

Hydrodynamic theory of polar active fluids

February 2022

1 Onsager reciprocal relations

Consider following free energy function for a system in contact with a heat bath of temperature T

$F \equiv F(\{\phi_i\})$ Here, $\{\phi_i\}$ is a set of independent state variables *i.e.* Temperature, Volume, Position

Variation of this free energy

$$\delta F = \sum_i \frac{\delta F}{\delta \phi_i} \delta \phi_i = - \sum_i f_i \delta \phi_i. \quad \text{With } f_i = -\frac{\delta F}{\delta \phi_i}.$$

The term f_i is the force conjugate to ϕ_i . Consequently, rate of change in free energy will be

$$\frac{dF}{dt} = - \sum_i f_i \frac{d\phi_i}{dt} = - \sum_i f_i \lambda_i$$

Onsager claimed that the fluxes can be written as linear functions of the generalized thermodynamic forces Onsager¹. For some non-equilibrium systems, studies using the principles of statistical mechanics have rigorously demonstrated that this linearity assumption is valid for small fluxes/forces. [Giordano] (If you know more references in this context please let me know). So we have,

$$\lambda_i = \sum_j \mathcal{O}_{ij} f_j \tag{1}$$

\mathcal{O} is a matrix of *Onsager coefficients*, also sometimes called as *kinetic matrix*. It is easy to see that these relations lead to entropy production rate that is quadratic in conjugate force

$$T\theta = -\frac{dF}{dt} = \sum_{ij} \mathcal{O}_{ij} f_i f_j$$

Since $\theta \geq 0$, it follows that \mathcal{O} must be positive definite matrix. For an equilibrium system, one can prove following relations

$$\beta \langle \phi_i f_j \rangle = -\delta_{ij} \quad \langle \phi_i \lambda_j \rangle = -\mathcal{O}_{ji}$$

From this, the following property of the "kinetic matrix" can be derived.

$$\mathcal{O}_{ij} = \epsilon_i \epsilon_j \mathcal{O}_{ji} \quad \epsilon_i \text{ is a time reversal signature of variable } \phi_i$$

So, one can decompose kinetic matrix as follows

$$\mathcal{O}_{ij} = \mathcal{O}_{ij}^d + \mathcal{O}_{ij}^r \quad \text{with, } \mathcal{O}_{ij}^d = \mathcal{O}_{ji}^d \quad \mathcal{O}_{ij}^r = -\mathcal{O}_{ji}^r$$

\mathcal{O}_{ij}^d , dissipative part of the kinetic matrix, describes the dynamics of irreversible processes and hence contributes to entropy production. Reactive part \mathcal{O}_{ij}^r corresponds to reversible processes.

¹Onsager's reciprocal relations is, originally presented as generalisation of Rayleigh's principle of the least energy dissipation.

Time reversal signature

ϵ_i of a state function/variable ϕ_i describes its the behaviour under time reversal transformation.

$$\phi_i(t) = \epsilon_i \phi_i(-t)$$

Invariant under time reversal *i.e* $\epsilon = 1$ position \vec{r} , polarity of particle \vec{p} , concentration ,
chemical activity μ , acceleration $\frac{d^2\vec{r}}{dt^2}$, Stress σ

Reversed under time reversal *i.e* $\epsilon = -1$ velocity $\frac{d\vec{r}}{dt}$, strain rate $\vartheta_{\alpha\beta}$, vorticity ω ,
reaction rate $r_i \sim \frac{dc}{dt}$
 \implies time derivatives changes the sign of ϵ

2 Conservation Laws

Mass Conservation

$$\partial_t \rho + \partial_\alpha (\rho \vartheta_\alpha) = 0 \quad (2)$$

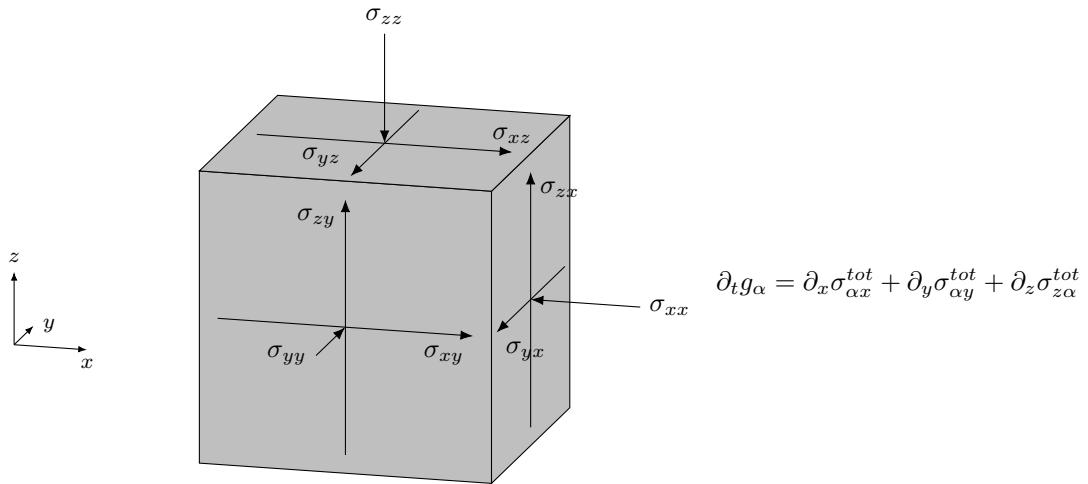
ρ is mass density, ϑ_α is the α -component of the velocity $\boldsymbol{\vartheta}$. ∂_α is derivative w.r.t. co-ordinate x_α . We consider three-dimensional fluid *i.e.* $\alpha \in \{x, y, z\}$. Above equation can be written using substantial/Lagrangian derivative $d/dt = \partial_t + \vartheta_\alpha \partial_\alpha$ as follows,

$$\frac{d\rho}{dt} = -\rho \partial_\alpha \vartheta_\alpha. \quad \text{For in-compressible flow } \rho \text{ is constant, we get } \partial_\alpha \vartheta_\alpha = 0 \quad (3)$$

Momentum Conservation

$$\partial_t g_\alpha = \partial_\beta \sigma_{\alpha\beta}^{tot} \quad (4)$$

$g_\alpha = \rho \vartheta_\alpha$ is a momentum vector and $\sigma_{\alpha\beta}^{tot}$ is the Cauchy stress tensor. For stress tensor, α denotes the direction of the force which is acting on surface area characterised by the unit normal vector β .



(5)

Angular momentum conservation

$$\partial_t l_{\alpha\beta}^{tot} = \partial_\gamma M_{\alpha\beta\gamma}^{tot} \quad (6)$$

$l_{\alpha\beta}^{tot} = \epsilon_{\alpha\beta\gamma} l_\gamma^{tot}$ is an anti-symmetric tensor that describes angular momentum density.

