

Analytical first derivatives of the RE-squared interaction potential

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Abstract

We derive exact expressions for the forces and torques between biaxial molecules interacting via the RE-squared potential, a recent variant of the Gay–Berne potential. Moreover, efficient routines have been provided for rigid body MD simulations, resulting in 1.6 times speedup compared to the two-point finite difference approach. It has also been shown that the time cost of a MD simulation will be almost equal to a similar MC simulation, making use of the provided routines. © 2006 Elsevier Inc. All rights reserved.

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1. Introduction

In molecular simulations, the van der Waals interactions have a prominent and essential contribution to the non-bonded interactions and are typically described using the Lennard–Jones(6–12) potential or its variants [1,2]. An interaction potential of this type between two extended molecules is assumed to be a double summation over the respective atomic interaction sites:

$$U_{\text{int}}(\mathcal{M}_1, \mathcal{M}_2) = \sum_{i \in \mathcal{M}_1} \sum_{j \in \mathcal{M}_2} U_a(r_{ij}; i, j), \quad (1)$$

where \mathcal{M}_1 and \mathcal{M}_2 denote the interacting molecules and $U_a(\cdot)$ is the atomic interaction potential, e.g. the Lennard–Jones(6–12) potential. The required computation time for the exact evaluation of this double sum is quadratic in the number of interacting sites. In practice, a large distant interaction cutoff accompanied by a proper tapering is used to reduce the computation cost. More sophisticated and efficient approximate summation methods such as Ewald summation and the Method of Lights [3] are also widely used.

As an alternative approach, Gay and Berne [4] proposed a more complicated single-site interaction potential (in contrast to a more sophisticated summation) for uniaxial rigid molecules which was generalized to

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dissimilar and biaxial molecules by Berardi et al. as well [5]. In response to the criticism of the unclear microscopic interpretation of the Gay–Berne potential [6], we have recently used results from colloid science to derive an interaction potential through a systematic approximation of the Hamaker integral [7] for mixtures of ellipsoids of arbitrary size and shape, namely the RE-squared potential [8]. The parameter space of the RE-squared potential is almost identical to that of Berardi, Fava and Zannoni [5], agrees significantly better with the numerically evaluated continuum approximation of Eq. (1) and has no nonphysical large distant limit. It has been verified that the new potential is superior to the biaxial Gay–Berne potential in representing the atomistic interactions of small organic molecules as well [9]. Moreover, the potential of mean force is representable with the same functional form of the RE-squared potential with negligible error [9].

In an anisotropic coarse-grained potential model, a molecule is treated and described like a rigid body, leading to a considerable speedup in computer simulations while preserving the fundamental features of atomistic potentials. Neglecting the atomic details, each molecule is characterized by the position of its center (a vector \mathbf{r}) and its orientation (a unitary operator \mathbf{A} or a unit quaternion q).

Due to the complexity of the functional form of such potentials, numerical finite differences are widely used for the evaluation of forces and torques in rigid body molecular dynamics simulations. The numerical differentiation methods are prone to round-off errors and are generally expensive in large scale simulations.

In this article, we will derive analytic expressions for the forces and torques between two molecules interacting via the RE-squared potentials. A set of optimized routines will be suggested for an efficient implementation of the given expressions. Finally, a time comparison between the two-point finite difference and the analytic derivatives will be presented.

2. The RE-squared potential

As mentioned earlier, the RE-squared potential [8] is a coarse-grained description of the attractive and repulsive interactions between two biaxial molecules. Each molecule is treated like a biaxial ellipsoid and is described by two characteristic diagonal tensors (in the principal basis of the molecule) \mathbf{S} and \mathbf{E} , representing the principal radii of the molecule and the strength of the pole contact interactions, respectively. As mentioned earlier, the orientation of a molecule is described by a center position vector \mathbf{r} and a unitary operator \mathbf{A} , revolving the bases of lab frame to the principal frame of the molecule.

The attractive and repulsive contributions of the RE-squared potential between two molecules with a relative center displacement of $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ and respective orientation tensors \mathbf{A}_1 and \mathbf{A}_2 are, respectively:

$$U_{\mathbf{A}}^{\text{RE-squared}}(\mathbf{A}_1, \mathbf{A}_2, \mathbf{r}_{12}) = -\frac{A_{12}}{36} \left(1 + 3\eta_{12}\chi_{12} \frac{\sigma_c}{h_{12}} \right) \times \prod_{i=1}^2 \prod_{e=x,y,z} \left(\frac{\sigma_e^{(i)}}{\sigma_e^{(i)} + h_{12}/2} \right), \quad (2a)$$

