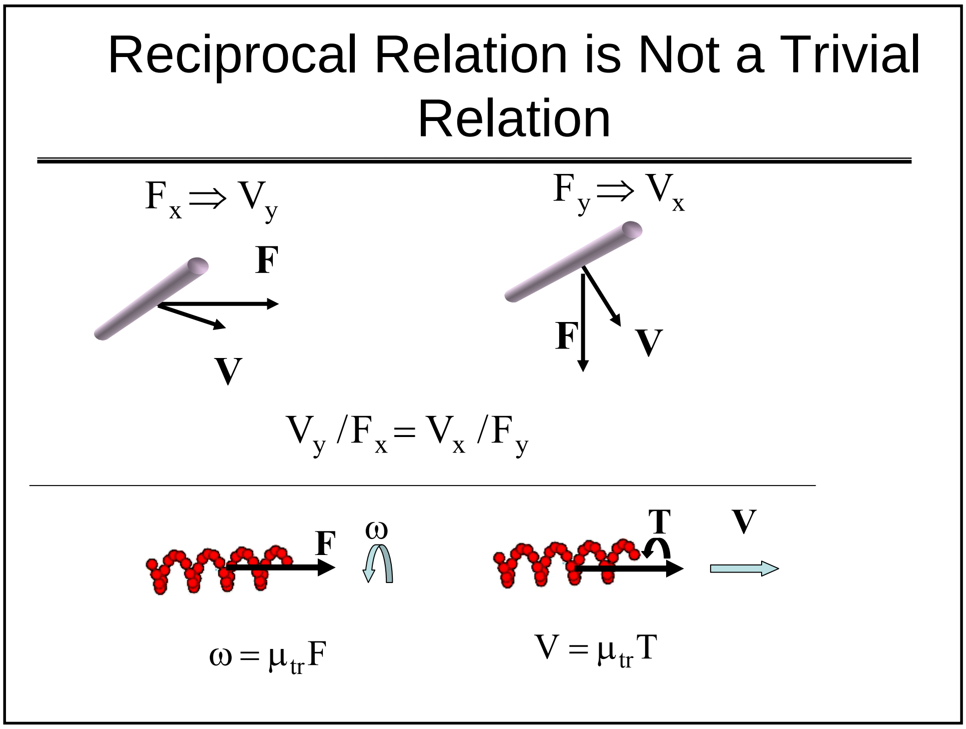
$U(x_i)$ Potential energy

Time evolution equation

$$\sum \zeta_{ij}\dot{x}_j = -\frac{\partial U}{\partial x_i} \qquad \zeta_{ij} = \zeta_{ji}$$

Lorentz reciprocal theorem

$$\boxed{R = \frac{1}{2}\sum \zeta_{ij}\dot{x}_i\dot{x}_j + \sum \frac{\partial U}{\partial x_i}\dot{x}_i}$$



Reciprocal Relation is Not a Trivial Relation

$F_x \Rightarrow V_y$

$F_y \Rightarrow V_x$

$$V_y / F_x = V_x / F_y$$

$\omega = \mu_{tr} F$

$V = \mu_{tr} T$

Proof of the reciprocal relation

1.Proof by hydrodynamics (Lorentz)
2.Proof by phenomenology (Onsager)
3.Pfoof by statisitical mechanics (Kubo et al)

Hydrodynamic proof

Configurational change　　Fluid velocity　　Frictional force

$$\begin{tikzcd}
\dot{x}_i^{(1)} \arrow[r] & \mathbf{v}^{(1)} \arrow[r] & F_i^{(1)} \\
\dot{x}_i^{(2)} \arrow[r] & \mathbf{v}^{(2)} \arrow[r] & F_i^{(2)}
\end{tikzcd}$$

We prove

$$\begin{tikzcd}
 & \sum F_i^{(1)}\dot{x}_i^{(2)} = \sum F_i^{(2)}\dot{x}_i^{(1)} \arrow[dl] \arrow[dr] & \\
\sum \zeta_{ij}\dot{x}_i^{(1)}\dot{x}_j^{(2)} & & \sum \zeta_{ij}\dot{x}_i^{(2)}\dot{x}_j^{(1)}
\end{tikzcd}$$

$$\sum F_i^{(1)}\dot{x}_i^{(2)} = -\int dS G_{i\alpha}(\mathbf{r})\sigma_{\alpha\beta}^{(1)} n_\beta \dot{x}_i^{(2)}$$

$$= -\int dS \sigma_{\alpha\beta}^{(1)} n_\beta v_\alpha^{(2)} = -\int dS \sigma_{\alpha\beta}^{(2)} n_\beta v_\alpha^{(1)} = \sum F_i^{(2)}\dot{x}_i^{(1)}$$

