2013/01/09 Newton Institute Cambridge

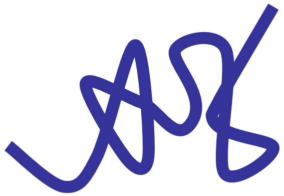
Onsager's Variational Principle in Soft Matter Dynamics

Masao Doi

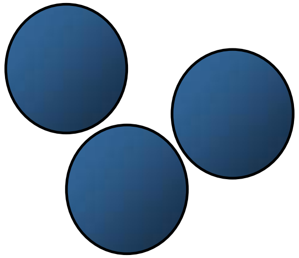
Toyota Physical and Chemical Research Institute

Introduction

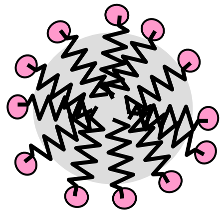
Polymer



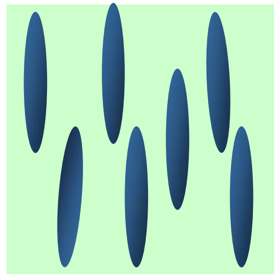
Colloids



Surfactants



Liquid crystals



- Complex fluids
  - Something between fluid and solid
  - Non-linear response

Such phenomena can be discussed quite generally based on Onsager’s variational principle.

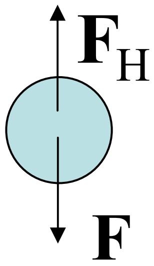
L. Onsager, Phys. Rev. 37 405- (1931), 38 2265-2279 (1931)

Outline

1. The variational principle in Stokesian hydrodynamics
2. Onsager's variational principle in irreversible thermodynamics
   - What it is
   - When it works
   - A useful formula
3. Applicaitons
   - Colloidal solutions
   - Gels
   - Liquid crystals
4. Summary

The Variational Principle in Stokesian Hydrodynamics

Particle motion 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

$$\zeta \dot{\mathbf{R}} + \frac{\partial U}{\partial \mathbf{R}} = 0$$

$$\Longleftrightarrow$$

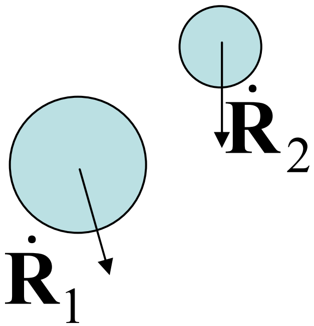
Minimize Rayleighian

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

The principle of the least dissipation of energy

Rayleigh 1883

Motion of two interacting particles in a viscous fluid



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

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

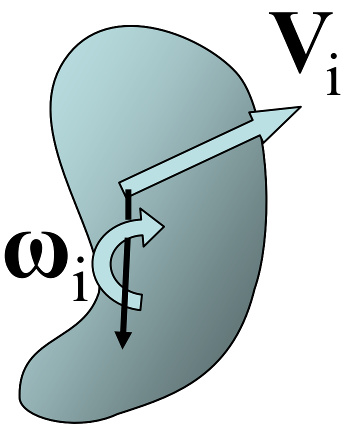
$$\zeta_{ij} = (\zeta_{ji})^t$$

Reciprocal relation

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

Reciprocal relation in the friction coefficients

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



$$F_{Hi} = -\sum \zeta_{ij} \dot{x}_j \qquad \zeta_{ij} = \zeta_{ji}$$

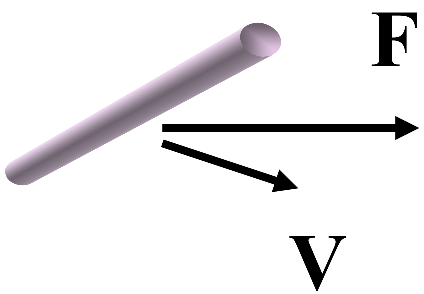
Time evolution equation $\displaystyle \sum \zeta_{ij} \dot{x}_j = -\frac{\partial U}{\partial x_i}$

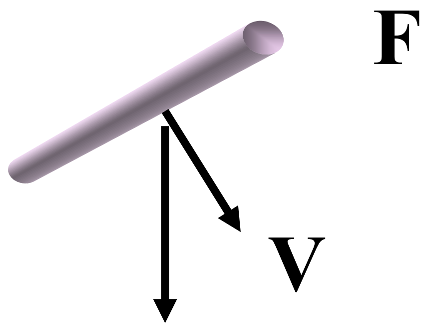
$$R = \frac{1}{2} \sum \zeta_{ij} \dot{x}_i \dot{x}_j + \sum \frac{\partial U}{\partial x_i} \dot{x}_i$$