$$l_{\alpha\beta}^{tot} = \begin{bmatrix} 0 & -l_z^{tot} & l_y^{tot} \\ l_z^{tot} & 0 & -l_x^{tot} \\ -l_y^{tot} & l_x^{tot} & 0 \end{bmatrix}$$

l_γ^{tot} is an angular momentum density pseudo-vector. $M_{\alpha\beta\gamma}^{tot}$ is a angular momentum flux and it is anti-symmetric in indices α & β . First two indices shows the torque is in $\alpha\beta$ plane acting on the surface normal to γ . Angular momentum density corresponding to the motion of the fluid $x_\alpha g_\beta - x_\beta g_\alpha$, and intrinsic spin of individual fluid particles is $l_{\alpha\beta}$. So, $l_{\alpha\beta}^{tot} = l_{\alpha\beta} + x_\alpha g_\beta - x_\beta g_\alpha$. Similarly $M_{\alpha\beta\gamma}^{tot}$ can be decomposed as $M_{\alpha\beta\gamma}^\pi + x_\alpha \sigma_{\beta\gamma} - x_\beta \sigma_{\alpha\gamma}$. Here, $M_{\alpha\beta\gamma}^\pi$ is intrinsic angular momentum flux and the other two terms corresponds to orbital angular momentum flux. Lets substitute these values in the Equation 6. Consider following expression

$$\begin{aligned} \partial_t(x_\alpha g_\beta - x_\beta g_\alpha) + \partial_\gamma(x_\alpha \sigma_{\beta\gamma} - x_\beta \sigma_{\alpha\gamma}) &= g_\alpha g_\beta - g_\beta g_\alpha + x_\alpha \partial_t g_\beta - x_\beta \partial_t g_\alpha \\ &\quad \delta_{\gamma\alpha} \sigma_{\beta\gamma} + \delta_{\gamma\beta} \sigma_{\alpha\gamma} + x_\alpha \partial_\gamma \sigma_{\beta\gamma} - x_\beta \partial_\gamma \sigma_{\alpha\gamma} \end{aligned}$$

Now using the momentum conservation equation 4, we have

$$\partial_t(x_\alpha g_\beta - x_\beta g_\alpha) + \partial_\gamma(x_\alpha \sigma_{\beta\gamma} - x_\beta \sigma_{\alpha\gamma}) = \sigma_{\beta\alpha} - \sigma_{\alpha\beta} = 2\sigma_{\alpha\beta}^a.$$

Superscript ' a ' is used to indicate the anti-symmetric part of the stress. From equation 6, it follows that

$$\partial_t l_{\alpha\beta} - \partial_\gamma M_{\alpha\beta\gamma}^\pi = -2\sigma_{\alpha\beta}^a$$

For a simple fluid, $\sigma_{\alpha\beta}^a = 0$ as well as $l_{\alpha\beta} = 0$ so angular momentum equation does not give any new information. But in active fluids, as we will see, anti-symmetric part of the stress tensor need not be zero.

Particle number conservation during chemical reaction

$$\partial_t n_i + \partial_\alpha J_\alpha^i = r_i \quad \text{with, } J_\alpha^i = j_\alpha^i + n_i \vartheta_\alpha \quad (7)$$

$n_i = N_i/V$ is the local number density of i^{th} component. V is the **volume of the control volume** and N_i is the total number of molecules of i^{th} species. J_α^i is particle density flux vector and j_α^i is relative flux, such that

$$n_i \vartheta_\alpha^i = n_i \vartheta_\alpha + j_\alpha^i \quad (8)$$

ϑ_α^i is the velocity of the i^{th} chemical species and ϑ_α is the center of mass velocity. The fluid consists of total \mathcal{N} number of species. Local density of this multi-component fluid is

$$\rho = \sum_{i=1}^{\mathcal{N}} m_i n_i.$$

m_i is the mass of the i^{th} component. Center of mass velocity ϑ_α will be

$$\vartheta_\alpha = \frac{1}{\rho} \sum_{i=1}^{\mathcal{N}} m_i n_i \vartheta_\alpha^i$$

From above equation, it is easy to see that

$$\sum_{i=1}^{\mathcal{N}} m_i n_i \vartheta_\alpha = \sum_{i=1}^{\mathcal{N}} m_i n_i \vartheta_\alpha^i \implies \therefore \text{ from equation 8, we find } \sum_{i=1}^{\mathcal{N}} m_i j_\alpha^i = 0. \quad (9)$$

Let's assume that, in this fluid, there are total R number of reactions taking place. These reactions can be expressed as follows

$$\sum_{i=1}^{\mathcal{N}} a_i^I C_i \rightleftharpoons 0 \implies \sum_{i=1}^{\mathcal{N}} a_i^I m_i = 0. \quad (10)$$

C_i represents the chemical symbol of the i^{th} species. a_i^I is the stoichiometric coefficient. Second equation states that mass is conserved. The total rate of production for i^{th} species will be sum of rate of consumption and production of that species in each chemical reaction,

$$-\sum_{I=1}^{\mathcal{R}} a_i^I r^I = r_i$$

r^I is reaction rate of I^{th} reaction. Using this and eq (10) one can show the following

$$\sum_{i=1}^{\mathcal{N}} m_i r_i = \sum_{I=1}^{\mathcal{R}} r^I \sum_{i=1}^{\mathcal{N}} m_i a_i^I = 0. \quad (11)$$

Juggling the divergence operator : uv rule (integration by parts) for higher dimensions .

Consider following integral

$$\int dV \partial_\gamma (s_{\alpha\beta} t_{\beta\gamma}) = \int dV \partial_\gamma (s_{\alpha\beta}) t_{\beta\gamma} + \int dV s_{\alpha\beta} \partial_\gamma (t_{\beta\gamma})$$

Using Gauss divergence theorem, we can write

$$\int dV \partial_\gamma (s_{\alpha\beta}) t_{\beta\gamma} = - \int dV s_{\alpha\beta} \partial_\gamma (t_{\beta\gamma}) + \oint dS_\gamma s_{\alpha\beta} t_{\beta\gamma}$$

3 Mit Kanonen auf Spatzen schießen : Naiver-stroke equations

This example is also discussed during biological hydrodynamics course offered by Benjamin M. Friedrich, Jan Bruges.

As a fun exercise, in this section, we will use Onsager relations to derive Naiver-stroke equations. Let's start with writing an expression of free energy for a single-component fluid

$$F = pV + \int dV \frac{1}{2} \rho \vec{v}^2$$

using $\vec{g} = \rho \vec{v}$

$$\begin{aligned} \frac{dF}{dt} &= -p \frac{dV}{dt} + \int dV \frac{1}{2} \frac{d}{dt} \left(\frac{\vec{g}^2}{\rho} \right) \\ &= -p \frac{dV}{dt} + \int dV \left(\frac{g_\alpha}{\rho} \frac{dg_\alpha}{dt} - \frac{g_\alpha^2}{\rho^2} \frac{d\rho}{dt} \right) + \oint dS_\beta v_\beta \frac{1}{2} \frac{g_\alpha^2}{\rho^2} \\ &= -p \frac{dV}{dt} + \int dV \left(v_\alpha \frac{dg_\alpha}{dt} - v_\alpha^2 \frac{d\rho}{dt} \right) + \oint dS_\beta v_\beta \frac{1}{2} \frac{g_\alpha^2}{\rho^2} \end{aligned}$$

Using mass conservation (3), momentum conservation (4) and $dV/dt = \int \partial_\alpha v_\alpha dV$

$$= \int dV \left(v_\alpha (\partial_\beta \sigma_{\alpha\beta}^{tot}) + v_\alpha^2 \partial_\beta (\rho v_\beta) - p \partial_\alpha v_\alpha \right) + \oint dS_\beta v_\beta \frac{1}{2} \frac{g_\alpha^2}{\rho^2}$$

Juggling the divergence operator for first two terms, we get

$$\begin{aligned}\frac{dF}{dt} &= \int dV \left(-\partial_\beta \vartheta_\alpha \sigma_{\alpha\beta}^{tot} - \rho \vartheta_\alpha \vartheta_\beta (\partial_\beta \vartheta_\alpha) - p \partial_\alpha \vartheta_\alpha \right) + \oint dS_\beta \left(\vartheta_\beta \frac{1}{2} \frac{g_\alpha^2}{\rho^2} - \sigma_{\beta\alpha}^{tot} \vartheta_\alpha - \rho \vartheta_\alpha^2 \vartheta_\beta \right) \\ &= - \int dV \left(\sigma_{\alpha\beta}^{tot} + \rho \vartheta_\alpha \vartheta_\beta + p \delta_{\alpha\beta} \right) \partial_\beta \vartheta_\alpha + \text{surface integral terms}\end{aligned}$$

$\sigma_{\alpha\beta}^{tot}$ is always symmetric. One can show this with simple scaling-argument (which is also called Cauchy's argument. I am not completely sure about this as I could not find original citation), One can also show the symmetric property by invoking conservation of angular moment. Since the double contraction of the anti-symmetric matrix with symmetric matrix is zero, symmetric part of $\partial_\beta \vartheta_\alpha$ is non-zero contribution to free energy source.

