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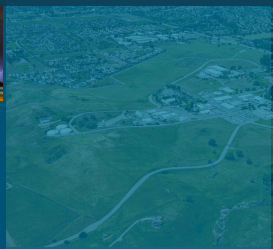
General approximation of single chain models with extensible links

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Presented by:

Michael R. Buche (mrbuche@sandia.gov)

Michael R. Buche[1], Matthew Grasinger[2], Jason Mulderrig[2]

[1]Sandia National Laboratories, [2]Air Force Research Laboratory

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Abstract

Physically-based constitutive models enable predictions of polymer solid mechanics.

- Models using continuum mechanics alone sometimes rely on heuristics.
- Relations obtained from molecular statistical mechanics provide a physical basis.

These relations are often obtained using idealized single-chain models.

- Analytic force-extension relations are available for certain ensembles and models.
- Approximations or numerical solutions are generally difficult in other cases.

Large-deformation models for polymers must incorporate chain extensibility.

- Extensible single-chain models are typically unsolvable and numerically difficult.
- Inextensible single-chain models, if not solvable, are at least numerically easy.
- One remedy is to approximate link extensibility in a broad inextensible model class.

Background

Consider discrete single-chain models with separable potential energy functions.

$$\Pi(\ell, \theta, \phi) = U_0(\theta, \phi) + U_1(\ell) - \mathbf{f} \cdot \boldsymbol{\xi} \tag{1}$$

In most cases, each link contribution is separate and from the same function.

$$U_1(\ell) = \sum_{i=1}^{N_b} u(\ell_i) \tag{2}$$

Approximate the link potential energy as harmonic, and write in nondimensional form.

$$\beta U_1 \sim \frac{\kappa}{2} \sum_{i=1}^{N_b} (\lambda_i - 1)^2 \tag{3}$$

Eq. (1) applies to most discrete single-chain models [1] in the isotensional ensemble [2].

Asymptotics

General partition function with a special set of degrees of freedom and related potential.

$$Z = \int d\Gamma_0 \int dX \, e^{-\beta H_0(\Gamma_0, X)} \, e^{-\beta U_1(X)} \tag{4}$$

Separate contributions in nondimensional form, where $\phi'(\hat{x}_i) = 0$ and $\phi''(\hat{x}_i) = 1$.

$$\beta U_1(X) = \sum_{i=1}^{N} \kappa_i \phi_i(x_i) \tag{5}$$

For steep ($\kappa_i \gg 1$) potentials, an asymptotic approximation upon the reference system [3].

$$Z \sim \left(\prod_{i=1}^{N} \sqrt{\frac{2\pi}{\kappa_i}} \right) \left[Z_0(\hat{X}) + \sum_{j=1}^{N} \frac{g_j(\hat{x}_j)}{\kappa_j} + \operatorname{ord}\left(\kappa_j^{-2}\right) \right] \tag{6}$$

One simple example is correcting upon the rigid-rotor-harmonic-oscillator approximation.

Derivation

The reference system is the inextensible single-chain model for some set of link lengths.

$$Z_0(\eta,\lambda) = \lambda^2 \int \sin\theta \, d\theta \int d\phi \, e^{\beta \mathbf{f}\cdot\boldsymbol{\xi} - \beta U_0} \tag{7}$$

The asymptotic approach yields an approximation for the extensible single-chain model.

$$Z(\eta) \sim \left(\frac{2\pi}{\kappa}\right)^{N_b/2} \left[Z_0(\eta,1) + \frac{1}{2\kappa} \sum_{j=1}^{N_b} \left. \frac{\partial^2 Z_0}{\partial \lambda_j^2} \right|_{\lambda=1} + \operatorname{ord}\left(\kappa^{-2}\right) \right] \tag{8}$$

The nondimensional relation for the average mechanical response can then be calculated.

$$\gamma(\eta) \sim \gamma_0(\eta) + \frac{1}{\kappa} \left\{ \frac{1}{N_b} \left[2\gamma_0(\eta) + 3\eta\gamma_0'(\eta) + \tfrac{1}{2}\eta^2\gamma_0''(\eta) \right] + \eta\gamma_0^2(\eta) + \eta^2\gamma_0(\eta)\gamma_0'(\eta) \right\} \tag{9}$$

This relation only requires ensemble-averaged information about the reference system.

Verification

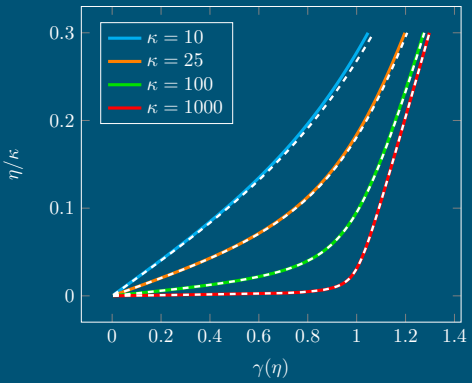
The freely jointed chain is analytically tractable.

$$\gamma(\eta) \sim \mathcal{L}(\eta) + \frac{1}{\kappa}\left[\coth(\eta) - \eta\,\mathrm{csch}^2(\eta)\right] + \frac{\eta}{\kappa}$$

The result is comparable to a previous result [4].

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

The former matches the latter to within $\mathrm{ord}\left(\kappa^{-2}\right)$, and the latter is coincidentally accurate to within transcendentally small terms [3, 5].



The general asymptotic relation is verified in one case, but it should not depend on N_b here.

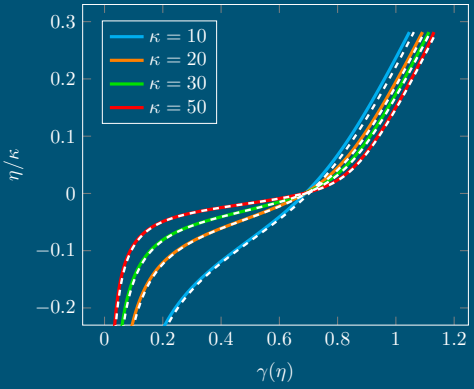
Validation

The freely rotating chain is analytically intractable.

$$\gamma(\eta) \sim \gamma_0(\eta) + \kappa^{-1} h(\eta) + \operatorname{ord}\left(\kappa^{-2}\right)$$

Monte Carlo methods in the isometric ensemble.

- Random walks for entire curves in one shot.
- Micro-canonical ensemble when inextensible.
- Independent bond sampling when extensible.†
- One trillion samples, one thousand bins.
- Numerical calculations to obtain $\gamma(\eta)$.



† Difficulties for large extension and large stiffness values from sample rarity.

The general asymptotic relation appears to be valid, but needs further study (N_b, θ_b, error).

Conclusion

Physically-based constitutive models enable predictions of polymer solid mechanics.

- Idealized single-chain models that are asserted to be physically representative.
- Extensibility must be included to accurately model large deformation or fracture.

An asymptotic theory for extensible links in a broad class of single-chain models is desired.

- Analytic approximations built upon the more easily solvable inextensible model.
- Preliminary results are promising but incomplete, requiring further investigation.
- Successful ventures so far have not considered multi-dimensional coupling [5–7].

Future work involves revisited continuum models and additional single-chain modeling.

- Attempt to improve existing constitutive modeling efforts for polymer failure [8–12].
- Derive extensions for anharmonic potentials, continuous degrees of freedom [13].

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