Happel J. and Brenner H. 1963 Low Reynolds Number Hydrodynamics Kluwer
Kim S., Karrila S. J. 1991 Microhydrodynamics Butterworth-Heinemann

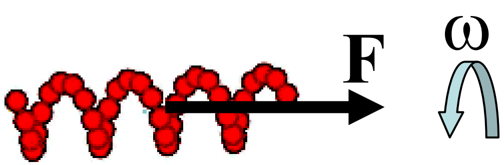
Reciprocal relation is NOT a trivial relation

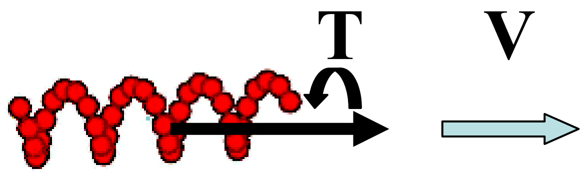
$$F_x \Rightarrow V_y \qquad F_y \Rightarrow V_x$$





$$V_y / F_x = V_x / F_y$$





$$\omega = \mu_{tr} F \qquad V = \mu_{tr} T$$

Lagrangean mechanics

$$x = (x_1, \ldots x_f)$$ Generalized coordinate

$$L = K(x, \dot{x}) - U(x)$$

$$\cancel{\frac{d}{dt}\left(\frac{\partial K}{\partial \dot{x}_i}\right)} - \left(\frac{\partial U}{\partial x_i}\right) = \left(\frac{\partial \Phi}{\partial \dot{x}_i}\right) \qquad \Phi = \frac{1}{2}\sum \zeta_{ij}\dot{x}_i\dot{x}_j$$

Ignore the inertia term

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

Onsager's Variational Principle in Irreversible Thermodynamics

Onsager's reciprocal relation

Onsager 1931

$(x_1, x_2, x_3 \ldots)$ Slow variables describing non-equilibrium state

$$\dot{x}_i = \sum L_{ij}(x) \frac{\partial S}{\partial x_j} \qquad S = S(x_1, x_2, x_3 \ldots)$$

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

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

$$\dot{S} = \sum \frac{\partial S}{\partial x_i} \dot{x}_i - \frac{1}{2} \sum (L^{-1})_{ij} \dot{x}_i \dot{x}_j$$

Onsager's variational principle

If T(temperature) is constant:

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

$x = (x_1, x_2, \ldots)$ Slow variables defining the non-equilibrium state

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

$2\Phi = \sum \zeta_{ij}(x)\dot{x}_i\dot{x}_j$ Work done to the dissipative system per unit time

$A = A(x)$ Free energy of the system

Onsager's proof of the reciprocal relation

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

$$\dot{x} = -\frac{1}{\zeta} \frac{\partial U}{\partial x}$$

Assume the system is close to equilibrium

$$S(x) = -\frac{1}{2} \sum k_{ij} x_i x_j$$

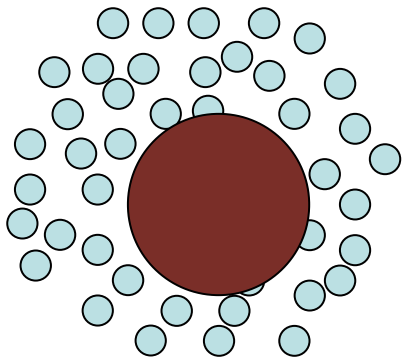
Calculate $\left\langle x_i(t) x_j(0) \right\rangle$

Use $\left\langle x_i(t) x_j(0) \right\rangle = \left\langle x_i(-t) x_j(0) \right\rangle = \left\langle x_j(t) x_i(0) \right\rangle$

⇩

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

Proof based on Kubo formula



$H(\Gamma, x)$ Hamiltonian

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

$$\langle F_i(t) \rangle = -\frac{\partial A}{\partial x_i} - \sum \tilde{\zeta}_{ij}(x,t)\dot{x}_j$$

$$\tilde{\zeta}_{ij}(x,t) = \frac{1}{k_B T}\int_0^t dt' \langle F_{ri}(t')F_{rj}(0)\rangle_x \qquad F_{ri} = \hat{F}_i(\Gamma, x) - \langle \hat{F}_i(\Gamma, x) \rangle$$

If the correlation time of the force is short

$$\langle F_i(t) \rangle = -\frac{\partial A}{\partial x_i} - \sum \zeta_{ij}(x)\dot{x}_j$$

