NonEquilibrium Thermodynamics of Flowing Systems: 1

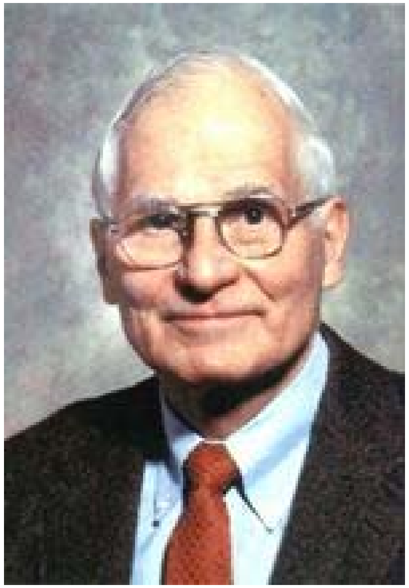
Antony N. Beris

University of Delaware
Chemical Engineering

Multiscale Modeling and Simulation of Complex Fluids
Center for Scientific Computing and Mathematical Modeling
University of Maryland, College Park

Schedule:

1. **4/13/07, 9:30 am Introduction. One mode viscoelasticity.**
2. **4/13/07, 10:15 am Coupled transport: Two-fluid model.**
3. **4/14/07, 2:00 pm Modeling under constraints: Liquid crystals.**
4. **4/14/07, 3:00 am Non-homogeneous systems: Surface effects.**



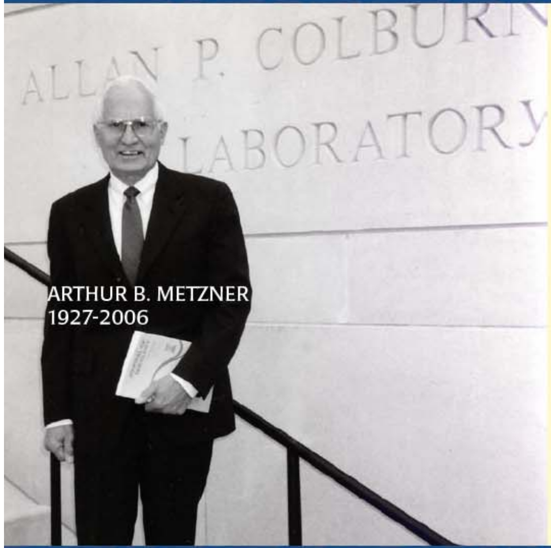
Art Metzner, 04/13/1927 – 05/02/2006

Commemorative Symposium: May 14, 2007, Dept. of Chem. Engrg., Univ. of Delaware

COMMEMORATIVE SYMPOSIUM

May 14, 2007

John M. Clayton Hall
Newark, Delaware



ARTHUR B. METZNER
1927-2006

In honor of

ARTHUR B. METZNER

The University of Delaware's
H. Fletcher Brown Professor Emeritus
of Chemical Engineering

Symposium Information

The Department of Chemical Engineering will be hosting this symposium in honor of Dr. Metzner.

Information is also available by visiting us at `www.che.udel.edu/forms/metzner.`

PROGRAM - JOHN M. CLAYTON HALL

8:30 a.m.	**Continental Breakfast**
9:00	Greetings
9:10	Morton Denn: *"Short Overview on the Scientific Contributions of Art Metzner"*
9:30	Jan Mewis: *"Suspension Rheology and Thixotropy"*
9:50	David Boger: *"Observation of Elastic Effects in the Flow of Polymer Solutions"*
10:10	Antony Beris: *"Polymer-Induced Drag Reduction"*
10:30	**Coffee Break**
10:50	Rakesh Gupta: *"Flow and Heat Transfer in Nanofiber Suspensions"*
11:10	Arup Chakraborty: *"How T cells "See" Antigen: Simplicity in Complexity a-la Metzner"*
11:30	Morton Denn: *"Orientational Multiplicity and Transitions in Liquid Crystalline Droplets"*
Noon-1:30	**Lunch - Clayton Hall**
1:30 p.m.	Kurt Wissbrun: *"Art Metzner's contributions to the Society of Rheology"*
1:50	Kenneth Chrisman: *"Art Metzner's Contribution to the Alyeska Pipeline"*
2:15	Family, Friends, Colleagues and Students: *"Remembering Arthur Metzner - Teacher, Research Advisor, Colleague, Family Man, and International Mentor"*
4:30-6:30	**Reception - Clayton Hall**

UNIVERSITY OF DELAWARE

Motivation

- To use a framework that it 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*

See also: H.C. Oettinger, Beyond Equilibrium Thermodynamics, Wiley, 2006

- The most general formalism for the dynamics of a structured system, macroscopic as well as microscopic, described by **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 **x**.