$$U_{\mathbf{R}}^{\text{RE-squared}}(\mathbf{A}_1, \mathbf{A}_2, \mathbf{r}_{12}) = \frac{A_{12}}{2025} \left(\frac{\sigma_c}{h_{12}} \right)^6 \left(1 + \frac{45}{56}\eta_{12}\chi_{12} \frac{\sigma_c}{h_{12}} \right) \times \prod_{i=1}^2 \prod_{e=x,y,z} \left(\frac{\sigma_e^{(i)}}{\sigma_e^{(i)} + h_{12}/60^{\frac{1}{3}}} \right). \quad (2b)$$

where A_{12} is the Hamaker constant (the energy scale), σ_c is the atomic interaction radius and $\sigma_x^{(i)}$, $\sigma_y^{(i)}$ and $\sigma_z^{(i)}$ are the half-radii of i th ellipsoid ($i = 1, 2$). η_{12} and χ_{12} are purely orientation dependant terms, describing the anisotropy of the molecules and h_{12} is the least contact distance between the ellipsoids.

The structure tensor \mathbf{S}_i and the relative well-depth tensor \mathbf{E}_i are diagonal in the principal basis of i th molecule and are defined as:

$$\mathbf{S}_i = \text{diag} \left\{ \sigma_x^{(i)}, \sigma_y^{(i)}, \sigma_z^{(i)} \right\}, \quad (3a)$$

$$\mathbf{E}_i = \text{diag} \left\{ E_x^{(i)}, E_y^{(i)}, E_z^{(i)} \right\}, \quad (3b)$$

where $E_x^{(i)}$, $E_y^{(i)}$ and $E_z^{(i)}$ are dimensionless energy scales inversely proportional to the well-depths of the respective orthogonal configurations of the interacting molecules. For large molecules with uniform constructions, it has been shown [8] that the energy parameters are approximately representable in terms of the local contact curvatures using the Derjaguin expansion [8,10]:

$$\mathbf{E}_i = \sigma_c \text{diag} \left\{ \frac{\sigma_x}{\sigma_y \sigma_z}, \frac{\sigma_y}{\sigma_x \sigma_z}, \frac{\sigma_z}{\sigma_x \sigma_y} \right\}. \quad (4)$$

The term χ_{12} quantifies the strength of interaction with respect to the local atomic interaction strength of the molecules and is defined as:

$$\chi_{12}(\mathbf{A}_1, \mathbf{A}_2, \hat{\mathbf{r}}_{12}) = 2\hat{\mathbf{r}}_{12}^T \mathbf{B}_{12}^{-1}(\mathbf{A}_1, \mathbf{A}_2) \hat{\mathbf{r}}_{12}, \quad (5)$$

where \mathbf{B}_{12} is defined in terms of the orientation tensors \mathbf{A}_i and relative well-depth tensors \mathbf{E}_i :

$$\mathbf{B}_{12}(\mathbf{A}_1, \mathbf{A}_1) = \mathbf{A}_1^T \mathbf{E}_1 \mathbf{A}_1 + \mathbf{A}_2^T \mathbf{E}_2 \mathbf{A}_2. \quad (6)$$

The term η_{12} describes the effect of contact curvatures of the molecules in the strength of the interaction and is defined as:

$$\eta_{12}(\mathbf{A}_1, \mathbf{A}_2, \hat{\mathbf{r}}_{12}) = \frac{\det[\mathbf{S}_1]/\sigma_1^2 + \det[\mathbf{S}_2]/\sigma_2^2}{[\det[\mathbf{H}_{12}]/(\sigma_1 + \sigma_2)]^{1/2}}, \quad (7)$$

where σ_i is the projected radius of i th ellipsoid along $\hat{\mathbf{r}}_{12}$:

$$\sigma_i(\mathbf{A}_i, \hat{\mathbf{r}}_{12}) = (\hat{\mathbf{r}}_{12}^T \mathbf{A}_i^T \mathbf{S}_i^{-2} \mathbf{A}_i \hat{\mathbf{r}}_{12})^{-1/2} \quad (8)$$

and the tensor \mathbf{H}_{12} is defined as:

$$\mathbf{H}_{12}(\mathbf{A}_1, \mathbf{A}_2, \hat{\mathbf{r}}_{12}) = \frac{1}{\sigma_1} \mathbf{A}_1^T \mathbf{S}_1^2 \mathbf{A}_1 + \frac{1}{\sigma_2} \mathbf{A}_2^T \mathbf{S}_2^2 \mathbf{A}_2. \quad (9)$$

No trivial solution is available for the least contact distance between two arbitrary ellipsoids (h_{12}) [6]. The Gay–Berne approximation [4,6] is usually employed for its low complexity and acceptable performance:

$$h_{12}^{\text{GB}} = \|\mathbf{r}_{12}\| - \sigma_{12}, \quad (10)$$

where the anisotropic distance function σ_{12} [5] is defined as:

$$\sigma_{12} = \left(\frac{1}{2} \hat{\mathbf{r}}_{12}^T \mathbf{G}_{12}^{-1} \hat{\mathbf{r}}_{12} \right)^{-1/2}, \quad (11)$$

and the symmetric overlap tensor \mathbf{G}_{12} is:

$$\mathbf{G}_{12} = \mathbf{A}_1^T \mathbf{S}_1^2 \mathbf{A}_1 + \mathbf{A}_2^T \mathbf{S}_2^2 \mathbf{A}_2. \quad (12)$$

We will also employ this approximation in our derivation and will omit the superscript GB for shorthand in the rest of the article.