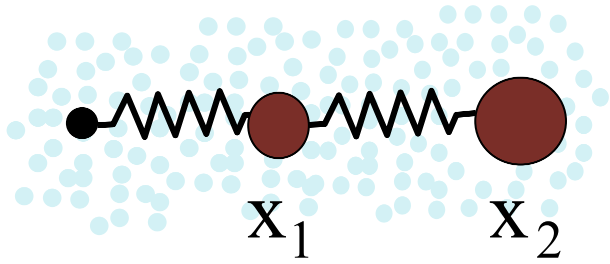
$$\zeta_{ij}(x) = \frac{1}{k_B T}\int_0^\infty dt' \langle F_{ri}(t')F_{rj}(0)\rangle_0 \qquad \zeta_{ij}(x) = \zeta_{ji}(x)$$

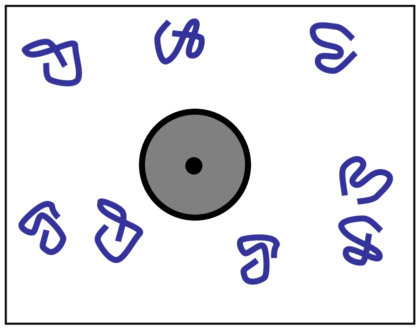
When Onsager's prinicple is valid?

$x = (x_1, x_2, \ldots)$ is a proper set of slow variables.

•All slow variables are listed.

Given $(x_1, x_2, \ldots)$, $(\dot{x}_1, \dot{x}_2, \ldots)$ is uniquely determined.

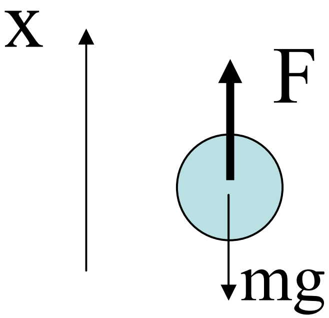




State variables (x_1, x_2) or $\psi(x_1, x_2)$

•The fast variables are close to equilibrium

A useful formula



Forces neede to move the partcle at a controlled rate $\dot{x}$

$$F = \zeta \dot{x} + mg$$

$$= \frac{\partial R}{\partial \dot{x}}$$

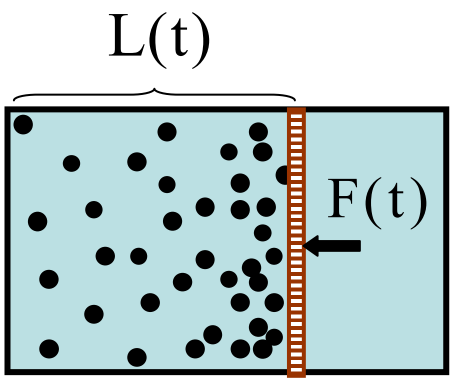
$$R = \frac{1}{2}\zeta \dot{x}^2 + mg\dot{x}$$

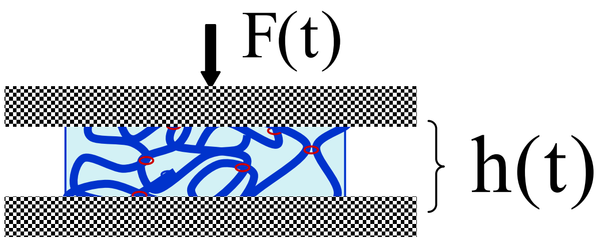
Forces neede to change external parameters

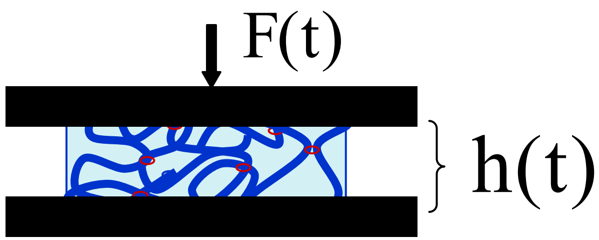
$$R = R(\dot{x}, x; \underline{L, \dot{L}})$$

External parameters

$$F = \frac{\partial R}{\partial \dot{L}}$$ The force needed to change an external parameter p



