NonEquilibrium Thermodynamics of Flowing Systems: 1

Antony N. Beris

Schedule: (all lectures at 409 Lind Hall)

1. 1/11/05, 10:10 am       Introduction. One mode viscoelasticity.
2. 1/14/05, 11:15 am       Coupled transport: Two-fluid model.
3. 1/21/05, 11:15 am       Modeling under constraints: Liquid crystals.
4. 1/28/05, 10:00 am       Non-homogeneous systems: Surface effects.
Motivation

- To use a framework that allows the imposition “ab initio” of the most restrictive physically possible guidelines governing the dynamics of complex systems.

- Certain limitations are inevitable: most importantly, that the system we study is “close enough” to equilibrium; yet we want the formalism to not be introducing arbitrary constraints. Here we also limit ourselves to macroscopic descriptions.
General Features

• The general formalism has to reduce to well-established ones at characteristic limiting cases:
  – In the limit of infinite time: Equilibrium (Gibbs) thermodynamics
  – In the limit of reversible dynamics: Hamiltonian dynamics
  – In the limit of infinitesimally small deviations from equilibrium: Linear Irreversible Thermodynamics (Onsager relations)
**GENERIC**

- The most general formalism for the dynamics of a structured system, macroscopic as well as microscopic, described by \( \mathbf{x} \), is the one developed (after many years multiple-investigator efforts) by Oettinger and Grmela and called as “GENERIC” (for General Equation for Non-Equilibrium Reversible-Irreversible Coupling):

\[
\frac{d\mathbf{x}}{dt} = L \frac{\delta E}{\delta \mathbf{x}} + M \frac{\delta S}{\delta \mathbf{x}}
\]

where \( L \) and \( M \) are linear differential operators of specific structure (Poissonian and Dissipation) subject to the additional degeneracy requirements:

\[
L \frac{\delta S}{\delta \mathbf{x}} = 0; \quad M \frac{\delta E}{\delta \mathbf{x}} = 0
\]

and \( E, S \) are the total energy (Hamiltonian) and total entropy, functionals of \( \mathbf{x} \).

Poisson Structure

• Defined for two arbitrary functionals $F, G$ as the bilinear functional $\{F, G\}$:

$$\{F, G\} \equiv \int \frac{\delta F}{\delta x} L \frac{\delta G}{\delta x} d\Omega$$

• such that:
  – It is antisymmetric: $\{F, G\} = - \{G, F\}$
  – It satisfies the Jacobi identity:
    $$\{F,\{G, H\}\} + \{G,\{H, F\}\} + \{H,\{F, G\}\} = 0$$
Dissipation Structure

- Defined for two arbitrary functionals $F, G$ as the bilinear functional $[F,G]$: 

$$ [F,G] \equiv \int \frac{\delta F}{\delta x} M \frac{\delta G}{\delta x} d\Omega $$

- such that the matrix operator $M_{ij}$, in the limit of small departures from equilibrium:
  - is symmetric or antisymmetric with respect to an interchange of $i, j$ depending on whether the corresponding $x_i, x_j$ components have the same or different parities upon time reversal (Generalized Onsager-Casimir relations of Linear Irreversible Thermodynamics)
Features of GENERIC

- It can be shown to be consistent with all well accepted dynamic transport equations ranging from the very microscopic (Maxwell-Boltzmann) to the microscopic (kinetic theory in polymers) and macroscopic (transport phenomena) levels
- It can provide corrections/suggestions to many complex modeling problems, such as:
  - Reptation theory models
  - Closure approximations

see Oettinger’s homepage: http://www.polyphys.mat.ethz.ch/
Single Generator Approximation

• For macroscopic systems, it is possible to deduce a simpler structure given the local equilibrium approximation according to which there is a local system entropy density that can alternatively be used to characterize the system
  – the entropy and energy potentials are directly related
  – we can express the dynamics solely in terms of energy (Hamiltonian) potentials
Hamiltonian functional formalism*


- For any arbitrary functional $F$, its time evolution can be described as the sum of two contributions:
  - a reversible one, represented by a Poisson bracket:
    - $\{F, H\}$
  - an irreversible one, represented by a dissipative bracket:
    - $[F, H]$
- The final dynamic equations are recovered through a direct comparison with the expression derived by differentiation by parts:

$$ \frac{dF}{dt} = \{F, H\} + [F, H] = \int \frac{\delta F}{\delta x} \cdot \frac{dx}{dt} \, dV $$
Advantages of Hamiltonian Formalism (1)

- It only requires knowledge of the following:
  - A set of macroscopic variables, taken uniformly as volume densities. The include, in addition to the equilibrium thermodynamic ones (the component mass density, $\rho_i$, for every component i, the entropy density $s_i$), the momentum density, $\rho \mathbf{v}$, and any additional structural parameter, again expressed as a density
  - The total energy of the system or any suitable Lagrange transform of it, typically the total Helmholtz free energy, expressed as a functional of all other densities with the temperature substituting for the entropy density
  - The Poisson bracket, $\{F,H\}$
  - The dissipation bracket, $[F,H]$
Advantages of Hamiltonian Formalism (2)