3. Analytic expressions for forces and torques

The algebraic structure of the attractive and repulsive contributions of the RE-squared potential are essentially the same. Thus, both of the contributions are expressible with a proper template structure, defined as:

$$U_{\alpha}^{\text{RE-squared}} = \frac{A_{12}}{A_{\alpha}} \left(\frac{\sigma_c}{h_{12}} \right)^{n_{\alpha}} \left(1 + b_{\alpha} \eta_{12} \chi_{12} \frac{\sigma_c}{h_{12}} \right) \times \prod_{i=1}^2 \prod_{e=x,y,z} \left(\frac{\sigma_e^{(i)}}{\sigma_e^{(i)} + h_{12}/c_x} \right). \quad (13)$$

We will work through this template in the derivation. One reaches to the explicit form of each of the contributions by giving appropriate values to the α -subscripted parameters according to Eqs. (2a) and (2b).

In an interaction between the molecules \mathcal{M}_1 and \mathcal{M}_2 , the exerted force and torque on the molecule \mathcal{M}_2 is most easily evaluated by applying proper virtual displacements and infinitesimal rotations to the interaction potential. The exerted force and torque on \mathcal{M}_1 is trivially obtained using the Newton's third law, afterwards.

We denote the first-order translational and rotational variation operators on the coordinates of \mathcal{M}_2 by δ_{T} and δ_{R} , respectively. The translational variation operator is formally defined on a scalar function F as:

$$\delta_{\text{T}}[F(\mathbf{A}_1, \mathbf{A}_2, \mathbf{r}_{12}); \hat{\rho}, \epsilon] := \epsilon \frac{\partial}{\partial \epsilon} F(\mathbf{A}_1, \mathbf{A}_2, \mathbf{r}_{12} + \epsilon \hat{\rho})|_{\epsilon=0}, \quad (14)$$

where the unit vector $\hat{\rho}$ points to the direction of translational variation and ϵ is an (infinitesimal) scalar for which the variations are valued. The proper definition of the rotational variation is more involved. The projection of the exerted torque on \mathcal{M}_2 along the unit vector $\hat{\mathbf{n}}$ is obtained by applying the infinitesimal orthogonal operator $\mathbf{I} + \epsilon \hat{\mathbf{n}} \cdot \sigma$ to the operator revolving *the molecule* from the lab frame to its current frame, i.e. \mathbf{A}_2^T . The resulting orientation operator would be $((\mathbf{I} + \epsilon \hat{\mathbf{n}} \cdot \sigma) \mathbf{A}_2^T)^T = \mathbf{A}_2 - \epsilon \mathbf{A}_2 \hat{\mathbf{n}} \cdot \sigma$, according to the anti-symmetry of the principal rotation generators (σ). The discussion suggests the definition:

$$\delta_R[F(\mathbf{A}_1, \mathbf{A}_2, \mathbf{r}_{12}); \hat{\mathbf{n}}, \epsilon] := \epsilon \frac{\partial}{\partial \epsilon} F(\mathbf{A}_1, \mathbf{A}_2 - \epsilon \mathbf{A}_2 \hat{\mathbf{n}} \cdot \sigma, \mathbf{r}_{12})|_{\epsilon=0}, \quad (15)$$

where $\boldsymbol{\Omega} = \hat{\mathbf{n}} \cdot \sigma$ is the rotation generator corresponding to the direction $\hat{\mathbf{n}}$. Acting exclusively on the coordinates of the second molecule (\mathcal{M}_2), the operators may be used to define the exerted force and torque along $\hat{\rho}$ and around $\hat{\mathbf{n}}$, respectively, as:

$$\mathbf{F}_{\mathcal{M}_2, \hat{\rho}} = - \frac{\delta_T(U_A + U_R)}{\epsilon} \hat{\rho}, \quad (16a)$$

$$\mathbf{N}_{\mathcal{M}_2, \hat{\mathbf{n}}} = - \frac{\delta_R(U_A + U_R)}{\epsilon} \hat{\mathbf{n}}. \quad (16b)$$

Applying either of the operators to the template potential U_α , we get:

$$\delta U_\alpha / U_\alpha = \sigma b_x \frac{\eta_{12} \delta \chi_{12} + \delta \eta_{12} \chi_{12}}{h_{12} + \sigma b_x \chi_{12} \eta_{12}} - \delta h_{12} \left(\frac{n_x + 1}{h_{12}} - \frac{1}{h_{12} + b_x \eta_{12} \chi_{12} \sigma} + \sum_{i=1}^2 \sum_{e=x,y,z} \frac{1}{c_x \sigma_e^{(i)} + h_{12}} \right). \quad (17)$$

We will complete the derivation by providing explicit expressions for the first-order variations appearing in Eq. (17).

