

Note: smooth torsional potentials for degenerate dihedral angles

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A general method is proposed for smoothing torsional potentials when the dihedral angle becomes undefined.

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Torsional potentials impose steric or geometric constraints between four bonded particles, e.g., the rotational barriers between conformations of the carbon backbone in atomistic models for hydrocarbons.^{1,2} Typically, torsional potentials are functions of the dihedral angle ϕ between a plane A containing three particles at $\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3\}$ and a plane B containing particle positions $\{\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4\}$ (Figure 1). The planes A and B have normal vectors $\mathbf{n}_A = \mathbf{r}_{12} \times \mathbf{r}_{23}$ and $\mathbf{n}_B = \mathbf{r}_{23} \times \mathbf{r}_{34}$, respectively, where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. The dihedral angle between the planes is³

$$\cos \phi = \frac{\mathbf{n}_A \cdot \mathbf{n}_B}{|\mathbf{n}_A| |\mathbf{n}_B|}. \quad (1)$$

In most cases, this definition can be straightforwardly applied to compute the torsional energy and forces.⁴ However, a degenerate state exists when $\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3\}$ or $\{\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4\}$ are collinear, and it is no longer possible to uniquely construct the required planes. The dihedral angle and torsional potential are then undefined, and the torsional forces are singular. Near this degenerate state, particles can be subjected to large forces, resulting in numerical integration errors or a complete crash for a molecular dynamics simulation.³ The singular nature of the torsional forces may also lead to unphysical motion or undesired restriction of conformations.

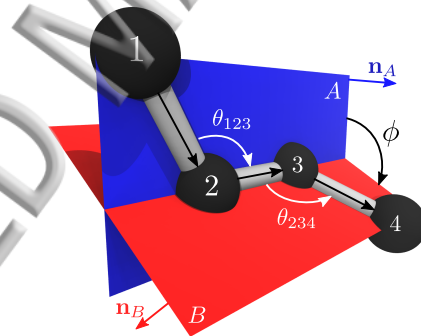


FIG. 1. Dihedral angle ϕ and bond angles θ_{ijk} formed from particles $\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4\}$. The positive orientation of ϕ is indicated according to the IUPAC convention.⁵ Image rendered using Visual Molecular Dynamics 1.9.3.⁶

Fortunately, such degenerate conformations are rarely, if ever, observed in atomistic models for particles participating in torsional potentials because the bond angle θ_{ijk} between them (Figure 1),³

$$\cos \theta_{ijk} = -\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{|\mathbf{r}_{ij}| |\mathbf{r}_{jk}|}, \quad (2)$$

restricted by additional interactions to values far from the collinear conformations. However, some coarse-grained polymer models impose significantly softer interactions,⁷⁻⁹ leading to a finite probability of observing a degenerate conformation, $\theta_{ijk} = 180^\circ$. It is necessary to somehow modify the torsional potential in such a case in order to obtain physical, well-defined behavior in molecular dynamics simulations.

The steric interactions approximated by a torsional potential are expected to weaken when the end particles are farther apart, and should be negligible when $\theta_{ijk} = 180^\circ$. Singular torsional forces can then be removed by modifying the potential so that forces go smoothly to zero when θ_{ijk} approaches 180° . Other authors have demonstrated the effectiveness of this approach for certain polymer models.¹⁰⁻¹³ However, the functional forms of the potentials chosen in their works offer little control over the range of bond angles for which the potential is modified, which may be problematic for some geometries.

In this note, we propose a simple, general approach for smoothing a torsional potential as a function of the bond angle. The proposed method can be applied to existing torsional potentials over a controllable smoothing range and gives well-defined behavior in the degenerate case. Motivated by a common method for smoothing truncated pair potentials in molecular simulations, we define a smoothed torsional potential,

$$V(\phi) = (V_0(\phi) - V_s)s(\cos \theta_{123})s(\cos \theta_{234}) + V_s, \quad (3)$$

where $V_0(\phi)$ is the unsmoothed potential, V_s is the value to which the potential is smoothed, and s is a smoothing function. The force on particle n is

$$\begin{aligned} \mathbf{F}_n(\phi) = & \mathbf{F}_{0,n}(\phi)s(\cos \theta_{123})s(\cos \theta_{234}) \\ & - (V_0(\phi) - V_s)\nabla_n (s(\cos \theta_{123})s(\cos \theta_{234})), \end{aligned} \quad (4)$$

where $\mathbf{F}_{0,n}(\phi)$ is the force on particle n in the absence of smoothing and ∇_n is the gradient with respect to \mathbf{r}_n . The smoothing function must satisfy the following conditions:

1. $s(\cos \theta_s) = 1$ at the onset of smoothing (angle θ_s),
2. $s(\cos \theta_c) = 0$ at the end of smoothing (angle θ_c),
3. The first derivatives of s are zero at θ_s and θ_c so that $\mathbf{F}_n = \mathbf{F}_{0,n}$ at θ_s and $\mathbf{F}_n^s = \mathbf{0}$ at θ_c , and

s must decay sufficiently quickly so that V and \mathbf{F}_n have well-defined limits for all bond angles.

