Supplement to the "AN ENERGETIC VARIATIONAL APPROACH FOR ION TRANSPORT" by Shixin Xu, Ping Sheng and Chun Liu in CMS

Motivated by the seminarial work of Onsager and Rayleigh, the frame work of the Energy Variational Approaches had been employed to study many complex fluids systems [Liu2001], [Yue2004], [Eisenberg2010]. Although there is a vast body of literatures on various applications, there lacks a comprehensive reference on the topic. The purpose of the paper " AN ENERGETIC VARIATIONAL APPROACH FOR ION TRANSPORT" is on the specific applications on Poisson-Nernst-Planck system and Poisson-Nernst-Planck-Navier-Stokes system. Due to the 10 pages limitation, we left out some details in that manuscript. This is the motivation of this supplement.

1 Some basic examples of Energetic Variational Approach

1). Hookean Spring : This is the original example by the Rayleigh [Strutt 1873]

The (Least) Action Principle is the reformulation of the fact that $force \times distance = work$. Hence variation of the energy with respect to flow map $x(X,t)$ yields the (conservative) force. Let x denote the displacement of the lower end of the spring form its equilibrium position. Then the traditional equation used to describe the spring is

$$mx_{tt} + \gamma x_t + kx = 0, \tag{0.1}$$

where mx_{tt} is the inertia, γx_t is damping, and kx is elastic force.

Multiplying (0.1) by x_t and integrating by parts, it yields

$$\frac{d}{dt}(\frac{1}{2}mx_t^2 + \frac{1}{2}kx^2) = -\gamma x_t^2, \tag{0.2}$$

where the total energy is $E^{total} = \frac{1}{2}mx_t^2 + \frac{1}{2}kx^2$, and the dissipation functional is quadratic on velocity $u = x_t$, $\Delta = -\gamma x_t^2$.

Reversely, if we start from energy dissipation law (0.2), the action functional is

$$A = \int_0^{t^*} \left(\frac{1}{2} m x_t^2 - \frac{1}{2} k x^2 \right) dt. \tag{0.3}$$

By LAP and taking variation of A with respect to x, we get immediately

$$F_{con} = -m x_{tt} - kx, \tag{0.4}$$

which is exactly the conservative force for the Hookean spring.

Next we treat the dissipative part. If we denote $x_t = u$, by MDP, it yields, for any smooth test function v,

$$\frac{d}{d\varepsilon}\Big|_{\varepsilon=0} \frac{1}{2}\Delta(u + \varepsilon v) = \frac{d}{d\varepsilon}\Big|_{\varepsilon=0} (\frac{1}{2}\gamma(u + \varepsilon v)^2) = \gamma u \cdot v, \tag{0.5}$$

which is also consistent with the optimal transportation [Villani2003]. This yields the dissipative force

$$F_{dis} = \gamma x_t. \tag{0.6}$$

Now we have both the dissipative part (0.6) and the Hamiltonian part (0.4) of the system. The equation for the entire system comes from the force balance $F_{con} = F_{dis}$:

$$-m x_{tt} - kx = \gamma x_t, \tag{0.7}$$

which is equivalent with equation (0.1).

2) Simple Diffusion

Various forms of this derivation can be found in many literatures, for instance, [Xu2013]. Here we take the simple heat equation as example. The diffusion equation

$$f_t = c\triangle f, \tag{0.8}$$

can be viewed as special case in this energetic variational framework. Equation (0.8) can be rewritten as

$$\begin{cases} f_t + \nabla \cdot (\mathbf{u} f) = 0, \\ -c\nabla f = f\mathbf{u}. \end{cases} \tag{0.9}$$

Multiplying the first equation in (0.9) by $c(\ln f + 1)$ and integrating by parts, it yields,

$$\begin{aligned} & \frac{d}{dt}\int_\Omega cf\ln f dx = \int_\Omega f_t c(1+\ln f)dx \\ = & \int_\Omega f\mathbf{u}c\nabla(1+\ln f)dx = \int_\Omega f\mathbf{u}c\frac{\nabla f}{f}dx \\ = & -\int_\Omega f|\mathbf{u}|^2 dx. \end{aligned} \tag{0.10}$$

Reversely, we start with the kinematic assumption of density f (conservation law) and energy dissipation law

$$\begin{cases} f_t + \nabla\cdot(\mathbf{u}f) = 0, \\ \frac{d}{dt}E^{total} = \frac{d}{dt}\int_\Omega cf\ln f dx = -\int_\Omega f|\mathbf{u}|^2 dx. \end{cases} \tag{0.11}$$