So we have pair of conjugate force and flux. Linear response theory:

$$\vartheta_{\alpha\beta} = \frac{1}{2\eta} \left(\sigma_{\alpha\beta}^{tot} + \rho \vartheta_\alpha \vartheta_\beta + p \delta_{\alpha\beta} \right) \quad \text{with,} \quad \vartheta_{\alpha\beta} = \frac{\partial_\alpha \vartheta_\beta + \partial_\beta \vartheta_\alpha}{2}$$

Substituting this in momentum equation 4,

$$\begin{aligned}\partial_t g_\alpha &= \partial_\beta (2\eta \vartheta_{\alpha\beta} - \rho \vartheta_\alpha \vartheta_\beta - p \delta_{\alpha\beta}) \\ \partial_t g_\alpha + \partial_\beta (\rho \vartheta_\alpha \vartheta_\beta) &= 2\eta \partial_\beta \vartheta_{\alpha\beta} - \partial_\alpha p\end{aligned}$$

For incompressible flow ρ is constant and $\partial_\alpha \vartheta_\alpha = 0$.

$$\begin{aligned}\partial_t g_\alpha + \rho \vartheta_\beta \partial_\beta (\vartheta_\alpha) &= 2\eta \partial_\beta \left(\frac{\partial_\alpha \vartheta_\beta + \partial_\beta \vartheta_\alpha}{2} \right) - \partial_\alpha p \\ \partial_t g_\alpha + \rho \vartheta_\beta \partial_\beta (\vartheta_\alpha) &= \eta \partial_\beta^2 \vartheta_\alpha - \partial_\alpha p\end{aligned}$$

$$\boxed{\rho \frac{D\vartheta_\alpha}{Dt} = \eta \partial_\beta^2 \vartheta_\alpha - \partial_\alpha p} \quad (12)$$

4 Force generation from chemical energy

This example is discussed in [Wang et al].

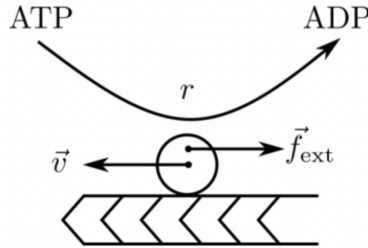


Figure 1: Conversion of chemical energy into mechanical work : Actomyosin-*like* system

Change in free energy for above system,

$$\delta F = -\delta x_\alpha \mathcal{F}_\alpha + \mu_{ATP} \delta c_{ATP} + \mu_{ADP} \delta c_{ADP} + \mu_P \delta c_P \quad (13)$$

Particle number conservation leads to following equations

$$\delta c_{ATP} + \delta c_{ADP} = 0$$

$$\delta c_{ATP} + \delta c_P = 0$$

We substitute above information into equation 13.

$$\begin{aligned}\delta F &= -\delta x_\alpha \mathcal{F}_\alpha + (\mu_{ATP} - \mu_{ADP} - \mu_P) \delta c_{ATP} \\ &= -\delta x_\alpha \mathcal{F}_\alpha + \Delta\mu \delta c_{ATP}\end{aligned}$$

So rate of dissipation is

$$-\frac{dF}{dt} = \vartheta_\alpha \mathcal{F}_\alpha + \Delta\mu r \quad \text{with,} \quad \frac{dc_{ATP}}{dt} = -r$$

This gives a set of conjugate force and fluxes. Now let's look at the nature of coupling between these variables.

	F_n	\mathcal{F}_α	$\Delta\mu$
J_n	ϵ	1	1
ϑ_α	-1	\mathcal{O}_{11}	\mathcal{O}_{12}
r	-1	\mathcal{O}_{12}	\mathcal{O}_{22}

All couplings are dissipative. The coupling \mathcal{O}_{12} relates a vector to scalar, hence it will be only physically meaningful if it is a rank one tensor. On top of this, this coupling should respect the symmetries of a given system. (This is, in general, called Curie's symmetry principle). Here, polarity of filament p_α is a natural choice for a rank one tensor which can be conjugated with \mathcal{O}_{12} .

Now we are ready to do linear response theory,

$$\begin{bmatrix} \vartheta_\alpha \\ r \end{bmatrix} = \begin{bmatrix} \mathcal{O}_{11} & \mathcal{O}_{12} p_\alpha \\ \mathcal{O}_{12} p_\alpha & \mathcal{O}_{22} \end{bmatrix} \begin{bmatrix} \mathcal{F}_\alpha \\ \Delta\mu \end{bmatrix}$$

Since entropy must always increase, above matrix must be positive definite *i.e.* $\mathcal{O}_{11}\mathcal{O}_{22} - \mathcal{O}_{12}^2 > 0$, $\mathcal{O}_{11} > 0$ & $\mathcal{O}_{22} > 0$.

Let's consider a simpler 1D model. We take $\mathcal{O}_{11} = \mathcal{O}_{22} = 1$. So, $0 < \mathcal{O}_{12} < 1$. For an example, let's take $\mathcal{O}_{12} = 0.7$. We now have two variables : \mathcal{F} and $\Delta\mu$. Figure 2 shows a different regimes for this actomyosin system.

5 Equilibrium thermodynamics of a multi-component Polar fluid

The total mass density ρ of a fluid consisting of \mathcal{N} number of species

$$\rho = \sum_{i=1}^{\mathcal{N}} m_i n_i.$$

Note that the density is the function of n_i . Center of mass velocity ϑ_α will be

$$\vartheta_\alpha = \frac{1}{M} \sum_{i=1}^{\mathcal{N}} m_i N_i \vartheta_\alpha^i \quad \text{where} \quad M = \sum_{i=1}^{\mathcal{N}} m_i N_i$$

Here, ϑ_α^i is the α component of the velocity vector of i^{th} chemical species. Consider a volume element of volume V , total momentum of the volume will be $G_\alpha = M\vartheta_\alpha = \rho V\vartheta_\alpha = g_\alpha V$. Here g_α is the momentum density. Our starting will be following free energy density,

$$f(T, n_i, p_\alpha, \partial_\alpha p_\beta, g_\alpha) = \frac{g_\alpha^2}{2\rho} + f_0(T, n_i, p_\alpha, \partial_\alpha p_\beta)$$

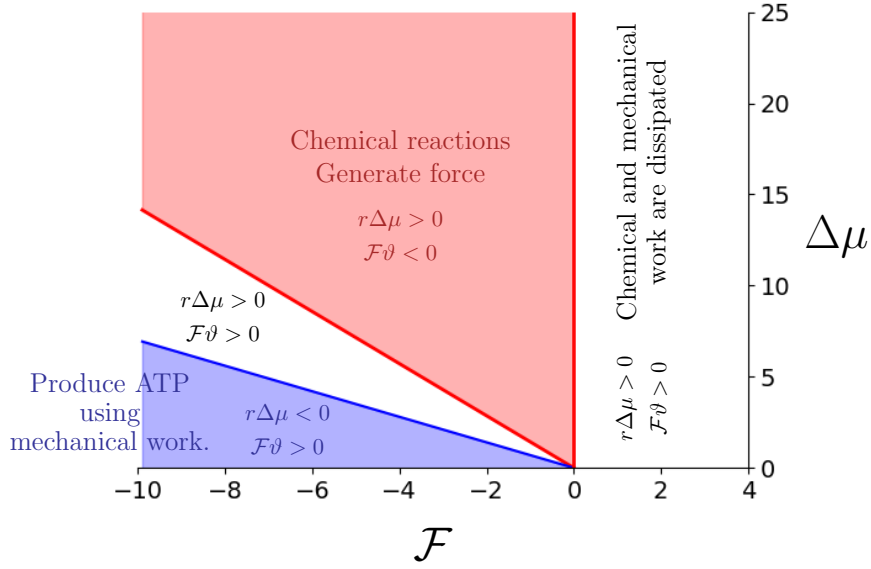


Figure 2: For the parameters in **red** region : Chemical work gets converted into mechanical work(*Regime of molecular motor.*) In the **blue** region : Mechanical work drives phosphorylation of ADP to ATP.