$$\sigma_{\alpha\beta}^{(1)} = \eta[\partial_\beta v_\alpha^{(1)} + \partial_\alpha v_\beta^{(1)}] - p^{(1)}\delta_{\alpha\beta}$$

$$-\int dS \sigma_{\alpha\beta}^{(1)} n_\beta v_\alpha^{(2)} = \int d\mathbf{r}\, \partial_\beta(\sigma_{\alpha\beta}^{(1)} v_\alpha^{(2)})$$

$$= \int d\mathbf{r}[v_\alpha^{(2)}\partial_\beta \sigma_{\alpha\beta}^{(1)} + \sigma_{\alpha\beta}^{(1)}\partial_\beta v_\alpha^{(2)}]$$

$$= \int d\mathbf{r} \sigma_{\alpha\beta}^{(1)}\partial_\beta v_\alpha^{(2)} = (1/2)\int d\mathbf{r}[\partial_\beta v_\alpha^{(1)} + \partial_\alpha v_\beta^{(1)}][\partial_\beta v_\alpha^{(2)} + \partial_\alpha v_\beta^{(2)}]$$

Onsager's proof 1/2

Assume that the friction matrix depends only on x and independent of U

$$-\sum \zeta_{ij}\dot{x}_j - \frac{\partial U}{\partial x_i} + F_{ri}(t) = 0$$

Assume that $x_i(t)$ is fluctuating around x_{i0}

$$\xi_i(t) = x_i(t) - x_{i0}$$

$$U(\xi) = \frac{1}{2}\sum k_{ij}\xi_i\xi_j$$

We can apply a hypothetical force to balance $-\partial U / \partial x_i$

$$-\sum \zeta_{ij}\dot{\xi}_j - \sum k_{ij}\xi_j + F_{ri}(t) = 0$$

where $\zeta_{ij} = \zeta_{ij}(x_0)$

Calculate $\langle \xi_i(t+\Delta t)\xi_j(t)\rangle$

Use the the symmetry $\langle \xi_i(t)\xi_j(t')\rangle = \langle \xi_j(t)\xi_i(t')\rangle$

$$\Downarrow$$

$$\zeta_{ij} = \zeta_{ji}$$

Time correlation at equilibrium has time reversal symmetry:
$\langle A(t)B(0)\rangle = \langle B(t)A(0)\rangle$

Onsager's proof 2/2

$$-\sum \zeta_{ij}\dot{\xi}_j - \sum k_{ij}\xi_j + F_{ri}(t) = 0$$

$$\dot{\xi}_i = -\sum \alpha_{ij}\xi_j + v_{ri}(t) \qquad \alpha_{ij} = \sum \left(\zeta^{-1}\right)_{im} k_{mj}$$

$$\xi_i(t+\Delta t) = \xi_i(t) - \Delta t \sum \alpha_{ij}\xi_j(t) + \int_t^{t+\Delta t} dt' v_{ri}(t')$$

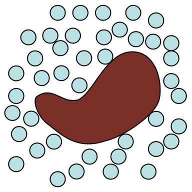
$$\begin{aligned}&\left\langle \xi_i(t+\Delta t)\xi_j(t)\right\rangle \\ &= \left\langle \xi_i(t)\xi_j(t)\right\rangle - \Delta t \sum \alpha_{ik}\left\langle \xi_k(t)\xi_j(t)\right\rangle \\ &= k_B T\left[\left(k^{-1}\right)_{ij} - \Delta t \sum \alpha_{ik}\left(k^{-1}\right)_{kj}\right] \\ &= k_B T\left[\left(k^{-1}\right)_{ij} - \Delta t \sum \left(\zeta^{-1}\right)_{ij}\right]\end{aligned} \qquad \left\langle \xi_i(t)\xi_j(t)\right\rangle = \left(k^{-1}\right)_{ij} k_B T$$

$$\left\langle \xi_i(t+\Delta t)\xi_j(t)\right\rangle = \left\langle \xi_j(t+\Delta t)\xi_i(t)\right\rangle$$

$$\Downarrow$$

$$\zeta_{ij} = \zeta_{ji}$$

Proof by statisitical mechanics 2/2



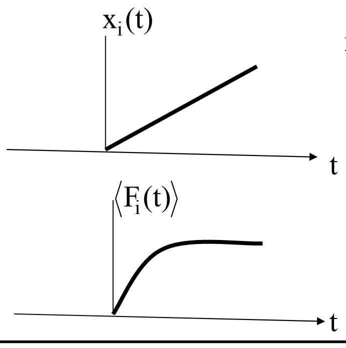
$H(\Gamma;x)$

- Parameters representing the configuration of Brownian particles
- Phase space variables representing the configuration of solvent molecules

