

The trimer paradox

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We reconsider the classical problem of a freely joined chain of Brownian particles connected by elastic springs and study its conformational probability distribution function in the limit of infinite stiffness of constraints. We show that the well-known solution by Fixman is missing a shape-related term, later alluded to but not computed by Helfand. In our approach, the shape term, also termed zero-point energy, arises explicitly from a careful treatment of the distributional limit. We present a computationally feasible method of calculation of the shape term and demonstrate its validity in a couple of examples.

I. INTRODUCTION

Molecular Dynamics (MD) and Brownian Dynamics (BD) simulations are now standard tools for detailed modelling of plethora of molecular and mesoscopic systems, where structural complexity poses a challenge to theoretical calculations. Upon the introduction of a suitable coarse-graining scheme to represent the composition of a given molecule, its conformational space is prescribed by specifying intramolecular interactions, such as chemical bonds or electrostatic forces, between the subunits. The nature of these interactions endows molecular models with flexibility, which then in turns affects their conformational variability, as well as macroscopic and statistical properties, such as rheology, diffusivity, and thermodynamics.

A popular idealisation for a wide variety of systems is purely mechanical, where the molecule is represented by beads connected with springs, an idea which probably originated from Kramers [1], who built on concepts of Kuhn, and termed it the pearl-necklace model. Variations of this idea are now the cornerstone of polymer physics [2], but have also been used to describe other classical many-body systems. Physically, the introduction of interactions leads to a constrained dynamics with multiple time scales. Typically, the characteristic time scales associated with internal vibrations of molecular bonds are much shorter than those of translational and rotational motion, or bond angle dynamics. The disparity of time scale of relaxation of stiff degrees of freedom (such as bond lengths) in comparison to soft degrees of freedom (such as bond angles) is a source of stiffness in the problem and hinders fast numerical simulation of such systems [3].

In many applications, the dynamics of the stiff degrees of freedom are of secondary importance, and one method of circumventing this difficulty is to treat them as fully constrained (i.e. rigid), thus eliminating the short timescale, and enabling faster calculation. This is the basic of many algorithms, such as SHAKE [4] and its further extensions. During the development of such rigid models, a disconnect between equilibrium bond angle distributions in the rigid simulations and simulations with

bonds modelled as very stiff springs was discovered.

The simplest example where complexity of the constrained dynamics can be appreciated is the case of a flexible trimer: a hypothetical molecule containing 3 atoms and 2 harmonic bonds, depicted in Fig. 1a. The angle between the two bonds is denoted by ψ . In Ref. [3], Frenkel and Smit present an apparently paradoxical result: the marginal distribution of the bond angle in the case of rigid bonds dp_{rigid} and the limiting distribution of spring-like bonds where spring stiffness k is taken to infinity $dp_{k \rightarrow \infty}$ do not coincide. More precisely,

$$dp_{k \rightarrow \infty} = N_1 \sin \psi \, d\psi \quad (1)$$

$$dp_{rigid} = N_2 \sin \psi \sqrt{1 - \frac{\cos^2 \psi}{4}} \, d\psi \quad (2)$$

for appropriate normalisation constants N_1 and N_2 . Qualitatively, the distribution (1) corresponds to a spherically uniform distribution of the second bond direction when the coordinates are aligned with the first bond, while in the case of Eq. (2) it seems that an additional force resists bond alignment.

In an early work, Fixman [5] presented a derivation to argue that the ratio of the two probability densities (1) and (2) can be computed with the knowledge of the constraining surfaces alone. This presupposes that both of these distributions are well defined whenever the constraint is given.

In this contribution, we show by clarifying the mathematical procedure leading to the aforementioned limits, that the distribution given by Eq. (1) is not completely determined by fixing the bond lengths and in particular that harmonic springs do not give the distribution with maximum entropy. In order to correctly predict the limiting distribution, knowledge about the nature of the confinement is needed. Furthermore, we demonstrate that expressions for the stiff limit are missing a term, which is important even in the case of harmonic springs.

II. STIFF VS. RIGID CONSTRAINTS

We consider a coarse-grained bead-spring model of a macromolecule, com...