A suitable polynomial for s is

$$s(x) = \begin{cases} 0 & x < x_c \\ \frac{(x_c^2 - x^2)^m (x_c^2 + mx^2 - (m+1)x_s^2)}{(x_c^2 - x_s^2)^{m+1}} & x_c \leq x < x_s \\ 1 & x \geq x_s \end{cases} \quad (5)$$

where $x_s = \cos \theta_s$, $x_c = \cos \theta_c$, and $m \geq 2$. (In writing s piecewise, we assume without loss of generality that $\theta_c > \theta_s$.) The values of θ_s , θ_c , and m set the range and steepness of smoothing. The gradients of s can be computed by chain rule, $\nabla_n s(\cos \theta_{ijk}) = s'(\cos \theta_{ijk}) \nabla_n \cos \theta_{ijk}$, where

$$s'(x) = \begin{cases} \frac{2m(m+1)x(x_c^2 - x^2)^{m-1}(x_s^2 - x^2)}{(x_c^2 - x_s^2)^{m+1}} & x_s \leq x < x_c \\ 0 & \text{otherwise} \end{cases} \quad (6)$$

and

$$\nabla_n \cos \theta_{ijk} = -\frac{1}{|\mathbf{r}_{ij}||\mathbf{r}_{jk}|} \left[(\nabla_n \otimes \mathbf{r}_{ij}) \left(\mathbf{r}_{jk} - \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{\mathbf{r}_{ij} \cdot \mathbf{r}_{ij}} \mathbf{r}_{ij} \right) + (\nabla_n \otimes \mathbf{r}_{jk}) \left(\mathbf{r}_{ij} - \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{\mathbf{r}_{jk} \cdot \mathbf{r}_{jk}} \mathbf{r}_{jk} \right) \right]. \quad (7)$$

Here, $\nabla_n \otimes \mathbf{r}_{ij}$ denotes the outer product and is equal to the identity matrix \mathbf{I} when $n = j$, $-\mathbf{I}$ when $n = i$, and the zero matrix $\mathbf{0}$ otherwise. In the degenerate limit, the unsmoothed torsional forces⁴ diverge as $1/\sin \theta_{ijk}$. If $\theta_c = 0^\circ$ or 180° , $s' \sim (1 - \cos^2 \theta_{ijk})^{m-1} \sim \sin^{2(m-1)} \theta_{ijk}$, and \mathbf{F}_n has a well-defined limit for $m \geq 2$.

The proposed smoothing function was tested for a simple torsional potential, $V_0(\phi) = -\cos \phi/2 + \cos^2 \phi$. The dihedral angle was initially fixed at $\phi = 120^\circ$ with $\mathbf{r}_1 = (-1, 0, 1)$, $\mathbf{r}_2 = (-1, 0, 0)$, $\mathbf{r}_3 = (0, 0, 0)$, and $\mathbf{r}_4 = (0, -\sin \phi, \cos \phi)$. The angle θ_{234} was then varied from its initial value of 90° by rotating \mathbf{r}_4 around \mathbf{r}_3 in plane B , causing the dihedral angle to jump to -60° as θ_{234} passed through 180° . Figure 2 shows the z -component of the torsional force on particle 4, $F_{4,z}$, as a function of θ_{234} for different smoothing ranges. As expected, the unsmoothed force diverges at $\theta_{234} = 180^\circ$. The smoothed force is equal to the unsmoothed force until θ_s , at which point $F_{4,z}$ goes continuously to zero at $\theta_{234} = 180^\circ$ before returning to the unsmoothed value at θ_s for $\phi = -60^\circ$.

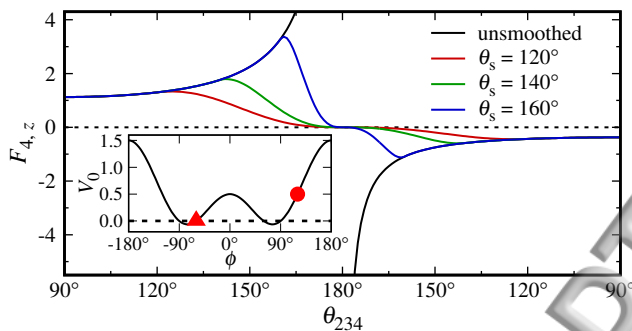


FIG. 2. Smoothed torsional force in z -direction on particle 4 as a function of bond angle θ_{234} for $V_s = 0.5$, $m = 2$, $\theta_c = 180^\circ$, and varied θ_s . Inset: unsmoothed potential with initial (circle) and final (triangle) dihedral angles marked.

The chosen form of s is particularly computationally convenient because (1) s and $\nabla_n s$ can be calculated from quantities that are already required for the unsmoothed potential, and (2) no additional square-root evaluations are necessary if smoothing is applied symmetrically around 90° to eliminate both possible degeneracies (i.e., $\theta_c = 180^\circ$ also implies smoothing toward $\theta_c = 0^\circ$). We encourage the use of the smoothed torsional potential especially during the development of coarse-grained models, using s as an additional adjustable parameter, in order to obtain correct simulation behavior and physics.

SUPPLEMENTARY MATERIAL

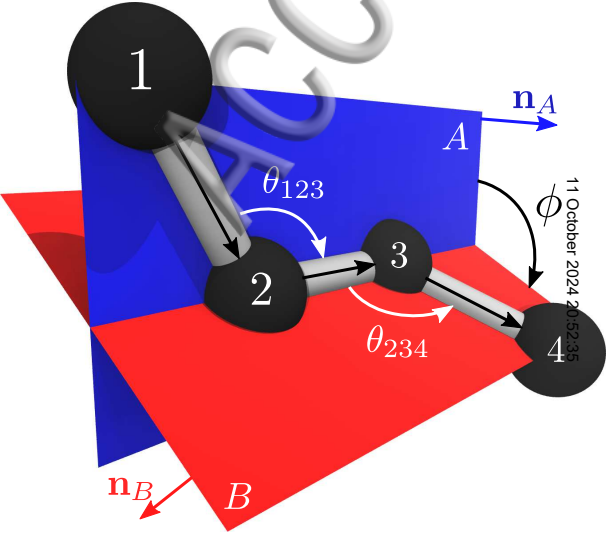
See supplementary material for an example implementation of the smoothed torsional potential.

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