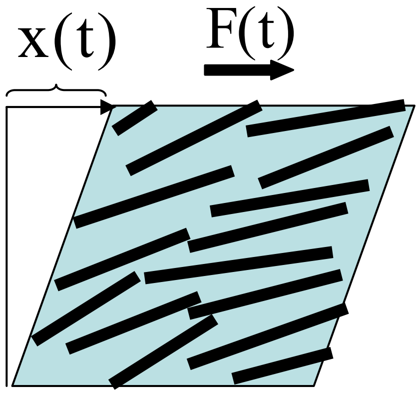




$$F = \frac{\partial R}{\partial \dot{L}}$$

$$F = \frac{\partial R}{\partial \dot{h}}$$

Microscopic expression for stress tensor



$$F = \frac{\partial R}{\partial \dot{x}}$$

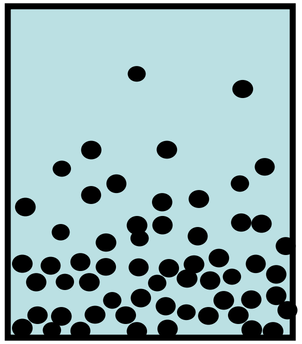
If R involves a velocity gradient tensor, the stress tensor is given by

$$\kappa_{\alpha\beta} = \frac{\partial v_\alpha}{\partial r_\beta}$$

$$\sigma_{\alpha\beta} = \frac{\partial R}{\partial \kappa_{\alpha\beta}}$$

Applications

Sedimentation of colloidal particles



State variables $\phi(\mathbf{r};t)$

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

$$R[\dot{\phi};\phi] = \Phi[\dot{\phi};\phi] + \dot{A}[\dot{\phi};\phi]$$

$$\dot{\phi} = -\nabla \bullet (\phi \mathbf{v}_p)$$

Dissipation function $\Phi = \frac{1}{2}\int d\mathbf{r}\,\xi(\phi)\mathbf{v}_p{}^2$

Free energy $A[\phi] = \int d\mathbf{r}\left[f(\phi) - \rho\mathbf{g}\bullet\mathbf{r}\phi\right]$

Time evolution equation

$$A[\phi] = \int d\mathbf{r}\left[f(\phi) - \rho\mathbf{g}\bullet\mathbf{r}\phi\right]$$

$$\begin{aligned}
\dot{A} &= \int d\mathbf{r}\ \dot{\phi}\left[f'(\phi) - \rho\mathbf{g}\bullet\mathbf{r}\right] \\
&= \int d\mathbf{r}\ \left[-\nabla\bullet(\phi\mathbf{v}_p)\right]\left[f'(\phi) - \rho\mathbf{g}\bullet\mathbf{r}\right] \\
&= \int d\mathbf{r}\ \phi\mathbf{v}_p\bullet\nabla\left[f'(\phi) - \bullet\mathbf{r}\right] \\
&= \int d\mathbf{r}\ \mathbf{v}_p\bullet\left[\nabla\Pi - \rho\mathbf{g}\phi\right]
\end{aligned}$$

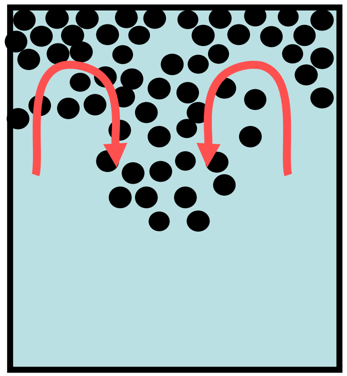
$$\Pi(\phi) = \phi f' - f$$

Osmotic pressure

$$R = \frac{1}{2}\int d\mathbf{r}\xi(\phi)\mathbf{v}_p{}^2 + \int d\mathbf{r}\mathbf{v}_p\bullet\left[\nabla\Pi + \rho g\phi\right]$$

$$\mathbf{v}_p = -\frac{1}{\xi}\left[\nabla\Pi - \rho\mathbf{g}\phi\right] \qquad \frac{\partial\phi}{\partial t} = \nabla\left[\frac{\phi}{\xi}\left(\nabla\Pi - \rho\mathbf{g}\phi\right)\right]$$

Coupling with hydrodynamics



$\mathbf{v}_p$ polymer velocity

$\mathbf{v}_s$ Solvent velocity

$$\mathbf{v} = \phi \mathbf{v}_p + (1-\phi)\mathbf{v}_s$$

Material velocity

$$\Phi = \frac{1}{2}\int d\mathbf{r}\left[\xi(\phi)(\mathbf{v}_p - \mathbf{v})^2 + \frac{1}{2}\eta(\phi)\left(\nabla \mathbf{v}\right)^2\right]$$