The calculations of the equilibrium properties of flexible polymers can be traced to the papers by Kramers [1], Gō and Sheraga [6] and Fixman [5]. Results of the latter paper were used essentially without changes in works such as [7–10].

Gō and Sheraga, in a quantum-mechanical treatment of the problem, correctly identify both projected volume elements (in their work denoted as $\det(\mathbf{g})$) and zero point energy (in their work denoted as ϵ) contributions to the coordinate expressions for the equilibrium probability density of the soft coordinates but erroneously state that these contributions vary less with soft coordinates than the energy of the configuration where hard coordinates take equilibrium values. Fixman, on the other hand, attempts purely classical calculation of the limiting distribution correctly writing out action of the limiting distribution on a test function but erroneously assuming that the constraining potential depends only on hard coordinates, as a result details of the confining potential cannot appear in the final expressions of Fixman which contain only the volume element terms. By focusing on a concrete two-dimensional example with one constraint, Helfand [11] correctly identifies rigid-rod type distribution as a uniform distribution on the constraining manifold and computes stiff-spring limit in a similar simple case, unfortunately these results are not expressed in a form applicable to a higher dimensional examples with multiple constraints. This lack of generality later results in works such as that of Hinch [8] citing Helfand [11] as a reference to an erroneous claim that bond angle distribution becomes non-uniform in case of rigid-rod system. Hinch [8] adopts yet another method of approaching the problem by attempting to manipulate Langevin equations (which are notoriously difficult to handle) and erroneously assumes that details of the confining potential are of little importance to the equilibrium distribution of the constrained configurations. Van Kampen and Lodder [12] note that approach of Helfand [11] is generally applicable and comment that the discrepancy between stiff-spring and rigid-rod distributions in the case of the trimer molecule is due to the fact that “*the width of this gully is not the same everywhere*” – how to quantify such width in a high-dimensional case is unfortunately not spelled out even though “*it can of course be checked in detail*” as claimed by the authors. The knowledge of the influence of the shape of the constraining potential appears to have been lost as multiple works (for example [3, 13, 14]) mention only the volume element densities and omit the *zero point energy* or equivalently *shape* terms from their descriptions of constrained dynamics using the work of Fixman [5] as their reference.

III. THE STIFF SPRING LIMIT

First we compute the stiff spring limit. We will consider a molecule with a number of atoms and N degrees of freedom in a heat bath with $\beta = 1/k_B T$, the potential energy $U(\mathbf{q})$ dependent on the conformation \mathbf{q} and the confining springs potential $k^2 W(\mathbf{q})$ where k is a large parameter describing spring stiffness. Note that k here would correspond to the square root of a harmonic spring constant. We parameterise conformations by Cartesian coordinates of atoms q_i with $i \in 1 \dots N$.

The potential energy has two components: the conformation-dependent energy $U(\mathbf{q})$ and the confining (springs) potential $k^2 W(\mathbf{q})$ where k is a large parameter describing spring stiffness.

The probability density p_k of the equilibrium distribution of the system configuration with respect to the Lebesgue measure $d\mathbf{q}$ is given by the Boltzmann distribution

$$p_k = N(k) \exp \left[-\beta(U(\mathbf{q}) + k^2 W(\mathbf{q})) \right], \quad (3)$$

with an appropriate normalising function $N(k)$.

Suppose now that the spring potential is non-negative, $W(\mathbf{q}) \geq 0$, and attains a minimum for a configuration lying on a smooth submanifold \mathcal{M} of dimension M , so that $W(\mathbf{q}) = 0 \iff \mathbf{q} \in \mathcal{M}$. To determine the weak limit of p_k , we will consider integrals I_k for a smooth compactly supported $\phi(\mathbf{q})$ given by