Force exerted on the particle by fluid molecules

$$\hat{F}_i(\Gamma,x) = -\frac{\partial H}{\partial x_i}$$

Assume



$$x_i(t) = x_{i0} + v_i t \qquad t > 0$$

$$\langle F_i(t)\rangle = \left\langle -\frac{\partial H}{\partial x_i}\right\rangle = -\int d\Gamma P(\Gamma;x,t)\frac{\partial H}{\partial x_i}$$

Proof by statisitical mechanics

$$\langle F_i(t)\rangle = \int d\Gamma \left(-\frac{\partial H}{\partial x_i} \right) P(\Gamma; x, t)$$

$t < 0$ $\quad P(\Gamma; x, t) \propto \exp[-\beta H(\Gamma; x_0)]$

$$\langle F_i \rangle = -\frac{\partial A(x_0)}{\partial x_{i0}} = \bar{F}_i(x_0) \qquad A(x_0) = -\frac{1}{\beta} \ln \int d\Gamma e^{-\beta H(\Gamma; x_0)}$$

$t > 0$ $\quad$ Perturbative solution for $\frac{\partial P}{\partial t} = (L + L')P$ gives the following result.

$$\langle F_i(t)\rangle = -\frac{\partial A}{\partial x_i} - \int_0^t dt' \sum \dot{\zeta}_{ij}(t') v_j \qquad \dot{\zeta}_{ij}(t) = \frac{1}{k_B T} \langle F_{ri}(t) F_{rj}(0) \rangle_0$$

Especially for $t > \tau_F$

$$\langle F_i(t)\rangle = -\frac{\partial A}{\partial x_i} - \sum \zeta_{ij} v_j \qquad \zeta_{ij} = \frac{1}{k_B T} \int_0^\infty dt' \langle F_{ri}(t') F_{rj}(0) \rangle_0$$

Onsager's Variational Principle in Irreversible Thermodynamics

Onsager's Reciprocal Relation

Onsager 1931

$(x_1, x_2, x_3 ...)$ State variables describing non-equilibrium state

$$S = S(x_1, x_2, x_3 ...)$$

$$\dot{x}_i = \sum L_{ij} \frac{\partial S}{\partial x_j}$$

Onsager's reciprocal relation

$$\boxed{L_{ij} = L_{ji}}$$

Can be proven by time reversal symmetry in the fluctuation at equilibrium state

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Onsager's Variational Principle

Onsager 1931

$$x_i = \sum L_{ij} \frac{\partial S}{\partial x_j}$$

$$L_{ij} = L_{ji}$$

$$O = -\frac{1}{2} \sum (L^{-1})_{ij} \dot{x}_i \dot{x}_j + \sum \frac{\partial S}{\partial X_i} \dot{x}_i$$ variational principle

If T(temperature) is constant:

$$\boxed{R = \frac{1}{2} \sum \zeta_{ij} \dot{x}_i \dot{x}_j + \sum \frac{\partial A}{\partial x_i} \dot{x}_i}$$

$A = A(x_i)$

free energy of the system

Application 1

Diffusion in Concentrated Colloidal Particles

Recipe to Make Kinetic Equations

(1)Choose proper state variables $(x_1, x_2, x_3 ...)$

(2)Construct the free energy function $A = A(x_i)$

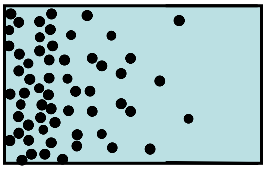
(3)Construct the dissipation function $(1/2)\sum \zeta_{ij} V_i V_j$

(4)Minimize $R = \frac{1}{2}\sum \zeta_{ij}\dot{x}_i\dot{x}_j + \sum \frac{\partial A}{\partial x_i}\dot{x}_i$

$$\sum \zeta_{ij}\dot{x}_j = -\frac{\partial A}{\partial x_i}$$

Diffusion of Colloidal Particles

Diffusion of particles in quiescent solution



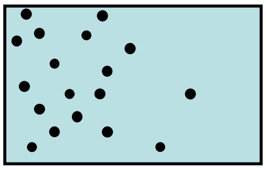
State variable $n(x,t)$ Volume fraction of particles

