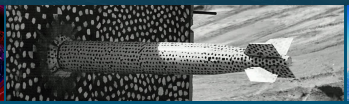
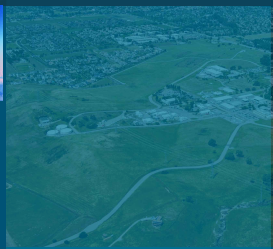
Sandia National Laboratories

A perspective on statistical physics in constitutive modeling




APS March Meeting 2024 – Minneapolis, Minnesota, USA

Presented by:

Michael R. Buche[1,*]

[1]Sandia National Laboratories
*mrbuche@sandia.gov

3/8/2024

U.S. DEPARTMENT OF ENERGY NNSA

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND NO. 2024-01747C

Abstract

Constitutive models are required to complete the governing equations for a material.

- Continuum mechanics and thermodynamics provide severely limited guidance.
- Statistical physics allows quantities to be derived from molecular constitution.

Background – statistical physics in constitutive modeling.

- Approach – some mathematical details from a high level.
- Example – polymer constitutive model using statistical thermodynamics.

Perspective – focus on polymers, some general conclusions.

- Successes – what has been working?
- Failures – what has not?
- Thoughts – what now?

Approach

Provide the molecular physics.

- Sufficient detail for desired behavior.
- Enough simplicity to remain tractable.
- Usually statistical thermodynamics [1].

$$H(p,q) = \sum_{j=1}^{N} \frac{p_j^2}{2m_j} + U(q)$$

$$Q(N,V,T) = \frac{1}{N!} \int dp \int dq \; e^{-H(p,q)/kT}$$

$$A(N,V,T) = -kT \ln Q(N,V,T)$$

Prescribe a macroscopic connection.

- Affine or non-affine deformation [2, 3].
- Representative volume elements [4].
- Sometimes not necessary (gases).

Phase 2

?

Apply continuum mechanics and thermodynamics.

- Frame invariance and the second law [5].
- Obtain the constitutive model.

$$\boldsymbol{\sigma} : \mathbf{L} \geq \dot{a} + s\dot{T}$$

$$\boldsymbol{\sigma} = \frac{1}{J} \frac{\partial a}{\partial \mathbf{F}} \cdot \mathbf{F}^T$$

Example

Provide the molecular physics.

- Single-chain model (uFJC) [6, 7].
- Evolving probability distribution of chains.
- Liouville equation, transition state theory.

$$\gamma(\eta) \sim \mathcal{L}(\eta) + \Delta\lambda(\eta)$$

$$\frac{\partial \mathscr{P}(\boldsymbol{\gamma}, t)}{\partial t} = -k'(\gamma)\mathscr{P}(\boldsymbol{\gamma}, t) + (\text{rev}) - \frac{\partial}{\partial \boldsymbol{\gamma}} \cdot \left[\dot{\boldsymbol{\gamma}}(\boldsymbol{\gamma}, t)\mathscr{P}(\boldsymbol{\gamma}, t)\right]$$

Prescribe a macroscopic connection.

- Affine deformation ($\dot{\boldsymbol{\gamma}} = \mathbf{L} \cdot \boldsymbol{\gamma}$).
- Exactly solve governing PDE.
- Simplifications (irreversible, transient).

$$\mathscr{P}(\boldsymbol{\gamma}, t) = \int_{-\infty}^{t} \mathscr{P}^{\text{eq}}\left[{}_{(t)}\mathbf{F}(\tau) \cdot \boldsymbol{\gamma}\right] \rho(\tau)\, d\Xi$$

$$\Xi(\boldsymbol{\gamma}, t, \tau) = \exp\left\{-\int_{\tau}^{t} k\left[{}_{(t)}\mathbf{F}(s) \cdot \boldsymbol{\gamma}\right] ds\right\}$$

Apply continuum mechanics and thermodynamics.

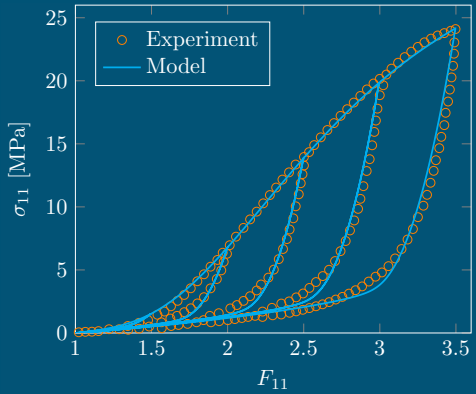
- Automatic solution and stability guarantees.
- See Buche and Silberstein (2021) for details [8].

$$\frac{\boldsymbol{\sigma} + p\mathbf{1}}{N_b n k T} = \iiint \mathscr{P}(\boldsymbol{\gamma}, t)\, \eta(\gamma) \left(\frac{\boldsymbol{\gamma}\boldsymbol{\gamma}}{\gamma}\right) d^3\boldsymbol{\gamma}$$

Successes

Triple network elastomer, sacrificial cross-links [9].