$$I_k = \int p_k(\mathbf{q}) \phi(\mathbf{q}) d\mathbf{q}. \quad (4)$$

Since our submanifold is smooth, we can use tubular embedding theorem to define new orthonormal coordinates $\mathbf{q} = (r_1, r_2, \dots, r_M, s_1, s_2, \dots)$ in the vicinity of \mathcal{M} , where $\mathbf{q} \in \mathcal{M} \iff \mathbf{s} = 0$. In other words, coordinates r_i represent the *soft* degrees of freedom and s_i represent the *stiff* directions. Since the new coordinates are orthonormal we know that the determinant of the transformation $(x_i) \mapsto (r_i, s_j)$ is 1. Additionally, I_k is finite by compactness of the support of ϕ and continuity of p_k , so we can replace the volume integral by an iterated one by Fubini's theorem. Then, I_k is given by

$$I_k = \iint p_k(\mathbf{r}, \mathbf{s}) \phi(\mathbf{r}, \mathbf{s}) d\mathbf{s} d\mathbf{r} \quad (5)$$

We proceed by expanding p_k in Taylor series with respect to \mathbf{s} to second order as $W(\mathbf{r}, \mathbf{s}) = \mathbf{s}^T \mathbf{H}(\mathbf{r}) \mathbf{s}$ to get

$$I_k = \iint N(k) \exp \left[-\beta U(\mathbf{r}, \mathbf{s}) - \beta k^2 (\mathbf{s}^T \mathbf{H}(\mathbf{r}) \mathbf{s} + o(\|\mathbf{s}\|^2)) \right] \phi(\mathbf{r}, \mathbf{s}) d\mathbf{s} d\mathbf{r} \quad (6)$$

Now we make a substitution $k\mathbf{s} = \mathbf{t}$ to arrive at

$$I_k = \iint \frac{N(k)}{k} \exp \left[-\beta U(\mathbf{r}, k^{-1}\mathbf{t}) - \beta \left(\mathbf{t}^T \mathbf{H}(\mathbf{r}) \mathbf{t} + \|\mathbf{t}\|^2 \frac{o(k^{-2}\|\mathbf{t}\|^2)}{k^{-2}\|\mathbf{t}\|^2} \right) \right] \phi(\mathbf{r}, k^{-1}\mathbf{t}) d\mathbf{t} d\mathbf{r} \quad (7)$$

Whenever W increases sufficiently fast with the distance from the constraining manifold, we may take a limit inside the integral by the dominated convergence theorem to arrive at limiting value $I = \lim_{k \rightarrow \infty} I_k$

$$I = \iint \left(\lim_{k \rightarrow \infty} \frac{N(k)}{k} \right) \exp \left[-\beta U(\mathbf{r}, \mathbf{0}) - \beta (\mathbf{t}^T \mathbf{H}(\mathbf{r}) \mathbf{t}) \right] \phi(\mathbf{r}, \mathbf{0}) d\mathbf{t} d\mathbf{r} \quad (8)$$

and, since \mathbf{H} is full rank, perform the $d\mathbf{t}$ integral to arrive at

$$I = L \int |\mathbf{H}(\mathbf{r})|^{-1/2} \exp[-\beta U(\mathbf{r}, \mathbf{0})] \phi(\mathbf{r}, \mathbf{0}) d\mathbf{r} \quad (9)$$

where the constant

$$L = \lim_{k \rightarrow \infty} \frac{N(k) \sqrt{(2\pi)^{N-M}}}{k}, \quad (10)$$

depends only on the values of N and M .

In a particular physical setting, finding the orthonormal coordinates (\mathbf{r}, \mathbf{s}) may be prohibitively difficult, but we can relax this strict requirement by considering another parametrisation $\mathbf{q} = \mathbf{q}(\mathbf{w})$ which still separates *soft* from *stiff* degrees of freedom by

$$\mathbf{q} \in \mathcal{M} \iff \forall i > M : w_i = \xi_i \quad (11)$$

for a set of constants ξ_i . This parametrisation is not necessarily orthonormal.

For convenience, we define a map $\zeta : \mathbb{R}^M \rightarrow \mathbb{R}^N$ such that $\zeta(w_1, w_2, \dots, w_M) = \mathbf{q}(w_1, w_2, \dots, w_M, \xi_{M+1}, \xi_{M+2}, \dots, \xi_N)$ which takes values of the *soft* coordinates and returns points on \mathcal{M} .