- However:
  - A set of macroscopic variables can easily be assumed depending on the physics that we want to incorporate to the problem.
  - The total Helmholtz free energy can also easily be constructed as the sum of kinetic energy plus an extended thermodynamic free energy that typically includes an easily derived expression (in terms of the structural parameters) in addition to a standard equilibrium expression.
  - The Poisson bracket, \( \{F,H\} \) is rarely needed by itself: only when an equation is put together for the first time characteristic of the variables involved in this system; otherwise, its effect is probably already known from previous work: it corresponds to a standard reversible dynamics. For viscoelastic flows, this corresponds to the terms defining an upper convected derivative.
  - The dissipation bracket, \([F,H]\) is the only one to contain major new information and is typically where our maximum ignorance lies. Barren any other information (say, by comparison against a microscopic theory) the main information that we can use is a linear irreversible thermodynamics expression: according to that, the dissipation bracket becomes a bilinear functional in terms of all the nonequilibrium Hamiltonian gradients with an additional nonlinear (in \(H\)) correction with respect to \(\delta F/\delta s\) (entropy correction) that can be easily calculated so that the conservation of the total energy is satisfied: \([H,H] = 0\).
Example Case: Single Mode Viscoelasticity

• Reference (available in electronic form):
  – A.N. Beris, Simple Nonequilibrium Thermodynamics Applications to Polymer Rheology (As it appeared on: RHEOLOGY REVIEWS 2003, The British Society of Rheology (publisher), 37-75)
Variables

- For an incompressible, homogeneous (uniform polymer concentration, $n$=chain number density is constant) system we have
  - $v$, the velocity
  - $s$, the entropy density (alternatively, $T$, temperature)
  - $c$, the conformation tensor where
    - $C = \langle RR \rangle$ (second moment of the end-to-end distribution function) = $nc$

- At equilibrium, $c=k_BT/K$ where $K$ is the equilibrium equivalent entropic elastic energy constant of the polymer chain
• The Hamiltonian (extended Helmholtz free energy of the system) is assumed to have the form:

\[ A = \int_v \left( \frac{1}{2} \rho v^2 + a \right) dV \]

where various expressions can be assumed to represent the elastic free energy density, \( a \), depending on the nature of the polymer phase (i.e., dilute solution, polymer melt etc). A list of the most widely used ones is supplied in Table 1 together, for convenience, with the corresponding expressions for the corresponding thermodynamic potential.
Poisson bracket: Reversible equations

• For an isothermal system, we get the standard reversible dynamics for an elastic medium (together with the divergence-free velocity constraint):

\[
\frac{D}{Dt} \rho \frac{D}{Dt} v = -\nabla p + \nabla \cdot T^T
\]

\[
\frac{D}{Dt} c - \nabla v^T \cdot c - c \cdot \nabla v = 0
\]

\[
T^T = 2c \cdot \frac{\partial a}{\partial c}
\]
The general dissipation bracket (within an entropy correction) can be easily formulated as a bilinear expression in terms of the nonequilibrium components of the Hamiltonian potential, $\frac{\delta H}{\delta c}$ and $\nabla (\frac{\delta H}{\delta v})$ as

$$[F,G] = -\int \Lambda_{\alpha\beta\gamma\epsilon} \frac{\delta F}{\delta c_{\alpha\beta}} \frac{\delta G}{\delta c_{\gamma\epsilon}} dV - \int Q_{\alpha\beta\gamma\epsilon} \nabla_{\alpha} \left( \frac{\delta F}{\delta v_{\beta}} \right) \nabla_{\gamma} \left( \frac{\delta G}{\delta v_{\epsilon}} \right) dV$$

$$- \int L_{\alpha\beta\gamma\epsilon} \nabla_{\alpha} \left( \frac{\delta F}{\delta v_{\beta}} \right) \frac{\delta G}{\delta c_{\gamma\epsilon}} dV - \int L_{\gamma\epsilon\alpha\beta} \nabla_{\alpha} \left( \frac{\delta G}{\delta v_{\beta}} \right) \frac{\delta F}{\delta c_{\gamma\epsilon}} dV$$

where, to preserve Onsager’s relations, the matrices $\Lambda$ and $Q$ are symmetric with respect to an exchange of $\gamma, \epsilon$ by $\alpha, \beta$ and, moreover, given the symmetry of $c$, the matrix $\Lambda$ does not change upon an exchange of $\gamma$ by $\epsilon$ and/or $\alpha$ by $\beta$; additional constraints on $Q$ can also be derived based on the principle of material indifference.
Typical Choices for $L$, $Q$

- If $L$ is symmetric upon change of $\gamma$ by $\varepsilon$ and/or $\alpha$ by $\beta$ it turns out that it does not contribute to the entropy production; thus there is no need for further constraints. A typical choice is therefore (following the simplest choice for $\Lambda$, see Table 2)

$$L_{\alpha\beta\gamma\varepsilon} = -\xi / 2 (c_{\alpha\gamma} \delta_{\beta\varepsilon} + \text{permutations of } \alpha \leftrightarrow \beta \text{ and } \gamma \leftrightarrow \varepsilon)$$

where $\xi$ is a scalar parameter between 0 and 1

Similarly, for $Q$, we use the expression which is valid for a homogeneous and isotropic (Newtonian) system of viscosity $\eta_s$:

$$Q_{\alpha\beta\gamma\varepsilon} = \eta_s (\delta_{\alpha\gamma} \delta_{\beta\varepsilon} + \delta_{\alpha\varepsilon} \delta_{\beta\gamma})$$
Typical Choices for $\Lambda$

- Various models can be generated using different expressions for the relaxation tensor $\Lambda$.
- A compilation of some of the most often employed forms can be found in Table 2.
Conclusions

• The Hamiltonian formalism can provide a uniform representation for viscoelastic models.
• New possibilities thus arise for new model development through “mix and match” of terms.
• In addition, the evaluation of thermodynamic consistency is facilitated: new constraints can be easily derived on acceptable parameter values and suitable approximations for the dissipative terms of the equations.
• The extension of the above-mentioned work to multimode models is straightforward! See the mentioned references (book and review) for several characteristic examples.