Group Seminar[a)]

Artur Avkhadiev[1, b)]
Department of Physics, Brown University, Providence RI 02912, USA

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Free polymer motion: minimizing the action and respecting the constraints. Progress report.

CONTENTS

I. PROBLEM SETUP AND FORMULATION

We showed that the kinetic energy of polymer motion around its center of mass — its internal kinetic energy — is given by

$$T = \frac{1}{2} m d^2 C_{ij} (\dot{\hat{\mathbf{\Omega}}}^i \cdot \dot{\hat{\mathbf{\Omega}}}^j)(\tau) \tag{1}$$

where $\dot{\hat{\mathbf{\Omega}}}$ are time derivatives of bond unit vectors indexed with from 1 to N_b, d is the fixed bond length, m is the mass of one atom in a polymer, and C is a matrix defined as

$$C_{ij} = C_{ji} = C_{N_\mathrm{b}+1-i,\, N_\mathrm{b}+1-j} = \frac{\min(i,\, j)(N_\mathrm{b}+1) - ij}{N_\mathrm{b}+1} \tag{2}$$

Bond unit vectors can change their orientation with time τ, but are constrained to have a norm of unity:

$$\sigma_i(\tau) = \left\| \hat{\mathbf{\Omega}}_i(\tau) \right\|^2 - 1 = 0 \quad \forall\, i \in (1, \ldots, N_\mathrm{b}) \tag{3}$$

We also specify the boundary conditions on initial ($\tau = 0$) and final ($\tau = t$) orientations of all bond unit vectors. Given these boundary conditions, we can solve the problem of free diffusion by minimizing the Lagrangian with constraints:

$$\begin{aligned} S &= \int_{\tau=0}^{\tau=t} T \,\mathrm{d}\tau \\ \sigma_i(\tau) &= 0 \end{aligned} \tag{4}$$

which is equivalent to solving the equations of motion with constraints (see appendix A)

$$\begin{aligned} C_{ij} \ddot{\hat{\mathbf{\Omega}}}^j(\tau) &= -\frac{2}{m d^2} \lambda_i(\tau) \hat{\mathbf{\Omega}}_i(\tau) \\ \sigma_i(\tau) &= 0 \end{aligned} \tag{5}$$

where $\lambda_i(\tau)$ are time-dependent Lagrange multipliers.

Given this setup, one has to either minimize the action directly or solve the equations of motion. Either way, one finds the time-dependent form of bond velocities $\dot{\hat{\mathbf{\Omega}}}(\tau)$, the solution to the problem of free polymer motion that respects the constraints.

II. SLERP

In the case when the cross terms in the kinetic energy expression vanish, equations of motion for each bond unit vector become decoupled. Apart from the weights C_{ii}, this motion is equivalent to the motion of N_b linear molecules. In that case, the solutions $\hat{\mathbf{\Omega}}(\tau)$ that minimize the Lagrangian are given by SLERP (since the bond vectors are now decoupled, the weights cancel out in the equations of motion and we may omit them). Recall that the SLERP solution is derived from the following parameterization of $\hat{\mathbf{\Omega}}(\tau)$[1]:

$$\hat{\mathbf{\Omega}}(\tau) = a(\tau)\hat{\mathbf{\Omega}}(0) + b(\tau)\hat{\mathbf{\Omega}}(t) + c(\tau)\hat{\boldsymbol{n}} \tag{6}$$

Where $\hat{\boldsymbol{n}} = \frac{\hat{\mathbf{\Omega}}(0)\times\hat{\mathbf{\Omega}}(t)}{\left\|\hat{\mathbf{\Omega}}(0)\times\hat{\mathbf{\Omega}}(t)\right\|}$ and the time-dependent coefficients a, b, and c respect the boundary conditions:

$$\begin{aligned} &a(0) = 1,\, a(t) = 0,\, \delta a(0) = \delta a(t) = 0 \\ &b(0) = 0,\, b(t) = 1,\, \delta b(0) = \delta b(t) = 0 \\ &c(0) = 0,\, c(t) = 0,\, \delta c(0) = \delta c(t) = 0 \end{aligned} \tag{7}$$

and the normalizaton constraint:

$$a^2(\tau) + b^2(\tau) + 2a(\tau)b(\tau)\cos\Delta\psi + c^2(\tau) - 1 = 0 \tag{8}$$

where $\Delta\psi$ is the angle between $\hat{\mathbf{\Omega}}(0)$ and $\hat{\mathbf{\Omega}}(t)$.