We now change variables under the integral from \mathbf{r} to \mathbf{w} to arrive at

$$I = \int \left(L |\mathbf{H}(\zeta(w_i))|^{-1/2} |\mathbf{J}^T \mathbf{J}|^{1/2} \exp[-\beta U(\zeta(w_i))] \phi(\zeta(w_i)) \right) dw_1 \dots dw_M \quad (12)$$

where \mathbf{J} is the Jacobian of $\zeta(\mathbf{w})$. Note that $\zeta : \mathbb{R}^M \rightarrow \mathbb{R}^N$, so the Jacobian is not a square matrix.

We can express the above using the Dirac- δ distributions. Taking

$$\delta(\mathbf{w}' - \xi') = \prod_{i=M+1}^N \delta(w_i - \xi_i) \quad (13)$$

the limiting integral amounts to

$$I = \int L \left(\frac{|\mathbf{J}^T \mathbf{J}|}{|\mathbf{H}|} \right)^{1/2} \exp[-\beta U(\mathbf{q}(\mathbf{w}))] \phi(\mathbf{q}(\mathbf{w})) \delta(\mathbf{w}' - \xi') dw_1 \dots dw_N \quad (14)$$

for an appropriate constant L , and since ϕ is arbitrary we arrive at $p_\infty = \lim_{k \rightarrow \infty} p_k$ such that

$$dp_\infty = L \left(|\mathbf{J}^T \mathbf{J}|^{1/2} |\mathbf{H}|^{-1/2} \exp[-\beta U(\mathbf{q}(\mathbf{w}))] \delta(\mathbf{w}' - \xi') \right) d\mathbf{w} \quad (15)$$

in the weak sense. We have thus arrived at the central result of this manuscript. The limiting distribution comprises of two parts: First, the metric term $|\mathbf{J}^T \mathbf{J}|$ describing the projection of the surface element of \mathcal{M} onto \mathbb{R}^M in the parametrisation $\mathbf{q}(w)$ – this term was correctly computed by Fixman [5]; Second, the *shape* term $|\mathbf{H}|$ (also called zero-point energy in the quantum-mechanical setting) which was often missing.

A. Computation of the shape term

A careful choice of parametrisation allows for computation of the metric term with relative ease, $|\mathbf{H}|$ term on the other hand can be harder to compute – in this section we present a computationally feasible approach to its computation.

Let \mathbf{B} be the full Hessian of W at a point \mathbf{q} ,

$$\mathbf{B}_{ij} = \frac{\partial^2}{\partial q_i \partial q_j} W(\mathbf{q}). \quad (16)$$

Since eigenvectors of \mathbf{B} are orthogonal, and zero eigenvectors lie inside the tangent space $T\mathcal{M}$, we can compute $|\mathbf{H}|$ from the product of the nonzero eigenvalues of \mathbf{B} . We can use the knowledge of the tangent space of \mathcal{M} to help us compute eigenvalues of \mathbf{B} . If our confining function is of the form $W(\mathbf{q}) = \sum_i P_i^2$ we can use the result of Ref. [15, proposition 8.15] to find vectors which lie in the normal space \mathcal{M}^\perp by computing

$$\mathbf{A}_{ji} = \frac{\partial}{\partial q_j} P_i \quad (17)$$

The vectors $\{\mathbf{A}_{j,1}, \dots, \mathbf{A}_{j,N-M}\}$ are not pairwise orthogonal but are orthogonal to \mathcal{M} thus form a basis of the

normal space at \mathbf{q} . We can write the eigenvalue problem using an arbitrary vector b_i as

$$\lambda \mathbf{A}_{ki} b_i = \mathbf{B}_{kj} \mathbf{A}_{ji} b_i. \quad (18)$$

This is a system of N equations with $N - M$ unknowns. We can eliminate redundant equations by contracting each side with \mathbf{A}_{ij} to finally get

$$\lambda (\mathbf{A}^T \mathbf{A}) \mathbf{b} = (\mathbf{A}^T \mathbf{B} \mathbf{A}) \mathbf{b} \quad (19)$$

and thus the product of eigenvalues in this problem is simply

$$|\mathbf{H}| = \frac{|\mathbf{A}^T \mathbf{B} \mathbf{A}|}{|\mathbf{A}^T \mathbf{A}|}. \quad (20)$$

We see that there are two terms in this expression. The denominator $|\mathbf{A}^T \mathbf{A}|$ measures the angles between gradients of the constraining functions, while the numerator $|\mathbf{A}^T \mathbf{B} \mathbf{A}|$ measures the shape and strength of the the confining field in these directions.