3.1. Derivation of the first-order variations

3.1.1. Rotational variation of η_{12}

Applying δ_R operator to η_{12} (Eq. (7)) and dropping off the constant terms, we arrive at:

$$\frac{\delta_R \eta_{12}}{\eta_{12}} = \frac{1}{2} \frac{\delta_R \sigma_2}{\sigma_1 + \sigma_2} - \frac{1}{2} \frac{\delta_R \det \mathbf{H}_{12}}{\det \mathbf{H}_{12}} - \frac{\delta_R \sigma_2}{\sigma_2^3} \frac{2 \det \mathbf{S}_2}{\det \mathbf{S}_1 / \sigma_1^2 + \det \mathbf{S}_2 / \sigma_2^2}. \quad (18)$$

The rotational variation of σ_2 is:

$$\frac{\delta_R \sigma_2}{\sigma_2} = - \frac{1}{2} \sigma_2^2 \delta_R (\hat{\mathbf{r}}_{12}^T \mathbf{A}_2^T \mathbf{S}_2^{-2} \mathbf{A}_2 \hat{\mathbf{r}}_{12}) \quad (19)$$

$$\begin{aligned} &= \frac{1}{2} \epsilon \sigma_2^2 \hat{\mathbf{r}}_{12}^T ((\mathbf{A}_2 \boldsymbol{\Omega})^T \mathbf{S}_2^{-2} \mathbf{A}_2 + \mathbf{A}_2^T \mathbf{S}_2^{-2} \mathbf{A}_2 \boldsymbol{\Omega}) \hat{\mathbf{r}}_{12} \\ &= \epsilon \sigma_2^2 \hat{\mathbf{r}}_{12}^T (\mathbf{A}_2 \boldsymbol{\Omega})^T \mathbf{S}_2^{-2} \mathbf{A}_2 \hat{\mathbf{r}}_{12}. \end{aligned} \quad (20)$$

We have used the symmetry and the anti-symmetry properties of \mathbf{S}^{-2} and $\boldsymbol{\Omega}$, respectively. The rotational variation of $\delta_R \mathbf{H}_{12}$ is required prior to $\delta_R \det \mathbf{H}_{12}$:

$$\delta_R \mathbf{H}_{12} = - \frac{\epsilon}{\sigma_2} (\mathbf{A}_2^T \mathbf{S}_2^2 \mathbf{A}_2 \boldsymbol{\Omega} + (\mathbf{A}_2 \boldsymbol{\Omega})^T \mathbf{S}_2^2 \mathbf{A}_2) - \frac{\delta_R \sigma_2}{\sigma_2^2} \mathbf{A}_2^T \mathbf{S}_2^2 \mathbf{A}_2. \quad (21)$$

It can be easily verified that,

$$\det[\boldsymbol{\Gamma} + \epsilon \boldsymbol{\Lambda}] = \det[\boldsymbol{\Gamma}] + \epsilon \sum_{i=1}^{\dim \boldsymbol{\Gamma}} \det[\boldsymbol{\Gamma}^{(i)}] + \mathcal{O}(\epsilon^2) \quad (22)$$

for arbitrary $\boldsymbol{\Gamma}$ and $\boldsymbol{\Lambda}$, where $\boldsymbol{\Gamma}^{(i)}$ is defined as:

$$\boldsymbol{\Gamma}_{kl}^{(i)} = \begin{cases} \boldsymbol{\Gamma}_{kl} & k \neq i, \\ \boldsymbol{\Lambda}_{il} & k = i. \end{cases} \quad (23)$$

An explicit expression for $\delta_R \det \mathbf{H}_{12}$ is feasible using Eqs. (21) and (22). Equating $\mathbf{\Gamma}$ and $\mathbf{\Lambda}$ to \mathbf{H}_{12} and $\delta_R \mathbf{H}_{12}/\epsilon$, respectively, the first-order terms of Eq. (22) will evidently be equal to the variation we are looking for.