We then have,

$$\left. \frac{\partial f}{\partial g_\alpha} \right|_{T, n_i, p_\alpha} = \vartheta_\alpha$$

Chemical potential,

$$\mu_i^{(0)} \equiv \left. \frac{\partial F_0}{\partial N_i} \right|_{T, p_\alpha} = \frac{\partial f_0}{\partial n_i}$$

Note, center of mass velocity of the volume element also depends of the number density n_i so $\partial F/\partial n_i \neq \partial F_0/\partial n_i$. One can define μ_i^{tot} as follows

$$\mu_i^{tot} = \left. \frac{\delta F}{\delta n_i} \right|_{\{g_\alpha, N_{j \neq i}, T, V\}} = \left. \frac{\partial}{\partial n_i} \frac{g_\alpha^2}{2\rho} \right|_{g_\alpha} + \left. \frac{\delta F_0}{\delta n_i} \right|_{\{N_{j \neq i}, T, V\}}$$

First term on the right hand side simplifies as follows,

$$\left. \frac{\partial}{\partial n_i} \frac{g_\alpha^2}{2\rho} \right|_{g_\alpha} = g_\alpha^2 \frac{\partial}{\partial n_i} \frac{1}{\sum_{l=1}^{\mathcal{N}} m_l n_l} = -\frac{1}{2} m_i \vartheta_\alpha^2$$

this gives,

$$\mu_i^{tot} = -\frac{1}{2} m_i \vartheta_\alpha^2 + \mu_i. \quad (14)$$

Hydro-static pressure,

$$\begin{aligned} P &= - \left. \frac{\partial F_0}{\partial V} \right|_{T, N_i, p_\alpha} = - \left. \frac{\partial (f_0 V)}{\partial V} \right|_{T, N_i, p_\alpha} \\ &= -f_0 - V \left. \frac{\partial f_0}{\partial n_k} \times \frac{\partial n_k}{\partial V} \right|_{T, N_i, p_\alpha} = -f_0 - V \mu_k^{(0)} \left. \frac{\partial (N_k/V)}{\partial V} \right|_{T, N_i, p_\alpha} \end{aligned}$$

$$= -f_0 + \sum_k \mu_k^{(0)} n_k \quad (15)$$

Functional derivative w.r.t. field y_i .

Consider an arbitrary free energy density function, $f(y_i, \partial_\alpha y_i)$, which depends not only a function of field y_i but also its spatial gradient $\partial_\alpha y_i$. Here we will show that, if one can ignore the boundary effects, the function derivative $\delta f / \delta y_i$ can be written as

$$\frac{\delta f}{\delta y_i} = \frac{\partial f}{\partial y_i} - \partial_\alpha \frac{\partial f}{\partial (\partial_\alpha y_i)}$$

Proof :

$$F_0 = \int dV f(y_i, \partial_\alpha y_i)$$

$$\delta F_0 = \int dV \left(\frac{\partial f}{\partial y_i} dy_i + \frac{\partial f}{\partial (\partial_\alpha y_i)} d\partial_\alpha y_i \right) = \int dV \left(\frac{\partial f}{\partial y_i} dy_i + \frac{\partial f}{\partial (\partial_\alpha y_i)} \partial_\alpha dy_i \right)$$

In the last step, we exchanged the position of the operators ∂_α and d as they are commutative. Now we perform integration by parts for the second term inside the integral, this gives

$$\int dV \frac{\partial f}{\partial (\partial_\alpha y_i)} \partial_\alpha dy_i = \oint dS_\alpha \frac{\partial f}{\partial (\partial_\alpha y_i)} dy_i - \int dV \partial_\alpha \frac{\partial f}{\partial (\partial_\alpha y_i)} dy_i.$$

Note, we are working three dimensions so the integration by parts will yield a surface integral instead of simple boundary terms which one gets in single dimensional case. Using above expression, we can finally write,

$$\delta F_0 = \int dV \left(\frac{\partial f}{\partial y_i} dy_i - \partial_\alpha \frac{\partial f}{\partial (\partial_\alpha y_i)} dy_i \right) + \oint dS_\alpha \frac{\partial f}{\partial (\partial_\alpha y_i)} dy_i$$

Now if we ignore boundary effects, we can write

$$\delta F_0 = \int dV \left(\frac{\partial f}{\partial y_i} dy_i - \partial_\alpha \frac{\partial f}{\partial (\partial_\alpha y_i)} dy_i \right).$$

We were interested in the change of f as y_i changes. Integration by parts allowed us to write integral such that it can be interpreted as $\delta F_0 = \int dV \delta f / \delta y_i dy_i$. This finally gives the following expression,

$$\frac{\delta f}{\delta y_i} = \frac{\partial f}{\partial y_i} - \partial_\alpha \frac{\partial f}{\partial (\partial_\alpha y_i)}$$

And, molecular field h_α ,

$$\begin{aligned} h_\alpha &= -\frac{\delta f}{\delta p_\alpha} \quad \text{Functional derivative} \\ &= -\frac{\partial f_0}{\partial p_\alpha} + \partial_\beta \frac{\partial f_0}{\partial (\partial_\beta p_\alpha)} \end{aligned} \quad (16)$$

Molecular field is a thermodynamic quantity (It does not include the boundary effects). Considering boundary effects, the change in the free energy as infinitesimal change δp_α in the polar field p_α will be

$$\delta F = - \int dV h_\alpha \delta p_\alpha + \oint dS_\beta \frac{\partial f}{\partial (\partial_\beta p_\alpha)} \delta p_\alpha$$

5.1 Translation invariance leads to Gibbs-Duhem relation

In this section, assuming no external fields,, we will impose translation invariance to the free energy functional and as a consequence see how it leads to Gibbs-Duhem equation. Consider a volume element Ω in a polar active fluid. If we purely translate this volume element by a small and constant vector δx_α , the free energy of the enclosed inside the new volume $\tilde{\Omega}$ should be same. In other words, the free energy of fluid enclosed in the volume should not depend on the position of the volume element. We will first calculate the expression for the change in free energy due to infinitesimal translation and then equate it to zero. Analogous to Reynold's transport theorem, for the case of pure translation, the change in Free energy δF can be written as

$$\delta F = \int dV \delta f + \oint dS_\alpha \delta x_\alpha f \quad (17)$$

$$\begin{aligned} \delta F &= \int dV \left[\vartheta_\alpha \delta g_\alpha + \mu_i^{tot} \delta n_i - h_\alpha \delta p_\alpha \right] + \oint dS_\beta \frac{\partial f}{\partial (\partial_\beta p_\alpha)} \delta p_\alpha + \oint dS_\alpha \delta x_\alpha f \\ &= \int dV \left[\vartheta_\alpha \delta g_\alpha + \mu_i^{tot} \delta n_i - h_\alpha \delta p_\alpha \right] + \oint dS_\beta \left(\frac{\partial f}{\partial (\partial_\beta p_\alpha)} \delta p_\alpha + f \delta x_\alpha \delta_{\alpha\beta} \right) \end{aligned} \quad (18)$$