IV. CALCULATION FOR THE TRIMER PROBLEM

In case of the trimer we have 3 atoms located at $\mathbf{r}_a, \mathbf{r}_b$ and \mathbf{r}_c with bond extensions P_a, P_c given by

$$P_a = |\mathbf{r}_a - \mathbf{r}_b| - l_0 \quad (21)$$

$$P_c = |\mathbf{r}_c - \mathbf{r}_b| - l_0 \quad (22)$$

and confining potential given by

$$W(\mathbf{q}) = P_a^2 + P_c^2. \quad (23)$$

we pick parametrisation $\mathbf{q}(\mathbf{w})$ with $\mathbf{w} = [x, y, z, \alpha, \beta, \gamma, \psi, l_a, l_c]^T$ given by

$$\mathbf{r}_a = [x, y, z]^T + l_a \mathbf{E}_{\alpha\beta\gamma} [1, 0, 0]^T \quad (24)$$

$$\mathbf{r}_b = [x, y, z]^T \quad (25)$$

$$\mathbf{r}_c = [x, y, z]^T + l_c \mathbf{E}_{\alpha\beta\gamma} [\cos \psi, \sin \psi, 0]^T \quad (26)$$

Where $\mathbf{E}_{\alpha\beta\gamma}$ is a rotation matrix defined in terms of the Euler angles as specified in the appendix. Thus $P_a = l_a - l_0$ and $P_c = l_c - l_0$.

We compute the metric term

$$|\mathbf{J}^T \mathbf{J}| = \frac{1}{2} l_0^8 \sin^2 \beta \sin^2 \psi (7 - \cos 2\psi) \quad (27)$$

from the \mathbf{J} matrix listed in appendix. Next we compute the shape term as

$$\mathbf{A}^T \mathbf{A} = \begin{bmatrix} 2 & \cos \psi \\ \cos \psi & 2 \end{bmatrix} \quad (28)$$

$$\mathbf{A}^T \mathbf{B} \mathbf{A} = \begin{bmatrix} 9 + \cos 2\psi & 8 \cos \psi \\ 8 \cos \psi & 9 + \cos 2\psi \end{bmatrix} \quad (29)$$

thus

$$|\mathbf{H}| = \frac{|\mathbf{A}^T \mathbf{B} \mathbf{A}|}{|\mathbf{A}^T \mathbf{A}|} = 2(7 - \cos 2\psi) \quad (30)$$

to finally get

$$\begin{aligned} dp_\infty &= \left(\frac{|\mathbf{J}^T \mathbf{J}|}{|\mathbf{H}|} \right)^{1/2} \\ &= N \sin \beta \sin \psi \, dx dy dz d\alpha d\beta d\gamma d\psi \end{aligned} \quad (31)$$

where N is a normalization constant, therefore marginal density of the bond angle is proportional to $\sin \psi$ as expected. This is, however, not simply the case of the uniform distribution – that distribution corresponds to $|\mathbf{H}| = \text{const}$. The unexpected aspect lies in the cancellation of the $(7 - \cos 2\psi)$ term, rather than its absence. This is best highlighted by an example where no such cancellation occurs.