Given these parameterizations, one substitutes $\hat{\mathbf{\Omega}}(a(\tau), b(\tau), c(\tau))$ into the Lagrangian $L = \frac{1}{2}md^2\sum_i\left(\dot{\hat{\mathbf{\Omega}}}_i \cdot \dot{\hat{\mathbf{\Omega}}}_i - \lambda_i\sigma_i(\hat{\mathbf{\Omega}}_i)\right)$, and proceeds to vary the action and obtain Euler-Lagrange equations of motion for a, b, and c. Omitting the time dependence, they are[1]:

$$\begin{aligned} A &= \ddot{a} + \ddot{b}\cos\Delta\psi + \lambda\left(a + b\cos\Delta\psi\right) = 0 \\ B &= \ddot{b} + \ddot{a}\cos\Delta\psi + \lambda\left(b + a\cos\Delta\psi\right) = 0 \\ C &= \ddot{c} + \lambda c = 0 \\ \tau\sqrt{\lambda} &= \Delta\psi \end{aligned} \tag{9}$$

for each bond vector. Solving these equations yields[1]

$$\begin{aligned} a(\tau) &= \frac{\sin\left(\left(1 - \frac{\tau}{t}\right)\Delta\psi\right)}{\sin(\Delta\psi)} \\ b(\tau) &= \frac{\sin\left(\frac{\tau}{t}\right)\Delta\psi}{\sin(\Delta\psi)} \\ c(\tau) &= 0 \end{aligned} \tag{10}$$

One can see that the SLERP solution describes planar motion. For each bond, the plane is defined by the initial and final orientation of the bond unit vector.

III. NEW PARAMETERIZATION

Consider the parameterization

$$\hat{\mathbf{\Omega}}(\tau) = \cos\left(\phi(\tau)\right)\left(a(\tau)\hat{\mathbf{\Omega}}(0) + b(\tau)\hat{\mathbf{\Omega}}(t)\right) + \sin\left(\phi(\tau)\right)\hat{\boldsymbol{n}} \tag{11}$$

where $a(\tau)$ and $b(\tau)$ are SLERP solutions from 10, and $\phi(\tau)$ is such that

$$\phi(0) = 0,\, \phi(t) = 0,\, \delta\phi(0) = \delta\phi(t) = 0 \tag{12}$$

so that the boundary conditions are respected.

The intuition behind this parameterization is that our solution should lie perturbabitvely close to the SLERP solution:

- In the absence of constraint forces, the bond vectors move in planes defined by their known initial and final orientations;

- The constraint forces push the bond vectors out of the plane;

- In the limit of the dimininshing difference between the initial and final times, the solution should be getting arbitrarily close to the SLERP solution.

The reason for choosing trigonometric functions is pragmatic: the normalization constraint is respected exactly with the fundamental trig identity.

Further, we make an ansatz on the form of the time dependence of ϕ in the limit of the small time step. In this limit (and this limit only), it makes sense that $\phi(\tau)$ will have single peak value at $\frac{t-0}{2}$ that would be small in the sense that $\phi(\frac{t}{2}) \ll \frac{\pi}{2}$. Trying to choose the simplest functional form, we take $\phi(\tau)$ to exhibit a projectile motion with some initial velocity and a constant downward acceleration. It is easy to show that in this case

$$\phi(\tau) = \tau v \left(1 - \frac{\tau}{t}\right) + \mathcal{O}\left(\tau^3\right) \tag{13}$$

Using the equations above, we can work out the form of the action and minimize it with respect to the initial velocities v_i of $\phi_i(\tau)$ for each bond vector. This means that

$$\frac{\delta S}{\delta v_i} = \int_{\tau=0}^{\tau=t} \left(\frac{1}{2} m d^2 C_{ij} \left(\left(\left(\frac{\partial}{\partial v}\dot{\hat{\mathbf{\Omega}}}^i\right) \cdot \dot{\hat{\mathbf{\Omega}}}^j\right)(\tau) + \left(\dot{\hat{\mathbf{\Omega}}}^i \cdot \frac{\partial}{\partial v}\dot{\hat{\mathbf{\Omega}}}^j\right)(\tau)\right)\right) \mathrm{d}\tau \tag{14}$$

is set to 0 for all i, and the set of initial "velocities" v_i is determined from the resulting system of equations.