We will now express the differentials in terms of gradients, *e.g.* $\delta z(x) = -\partial_\beta z \delta x_\beta$, this gives

$$\delta F = \int dV \left[-\vartheta_\alpha (\partial_\beta g_\alpha) \delta x_\beta - \mu_i^{tot} (\partial_\beta n_i) \delta x_\beta + h_\alpha (\partial_\beta p_\alpha) \delta x_\beta \right] + \oint dS_\beta \left(-\frac{\partial f}{\partial (\partial_\beta p_\alpha)} (\partial_\beta p_\alpha) \delta x_\beta + f \delta x_\alpha \delta_{\alpha\beta} \right)$$

Using integration by parts, once can shift the exchange divergence operator acting variables to their conjugate fields *e.g.*

$$\delta x_\beta \int \vartheta_\alpha (\partial_\beta g_\alpha) = \delta x_\beta \oint dS_\beta \vartheta_\gamma g_\gamma - \delta x_\beta \int dV \partial_\beta \vartheta_\alpha g_\alpha$$

By definition, δx_β is constant so it is taken out of integral. This yields,

$$\delta F = \int dV \left[(\partial_\beta \vartheta_\alpha) g_\alpha + (\partial_\beta \mu_i^{tot}) n_i + h_\alpha (\partial_\beta p_\alpha) \right] \delta x_\beta + \oint dS_\beta \left[\left(f - \vartheta_\gamma g_\gamma - \mu_i^{tot} n_i \right) \delta_{\beta\alpha} \delta x_\alpha - \frac{\partial f}{\partial (\partial_\beta p_\kappa)} (\partial_\alpha p_\kappa) \delta x_\alpha \right]$$

Term $f - \vartheta_\gamma g_\gamma - \mu_i^{tot} n_i$, is nothing but hydrostatic pressure.

$$\begin{aligned} f - \vartheta_\gamma g_\gamma - \mu_i^{tot} n_i &= f_0 + \frac{g_\gamma^2}{2\rho} - \frac{g_\gamma^2}{\rho} - \mu_i^{tot} n_i \\ &= f_0 - \frac{g_\gamma^2}{2\rho} - \left(\frac{1}{2} m_i \vartheta_\alpha^2 + \mu_i \right) n_i \\ &= f_0 - \mu_i n_i = -\Pi \quad \frac{1}{2} m_i n_i \vartheta_\alpha^2 = \frac{\rho}{2} \vartheta_\alpha^2 = \frac{g_\alpha^2}{2\rho} \end{aligned}$$

The surface contribution, usually identified as equilibrium stress (also called Ericksen stress in the context of liquid crystals) is

$$\sigma_{\beta\alpha}^{eq} = (f_0 - \mu_i n_i) \delta_{\alpha\beta} - \frac{\partial f}{\partial (\partial_\beta p_\kappa)} (\partial_\alpha p_\kappa) \quad (19)$$

As discussed earlier, $\delta F = 0$. So one can straightforwardly write,

$$\begin{aligned} -\partial_\alpha \sigma_{\beta\alpha}^{eq} &= (\partial_\beta \vartheta_\alpha) g_\alpha + (\partial_\alpha \mu_i^{tot}) n_i + h_\beta (\partial_\alpha p_\beta) \\ &= (\partial_\alpha \mu_i) n_i + h_\beta (\partial_\alpha p_\beta) \end{aligned} \quad (20)$$

Above equation is generalisation of Gibbs-Duhem equation for polar systems.

6 Imposing rotational invariance: Characteristic oddity

Consider active transformation: infinitesimal rotation of fluid element by some angle θ_α . The resultant displacement field will be

$$\delta x_\alpha = \epsilon_{\alpha\beta\gamma} \theta_\beta x_\gamma$$

A solid rotation, as above, should not change the free energy of the fluid, hence we expect that δF for above transformation must be zero. Our starting point is the equation 18.

$$\delta F = \int dV \left[\vartheta_\alpha \delta g_\alpha + \mu_i^{tot} \delta n_i - h_\alpha \delta p_\alpha \right] + \oint dS_\beta \left(\frac{\partial f}{\partial (\partial_\beta p_\alpha)} \delta p_\alpha + f \delta x_\alpha \delta_{\alpha\beta} \right) \quad (21)$$

Let's first simplify the terms inside the volume integral. Each momentum vector is getting rotated as well as translated, hence the change in momentum vector is

$$\delta g_\alpha = \epsilon_{\alpha\beta\gamma} \theta_\beta g_\gamma - \partial_\beta g_\alpha \delta x_\beta \quad (22)$$

Now, note that the divergence of the displacement field is zero.

$$\partial_\beta \delta x_\beta = \partial_\beta (\epsilon_{\beta\kappa\gamma} \theta_\kappa x_\gamma) = \epsilon_{\beta\kappa\gamma} \theta_\kappa \delta_{\beta\gamma} = 0 \quad \because \epsilon_{\beta\kappa\beta} = 0$$

From this observation, it follows that,

$$\oint dS_\beta \vartheta_\alpha g_\alpha \delta x_\beta = \int dV \partial_\beta (\vartheta_\alpha g_\alpha) \delta x_\beta.$$

We can now simplify following integral

$$\begin{aligned} \int dV \vartheta_\alpha \delta g_\alpha &= \int dV \left[(\epsilon_{\alpha\beta\gamma} \theta_\beta g_\gamma) \vartheta_\alpha - \vartheta_\alpha \partial_\beta g_\alpha \delta x_\beta \right] \\ &= \int dV (\epsilon_{\alpha\beta\gamma} \theta_\beta g_\gamma) \vartheta_\alpha - \oint dS_\beta \delta x_\beta \vartheta_\alpha g_\alpha + \int dV g_\alpha (\partial_\beta \vartheta_\alpha) \delta x_\beta \\ &= - \oint dS_\beta \delta x_\beta \vartheta_\alpha g_\alpha + \int dV g_\alpha (\partial_\beta \vartheta_\alpha) \delta x_\beta \end{aligned} \quad (23)$$

Using vector triple product, it follows that that first term in second expression is zero. $\because \vartheta_\alpha \parallel g_\alpha$. Polarity vector p_α will transform similar under rotation like momentum vector (22), hence

$$\int dV h_\alpha \delta p_\alpha = \int dV (\epsilon_{\alpha\beta\gamma} \theta_\beta p_\gamma - h_\alpha (\partial_\beta p_\alpha) \delta x_\beta). \quad (24)$$

Scalar like n_i will tranform as $\delta n_i = -\partial_\beta n_i \delta x_\beta$. Therefore

$$\int dV \mu_i^{tot} \delta n_i \delta x_\beta = \oint dS_\beta \delta x_\beta \mu_i^{tot} n_i - \delta x_\beta \int dV \partial_\beta \mu_i^{tot} n_i. \quad (25)$$

Substituting 23, 24 and 25 in equation 21, we get

$$\delta F = \int dV \left[(\partial_\beta \mu_i) n_i \delta x_\beta - h_\alpha \epsilon_{\alpha\beta\gamma} \theta_\beta p_\gamma + h_\alpha (\partial_\beta p_\alpha) \delta x_\beta \right] + \oint dS_\beta \left[(f_0 - \mu_i n_i) \delta x_\beta + \frac{\partial f}{\partial (\partial_\beta p_\kappa)} (\epsilon_{\kappa\delta\gamma} \theta_\delta p_\gamma - \partial_\alpha p_\kappa \delta x_\alpha) \right]$$