V. CYCLIC TETRAMER

For sake of brevity we show the case of a cyclic tetramer a 4 atom molecule joined into a quadrilateral in 2D. Calculation in 3D is completely analogous but involves much longer intermediate expressions due to the additional rotational degrees of freedom and a dihedral angle. We pick parametrisation where the 4 atoms are located at $\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c$ and \mathbf{r}_d with locations given by

$$\mathbf{r}_a = [x, y]^T + l_a \mathbf{E}_\alpha [1, 0]^T \quad (32)$$

$$\mathbf{r}_b = [x, y]^T \quad (33)$$

$$\mathbf{r}_c = [x, y]^T + l_c \mathbf{E}_\alpha [\cos \phi, \sin \phi]^T \quad (34)$$

$$\mathbf{r}_d = [x, y]^T + \mathbf{E}_\alpha ((1 + \delta) \mathbf{v}_\delta + \epsilon \mathbf{v}_\epsilon) \quad (35)$$

$$\mathbf{v}_\delta = \frac{[l_a + l_c \cos \psi, l_c \sin \psi]^T}{2} \quad (36)$$

$$\mathbf{v}_\epsilon = \frac{[l_a - l_c \cos \psi, -\sin \psi]^T}{2} \quad (37)$$

where \mathbf{E}_α is a rotation matrix defined in appendix. The four constraining surfaces are given by

$$P_a = |\mathbf{r}_a - \mathbf{r}_b| - l_0 \quad (38)$$

$$P_b = |\mathbf{r}_b - \mathbf{r}_c| - l_0 \quad (39)$$

$$P_c = |\mathbf{r}_c - \mathbf{r}_d| - l_0 \quad (40)$$

$$P_d = |\mathbf{r}_d - \mathbf{r}_a| - l_0 \quad (41)$$

and \mathcal{M} is given by $l_a = l_c = l_0, \delta = 1, \epsilon = 0$.

The metric term is simply constant with $|\mathbf{J}^T \mathbf{J}| = 16l_0^4$ while the shape term is non-trivial. Denoting $\cos \psi = c_\psi$

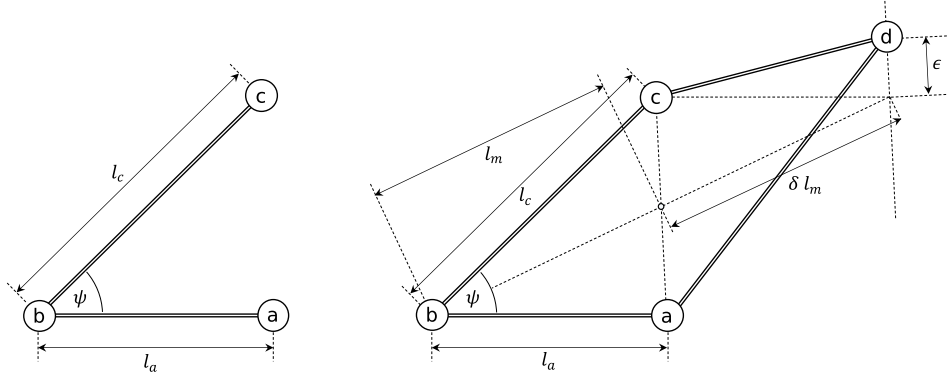


FIG. 1. Parametrisation used in the calculations of the trimer and cyclic tetramer problems. Final rigid body rotation around the "b" atom omitted for clarity.

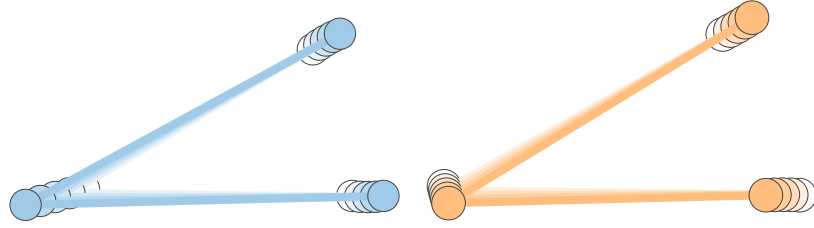


FIG. 2. Motion along the symmetric and anti-symmetric eigen-vectors of the hessian \mathbf{H} of the confinement function in the trimer problem. Note that central bead has to move for the motion to be orthogonal to the constraining manifold \mathcal{M} .