- Model predictions of mechanics [8].
  - Mostly predicts loading path.
    - Nearly without any fitting [8].
  - Captures damage and dissipation.
    - Irreversible bond breaking.
  - Across model flavors [3, 10].
- Mechanoluminescence (not shown).
  - Decent qualitative prediction [8].

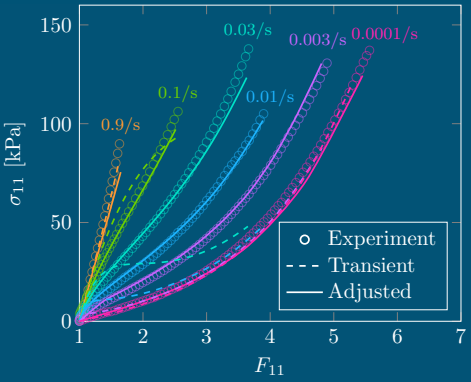


Summary:
This modeling approach tends to accurately predict rate-independent elasticity and damage.

Failures

Dual (permanent and transient) cross-link gel [11].

- Qualitative rate dependence.
  - Perhaps one rate, not more [8, 12].
- Quantitative rate dependence.
  - With e^{-kt} ? In your dreams!
    - Thanks, transition state theory [8].
  - Transient $\neq$ equilibrium, right?
    - Invalid separation of timescales.
  - Phenomenological better [13].



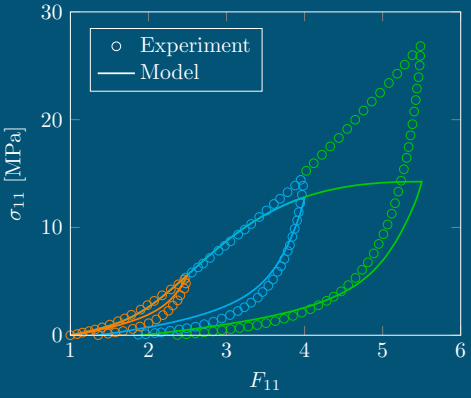
Summary:

Kinetics from transition state theory and similar theories are unpredictive and possibly invalid.

Failures

Metal-coordination cross-linked hydrogel [14].

- Substantial "viscoplastic" dissipation.
  - Bonds reforming stress-free [8, 15].
- Insufficient "viscoelastic" dissipation.
  - Support either loading or dissipation.
    - Pathology of break/reform kinetics.
  - No interchain interactions.
    - Intractable molecular model.
  - Phenomenological predominant [14].



Summary:

Viscosity from the statistical thermodynamics of tractable molecular models is not sufficient.

Thoughts

Transition-state-like non-equilibrium theories:

- Phase space regions in local equilibrium.
  - Relaxation rate $\gg$ reaction rate.
    - "This separation of time scales is generally hard to justify..." [16]
  - Equilibrium principles, extra steps.
- Always produces some flavor of e^{-kt}.
  - Rarely seems to be predictive [8], phenomenological often better.

Summary:

Something drastically different than transition state theory is needed to improve model results.

Thoughts

Provide the molecular physics.

- Partition phase space without assumptions.
- Nonequilibrium evolution via Liouville [1, 8].
- Advance without transition state theory?

$$\frac{\partial \mathscr{P}}{\partial t} = \mathcal{R}'' - \mathcal{R}' - \frac{\partial}{\partial \boldsymbol{\gamma}} \cdot (\dot{\boldsymbol{\gamma}} \mathscr{P})$$

$$\mathcal{R}' = \left\langle \frac{p}{m} \Theta(p)\, \delta(q^{\ddagger} - q) \delta^3(\boldsymbol{\gamma}' - \boldsymbol{\gamma}) \right\rangle$$

$$\dot{\boldsymbol{\gamma}} = \left\langle \dot{\boldsymbol{\gamma}}' \Theta(q^{\ddagger} - q) \delta^3(\boldsymbol{\gamma}' - \boldsymbol{\gamma}) \right\rangle$$

Prescribe a macroscopic connection.