Now using Gibbs-Duhem Equation (20), we get

$$\begin{aligned} \delta F &= \int dV \left[\partial_\alpha (-\sigma_{\beta\alpha}^{eq}) \delta x_\beta - h_\alpha \epsilon_{\alpha\beta\gamma} \theta_\beta p_\gamma \right] + \oint dS_\beta \left[\sigma_{\beta\alpha}^{eq} \delta x_\alpha + \frac{\partial f}{\partial (\partial_\beta p_\kappa)} (\epsilon_{\kappa\delta\gamma} \theta_\delta p_\gamma) \right] \\ &= \int dV \left[(-\sigma_{\alpha\beta}^{eq} + p_\beta h_\alpha) \epsilon_{\kappa\beta\alpha} \theta_\kappa \right] + \oint dS_\beta \left[\frac{\partial f}{\partial (\partial_\beta p_\alpha)} p_\gamma \epsilon_{\kappa\gamma\alpha} \theta_\kappa \right] \end{aligned}$$

The surface terms show the contribution to δF due to Equilibrium intrinsic angular momentum flux $M_{\alpha\beta\gamma}^e$. Where,

$$M_{\alpha\beta\gamma}^e = \frac{\partial f}{\partial(\partial_\gamma p_\alpha)} p_\alpha - \frac{\partial f}{\partial(\partial_\gamma p_\beta)} p_\beta \quad (26)$$

Angular momentum flux across the small surface dS_γ is $M_{\alpha\beta\gamma}^e dS_\gamma$. So the change in the free energy will be the work done due to this torque. Since the $\delta F = 0$ is for any small θ_κ , we finally have

$$\partial_\gamma M_{\alpha\beta\gamma}^e = 2\sigma_{\alpha\beta}^{e,a} + (p_\alpha h_\beta - p_\beta h_\alpha) \quad (27)$$

Note that while defining the free energy, we did not take into account the kinetic energy contribution due to intrinsic rotation. This is equivalent of saying $l_{\alpha\beta} = 0$. So the angular momentum conservation will get modified to

$$\partial_\gamma M_{\alpha\beta\gamma}^\pi = 2\sigma_{\alpha\beta}^{tot,a} \quad (28)$$

Subtracting equation 27 from 28

$$\partial_\gamma M_{\alpha\beta\gamma}^\pi - \partial_\gamma M_{\alpha\beta\gamma}^e = 2(\sigma_{\alpha\beta}^{tot,a} - \sigma_{\alpha\beta}^{e,a}) - (p_\alpha h_\beta - p_\beta h_\alpha) \quad (29)$$

This suggest that, at non-equilibrium, there will be contribution to the stress due to molecular field.

7 Putting everything together: Finding conjugate pairs

$$\frac{dF}{dt} = \int dV \left[\vartheta_\alpha \frac{\partial g_\alpha}{\partial t} + \mu_i^{tot} \frac{\partial n_i}{\partial t} - h_\alpha \frac{\partial p_\alpha}{\partial t} \right] + \oint dS_\beta \left(\frac{\partial f}{\partial (\partial_\beta p_\alpha)} \frac{\partial p_\alpha}{\partial t} \right)$$

Using momentum conservation (4) and particle number conservation (7) ,

$$\begin{aligned} &= \int dV \left[\vartheta_\alpha (\partial_\beta \sigma_{\alpha\beta}^{tot}) + \mu_i^{tot} (r_i - \partial_\alpha (n_i \vartheta_\alpha + j_\alpha^i)) - h_\alpha \frac{\partial p_\alpha}{\partial t} \right] + \oint dS_\beta \left(\frac{\partial f}{\partial (\partial_\beta p_\alpha)} \frac{\partial p_\alpha}{\partial t} \right) \\ &= \int dV \left[-(\partial_\beta \vartheta_\alpha) \sigma_{\alpha\beta}^{tot} + \mu_i^{tot} (r_i - \partial_\alpha (n_i \vartheta_\alpha + j_\alpha^i)) - h_\alpha \frac{\partial p_\alpha}{\partial t} \right] + \oint dS_\beta \left(\vartheta_\beta \sigma_{\alpha\beta}^{tot} + \frac{\partial f}{\partial (\partial_\beta p_\alpha)} \frac{\partial p_\alpha}{\partial t} \right) \\ &= \int dV \left[-(\partial_\beta \vartheta_\alpha) \sigma_{\alpha\beta}^{tot} + \mu_i^{tot} r_i + (n_i \vartheta_\alpha + j_\alpha^i) (\partial_\alpha \mu_i^{tot}) - h_\alpha \frac{\partial p_\alpha}{\partial t} \right] \\ &\quad + \oint dS_\beta \left(\vartheta_\beta \sigma_{\alpha\beta}^{tot} - \mu_i^{tot} J_\alpha^i + \frac{\partial f}{\partial (\partial_\beta p_\alpha)} \frac{\partial p_\alpha}{\partial t} \right) \end{aligned}$$

Writing $\partial_\alpha \mu_i^{tot}$ as $(-m_i \vartheta_\gamma \partial_\alpha \vartheta_\gamma + \partial_\alpha \mu_i)$, (See Eq14) , and then using equations 10 and 11, we get

$$\begin{aligned} &= \int dV \left[-(\partial_\beta \vartheta_\alpha) \sigma_{\alpha\beta}^{tot} + \mu_i r_i - \rho \vartheta_\alpha \vartheta_\beta \partial_\alpha \vartheta_\beta + n_i \vartheta_\alpha \partial_\alpha \mu_i + j_\alpha^i \partial_\alpha \mu_i - h_\alpha \frac{\partial p_\alpha}{\partial t} \right] \\ &\quad + \oint dS_\beta \left(\vartheta_\beta \sigma_{\alpha\beta}^{tot} - \mu_i^{tot} J_\alpha^i + \frac{\partial f}{\partial (\partial_\beta p_\alpha)} \frac{\partial p_\alpha}{\partial t} \right) \end{aligned}$$

Now adding and subtracing $\vartheta_\alpha h_\beta \partial_\alpha p_\beta$ and using Gibbs Duhem equation,

$$\begin{aligned} &= \int dV \left[-(\partial_\beta \vartheta_\alpha) \sigma_{\alpha\beta} + \mu_i r_i + \vartheta_\alpha (-\partial_\beta \sigma_{\alpha\beta}^e) + j_\alpha^i \partial_\alpha \mu_i - \vartheta_\alpha h_\beta \partial_\alpha p_\beta - h_\alpha \frac{\partial p_\alpha}{\partial t} \right] \\ &\quad + \oint dS_\beta \left(\vartheta_\beta \sigma_{\alpha\beta}^{tot} - \mu_i^{tot} J_\alpha^i + \frac{\partial f}{\partial (\partial_\beta p_\alpha)} \frac{\partial p_\alpha}{\partial t} \right) \\ &= \int dV \left[-(\partial_\beta \vartheta_\alpha) (\sigma_{\alpha\beta} - \sigma_{\alpha\beta}^e) + \mu_i r_i + j_\alpha^i \partial_\alpha \mu_i - h_\alpha \frac{dp_\alpha}{dt} \right] \\ &\quad + \oint dS_\beta \left(\vartheta_\alpha \sigma_{\alpha\beta}^{tot} - \vartheta_\alpha \sigma_{\alpha\beta}^{eq} - \mu_i^{tot} J_\alpha^i + \frac{\partial f}{\partial (\partial_\beta p_\alpha)} \frac{\partial p_\alpha}{\partial t} \right) \end{aligned}$$

Now, in surface integral, we substitute expression for $\sigma_{\alpha\beta}^{eq}$ from equation 19. simultaneously we expand μ_i^{tot} and J_α^i . After simplification, we get

$$\begin{aligned} &= \int dV \left[-(\partial_\beta \vartheta_\alpha) (\sigma_{\alpha\beta} - \sigma_{\alpha\beta}^e) + \mu_i r_i + j_\alpha^i \partial_\alpha \mu_i - h_\alpha \frac{dp_\alpha}{dt} \right] \\ &\quad + \oint dS_\beta \left(\vartheta_\alpha \sigma_{\alpha\beta} - \vartheta_\alpha f - \mu_i j_\alpha^i + \frac{\partial f}{\partial (\partial_\beta p_\alpha)} \frac{dp_\alpha}{dt} \right) \end{aligned}$$

This is already a lot of progress. Above expression for bulk free energy can be interpreted as work done due to the contributions by (gradient in velocity :shear flow?)stress, chemical reactions, movement of chemicals

within the fluid and change in polarity. Surface effects have contribution due to stresses, free energy as well chemical flux and [what is the meaning of final term?](#).