Our objective is to determine $\dot{n}(x,t)$

It is more convenient to consider $v_p(x,t)$ Solute velocity

$$\dot{n} = -\frac{\partial}{\partial x}(v_p n)$$

Case of Dilute Solution



Free Energy of the system

$$A[n(x)] = \int dx[k_B T n(x) \ln n(x)]$$

$$\begin{aligned} \dot{A} &= \int dx\ \dot{n}(k_B T \ln n + k_B T) \\ &= -\int dx \frac{\partial v_p n}{\partial x}(k_B T \ln n + k_B T) \\ &= \int dx\ v_p n \frac{\partial}{\partial x}(k_B T \ln n + k_B T) \\ &= k_B T \int dx\ v_p \frac{\partial n}{\partial x} \end{aligned}$$

Variational Calculation

$$R = \frac{1}{2}\int dx\zeta n v_p^2 + k_B T\int dx\ v_p \frac{\partial n}{\partial x} \qquad \zeta = 6\pi\eta a$$

$$\left.\begin{array}{l} \zeta n v_p + k_B T\dfrac{\partial n}{\partial x} = 0 \\[2em] \dot{n} = -\dfrac{\partial}{\partial x}(v_p n) \end{array}\right\} \quad \frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}$$

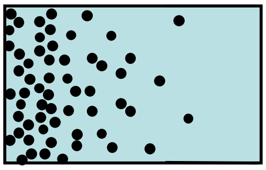
$$D = \frac{k_B T}{\zeta}$$

Case of Concentrated Solution

$$\phi = n\frac{4\pi}{3}a^3$$

$$A[\phi] = \int d\mathbf{r} f(\phi)$$

$$\begin{aligned} \dot{A} &= \int d\mathbf{r} f'(\phi)\dot{\phi} \\ &= -\int d\mathbf{r} f'(\phi)\nabla \bullet (\phi \mathbf{v}_p) \\ &= \int d\mathbf{r}\mathbf{v}_p \bullet \phi\nabla f'(\phi) \\ &= \int d\mathbf{r}\mathbf{v}_p \bullet \underline{\nabla\Pi} \end{aligned}$$



Osmotic pressure

$$\Pi(\phi) = \phi f' - f$$

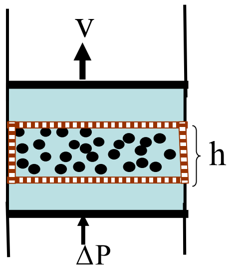
$$\nabla\Pi = (\nabla\phi)f' + \phi\nabla f' - \nabla f = \phi\nabla f'$$

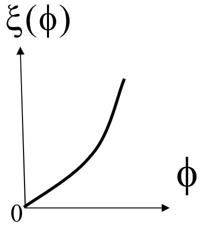
Dissipation Function

$$W = \int d\mathbf{r}\,\underbrace{\xi(\phi)}_{\uparrow}\,\mathbf{v}_p{}^2$$

Friction coefficient / volume

$$\Delta P \,/\, h \,=\, \xi v$$



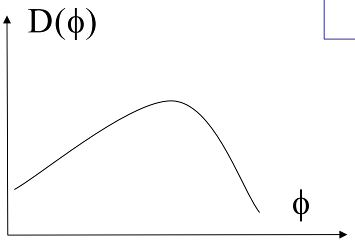


Variational Calculation

$$R = \frac{1}{2}\int d\mathbf{r}\,\xi(\phi)\,\mathbf{v}_p{}^2 + \int d\mathbf{r}\,\mathbf{v}_p \bullet \nabla\Pi$$

$$\left.\begin{array}{l} \mathbf{v}_p = -\dfrac{\nabla\Pi}{\xi(\phi)} \\[2ex] \dot{\phi} = -\nabla \bullet (\phi\mathbf{v}_p) \end{array}\right\} \quad \frac{\partial\phi}{\partial t} = \nabla\left(D\nabla\phi\right)$$

$$\boxed{D(\phi) = \frac{\phi}{\xi(\phi)}\,\frac{\partial\Pi}{\partial\phi}}$$



Reciprocal Relation in Diffusion Equation

Onsager’s kinetic equation

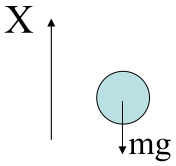
$$\dot{X}_i = \sum L_{ij} \frac{\partial A}{\partial X_j} \qquad L_{ij} = L_{ji}$$

Diffusion equation

$$\frac{\partial \phi}{\partial t} = \nabla\left(D\nabla\phi\right)$$

$$\frac{\partial \phi}{\partial t} = -\int d\mathbf{r}\int d\mathbf{r}'\mu(\mathbf{r},\mathbf{r}')\frac{\delta A}{\delta\phi(\mathbf{r}')} \qquad \mu(\mathbf{r},\mathbf{r}') = \mu(\mathbf{r}',\mathbf{r})$$