3.1.2. Rotational variation of χ_{12}

Using Eq. (5), it is straightforward to show that:

$$\frac{\delta_R \chi_{12}}{\chi_{12}} = \frac{\hat{\mathbf{r}}_{12}^T \delta_R (\mathbf{B}_{12}^{-1}) \hat{\mathbf{r}}_{12}}{\hat{\mathbf{r}}_{12}^T \mathbf{B}_{12}^{-1} \hat{\mathbf{r}}_{12}}, \quad (24)$$

where:

$$\delta_R \mathbf{B}_{12} = -\epsilon [(\mathbf{A}_2 \mathbf{\Omega})^T \mathbf{E}_2 \mathbf{A}_2 + \mathbf{A}_2^T \mathbf{E}_2 \mathbf{A}_2 \mathbf{\Omega}]. \quad (25)$$

Using the relation:

$$(\mathbf{\Gamma} + \epsilon \mathbf{\Lambda})^{-1} = -\epsilon \mathbf{\Gamma}^{-1} \mathbf{\Lambda} \mathbf{\Gamma}^{-1} + \mathcal{O}(\epsilon^2) \quad (26)$$

for infinitesimal ϵ , together with Eqs. (24) and (25) we finally reach to:

$$\delta_R \chi_{12} = 2\epsilon \hat{\mathbf{r}}_{12}^T \mathbf{B}_{12}^{-1} [(\mathbf{A}_2 \mathbf{\Omega})^T \mathbf{E}_2 \mathbf{A}_2 + \mathbf{A}_2^T \mathbf{E}_2 \mathbf{A}_2 \mathbf{\Omega}] \mathbf{B}_{12}^{-1} \hat{\mathbf{r}}_{12} = 4\epsilon \hat{\mathbf{r}}_{12}^T \mathbf{B}_{12}^{-1} \mathbf{A}_2^T \mathbf{E}_2 \mathbf{A}_2 \mathbf{\Omega} \mathbf{B}_{12}^{-1} \hat{\mathbf{r}}_{12}. \quad (27)$$

where the symmetry of \mathbf{E}_i , \mathbf{B}_{12} and their inverses have been used.

3.1.3. Rotational variation of h_{12}

We will use the Gay–Berne approximation for the least constant distance defined by Eq. (10). Accordingly, the rotational variation of h_{12} is a result of the change in the anisotropic distance function σ_{12} :

$$\delta_R h_{12} = \delta_R (r_{12} - \sigma_{12}) = -\delta_R \sigma_{12}, \quad (28)$$

where the rotationally constant term r_{12} drops out. The term $\delta_R \sigma_{12}$ is easily expressed in terms of $\delta_R \mathbf{G}_{12}^{-1}$:

$$\frac{\delta_R \sigma_{12}}{\sigma_{12}} = -\frac{1}{2} \frac{\delta_R \hat{\mathbf{r}}_{12}^T \mathbf{G}_{12}^{-1} \hat{\mathbf{r}}_{12}}{\hat{\mathbf{r}}_{12}^T \mathbf{G}_{12}^{-1} \hat{\mathbf{r}}_{12}} = -\frac{1}{4} \sigma_{12}^2 \hat{\mathbf{r}}_{12}^T (\delta_R \mathbf{G}_{12}^{-1}) \hat{\mathbf{r}}_{12}. \quad (29)$$

Eq. (12) together with Eq. (26) result in:

$$\delta_R \mathbf{G}_{12}^{-1} = \epsilon \mathbf{G}_{12}^{-1} [(\mathbf{A}_2 \mathbf{\Omega})^T \mathbf{S}_2^2 \mathbf{A}_2 + \mathbf{A}_2^T \mathbf{S}_2^2 \mathbf{A}_2 \mathbf{\Omega}] \mathbf{G}_{12}^{-1} = 2\epsilon \mathbf{G}_{12}^{-1} [\mathbf{A}_2^T \mathbf{S}_2^2 \mathbf{A}_2 \mathbf{\Omega}] \mathbf{G}_{12}^{-1}, \quad (30)$$

where the symmetry of \mathbf{S}_2 , \mathbf{G}_{12} and their inverses have been used. Thus, we finally reach to:

$$\delta_R h_{12} = \frac{1}{2} \epsilon \sigma_{12}^3 \hat{\mathbf{r}}_{12}^T \mathbf{G}_{12}^{-1} \mathbf{A}_2^T \mathbf{S}_2^2 \mathbf{A}_2 \mathbf{\Omega} \mathbf{G}_{12}^{-1} \hat{\mathbf{r}}_{12}. \quad (31)$$

3.1.4. Translational variation of η_{12}

The displacement of the molecule \mathcal{M}_2 results in a change in the direction of the connecting vector \mathbf{r}_{12} . Up to first order, this change is expressed as:

$$\hat{\mathbf{r}}_{12}^{(1)} = \frac{\mathbf{r}_{12}^{(0)} + \epsilon \hat{\rho}}{\|\mathbf{r}_{12}^{(0)} + \epsilon \hat{\rho}\|} = \hat{\mathbf{r}}_{12}^{(0)} + \frac{\epsilon}{r_{12}} (\hat{\rho} - (\hat{\rho} \cdot \hat{\mathbf{r}}_{12}) \hat{\mathbf{r}}_{12}) + \mathcal{O}(\epsilon^2). \quad (32)$$