By the LAP, we can get

$$F_{con} = \frac{\delta A}{\delta x} = -\frac{\delta E^{total}}{\delta x} = -c\nabla f \tag{0.12}$$

and by MDP, we can get

$$F_{dis} = \frac{\delta}{\delta \mathbf{u}}\frac{\Delta}{2} = f\mathbf{u}. \tag{0.13}$$

The force balance yields

$$-c\nabla f = f\mathbf{u}. \tag{0.14}$$

Combining above formula and the conservation law, we can get

$$f_t = c\triangle f. \tag{0.15}$$

2. The derivation of compressible Navier-Stokes equation

This is motivated by the classical derivations of Euler equation by (Least) Action Principle [Arnold1989] and also the (Maximum) Dissipation Principle of Onsager [Onsager1931a,Onsager1931b] which is another version of the linear response theory [Kubo1976]. The density ρ satisfies the kinematic assumption (conservation of mass),

$$\rho_t + \nabla\cdot(\rho\mathbf{u}) = 0. \tag{0.16}$$

From the energy variation point of view, the following energy dissipation law includes all the physics of Newtonian fluids

$$\frac{d}{dt}E^{total} = \frac{d}{dt}\int_\Omega \left(\frac{1}{2}\rho|\mathbf{u}|^2 + \omega(\rho)\right)dx = -\int_\Omega \left[\mu_1|\nabla\mathbf{u}|^2 + \mu_2|\nabla\cdot\mathbf{u}|\right]dx, \quad (0.17)$$

where μ_1 and μ_2 are viscosity constants, the Hemholtz free energy density $\omega(\rho)$ includes both the entropic contributions and the internal energy describing the particle interactions. The action functional in Lagrangian coordinates, after Legendre transformation, is

$$\begin{aligned} A(x) &= \int_0^{t^*}\int_\Omega \left(\frac{1}{2}\rho|\mathbf{u}|^2 - \omega(\rho)\right)dxdt \\ &= \int_0^{t^*}\int_{\Omega_0} \left(\frac{1}{2}\frac{\rho_0}{J}|x_t(X,t)|^2 - \omega(\frac{\rho_0}{J})\right)JdXdt \\ &= \int_0^{t^*}\int_{\Omega_0} \left(\frac{1}{2}\rho_0|x_t(X,t)|^2 dXdt - \omega(\frac{\rho_0}{J})J\right)dXdt, \end{aligned} \quad (0.18)$$

where $J = \det F$, $F(X,t) = \frac{\partial x(X,t)}{\partial X}$ is the deformation gradient. Taking the variation with respect to x yields, for any $y(X,t) = \tilde{y}(x(X,t),t)$ smooth with compact support

$$\begin{aligned} &\frac{d}{d\varepsilon}\Big|_{\varepsilon=0} A(x(X,t) + \varepsilon y(X,t)) = \frac{d}{d\varepsilon}\Big|_{\varepsilon=0} A(x+\varepsilon y) \\ = \;& \frac{d}{d\varepsilon}\Big|_{\varepsilon=0} \int_0^{t^*}\int_{\Omega_0} \frac{1}{2}\rho_0(X)|x_t + \varepsilon y_t|^2 - \omega\left(\frac{\rho_0(X)}{det(\frac{\partial(x+\varepsilon y)}{\partial X})}\right)\left(det(\frac{\partial(x+\varepsilon y)}{\partial X})\right)dXdt \\ = \;& \int_0^{t^*}\int_{\Omega_0} \rho_0(X)x_t y_t dXdt + \int_0^{t^*}\int_{\Omega_0} \omega_\rho(\frac{\rho_0(X)}{J})\frac{\rho_0(X)}{J^2}\cdot tr(\frac{\partial X}{\partial x}\frac{\partial y}{\partial X})\cdot J^2 \\ & -\omega(\frac{\rho_0(X)}{J})\cdot J\cdot tr(\frac{\partial X}{\partial x}\frac{\partial y}{\partial X})dXdt. \end{aligned} \quad (0.19)$$

Here we use the fact $\delta(\det F) = \det F\cdot tr(F^{-T}\frac{\partial\delta x}{\partial X})$.