for brevity the shape factors are given by

$$\mathbf{A}^T \mathbf{A} = \begin{bmatrix} 2 & c_\psi & 0 & -c_\psi \\ c_\psi & 2 & -c_\psi & 0 \\ 0 & -c_\psi & 2 & c_\psi \\ -c_\psi & 0 & c_\psi & 2 \end{bmatrix} \quad (42)$$

$$\mathbf{A}^T \mathbf{B} \mathbf{A} = 4 \begin{bmatrix} c_\psi^2 + 2 & 2c_\psi & -c_\psi^2 & -2c_\psi \\ 2c_\psi & c_\psi^2 + 2 & -2c_\psi & -c_\psi^2 \\ -c_\psi^2 & -2c_\psi & c_\psi^2 + 2 & 2c_\psi \\ -2c_\psi & -c_\psi^2 & 2c_\psi & c_\psi^2 + 2 \end{bmatrix} \quad (43)$$

Giving $|\mathbf{H}| = 256 \sin^2 \psi$, as a result we get that

$$dp_\infty \propto \frac{1}{\sin \psi} d\psi \quad (44)$$

p_∞ which is not integrable near zero. Physically as we go to the stiff spring limit tetramer spends more and more time in folded state and, unless some repulsive potential is added, in the limit of stiff springs looks like a trimer indefinitely (with atoms a-c or b-d coinciding).

This surprising result can be easily corroborated by a numerical simulation calculated with the package **pychastic** [16]. By choosing $k_B T$ as energy scale, l_0 as distance scale and l_0^2/D as timescale the equations of Brownian dynamics take a non-dimensional Langevin form

$$d\mathbf{r}_i = -\nabla U dt + \sqrt{2} d\mathbf{W}_i, \quad (45)$$

with $d\mathbf{W}_i$ denoting the Wiener process. We have performed $n_{\text{traj}} = 4000$ simulations with $k = 35$ for time up

to $t_{\text{max}} = 10$ with time step $\delta t = 10^{-5}$. A strong repulsive potential was added in the case of tetramer simulation to prevent atom overlap for distances smaller than 0.05. The final bond angle distribution shown in Figure 3 coincides well with $0.15/\sin \psi$.

VI. CONCLUSIONS

By rephrasing the problem as a mathematically rigorous limit we have shown that the classical expression given by Fixman [5] (later reproduced many times, for example in Frenkel and Smit [3]) is missing a critical term describing the shape of the confining potential: $|\mathbf{H}|$. This shows that reasoning in Frenkel and Smit [3] is fundamentally flawed. First, the dynamics and the distribution of a polymer connected with (stiff or not) springs is independent of the mass of the atoms in the overdamped regime, thus the limiting distribution cannot depend on the mass of the atoms. Second, putting aside the question of existence of rigid rod distribution (or lack thereof) it presupposes that stiff spring limit should be always the same regardless of the details of the confining potential – this is clearly not true, harmonic potentials will lead to different outcomes than springs realising uniform confinement around the constraining manifold with and the difference can be arbitrarily large as shown in the tetramer example.

To summarise we cannot disagree more with the statement: *However, to put things in perspective, we should*