- Could $\dot{\boldsymbol{\gamma}}$ incorporate viscous effects?
- Is Gibbs' postulate even valid here [1, 8]?
- Are interchain interactions simply vital?

$$a(t) = n_{\mathrm{A}}(t)\mu_{\mathrm{A}}(t) + n_{\mathrm{B}}(t)\mu_{\mathrm{B}}(t) - nkT$$

$$\mu_{\mathrm{A}}(t) = \iiint \frac{\mathscr{P}_{\mathrm{A}}(\boldsymbol{\gamma}, t)}{\mathscr{P}_{\mathrm{A}}^{\mathrm{tot}}(t)}\, \mu_{\mathrm{A}}^{*}(\boldsymbol{\gamma}, t)\, d^3\boldsymbol{\gamma}$$

$$\mu_{\mathrm{A}}^{*}(\boldsymbol{\gamma}, t) = \psi_{\mathrm{A}}^{*}(\boldsymbol{\gamma}) + kT \ln N_{\mathrm{A}}(t)$$

Apply continuum mechanics and thermodynamics.

- Compatible with nonequilibrium statistics?
- Emergent intrinsic material timescales [17]?

$$\pi(t) = a(t) + \operatorname*{\mathfrak{F}}_{0 \le s \le t} \Big\{ \mathbf{F}(s), T(s), \dots \Big\}$$

$$\Delta t_{\mathrm{mat}} = \int_0^t \frac{ds}{f(s)}, \qquad f(s) = f\big(\mathbf{F}, T\big)$$

Conclusion

Developing continuum constitutive models remains a sort of black art.

- Tradeoff between physics and practicality when providing the molecular model.
- Large deal of freedom and uncertainty when prescribing the macroscopic connection.

Recent constitutive models for polymers have not been entirely successful.

- Rate-independent elasticity and damage are predicted quite nicely.
- Rate-dependence and viscous dissipation can be predicted poorly.

In general, equilibrium principles limit the resulting constitutive model.

- Need to get away from kinetics that resemble transition state theory.
- Techniques from nonequilibrium statistical mechanics may be applicable.
    - They are certainly required for materials considered to be glassy.

References

[1] D. A. McQuarrie, *Statistical Mechanics*, (University Science Books, Mill Valley, CA, 2000).

[2] M. R. Buche and M. N. Silberstein, Phys. Rev. E **102**, 012501 (2020).

[3] J. P. Mulderrig, B. Li, and N. Bouklas, Mech. of Mater. **160**, 103857 (2021).

[4] M. Grasinger, J. Mech. Phys. Solids **175**, 105289 (2023).

[5] S. Paolucci, *Continuum Mechanics and Thermodynamics of Matter*, (Cambridge University Press, New York, NY, 2016).

[6] M. R. Buche, M. N. Silberstein, and S. J. Grutzik, Phys. Rev. E **106**, 024502 (2022).

[7] J. P. Mulderrig, B. L. Talamini, and N. Bouklas, J. Mech. Phys. Solids **174**, 105244 (2023).

[8] M. R. Buche and M. N. Silberstein, J. Mech. Phys. Solids **156**, 104593 (2021).

[9] E. Ducrot, Y. Chen, M. Bulters, R. P. Sijbesma, and C. Creton, Science **344**, 186 (2014).

[10] F. J. Vernerey, R. Brighenti, R. Long, and T. Shen, Macromolecules **51**, 6609 (2018).

[11] K. Mayumi, A. Marcellan, G. Ducouret, C. Creton, and T. Narita, ACS Macro Lett. **2**, 1065 (2013).

[12] F. J. Vernerey, J. Mech. Phys. Solids **115**, 230 (2018).

[13] R. Long, K. Mayumi, C. Creton, T. Narita, and C.-Y. Hui, Macromolecules **47**, 7243 (2014).

[14] J. Lin, S. Y. Zheng, R. Xiao, J. Yin, Z. L. Wu, Q. Zheng, and J. Qian, J. Mech. Phys. Solids **139**, 103935 (2020).

[15] S. C. Lamont, J. Mulderrig, N. Bouklas, and F. J. Vernerey, Macromolecules **54**, 10801 (2021).

[16] R. Zwanzig, *Nonequilibrium Statistical Mechanics*, (Oxford University Press, New York, NY, 2001).

[17] K. N. Cundiff, M. R. Buche, B. L. Talamini, S. J. Grutzik, J. M. Kropka, and K. N. Long, Sandia National Laboratories **14317** (2023).