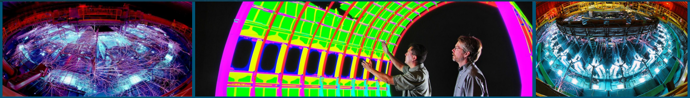
# Background and applications of statistical thermodynamics



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# Abstract

Statistical thermodynamics is a powerful tool.

- Only a few axioms and equations, but a lot of examples.
- Allows constitutive relations to be obtained from molecular physics.
- Nuances from ensemble and system size, state variables and equilibrium, etc.
- Applicable to quantum mechanical systems, of course.

Statistical thermodynamics is sometimes the right tool.

- Molecular stretching, some constitutive modeling, subcritical crack growth.
- Performs poorly when underlying axioms are invalid.
- Performs poorly when the model system is not representative.

Statistical thermodynamics research continues.

- It has historically has focused on computational and approximation techniques.
- New applications and clever model system choices provide further motivation.

# Background

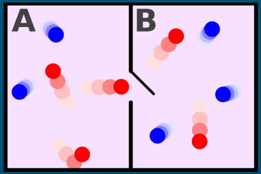
# Statistical mechanics

Statistical mechanics:

- Probabilistic interpretation of mechanics through $f(p, q, t)$.
- State variables are all atomic positions/momenta, time.

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_{j=1}^{3N} \left( \frac{\partial f}{\partial q_j} \dot{q}_j + \frac{\partial f}{\partial p_j} \dot{p}_j \right) = 0$$

- Fundamentally correct, but can be extremely unwieldy




Statistical thermodynamics:

- Statistical features do not evolve in time (equilibrium).
- Severely reduced number of state variables (ensemble).
- Macroscopic thermodynamics from constituent particles.

# Statistical thermodynamics

Partition functions:

- Probability normalization for all calculations.
- Compute once, if possible, for all states.
- Configuration integral is typically impossible.
- Connection to thermodynamics by inference.
- Laplace transforms change the ensemble.

$$Q(N,V,T) = \frac{1}{N!h^{3N}} \int \cdots \int e^{-H(p,q)/kT}\, dp\, dq$$

$$= \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} Z(N,V,T)$$

$$Z(N,V,T) = \int \cdots \int e^{-U(q)/kT}\, dq$$

Difference from macroscopic thermodynamics:

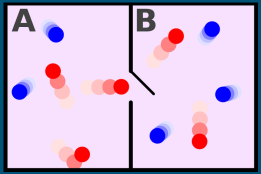
- Non-state variables are averages and fluctuate.
- Ensemble-dependent results for small systems.
- Calculate averages of molecular variables.
- Things like temperature become nebulous.

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

$$\langle x \rangle = \frac{1}{Q} \int \cdots \int x(q)\, e^{-U(q)/kT}\, dq$$

$$P = -\left. \frac{\partial A}{\partial V} \right|_{N,T}$$

# Statistical thermodynamics




Fundamental axioms [1]:

- Principle of equal *a priori* probabilities.
- The entropy is maximized at equilibrium.
- The entropy takes a specific form.
- Gibbs' postulate, (in)distinguishability of particles.

Two approximation techniques:

- If $U = U_0 + U_1$, where $U_1$ is weak ($U_1 \ll kT$) [2], i.e. derive van der Waals.

$$A \sim A_0 + \langle U_1 \rangle_0 - \frac{1}{2kT}\left[\langle U_1^2 \rangle_0 - \langle U_1 \rangle_0^2\right] + \cdots$$

- If $U = U_0 + U_1$, where $U_1$ is steep ($U_1 \gg kT$ and narrow) [3], i.e. correct RRHO.

$$A \sim A_0 + U_1\big|_0 + kT\left[\left(\frac{A_0'}{kT}\right)^2 - \frac{A_0''}{kT} + \cdots\right]_0 + \cdots$$

# Applications

# Molecular stretching

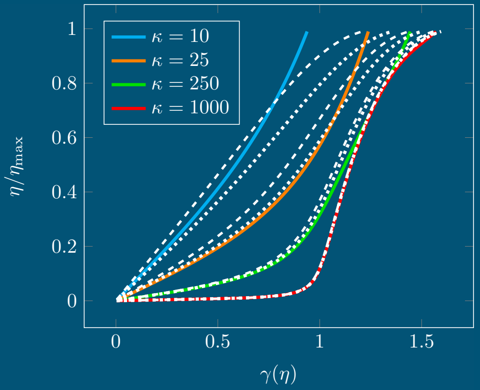
Freely jointed chain models with extensible links [4].