Defining a new auxiliary vector results in a cleaner derivation:

$$\mathbf{u} := \frac{\hat{\rho} - (\hat{\rho} \cdot \hat{\mathbf{r}}_{12}) \hat{\mathbf{r}}_{12}}{r_{12}}. \quad (33)$$

Accordingly, $\delta \hat{\mathbf{r}}_{12}$ is obviously ϵ times \mathbf{u} . Applying δ_T operator to η_{12} , we reach to:

$$\frac{\delta_T \eta_{12}}{\eta_{12}} = \frac{1}{2} \frac{\delta_T \sigma_1 + \delta_T \sigma_2}{\sigma_1 + \sigma_2} - \frac{1}{2} \frac{\delta_T \det \mathbf{H}_{12}}{\det \mathbf{H}_{12}} - 2 \frac{(\delta_T \sigma_1) \det \mathbf{S}_1 / \sigma_1^3 + (\delta_T \sigma_2) \det \mathbf{S}_2 / \sigma_2^3}{\det \mathbf{S}_1 / \sigma_1^2 + \det \mathbf{S}_2 / \sigma_2^2}. \quad (34)$$

We will follow the same steps as the rotational case. The translational variation of the projected diameter σ_i is:

$$\delta_T \sigma_i = -\frac{1}{2} \sigma_i^3 \delta_T (\hat{\mathbf{r}}_{12}^T \mathbf{A}_i^T \mathbf{S}_i^{-2} \mathbf{A}_i \hat{\mathbf{r}}_{12}) = -\frac{1}{2} \epsilon \sigma_i^3 (\mathbf{u}^T \mathbf{A}_i^T \mathbf{S}_i^{-2} \mathbf{A}_i \hat{\mathbf{r}}_{12} + \hat{\mathbf{r}}_{12}^T \mathbf{A}_i^T \mathbf{S}_i^{-2} \mathbf{A}_i \mathbf{u}) = -\epsilon \sigma_i^3 \mathbf{u}^T \mathbf{A}_i^T \mathbf{S}_i^{-2} \mathbf{A}_i \hat{\mathbf{r}}_{12}. \quad (35)$$

It is also easy to verify that:

$$\delta_T \mathbf{H}_{12} = -\frac{\delta_T \sigma_1}{\sigma_1^2} \mathbf{A}_1^T \mathbf{S}_1^2 \mathbf{A}_1 - \frac{\delta_T \sigma_2}{\sigma_2^2} \mathbf{A}_2^T \mathbf{S}_2^2 \mathbf{A}_2. \quad (36)$$

Finally, we may express $\delta_T \det[\mathbf{H}_{12}]$ explicitly using Eq. (22) in terms of \mathbf{H}_{12} and its translational variation, Eq. (36).

3.1.5. Translational variation of χ_{12}

Applying δ_T to χ_{12} , we get:

$$\frac{\delta_T \chi_{12}}{\chi_{12}} = \frac{\delta_T \hat{\mathbf{r}}_{12}^T \mathbf{B}_{12}^{-1} \hat{\mathbf{r}}_{12}}{\hat{\mathbf{r}}_{12}^T \mathbf{B}_{12}^{-1} \hat{\mathbf{r}}_{12}}. \quad (37)$$

The numerator simplifies to:

$$\delta_T \hat{\mathbf{r}}_{12}^T \mathbf{B}_{12}^{-1} \hat{\mathbf{r}}_{12} = \epsilon (\mathbf{u}^T \mathbf{B}_{12}^{-1} \hat{\mathbf{r}}_{12} + \hat{\mathbf{r}}_{12}^T \mathbf{B}_{12}^{-1} \mathbf{u}) = 2\epsilon \mathbf{u}^T \mathbf{B}_{12}^{-1} \hat{\mathbf{r}}_{12}. \quad (38)$$

We finally reach to:

$$\delta_T \chi_{12} = 4\epsilon \mathbf{u}^T \mathbf{B}_{12}^{-1} \hat{\mathbf{r}}_{12}. \quad (39)$$

We have used the symmetry and the translational invariance of \mathbf{B}_{12} .