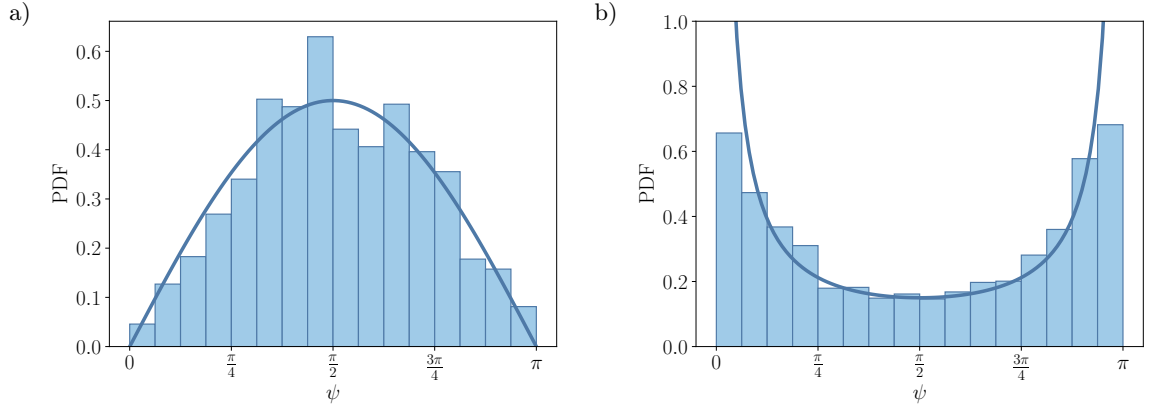


FIG. 3. Distribution of the bond angles in a numerical simulation compared with theoretical prediction for a) trimer b) cyclic tetramer.

add that, at least for bond length constraints of the type most often used in Molecular Dynamics simulations, the effect of the hard constraints on the distribution functions appears to be relatively small. [3, Chapter 15.1.1]. Especially since coming up finding a counterexample required adding only one atom to the molecule studied in the chapter.

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Appendix A: Auxiliary matrices used in calculations

Using notation $s_\alpha = \sin \alpha$, $c_\alpha = \cos \alpha$ we can compactly express used matrices. The 2D rotation matrix is given by

$$\mathbf{E}_\alpha = \begin{bmatrix} c_\alpha & -s_\alpha \\ s_\alpha & c_\alpha \end{bmatrix} \quad (\text{A1})$$

and the 3D rotation matrix is given by

$$\mathbf{E}_{\alpha\beta\gamma} = \begin{bmatrix} c_\alpha c_\beta c_\gamma - s_\alpha s_\gamma & -c_\alpha c_\beta s_\gamma - c_\gamma s_\alpha & c_\alpha s_\beta \\ c_\beta c_\gamma s_\alpha + c_\alpha s_\gamma & c_\alpha c_\gamma - c_\beta s_\alpha s_\gamma & s_\alpha s_\beta \\ -c_\gamma s_\beta & s_\beta s_\gamma & c_\beta \end{bmatrix} \quad (\text{A2})$$

For our parametrisation of the trimer \mathbf{J} can be expressed as a block matrix with 3×4 blocks \mathbf{Q}_i

$$\mathbf{J} = \begin{bmatrix} \mathbf{1} & \mathbf{Q}_1 \\ \mathbf{1} & \mathbf{Q}_2 \\ \mathbf{1} & \mathbf{Q}_3 \end{bmatrix} \quad (\text{A3})$$

writing $\gamma + \psi = \theta$ for brevity, the blocks \mathbf{Q}_i are given by

$$\mathbf{Q}_1^T = l_0 \begin{bmatrix} -s_\alpha c_\beta c_\gamma - c_\alpha s_\gamma & c_\alpha c_\beta c_\gamma - s_\alpha s_\gamma & 0 \\ -c_\alpha s_\beta c_\gamma & -s_\alpha s_\beta c_\gamma & -c_\beta c_\gamma \\ -s_\alpha c_\gamma - c_\alpha c_\beta s_\gamma & c_\alpha c_\gamma - s_\alpha c_\beta s_\gamma & s_\beta s_\gamma \\ 0 & 0 & 0 \end{bmatrix} \quad (\text{A4})$$

$$\mathbf{Q}_2^T = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (\text{A5})$$

$$\mathbf{Q}_3^T = l_0 \begin{bmatrix} -s_\alpha c_\beta c_\theta - c_\alpha s_\theta & c_\alpha c_\beta c_\theta - s_\alpha s_\theta & 0 \\ -c_\alpha s_\beta c_\theta & -s_\alpha s_\beta c_\theta & -c_\beta c_\theta \\ -s_\alpha c_\theta - c_\alpha c_\beta s_\theta & c_\alpha c_\theta - s_\alpha c_\beta s_\theta & s_\beta s_\theta \\ -s_\alpha c_\theta - c_\alpha c_\beta s_\theta & c_\alpha c_\theta - s_\alpha c_\beta s_\theta & s_\beta s_\theta \end{bmatrix} \quad (\text{A6})$$

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