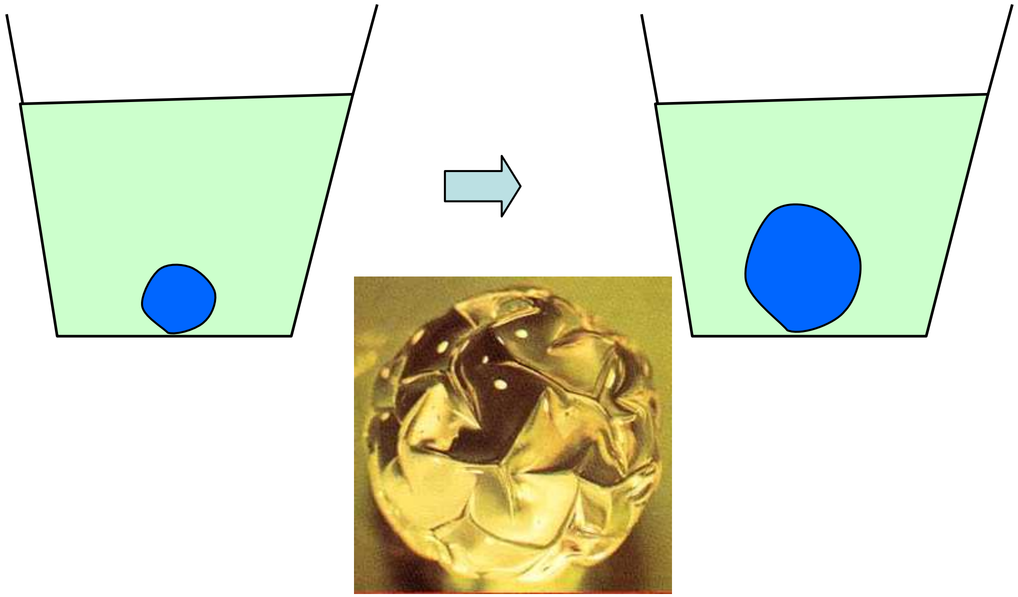
$$\mathbf{v}_p = \mathbf{v} - \frac{1}{\xi}\left[\nabla \Pi - \rho \mathbf{g}\phi\right]$$

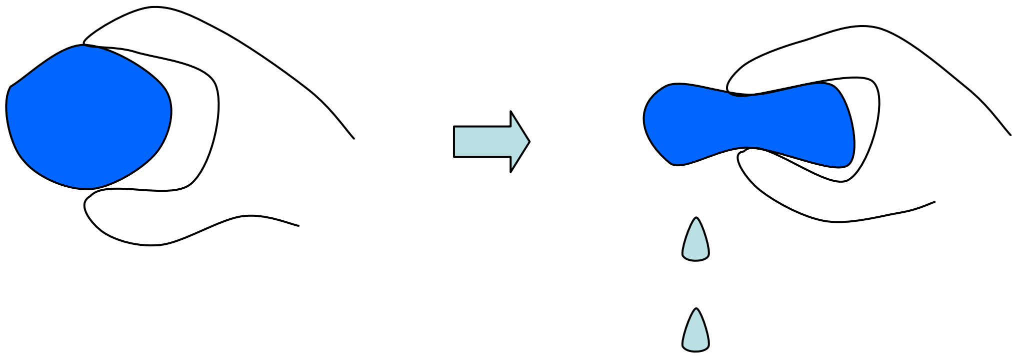
$$\nabla \bullet \mathbf{v} = 0$$

$$\nabla \eta\left[\nabla \mathbf{v} + \nabla \mathbf{v}^t\right]\mathbf{v}_p = \nabla(\Pi + p)\mathbf{v} - \rho \mathbf{g}\phi$$

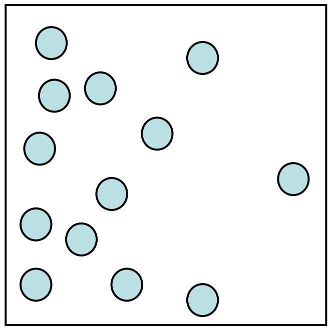
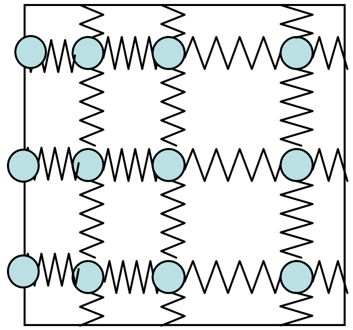
$$\dot{\phi} = -\nabla \bullet (\phi \mathbf{v}_p)$$