3.1.6. Translational variation of h_{12}

Both of the involving terms in the definition of h_{12} contribute to $\delta_T h_{12}$. The contribution of the center displacement is:

$$\delta_T r_{12} = \epsilon \hat{\mathbf{r}}_{12} \cdot \hat{\boldsymbol{\rho}} \quad (40)$$

and the variation of the anisotropic distance function may be expressed as:

$$\frac{\delta_T \sigma_{12}}{\sigma_{12}} = -\frac{1}{2} \frac{\delta_T \hat{\mathbf{r}}_{12}^T \mathbf{G}_{12}^{-1} \hat{\mathbf{r}}_{12}}{\hat{\mathbf{r}}_{12}^T \mathbf{G}_{12}^{-1} \hat{\mathbf{r}}_{12}}. \quad (41)$$

Expanding and simplifying the numerator, we reach to:

$$\delta_T \sigma_{12} = -\frac{1}{2} \epsilon \sigma_{12}^3 \mathbf{u}^T \mathbf{G}_{12}^{-1} \hat{\mathbf{r}}_{12}. \quad (42)$$

Adding up the above contributions, we finally get:

$$\delta_T h_{12} = \epsilon \hat{\mathbf{r}}_{12} \cdot \hat{\boldsymbol{\rho}} + \frac{1}{2} \epsilon \sigma_{12}^3 \mathbf{u}^T \mathbf{G}_{12}^{-1} \hat{\mathbf{r}}_{12}. \quad (43)$$

4. An efficient implementation for rigid-body molecular dynamics simulations

Most of the required matrix and vectors products in the evaluation of the first derivatives using the given expressions will be already available once one gets through the evaluation of the interaction energy beforehand. Without a careful implementation, a minimal speedup is expected due to the considerable redundancy of the algebra. Therefore, a proper integration between the variable spaces of all routines must be considered. The three provided routines demonstrate a suggested implementation. The first routine evaluates the interaction energy while the second and third routines calculate the torque and force. The latter routines depend on portions of variable space of the first routine in order to skip the redundant matrix products. We have also omitted the ϵ factors appearing in the variations beforehand as they will finally factor out, according to Eqs. (16a) and (16b). In practice, one call of the first routine accompanied by three calls of each of the second and third routines are mandatory in order to evaluate the three components of the force and the torque vec-

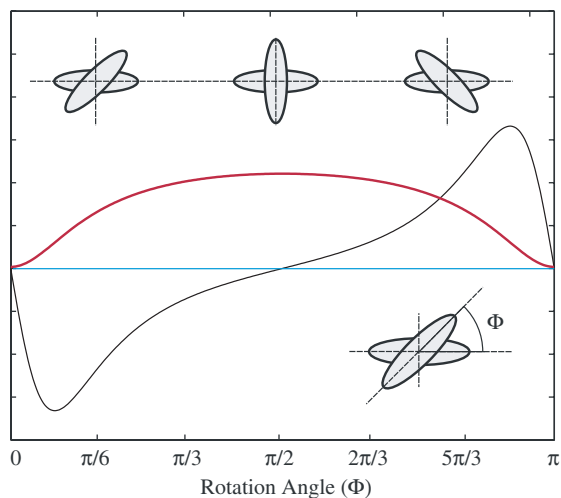


Fig. 1. Typical interaction energy (red thick line) and torque (black thin line) between two prolate molecules (in arbitrary units), continuously evolved from side-by-side to cross configuration. The ellipsoids are identical, having half-radii [11:2:0.5] (in arbitrary units) and vertically separated by 5 units of length. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

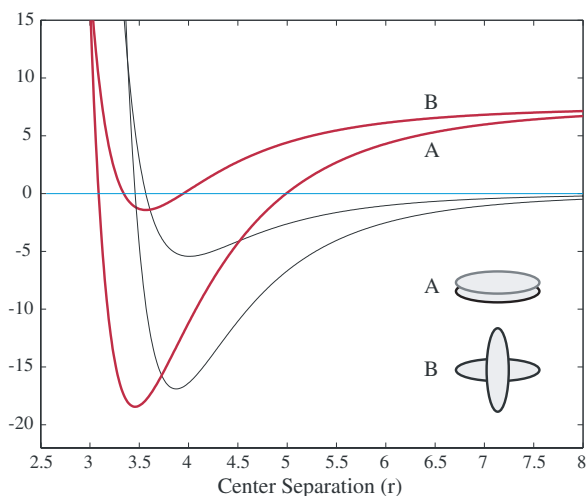


Fig. 2. Interaction energy (red thick lines) and vertical force (black thin lines) between two prolate molecules in two different configurations with respect to the vertical center separation (r). The ellipsoids are identical, having half-radii [11:2:0.5] (in arbitrary units). The y -axis ticks correspond to the vertical force (in arbitrary units). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tors. We have compared the computation time of an efficient C-language implementation of the proposed routines [11] against a numerical two-point finite differentiation. A large scale comparison (Pentium-M 1.7Ghz, GCC4) indicates that the an evaluation of the interaction energy and the force and torque vectors takes 38.6 μ s using the provided routines while the same calculation takes 62.2 μ s with the finite difference approach, leading to 1.6 times speedup. Figs. 1 and 2 have been drawn with the aid of the provided routines and show the typical behavior of interaction force and torque between two prolate molecules.