Now we will decompose the gradient of velocity into symmetric and skew-symmetric matrix.

$$\vartheta_{\alpha\beta} = \frac{1}{2}(\partial_\alpha \vartheta_\beta + \partial_\beta \vartheta_\alpha) \quad \omega_{\alpha\beta} = \frac{1}{2}(\partial_\alpha \vartheta_\beta - \partial_\beta \vartheta_\alpha) \quad (30)$$

$\vartheta_{\alpha\beta}$ is strain rate tensor and $\omega_{\alpha\beta}$ is called vorticity. Stress tensor can also has symmetric and anti-symmetric components. It is natural to decomposed velocity gradient as well as stress tensor in these components since the double contraction of symmetric and anti-symmetric tensor is zero. This gives,

$$(\partial_\beta \vartheta_\alpha)(\sigma_{\alpha\beta} - \sigma_{\alpha\beta}^e) = \vartheta_{\alpha\beta}(\sigma_{\alpha\beta}^s - \sigma_{\alpha\beta}^{e,s}) - \omega_{\alpha\beta}(\sigma_{\alpha\beta}^a - \sigma_{\alpha\beta}^{e,a}) \quad (31)$$

$$\begin{aligned} \frac{dF}{dt} = \int dV \left[-\vartheta_{\alpha\beta}(\sigma_{\alpha\beta}^s - \sigma_{\alpha\beta}^{e,s}) + \omega_{\alpha\beta}(\sigma_{\alpha\beta}^a - \sigma_{\alpha\beta}^{e,a} + h_\alpha p_\beta) + \mu_i r_i + j_\alpha^i \partial_\alpha \mu_i - h_\alpha \frac{Dp_\alpha}{Dt} \right] \\ + \oint dS_\beta \left(\vartheta_\alpha \sigma_{\alpha\beta} - \vartheta_\alpha f - \mu_i j_\alpha^i + \frac{\partial f}{\partial(\partial_\beta p_\alpha)} \frac{dp_\alpha}{dt} \right) \end{aligned}$$

In above step, $h_\alpha p_\beta \omega_{\alpha\beta}$ is added and subtracted, and the definition of co-rotational derivative $D/Dt = \partial_t + \vartheta_\gamma \partial_\gamma + \omega_{\alpha\beta}$ is used. Now using equation 29, we can simplify about equation further

$$\begin{aligned} = \int dV \left[-\vartheta_{\alpha\beta} \sigma_{\alpha\beta}^{d,s} + \frac{1}{2} \omega_{\alpha\beta} (\partial_\gamma M_{\alpha\beta\gamma}^d + (h_\beta p_\alpha + h_\alpha p_\beta)) + \mu_i r_i + j_\alpha^i \partial_\alpha \mu_i - h_\alpha \frac{Dp_\alpha}{Dt} \right] \\ + \oint dS_\beta \left(\vartheta_\alpha \sigma_{\alpha\beta} - \vartheta_\alpha f - \mu_i j_\alpha^i + \frac{\partial f}{\partial(\partial_\beta p_\alpha)} \frac{dp_\alpha}{dt} \right) \end{aligned}$$

In the above expression, deviatoric stress is defined as $\sigma_{\alpha\beta}^{d,s} = \sigma_{\alpha\beta}^s - \sigma_{\alpha\beta}^{e,s}$. Now, using $\omega_{\alpha\beta}(h_\beta p_\alpha + h_\alpha p_\beta) = 0$ and juggling the divergence operator from $M_{\alpha\beta\gamma}^d$ to $\omega_{\alpha\beta}$

$$\begin{aligned} = \int dV \left[-\vartheta_{\alpha\beta} \sigma_{\alpha\beta}^{d,s} - \frac{1}{2} (\partial_\gamma \omega_{\alpha\beta}) M_{\alpha\beta\gamma}^d + \mu_i r_i + j_\alpha^i \partial_\alpha \mu_i - h_\alpha \frac{Dp_\alpha}{Dt} \right] \\ + \oint dS_\beta \left(\vartheta_\alpha \sigma_{\alpha\beta} + \frac{1}{2} \omega_{\alpha\gamma} M_{\alpha\gamma\beta}^d - \vartheta_\alpha f - \mu_i j_\alpha^i + \frac{\partial f}{\partial(\partial_\beta p_\alpha)} \frac{dp_\alpha}{dt} \right) \end{aligned}$$

Writing down $M_{\alpha\beta\gamma}^d$ as $M_{\alpha\beta\gamma}^\pi - M_{\alpha\beta\gamma}^e$ and then using equation 26

$$\begin{aligned} = \int dV \left[-\vartheta_{\alpha\beta} \sigma_{\alpha\beta}^{d,s} - \frac{1}{2} (\partial_\gamma \omega_{\alpha\beta}) M_{\alpha\beta\gamma}^d + \mu_i r_i + j_\alpha^i \partial_\alpha \mu_i - h_\alpha \frac{Dp_\alpha}{Dt} \right] \\ + \oint dS_\beta \left(\vartheta_\alpha \sigma_{\alpha\beta} + \frac{1}{2} \omega_{\alpha\gamma} M_{\alpha\gamma\beta}^\pi - \frac{1}{2} \omega_{\alpha\gamma} \frac{\partial f}{\partial(\partial_\beta p_\gamma)} p_\alpha + \frac{1}{2} \omega_{\alpha\gamma} \frac{\partial f}{\partial(\partial_\beta p_\alpha)} p_\gamma - \vartheta_\alpha f - \mu_i j_\alpha^i + \frac{\partial f}{\partial(\partial_\beta p_\alpha)} \frac{dp_\alpha}{dt} \right) \end{aligned}$$

Simplifying surface integral using

$$-\frac{1}{2} \omega_{\alpha\gamma} \frac{\partial f}{\partial(\partial_\beta p_\gamma)} p_\alpha + \frac{1}{2} \omega_{\alpha\gamma} \frac{\partial f}{\partial(\partial_\beta p_\alpha)} p_\gamma = -\frac{1}{2} \omega_{\alpha\gamma} \frac{\partial f}{\partial(\partial_\beta p_\gamma)} p_\alpha - \frac{1}{2} \omega_{\gamma\alpha} \frac{\partial f}{\partial(\partial_\beta p_\alpha)} p_\gamma = -\omega_{\alpha\gamma} \frac{\partial f}{\partial(\partial_\beta p_\alpha)} p_\gamma,$$