Gel dynamics

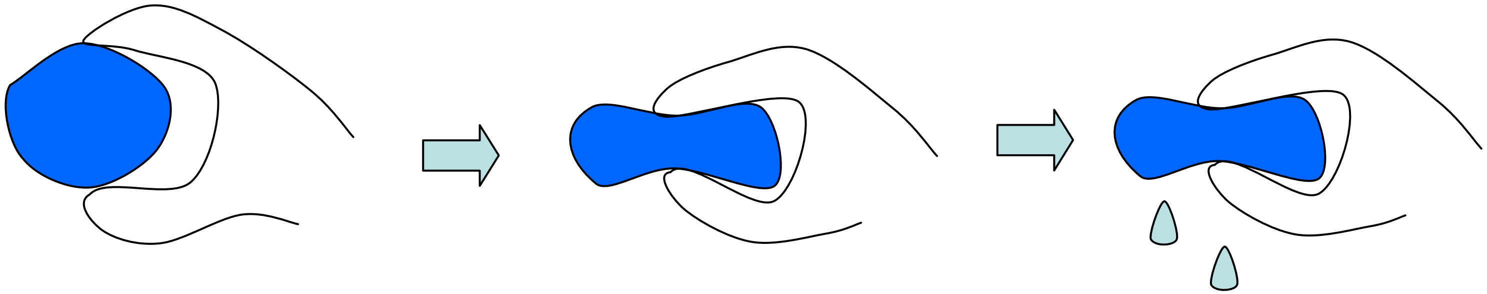




Sol vs Gel

	Sol	Gel
		
State variables	$\phi(\mathbf{r}, t)$	$\mathbf{u}(\mathbf{r}, t) = \mathbf{r}'(\mathbf{r}, t) - \mathbf{r}$
	$\dot{\phi} = -\nabla \bullet (\mathbf{v}_p \phi)$	$\dot{\mathbf{u}} = \mathbf{v}_p$
Free energy	$f(\phi)$	$f(\nabla \mathbf{u})$
Energy dissipation	$\xi(\phi)(\mathbf{v}_p - \mathbf{v})^2 + \frac{1}{2}\eta(\phi)(\nabla \mathbf{v})^2$	$\xi(\phi)(\mathbf{v}_p - \mathbf{v})^2$

For small deformation



$$A[\nabla \mathbf{u}] = \int d\mathbf{r} \left[\frac{1}{2} G (\nabla \mathbf{u})^2 + f(\phi) \right]$$

$$\phi = (1 - \nabla \bullet \mathbf{u}) \phi_0$$

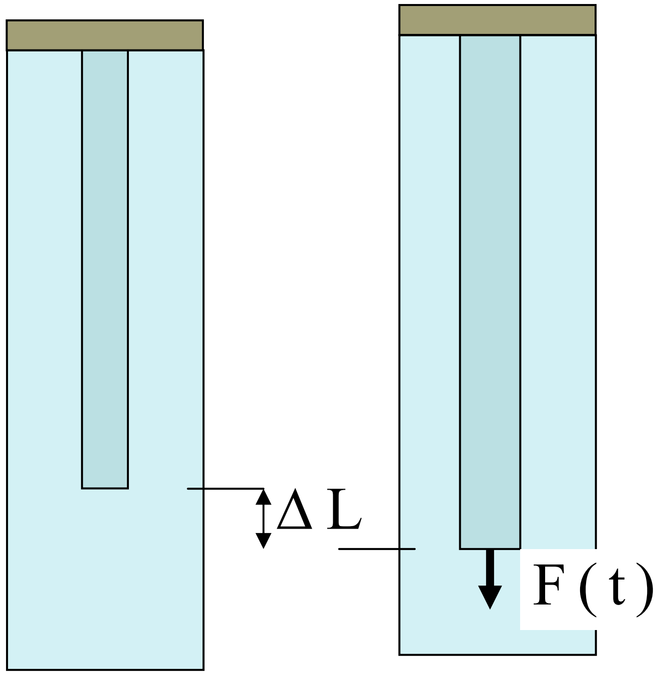
$$\dot{\mathbf{u}} = \mathbf{v}_s - \frac{1}{\xi} \nabla \bullet \boldsymbol{\sigma}$$

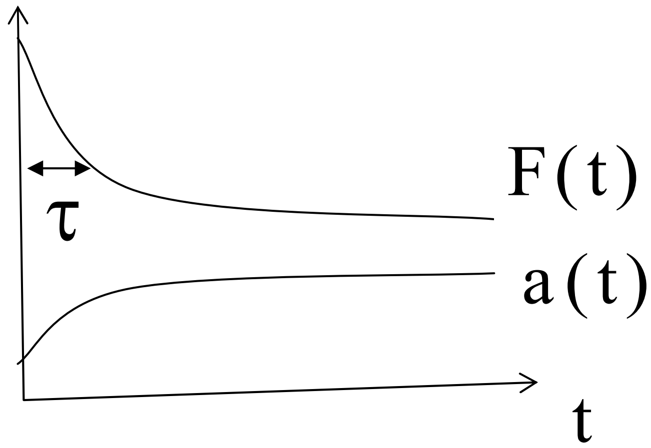
$$\nabla \bullet (\boldsymbol{\sigma} - p\mathbf{I}) = 0$$

$$\boldsymbol{\sigma} = G \left(\nabla \mathbf{u} + \nabla \mathbf{u}^t - \frac{2}{3} \mathbf{I} \nabla \bullet \mathbf{u} \right) - \Pi' \nabla \bullet \mathbf{u}$$