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* H. C. Oettinger and M. Grmela, Dynamics and thermodynamics of complex fluids. II. Illustrations of a general formalism, Phys. Rev. E 56, 6633-6655 (1997).

Poisson Structure

- Defined for two arbitrary functionals *F*, *G* as the bilinear functional {*F*,*G*}:

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

- 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*]:

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

- 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 Öttinger's homepage: http://www.polyphys.mat.ethz.ch/ and Öttinger H-C, Beyond Equilibrium Thermodynamics, Wiley 2005

Single Generaror Approximation

- For macroscopic systems, it is possible to deduce a simpler structure based on the local equilibrium approximation according to which there is a local system entropy density that can alternatively to the energy 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
- This is shown to be equivalent to GENERIC:
  - Edwards BJ, J. Non-Equil. Thermodyn., 23:300-332 (1998)

Hamiltonian Functional Formalism*

*Beris and Edwards, Thermodynamics of Flowing Systems, Oxford UP, 1994

- 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:

$$dF/dt = \{F,H\} + [F,H] = \int \delta F/\delta \mathbf{x} \cdot d\mathbf{x}/dt \, dV$$

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, ρ_i, for every component i, the entropy density si), the momentum density, ρ**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)

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 from beris@che.udel.edu):
  - **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** = <**RR**> (second moment of the end-to-end distribution function) = $n\mathbf{c}$
- At equilibrium, c=$k_B T/K$ where K is the equilibrium equivalent entropic elastic energy constant of the polymer chain

Hamiltonian

- The Hamiltonian (extended Helmholtz free energy of the system) is assumed to have the form:

$$A = \int_V \left(\tfrac{1}{2} \rho v^2 + a \right) \mathrm{dV}$$

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.

Table 1 List of commonly used expressions for the Helmholtz free energy energy density a and the corresponding thermodynamic potential, $\partial a / \partial \mathbf{c}$, with respect to the conformation tensor, **c**. The expressions are provided in dimensionless form. The free energy is made dimensionless with respect to nk_BT, where n is a chain number density, k_B is the Boltzmann factor and T the temperature, and **c** is made dimensionless with respect to the square of the equilibrium end-to-end chain distance, k_BT/K where K is the (apparent) elastic constant for the chain's elastic energy. In the random flight model, $k_BT/K=1/3Nl^2$, where N, l is the number, length of repeating (Kuhn) segments [Kuhn and Grün, 1942].

Model	$a(\mathbf{c})$	$\partial a / \partial \mathbf{c}$	Remarks /References
Maxwell Oldroyd-B	$\frac{1}{2}\left\{\mathrm{tr}(\mathbf{c})-\ln\left(\det(\mathbf{c})\right)\right\}$	$\frac{1}{2}\mathbf{I}-\frac{1}{2}\mathbf{c}^{-1}$	Also called Hookean or Linear Dumbbell model [Bird et al., 1987]
FENE-P	$-\frac{1}{2}L^2\ln\left(1-\frac{\mathrm{tr}(\mathbf{c})}{L^2}\right)$ $-\frac{1}{2}\ln\left(\det(\mathbf{c})\right)$	$\frac{1}{2}\left(\frac{1}{1-\frac{\mathrm{tr}(\mathbf{c})}{L^2}}\right)\mathbf{I}-\frac{1}{2}\mathbf{c}^{-1}$	L represents the dimensionless maximum chain extensibility; L^2 also appears as b [Bird et al., 1987]
Bird and DeAguiar (modified)	$\frac{1}{2}\left\{\mathrm{tr}(\mathbf{c})-\ln\left(\det(\mathbf{c})\right)\right\}$ $+\frac{(1-\alpha)}{2}\ln\left(\frac{\left(\frac{1}{3}\mathrm{tr}(\mathbf{c})\right)^3}{\det(\mathbf{c})}\right)$	$\frac{1}{2}\left(1-\frac{3(\alpha-1)}{\mathrm{tr}(\mathbf{c})}\right)\mathbf{I}$ $-\frac{1}{2}(2-\alpha)\mathbf{c}^{-1}$	α is an aniso-tropic mobility parameter; [Bird and DeAguiar, 1983]