Forces needed to change external parameters



$$R = \frac{1}{2}\zeta\dot{X}^2 + mg\dot{X}$$

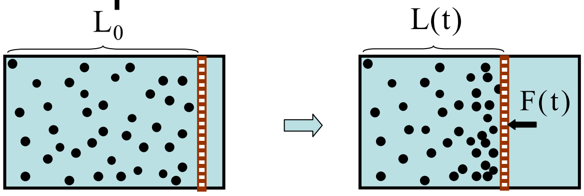
$$F = \frac{\partial R}{\partial \dot{X}} = \zeta\dot{X} + mg$$

In general $R = R(\underbrace{\dot{x}, x}_{\text{Internal variables}}, \underbrace{p, \dot{p}}_{\text{External parameters}})$

The forces needed to change the external parameter is

$$\boxed{F = \frac{\partial R}{\partial \dot{p}}}$$

Forces neede to move the semipermeable membrane



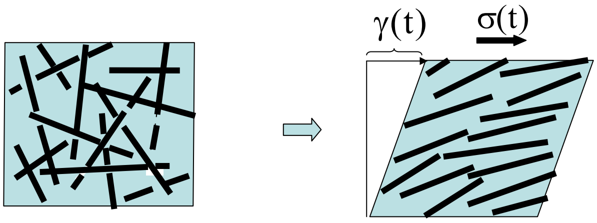
$$A = \int_0^L dx\ k_B T n(x) \ln n(x)$$

$$\dot{A} = -\int_0^L dx\ k_B T v_p \frac{\partial n}{\partial x} + \dot{L} n(L) k_B T$$

$$W = \int_0^L dx \zeta n v_p^2 + \zeta_m \dot{L}^2$$

$$F(t) = \frac{\partial R}{\partial \dot{L}} = \zeta_m \dot{L} - k_B T n(L)$$

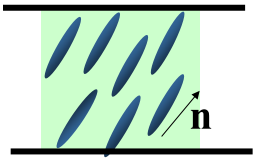
Rheology of rodlike polymers



$$\sigma(t) = \frac{\partial R}{\partial \dot{\gamma}}$$

Application 2
Liquid Crystals

Flow of Liquid Crystals



$\mathbf{n}(\mathbf{r},t)$ director

$\mathbf{v}(\mathbf{r},t)$ velocity

$$\tilde{\dot{n}}_\alpha = \dot{n}_\alpha - \omega_{\alpha\beta} n_\beta$$

$$\omega_{\alpha\beta} = \frac{1}{2}(\partial_\beta v_\alpha - \partial_\alpha v_\beta)$$

$$\dot{\varepsilon}_{\alpha\beta} = \frac{1}{2}(\partial_\beta v_\alpha + \partial_\alpha v_\beta)$$

Nemato-Hydrodynamics

$$W = \frac{A_1}{2}(n_\alpha n_\beta \dot{\varepsilon}_{\alpha\beta})^2 + \frac{A_2}{2}\dot{\varepsilon}_{\alpha\beta}\dot{\varepsilon}_{\alpha\beta} + \frac{A_3}{2} n_\mu n_\nu \dot{\varepsilon}_{\alpha\mu}\dot{\varepsilon}_{\beta\nu}$$

$$+ \frac{A_4}{2}(\tilde{\dot{n}}_\alpha)^2 + \frac{A_5}{2}\tilde{\dot{n}}_\alpha \dot{\varepsilon}_{\alpha\beta} n_\beta$$

$$A = \frac{1}{2}K_1(\nabla \bullet \mathbf{n})^2 + \frac{1}{2}K_2(\mathbf{n} \bullet \nabla \times \mathbf{n})^2 + \frac{1}{2}K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2$$

$$\dot{U} = \frac{\delta F}{\delta n_\alpha}\dot{n}_\alpha - \frac{\partial F}{\partial n_{\alpha,\beta}}(\partial_\mu n_\alpha)(\partial_\beta v_\mu)$$

⇨ Leslie-Ericksen equation

Conclusion

- Many kinetic equations in soft matter physics can be derived from the Rayleigh-Onsager’s variational principle
    - Brownian motion of colloidal particles
    - Phase separation kinetics in solutions
    - Swelling kinetics in gels
    - Flow in liquid crystals
    - Diffusio-phoresis, electro-phoresis etc
- The variational principle is simple and easy to use.

The Onsager’s variational principle is a general base of soft matter physics.