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

Stress Relaxation of a Stretched Gel

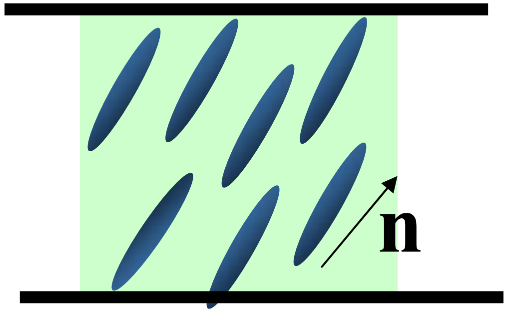




$$\frac{F(\infty)}{F(0)} = \frac{3K}{3K+G}$$

$$\tau \cong \frac{a^2}{\kappa K}$$

Ericksen-Leslie theory



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

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

Rayleighian $$R = \int d\mathbf{r}\left[\Phi(\dot{\mathbf{n}}, \mathbf{v}) + \dot{A} - h\mathbf{n} \bullet \dot{\mathbf{n}} - p\nabla \bullet \mathbf{v}\right]$$

$$\mathbf{n} \bullet \dot{\mathbf{n}} = 0, \quad \nabla \bullet \mathbf{v} = 0$$

$$\frac{\delta R}{\delta \dot{\mathbf{n}}} = 0, \quad \frac{\delta R}{\delta \mathbf{v}} = 0$$

⇨

Ericksen-Leslie equation for $\mathbf{n}(\mathbf{r}, t)$ and $\mathbf{v}(\mathbf{r}, t)$

Dissipation function and free energy

$$\Phi = \frac{a_1}{2}(n_\alpha n_\beta \dot{\varepsilon}_{\alpha\beta})^2 + \frac{a_2}{2}\dot{\varepsilon}_{\alpha\beta}\dot{\varepsilon}_{\alpha\beta} + \frac{a_3}{2} n_\mu n_\nu \dot{\varepsilon}_{\alpha\mu}\dot{\varepsilon}_{\beta\nu} + \frac{a_4}{2}(\tilde{\dot{n}}_\alpha)^2 + \frac{a_5}{2}\tilde{\dot{n}}_\alpha \dot{\varepsilon}_{\alpha\beta} n_\beta$$

$$\dot{\varepsilon}_{\alpha\beta} = \frac{1}{2}\left(\partial_\alpha v_\beta + \partial_\beta v_\alpha\right) \qquad \tilde{\dot{n}}_\alpha = \dot{n}_\alpha - \frac{1}{2}(\partial_\beta v_\alpha - \partial_\alpha v_\beta) n_\beta$$

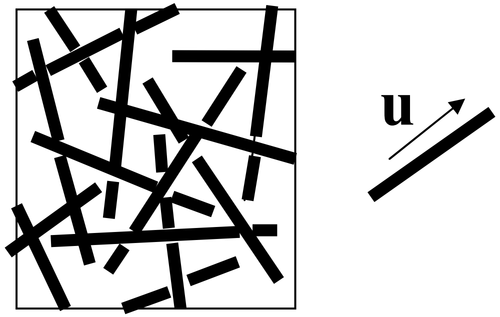
$$A_{tot} = \int d\mathbf{r}\ A \qquad A = \frac{1}{2}K_1(\nabla \bullet \mathbf{n})^2 + \frac{1}{2}K_2(\mathbf{n} \bullet \nabla \times \mathbf{n})^2 + \frac{1}{2}K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2$$

$$\dot{A}_{tot} = \int d\mathbf{r}\left[\frac{\delta A_{tot}}{\delta n_\alpha}\dot{n}_\alpha - \frac{\partial A}{\partial n_{\alpha,\beta}}(\partial_\mu n_\alpha)(\partial_\beta v_\mu)\right]$$

⇨ Ericksen-Leslie equation for $\mathbf{n}(\mathbf{r}, t)$ and $\mathbf{v}(\mathbf{r}, t)$