- Ensemble is links $N_b$, force $f$, temperature $T$.
- Resistance due to entropy and link stretching.
- Analytic relations using asymptotic approach.

$$\gamma(\eta) \sim \mathcal{L}(\eta) + \frac{\eta}{\kappa}\left[\frac{1 - \mathcal{L}(\eta)\coth(\eta)}{c + (\eta/\kappa)\coth(\eta)}\right] + \Delta\lambda(\eta)$$

Device effects in these stretching experiments [5].

- No device can apply a constant force or extension due to finite stiffness and size.
- Either ensemble provides a zeroth order approximation in certain device limits.
- Weak and steep theories provide corrections.



# Constitutive modeling

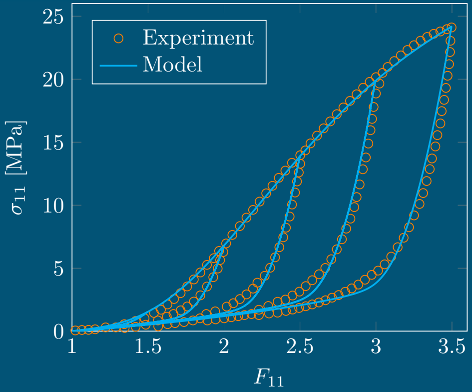
Triple network elastomer, sacrificial cross-links [6].

- Single chains to bulk constitutive model [7].
- Largely successful across model types [8–10].

Rate-dependence and viscous dissipation.

- Possible failure of underling physics.
  - Failure of transition-state-like theories.
  - Intermolecular interactions not tangible.
- Definite failure of resulting model forms.
  - Always some useless flavor of $e^{-kt}$.
  - Phenomenological models are better.

Is non-equilibrium statistical mechanics compatible with thermodynamic constitutive theory?



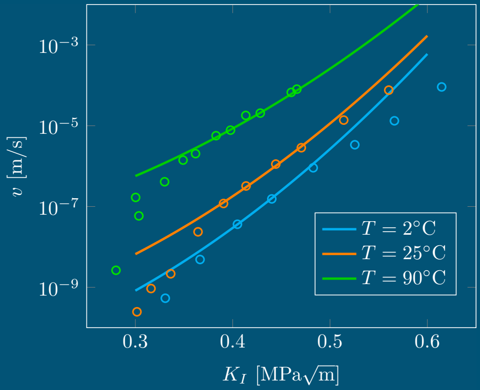
# Subcritical crack growth

Statistical mechanical model for crack growth [11].

- Harmonic bending, Morse potential bonds.
- Applied displacement or force ensembles.
- Velocity from transition state theory rate.
- Analytic solutions using assumptions:
  - Big system, steep potential, small stretch.

$$\frac{v}{b} \sim \frac{\omega_0}{\pi} \exp\left(\frac{f\Delta x^\ddagger - \Delta u^\ddagger}{kT}\right)\left(\frac{Rb^2}{2kT}\right)$$

- Similar to before, but better parameters now.
- SLS glass in water; no water in model [12, 13].
  - Possible explanation for $v$ overestimation.
  - Future work: environment, dimensions.



# Functional integrals

Infinite degrees of freedom.

- Continuous limit of discrete particles.
- Integrate over functions instead of numbers.
- Absolute free energies are not defined.

Asymptotic approach still applies [14].

- Worm-like polymer chain models [15].
- Nanoscale origami models [16].
- SPECtacular has similar expansions [17].
- Possibly applicable to quantum field theory.
  - Specifically, the path integral formulation.
  - Looking for a demonstrator problem.

$$Z = \int f(x)\, e^{-\lambda \phi(x)}\, \mathcal{D}x$$

$$\phi(x) = \frac{1}{2} \int \left[x(s) - x_0\right]^2 ds$$

$$\lambda \gg 1$$

$$A = \int e^{-\frac{1}{2} \int u^2(s)\, ds}\, \mathcal{D}u$$

$$Z \sim \frac{A}{\sqrt{\lambda}} f(x_0) \left[1 + \sum_{m=1}^{\infty} \frac{a_m}{\lambda^m}\right]$$

# Conclusion

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