IV. CALCULATION

Let us write out $\hat{\mathbf{\Omega}}(\tau,\, v)$ and $\dot{\hat{\mathbf{\Omega}}}(\tau,\, v)$:

$$\begin{aligned}
\hat{\mathbf{\Omega}}(\tau,\, v) &= \cos\left(\phi(\tau,\, v)\right) \hat{\mathbf{\Omega}}^{(0)}(\tau) + \sin\left(\phi(\tau,\, v)\right) \hat{\boldsymbol{n}} \\
\dot{\hat{\mathbf{\Omega}}}(\tau,\, v) &= \cos\left(\phi(\tau,\, v)\right) \dot{\hat{\mathbf{\Omega}}}^{(0)}(\tau) - \dot{\phi} \sin\left(\phi(\tau,\, v)\right) \hat{\mathbf{\Omega}}^{(0)}(\tau) + \dot{\phi} \cos\left(\phi(\tau,\, v)\right) \hat{\boldsymbol{n}}
\end{aligned} \tag{15}$$

where the SLERP solution for the bond unit vector has been denoted $\hat{\mathbf{\Omega}}^{(0)}(\tau)$, and $\hat{\boldsymbol{n}}$ is still equal to $\frac{\hat{\mathbf{\Omega}}^{(0)}(0) \times \hat{\mathbf{\Omega}}^{(0)}(t)}{\left\|\hat{\mathbf{\Omega}}^{(0)}(0) \times \hat{\mathbf{\Omega}}^{(0)}(t)\right\|}$.

Omitting the dependence on τ and v, $\frac{\partial \dot{\hat{\mathbf{\Omega}}}}{\partial v}$ is given by

$$\begin{aligned}
\frac{\partial \dot{\hat{\mathbf{\Omega}}}}{\partial v} = &- \left(\frac{\partial \phi}{\partial v} \sin\phi\right) \dot{\hat{\mathbf{\Omega}}}^{(0)} \\
&- \left(\frac{\partial \dot{\phi}}{\partial v} \sin\phi + \dot{\phi} \frac{\partial \phi}{\partial v} \cos\phi\right) \hat{\mathbf{\Omega}}^{(0)} \\
&+ \left(\frac{\partial \dot{\phi}}{\partial v} \cos\phi - \dot{\phi} \frac{\partial \phi}{\partial v} \sin\phi\right) \hat{\boldsymbol{n}}
\end{aligned} \tag{16}$$

The diagonal elements $\frac{\partial}{\partial v}\left(\dot{\hat{\mathbf{\Omega}}}^i \cdot \dot{\hat{\mathbf{\Omega}}}^i\right)(\tau)$ are rather simple, because $\hat{\boldsymbol{n}}_i \cdot \hat{\mathbf{\Omega}}_i^{(0)} = 0$ by definition, $\hat{\mathbf{\Omega}}_i^{(0)} \cdot \dot{\hat{\mathbf{\Omega}}}^{(0)}{}_i = 0$ by normalization, and $\hat{\boldsymbol{n}}_i \cdot \dot{\hat{\mathbf{\Omega}}}^{(0)}{}_i = 0$ since SLERP bond vectors exhibit planar motion.

Off-diagonal elements are gnarly because the above does not hold. However, if we assume that the time step is small enough that we can replace these time-dependent dot products with their averages over a period, the above

cross terms become constants easily integrable in time. Denote:

$$\begin{aligned}
\frac{1}{t}\int_{\tau=0}^{\tau=t}\left(\dot{\hat{\boldsymbol{\Omega}}}^{(0)}{}_i \cdot \dot{\hat{\boldsymbol{\Omega}}}^{(0)}{}_j\right)\mathrm{d}\tau &= A_{vv}^{ij}\\
\frac{1}{t}\int_{\tau=0}^{\tau=t}\left(\hat{\boldsymbol{\Omega}}_i^{(0)} \cdot \dot{\hat{\boldsymbol{\Omega}}}^{(0)}{}_j\right)\mathrm{d}\tau &= A_{rv}^{ij}\\
\frac{1}{t}\int_{\tau=0}^{\tau=t}\left(\hat{\boldsymbol{n}}_i \cdot \hat{\boldsymbol{\Omega}}_j^{(0)}\right)\mathrm{d}\tau &= A_{nr}^{ij}\\
\frac{1}{t}\int_{\tau=0}^{\tau=t}\left(\hat{\boldsymbol{n}}_i \cdot \dot{\hat{\boldsymbol{\Omega}}}^{(0)}{}_j\right)\mathrm{d}\tau &= A_{nv}^{ij}\\
\frac{1}{t}\int_{\tau=0}^{\tau=t}\left(\hat{\boldsymbol{n}}_i \cdot \hat{\boldsymbol{n}}_j\right)\mathrm{d}\tau &= A_{nn}^{ij}
\end{aligned} \tag{17}$$