Leonov	$W(a_1,a_{-1})$; $a_1 \equiv \frac{I_1}{I_3^{1/3}}$; $a_{-1} \equiv I_{-1} I_3^{1/3}$; $I_{-1} = \frac{I_2}{I_3}$	$\frac{\partial W}{\partial a_1}\frac{1}{I_3^{1/3}}\left(\mathbf{I} - \tfrac{1}{3} I_1 \mathbf{c}^{-1}\right) +$ $\frac{\partial W}{\partial a_{-1}}\frac{1}{I_3^{2/3}}(I_1\mathbf{I} - \mathbf{c} - \tfrac{2}{3} I_2 \mathbf{c}^{-1})$	I_n is the *n*-th invariant of **c**; in the original model I_3=1 [Leonov, 1976]
Marrucci and Acierno (modified)	$\tfrac{1}{2}(\chi+1)\left(\mathrm{tr}(\mathbf{c}) - \ln\left(\det(\mathbf{c})\right)\right)$ $-\tfrac{3}{2}\chi_0 \ln(\chi)$	$\tfrac{1}{2}(\chi+1)\left(\mathbf{I}-\mathbf{c}^{-1}\right)$	χ is the number of entanglements per chain [Marrucci et al., 1973, Acierno et al., 1976a,b]
MGI (modified)	$-\ln\left(\det\left(\frac{\mathbf{c}}{\left(\mathrm{tr}\left(\mathbf{c}^{1/2}\right)\right)^2}\right)\right)$ $= 6\ln\left(\mathrm{tr}\left(\mathbf{c}^{1/2}\right)\right) - \ln\left(\det(\mathbf{c})\right)$	$\frac{3\mathbf{c}^{-1/2}}{\mathrm{tr}\left(\mathbf{c}^{1/2}\right)} - \mathbf{c}^{-1}$	[Marrucci et al., 2001; Leygue et al., 2001]
Pompon	$\tfrac{1}{2}\left\{3\ln\left(\mathrm{tr}(\mathbf{c})\right) - \ln\left(\det(\mathbf{c})\right)\right\}$ $+\tfrac{3}{2}\left\{\begin{matrix}\lambda^{*2} - (\lambda^*-q)^2\,\mathrm{H}(\lambda^*-q) \\ -1-2\ln(\lambda^*)\end{matrix}\right\}$	$\tfrac{3}{2}\frac{\mathbf{I}}{\mathrm{tr}(\mathbf{c})} - \tfrac{1}{2}\mathbf{c}^{-1}$	λ^* is an extended stretch factor [Öttinger, 2001; McLeish and Larson, 1998]

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):

$$\rho \frac{\mathrm{D}}{\mathrm{Dt}} \mathbf{v} = -\nabla p + \nabla \cdot \mathbf{T}^T$$

$$\frac{\mathrm{D}}{\mathrm{Dt}} \mathbf{c} - \nabla \mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla \mathbf{v} = 0$$

$$\mathbf{T}^T = 2\mathbf{c} \cdot \frac{\partial a}{\partial \mathbf{c}}$$

General Dissipation Bracket

- 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, δH/δ**c** and ∇(δH/δ**v**) as

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

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

where, to preserve Onsager's relations, the matrices **Λ** and **Q** are symmetric with respect to an exchange of γ,ε by α,β and, moreover, given the symmetry of **c**, the matrix **Λ** does not change upon an exchange of γ by ε and/or α by β; 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 γ by ε and/or α by β 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 **Λ**, see Table 2)

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

where ξ 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 η_s:

$$Q_{\alpha\beta\gamma\varepsilon} = \eta_s(\delta_{\alpha\gamma}\delta_{\beta\varepsilon} + \delta_{\alpha\varepsilon}\delta_{\beta\gamma})$$