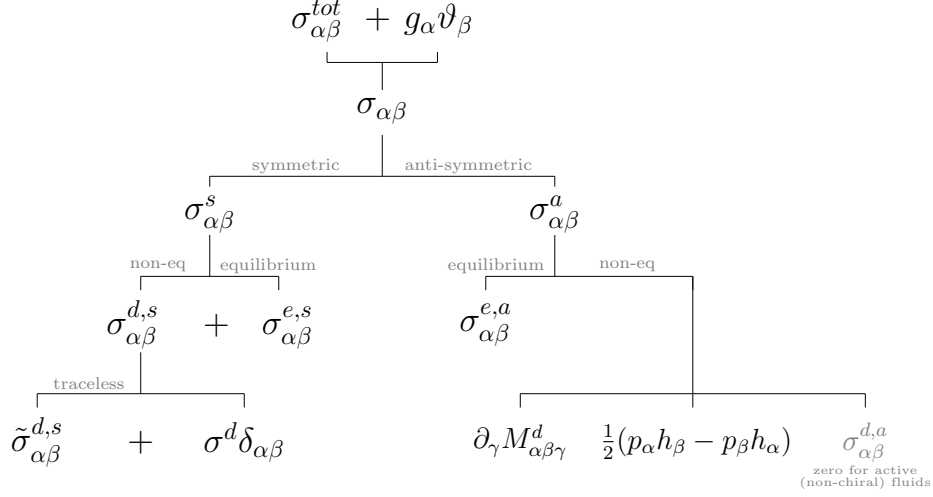


Figure 3: Decomposition of stress tensor

one finally gets the expression for rate of free energy change.

$$\begin{aligned} \frac{dF}{dt} = \int dV \left[-\vartheta_{\alpha\beta} \sigma_{\alpha\beta}^{d,s} - \frac{1}{2} (\partial_\gamma \omega_{\alpha\beta}) M_{\alpha\beta\gamma}^d + \mu_i r_i + j_\alpha^i \partial_\alpha \mu_i - h_\alpha \frac{Dp_\alpha}{Dt} \right] \\ + \oint dS_\beta \left(\vartheta_\alpha \sigma_{\alpha\beta} + \frac{1}{2} \omega_{\alpha\gamma} M_{\alpha\gamma\beta}^\pi - \vartheta_\alpha f - \mu_i j_\alpha^i + \frac{\partial f}{\partial(\partial_\beta p_\alpha)} \frac{Dp_\alpha}{Dt} \right) \end{aligned} \quad (32)$$

The volume integral (bulk term) is free energy source and it vanishes at equilibrium. The surface integral of the form $-\oint dS_\alpha J_\alpha^f$ represents total free energy flux. Total free energy flux per unit area $J_\alpha^f = f \vartheta_\alpha + j_\alpha^f$, with

$$j_\alpha^f = -\vartheta_\alpha \sigma_{\alpha\beta} - \frac{1}{2} \omega_{\alpha\gamma} M_{\alpha\gamma\beta}^\pi + \mu_i j_\alpha^i - \frac{\partial f}{\partial(\partial_\beta p_\alpha)} \frac{Dp_\alpha}{Dt}$$

The bulk contribution (*i.e.* free energy source) is related to entropy production θ such that

$$T\theta = \vartheta_{\alpha\beta} \sigma_{\alpha\beta}^{d,s} + \frac{1}{2} (\partial_\gamma \omega_{\alpha\beta}) M_{\alpha\beta\gamma}^d - \mu_i r_i + j_\alpha^i \partial_\alpha \mu_i + h_\alpha \frac{Dp_\alpha}{Dt}$$

The term $\mu_i r_i$ is an entropy production contribution due to chemical reaction, which can be written as

$$\sum_i \mu_i r_i = - \sum_i \mu_i \sum_I a_i^I r^I = - \sum_I r^I \sum_i \mu_i a_i^I = - \sum_I r^I \Delta\mu^I. \quad (33)$$

Here, $\Delta\mu^I$ is the total amount of chemical potential change for the I^{th} reaction. Note, in equation 33, first term is sum over chemical species and the last term is sum over chemical reactions. For a trace-less matrix M_{ij} , $M_{ij}\delta_{ij} = 0$, so we write

$$\vartheta_{\alpha\beta} \sigma_{\alpha\beta}^{d,s} = \tilde{\vartheta}_{\alpha\beta} \tilde{\sigma}_{\alpha\beta}^{d,s} + \partial_\gamma \vartheta_\gamma \frac{1}{3} \sigma_{\alpha\alpha}^{d,s} = \tilde{\vartheta}_{\alpha\beta} \tilde{\sigma}_{\alpha\beta}^{d,s} + \vartheta_\gamma \gamma \sigma^d$$

Using this and previous equation, we can, at last, write down the expression for entropy production

$$T\theta = \tilde{\vartheta}_{\alpha\beta} \tilde{\sigma}_{\alpha\beta}^{d,s} + \vartheta_\gamma \gamma \sigma^d + \frac{1}{2} (\partial_\gamma \omega_{\alpha\beta}) M_{\alpha\beta\gamma}^d + r^I \Delta\mu^I - j_\alpha^i \partial_\alpha \mu_i + h_\alpha \frac{Dp_\alpha}{Dt} \quad (34)$$

	F_n	$\tilde{\vartheta}_{\alpha\beta}$	$\Delta\mu^I$	h_α	$-\partial_\alpha\bar{\mu}_i$
J_n	ϵ	-1	1	1	1
$\tilde{\sigma}_{\alpha\beta}^{d,s}$	1	2η	ζ^I	ν_1	ν^i
r^I	-1	$-\zeta^I$	Λ^{II}	λ^I	λ^{iI}
$\frac{Dp_\alpha}{Dt}$	-1	$-\nu_1$	λ^I	$\frac{1}{\gamma_1}$	$-\kappa^i$
j_α^i	-1	$-\nu^i$	λ^{iI}	$-\kappa^i$	Λ^{ii}

Defining,

$$\tilde{q}_{\alpha\beta} = p_\alpha p_\beta - \frac{1}{3} p_\gamma p_\gamma \delta_{\alpha\beta}.$$

We are now well equipped to write down the reciprocal relations

$$\tilde{\sigma}_{\alpha\beta}^{d,s} = 2\eta\tilde{\vartheta}_{\alpha\beta} + \sum_I \zeta^I \Delta\mu^I \tilde{q}_{\alpha\beta} + \frac{\nu_1}{2} (h_\alpha p_\beta + h_\beta p_\alpha - \frac{2}{3} h_\gamma p_\gamma) - \sum_i (\nu^i \partial_\alpha \bar{\mu}_i p_\beta + \partial_\alpha \bar{\mu}_i p_\alpha - \frac{2}{3} \partial_\gamma \bar{\mu}_i p_\gamma) \quad (35)$$

$$r^I = -\zeta^I \tilde{\vartheta}_{\alpha\beta} \tilde{q}_{\alpha\beta} + \sum_J \Lambda^{IJ} \Delta\mu^J + \lambda^I h_\alpha p_\alpha - \sum_i (\lambda^{iI} p_\alpha \partial_\alpha \mu_i) \quad (36)$$

$$\frac{Dp_\alpha}{Dt} = -\nu_1 \tilde{\vartheta}_{\alpha\beta} p_\beta + \sum_I (\lambda^I \Delta\mu^I p_\alpha) + \frac{1}{\gamma_1} h_\alpha + \sum_i (\kappa_i \partial_\alpha \mu_i) \quad (37)$$

$$j_\alpha^i = -\nu^i \tilde{\vartheta}_{\alpha\beta} p_\beta + \sum_I (\lambda^{iI} \Delta\mu^I p_\alpha) - \kappa^i h_\alpha - \sum_j \Lambda^{ij} \partial_\alpha \mu_j \quad (38)$$