Then the calculations can be carried through using a computer algebra system. The result (obtained with *Mathematica*) is:

$$\begin{aligned}
\frac{\delta S}{\delta v_i} &= C_{ii}\left(\frac{2}{3}-\frac{t^2}{15}\right)tv_i + \mathcal{O}\left(t^5\right)\\
&+\sum_{i\neq j} C_{ij}\left(\frac{t}{3}A_{nn}^{ij}\left(v_i+v_j\right)\right.\\
&-\frac{t^2}{30}\left(\left(A_{nr}^{ji}v_i^2\right)+2v_iv_jA_{nr}^{ij}+(i\leftrightarrow j)\right)\\
&\left.-\frac{t^3}{420}\left(3A_{nn}^{ij}v_j\left(v_i^2-v_j^2\right)+4A_{rr}^{ij}v_iv_j^2+14A_{vv}^{ij}t^2v_i+(i\leftrightarrow j)\right)\right)+\mathcal{O}\left(t^5\right)
\end{aligned} \tag{18}$$

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[b]Electronic mail: artur_avkhadiev@brown.edu

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Appendices

A. LAGRANGIAN WITH CONSTRAINTS

Basic Lagrangian mechanics. Given a functional

$$S = \int_{\tau=0}^{\tau=t} L(\boldsymbol{q}(\tau),\, \dot{\boldsymbol{q}}(\tau), \tau)\,\mathrm{d}\tau$$

we wish to obtain the equations of motion $q(\tau)$. These functions $q(\tau)$ have to minimize our functional — the action S.

To do so, we use the calculus of variations. At a minimum, the variation of the action should be 0.

$$\begin{aligned}
\delta S &= \delta \int_{\tau=0}^{\tau=t} L(\boldsymbol{q}(\tau),\, \dot{\boldsymbol{q}}(\tau), \tau)\, \mathrm{d}\tau \\
&= \int_{\tau=0}^{\tau=t} \left(\frac{\partial L}{\partial q_i} \delta q_i + \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i \right) \mathrm{d}\tau \\
&= \int_{\tau=0}^{\tau=t} \left(\frac{\partial L}{\partial q_i} \delta q_i + \left(\frac{\partial}{\partial \tau} \left(\frac{\partial L}{\partial \dot{q}_i} \delta q_i \right) - \frac{\partial}{\partial \tau} \left(\frac{\partial L}{\partial \dot{q}_i} \right) \delta q_i \right) \right) \mathrm{d}\tau \\
&= \int_{\tau=0}^{\tau=t} \left(\frac{\partial L}{\partial q_i} - \frac{\partial}{\partial \tau} \frac{\partial L}{\partial \dot{q}_i} \right) \delta q_i \, \mathrm{d}\tau
\end{aligned}$$

where we integrated by parts and the full term $\frac{\partial}{\partial \tau} \left(\frac{\partial L}{\partial \dot{q}_i} \delta q_i \right)$ vanished at the boundaries: $\delta \boldsymbol{q}(\tau = 0) = \delta \boldsymbol{q}(\tau = t) = \mathbf{0}$. Since the variation δq_i is arbitrary and the integral is identically zero, we find Euler-Lagrange equations of motion for each coordinate q_i:

$$\frac{\partial}{\partial \tau} \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$$

Now, in addition minimizing the functional, we may have have to respect a set of constraints $\sigma_k((q)(\tau)) = 0$. Recall from calculus that finding a minimum $\boldsymbol{x}_0$ of a function $F(\boldsymbol{x})$ constrained to a set of surfaces $G_k(\boldsymbol{x}_0) = 0$ means that the normal vector $\frac{\partial F}{\partial x_i} \hat{\boldsymbol{x}}_i$ is a linear combination of normal vectors to constraint surfaces:

$$\frac{\partial F}{\partial x_i} \hat{\boldsymbol{x}}_i = \lambda_k \frac{\partial G^k}{\partial x_i} \hat{\boldsymbol{x}}_i$$

where λ_k are scalar constants (Lagrange multipliers). Note that minimizing $F(\boldsymbol{x})$ subject to constraints $G_k(\boldsymbol{x}_0) = 0$ is equivalent to minimizing $F(\boldsymbol{x}) - \lambda_k G^k(\boldsymbol{x})$ without constraints. Given the additional information that $G_k(\boldsymbol{x}_0) = 0$, the number of unknowns is equal to the number of equations.

This is all we need to do calculus of variations with constraints: modify the Lagrangian to include the constraints:

$$L'(\boldsymbol{q}(\tau), \dot{\boldsymbol{q}}(\tau), \tau) = L - \lambda_k(\tau) \sigma^k(\boldsymbol{q}(\tau), \tau)$$

except that now we are minimizing a functional, and our minimum is not at a point but a function (of time), and Lagrange multipliers are time-dependent. The Euler Lagrange equations for L', in addition to a set of algebraic equations $\sigma^k(\boldsymbol{q}(\tau), \tau) = 0$, give us the equations of motion.