Final Equations

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

$$\rho \frac{\mathrm{D}}{\mathrm{Dt}} \mathbf{v} = -\nabla p + \eta_s \Delta \mathbf{v} + \nabla \cdot \mathbf{T}^T$$

$$\frac{\mathrm{D}}{\mathrm{Dt}} \mathbf{c} - \nabla \mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla \mathbf{v} = -\frac{\xi}{2}\left(\dot{\boldsymbol{\gamma}} \cdot \mathbf{c} + \mathbf{c} \cdot \dot{\boldsymbol{\gamma}} \right) - \boldsymbol{\Lambda} : \frac{\partial a}{\partial \mathbf{c}}$$

$$\mathbf{T}^T = 2(1-\xi)\mathbf{c} \cdot \frac{\partial a}{\partial \mathbf{c}}$$

Typical Choices for **Λ**

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

Table 2 List of commonly used expressions for the fourth order relaxation tensor $\mathbf{\Lambda}$, made dimensionless by ${k_B T}\big/{\lambda_e n K^2}$ where λ_e represents an equilibrium relaxation time and the other parameters have been defined in Table 1. Note that only one of four equivalent contributions to the $\alpha\beta\gamma\varepsilon$ component is given, the others (represented as [perm.] in the table) arising from the following permutations of the original subscripts: $\alpha\beta\gamma\varepsilon \leftrightarrow \beta\alpha\gamma\varepsilon \leftrightarrow \alpha\beta\varepsilon\gamma \leftrightarrow \beta\alpha\varepsilon\gamma$ (this table is adapted from [Beris and Edwards, 1990]).

Model	$\Lambda_{\alpha\beta\gamma\varepsilon}$	Remarks/references
Elastic dumbbell (UCM, OldroydA, B, FENE-P)	$\frac{1}{2}\left(c_{\alpha\gamma}\delta_{\beta\varepsilon}+[perm.]\right)$	
Elastic dumbbell with hydrodynamic interactions	$\frac{1}{2}\left(c_{\alpha\gamma}\left(\delta_{\beta\varepsilon}-\frac{3}{4}h\sqrt{\frac{\pi}{\mathrm{tr}(\mathbf{c})}}\left(\delta_{\beta\varepsilon}+\frac{c_{\beta\varepsilon}}{\mathrm{tr}(\mathbf{c})}\right)\right)+[perm.]\right)$	$0 \le h \le \frac{2}{3}\sqrt{\frac{I_1}{\pi}}$; [Bird et al, 1987]
Modified encapsulated dumbbell	$\frac{1}{2}\left(\sigma c_{\alpha\gamma}\delta_{\beta\varepsilon}+(1-\sigma)\frac{1}{\mathrm{tr}(\mathbf{c})}c_{\alpha\beta}c_{\gamma\varepsilon}+[perm.]\right)$	$\sigma \ge 0$; [Bird and DeAguiar, 1983]

Giesekus	$\frac{1}{2}\left(c_{\alpha\gamma}\left((1-\alpha)\delta_{\beta\varepsilon}+\alpha c_{\beta\varepsilon}\right)+[perm.]\right)$	$0 \le \alpha \le 1$; [Giesekus, 1982a]
Leonov	$\left(c_{\alpha\varepsilon}c_{\gamma\beta}-\frac{1}{3}c_{\alpha\beta}c_{\gamma\varepsilon}+[perm.]\right)$	[Leonov, 1976]
Phan-Thien/Tanner (linear)	$\frac{1}{2}\left(1+\varepsilon\left(\mathrm{tr}\left(\mathbf{c}\right)-3\right)\right)\left(c_{\alpha\gamma}\delta_{\beta\varepsilon}+[perm.]\right)$	[Phan-Thien and Tanner, 1977]
Extended White/ Metzner	$\frac{1}{2}\frac{1}{\lambda^{*}(I_1,I_2,I_3)}\left(c_{\alpha\gamma}\delta_{\beta\varepsilon}+[perm.]\right)$	λ^{*} is a dimensionless, positive function of the invariants of **c**; for example, $\lambda^{*}=K(I_1)^{k}$ [Souvaliotis and Beris, 1992]
Leygue, Beris and Keunings	$\frac{1}{2}\left(c_{\alpha\gamma}\left(\alpha c_{\beta\varepsilon}+(1-\alpha)\frac{\mathrm{tr}\left(\mathbf{c}^{1/2}\right)}{3}c_{\beta\varepsilon}^{1/2}\right)+[perm.]\right)$	$0 \le \alpha \le 1$; [Leygue et al., 2001]

In the remarks column a number of sufficient conditions known to assure the non-negative character of the relaxation dissipation are listed (see [Beris and Edwards, 1994] for more details regarding their derivation).

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