Integrating by parts, above formula yields

$$\begin{aligned}
&\int_0^{t^*}\int_{\Omega_0} -\rho_0(X)x_{tt}y_t \\
&+\left(\omega_\rho\left(\frac{\rho_0(X)}{J}\cdot\right)\frac{\rho_0(X)}{J}-\omega\left(\frac{\rho_0(X)}{J}\cdot\right)\right)\cdot tr(\frac{\partial X}{\partial x}\frac{\partial y}{\partial X})JdXdt \\
= &\int_0^{t^*}\int_\Omega(-\rho(x)\frac{d}{dt}\mathbf{u}(x,t))\cdot\tilde{y} \\
&+(\omega_\rho(\rho(x,t))\rho(x,t)-\omega(\rho(x,t)))\cdot(\nabla_x\cdot\tilde{y})dxdt \\
= &\int_0^{t^*}\int_\Omega -(\rho(x,t)\frac{d}{dt}\mathbf{u}(x,t)+\nabla_x(\omega_\rho(\rho(x,t))\cdot\rho(x,t)-\omega(\rho(x,t))))\cdot\tilde{y}dxdt \\
= &\int_0^{t^*}\int_\Omega -(\rho(x,t)(\mathbf{u}_t+\mathbf{u}\cdot\nabla_x\mathbf{u})+\nabla_x\Pi(x,t))\cdot\tilde{y}dxdt, \qquad (0.20)
\end{aligned}$$

where $\Pi(x,t)=\omega_\rho(\rho(x,t))\cdot\rho(x,t)-\omega(\rho(x,t))$(*same result as Lemma* 1.1). Then we obtain the conservative force

$$F_{con}=-\left(\rho(x,t)(\mathbf{u}_t+\mathbf{u}\cdot\nabla_x\mathbf{u})+\nabla_x\Pi(x,t)\right). \qquad (0.21)$$

As to the dissipation part, the dissipation functional is
$\Delta=\int_\Omega\left[\mu_1|\nabla\mathbf{u}|^2+\mu_2|\nabla\cdot\mathbf{u}|\right]dx$. Maximum Dissipation Principle, as a reformulation of the linear response theory, takes the variation of Δ with respect to the rate function $\mathbf{u}$.

$$\begin{aligned}
&\frac{d}{d\varepsilon}\Big|_{\varepsilon=0}\frac{1}{2}\Delta(\mathbf{u}+\varepsilon\mathbf{v}) \\
= &\frac{d}{d\varepsilon}\Big|_{\varepsilon=0}\int_\Omega\frac{1}{2}\mu_1(x,t)|\nabla_x\mathbf{u}+\varepsilon\nabla_x\mathbf{v}|^2+\frac{1}{2}\mu_2(x,t)|\nabla_x\cdot\mathbf{u}+\varepsilon\nabla_x\cdot\mathbf{v}|^2dx \\
= &\int_\Omega\mu_1(x,t)\nabla_x\mathbf{u}:\nabla_x\mathbf{v}+\mu_2(x,t)(\nabla_x\cdot\mathbf{u})(\nabla_x\cdot\mathbf{v})dx \\
= &\int_\Omega(-\nabla_x(\mu_1(x,t)\nabla_x\mathbf{u})-\nabla_x(\mu_2(x,t)\nabla_x\cdot\mathbf{u})\cdot\mathbf{v}dx, \qquad (0.22)
\end{aligned}$$

where $\mathbf{v}$ is any test function with compact support. Hence the dissipative force is

$$F_{dis}=-\nabla_x(\mu_1\nabla_x\mathbf{u})+\nabla_x(\mu_2\nabla_x\cdot\mathbf{u}). \qquad (0.23)$$

Finally, by force balance $F_{con}=F_{dis}$, we can get the usual Navier-Stokes equation (momentum equation)

$$\rho(\mathbf{u}_t+\mathbf{u}\cdot\nabla\mathbf{u})+\nabla\Pi(\rho)=\nabla\cdot(\mu_1\nabla\mathbf{u})+\nabla(\mu_2\nabla\cdot\mathbf{u}). \qquad (0.24)$$

3. Interactions between particles

In a dissipation system, the particle interactions attribute to both the free energy functional and dissipation functional. The coarse graining derivation of the Helmholtz free energy $\mathcal{U} - T\mathcal{S}$, or equivalently, the equation of states, takes into account the free energy part . As in the standard statistical physics, the particles interactions contribute to the internal energy $\mathcal{U}$. Such interactions can be local, such as hard core interations or nonlocal, such as Coulomb electro static interactions. At the same time, however independently, the non-equilibrium thermaldynamics, following the linear response theory of Onsager [Onsager1931a,Onsager1931b]and Kubo [Kubo1976], the dissipative functional (the entropy production) is the sum of the quadratic powers of various rate variables. In PNP, the free energy includes the Gibbs entropy and the particle Columb interaction. The dissipation are quadratic of velocities.

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