Parodi’s relation is guranteed

Diffusion equation approach



$\psi(\mathbf{u}, t)$ Distribution function

$$\dot{\psi} = -\mathcal{R} \bullet (\boldsymbol{\omega}\psi)$$

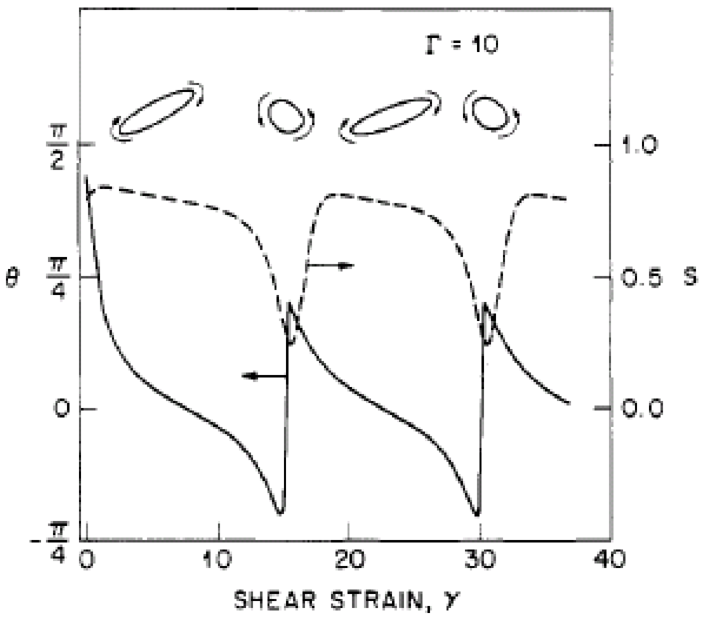
$$\begin{cases} \Phi = \dfrac{n\zeta_r}{2} \displaystyle\int d\mathbf{u}\, (\boldsymbol{\omega} - \boldsymbol{\omega}_0)^2 \psi \\ A = nk_B T \displaystyle\int d\mathbf{u}\, \psi \ln \psi - \dfrac{nU}{2} \displaystyle\int d\mathbf{u} \int d\mathbf{u}' (\mathbf{u} \bullet \mathbf{u}')^2 \psi(\mathbf{u})\psi(\mathbf{u}') \end{cases}$$

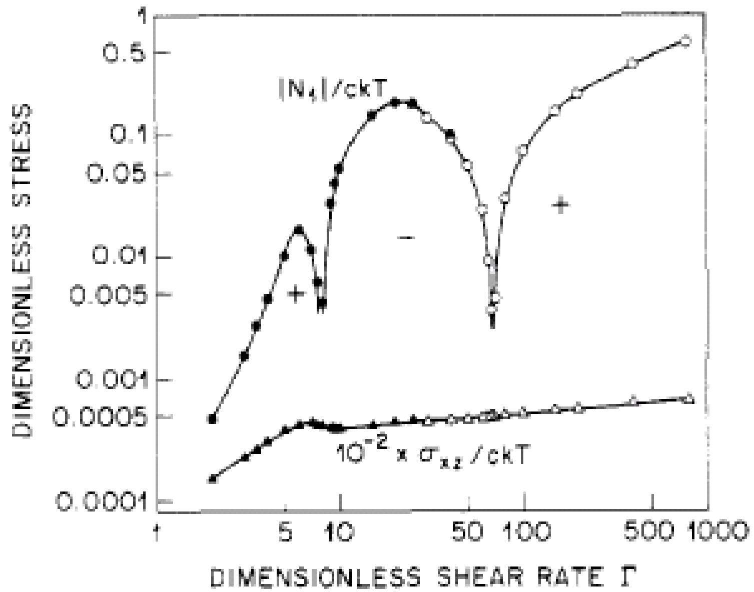
$$\begin{cases} \dfrac{\partial \psi}{\partial t} = D_r \mathcal{R} \bullet \left[\mathcal{R}\psi + \beta\psi\, \mathcal{R} w_{mf}\right] - \mathcal{R} \bullet (\boldsymbol{\omega}_0 \psi) \\ \sigma_{\alpha\beta} = nk_B T \left\langle u_\alpha u_\beta - \dfrac{1}{3}\delta_{\alpha\beta} \right\rangle + n \left\langle [\mathcal{R} w_{mf}(\mathbf{u})]_\alpha u_\beta \right\rangle - p\delta_{\alpha\beta} \end{cases}$$

$$w_{mf}(\mathbf{u}) = -nU \int d\mathbf{u}' (\mathbf{u} \bullet \mathbf{u}')^2 \psi(\mathbf{u}')$$

Non-linear viscoelasticity in nematic state

Larson, Macromolecules





Conclusion

- Many kinetic equations in soft matter dynamics can be derived from Onsager’s variational principle
    - Diffusion and sedimentation of colloidal particles
    - Gel dynamics
    - Hydrodynamics of liquid crystals
- The variational principle is simple and easy to use.

Onsager’s variational principle is a useful principle