5. The time cost of Monte-Carlo and molecular dynamics simulations

Monte-Carlo (MC) and Molecular Dynamics (MD) simulations are two main concerns in studying molecular systems. MC simulations are usually faster and more effective in the studying of steady states while MD

simulations play a more prominent role in the studying of transition states of certain systems. Furthermore, there are certain cases where MC simulations are of little interest (specially where the dynamical behavior is demanded).

A MC step is considered to be as *revealing* an a MD step once each molecule successfully move to a new position in the phase space. In a system of N molecules, each having an average number of M neighbors, the time consumption of a MC step roughly is:

$$T_{MC} = \alpha NM \times \tau_E, \quad (44)$$

where α is the inverse of the acceptance ratio (usually, $\alpha \approx 2$ with a proper conditioning) and τ_E is the average required time of an energy evaluation. The corresponding time consumption of an MD step would be:

$$T_{MD} = \frac{NM}{2} (\tau_E + \tau_F + \tau_T), \quad (45)$$

where τ_F and τ_T are the average excessive time required for a single force and torque evaluation in all three directions. Using the values obtained from a sample large-scale simulation (with an acceptance of 50%), the ratio of the time expenses turn out to be:

$$\frac{T_{MD}}{T_{MC}} = \frac{38.6 \text{ } (\mu\text{s})}{2 \times 2 \times 8.9 \text{ } (\mu\text{s})} \simeq 1.1 \quad (46)$$

using analytical first derivatives. The same ratio would be 1.7 using finite differences. Therefore, one will end up with a MD simulation almost as fast as a MC simulation using the provided analytical derivatives.

Routine 1: Evaluation of U_α

- 1: $\hat{\mathbf{r}}_{12} \leftarrow \mathbf{r}_{12} / \|\mathbf{r}_{12}\|$
- 2: $\mathbf{\Gamma}_1 \leftarrow \mathbf{A}_1^T \mathbf{S}_1^2 \mathbf{A}_1$
- 3: $\mathbf{\Gamma}_2 \leftarrow \mathbf{A}_2^T \mathbf{S}_2^2 \mathbf{A}_2$
- 4: $\mathbf{s} \leftarrow (\mathbf{\Gamma}_1 + \mathbf{\Gamma}_2)^{-1} \hat{\mathbf{r}}_{12}$
- 5: $\sigma_{12} \leftarrow 1 / \sqrt{\frac{1}{2} \mathbf{s}^T \hat{\mathbf{r}}_{12}}$
- 6: $\mathbf{z}_1 \leftarrow \mathbf{A}_1 \hat{\mathbf{r}}_{12}$
- 7: $\mathbf{z}_2 \leftarrow \mathbf{A}_2 \hat{\mathbf{r}}_{12}$
- 8: $\mathbf{v}_1 \leftarrow \mathbf{S}_1^{-2} \mathbf{z}_1$
- 9: $\mathbf{v}_2 \leftarrow \mathbf{S}_2^{-2} \mathbf{z}_2$
- 10: $\sigma_1 \leftarrow 1 / \sqrt{\mathbf{z}_1^T \mathbf{v}_1}$
- 11: $\sigma_2 \leftarrow 1 / \sqrt{\mathbf{z}_2^T \mathbf{v}_2}$
- 12: $\mathbf{H}_{12} \leftarrow \mathbf{\Gamma}_1 / \sigma_1 + \mathbf{\Gamma}_2 / \sigma_2$
- 13: $d_H \leftarrow \det \mathbf{H}_{12}$
- 14: $d_{S1} \leftarrow \det \mathbf{S}_1$
- 15: $d_{S2} \leftarrow \det \mathbf{S}_2$
- 16: $\lambda \leftarrow d_{S1} / \sigma_1^2 + d_{S2} / \sigma_2^2$
- 17: $v \leftarrow \sqrt{d_H / (\sigma_1 + \sigma_2)}$
- 18: $\mathbf{w} \leftarrow (\mathbf{A}_1^T \mathbf{E}_1 \mathbf{A}_1 + \mathbf{A}_2^T \mathbf{E}_2 \mathbf{A}_2)^{-1} \hat{\mathbf{r}}_{12}$
- 19: $h_{12} \leftarrow r_{12} - \sigma_{12}$
- 20: $\eta_{12} \leftarrow \lambda / v$
- 21: $\chi_{12} \leftarrow 2 \hat{\mathbf{r}}_{12}^T \mathbf{w}$
- 22: Evaluate U_α using Eq. (13)

Routine 2: Evaluation of $\delta_R U_\alpha$

Require: Evaluated variable space of Routine (1)

- 1: $\mathbf{\Lambda} \leftarrow -\mathbf{A}_2 (\hat{\mathbf{n}} \cdot \boldsymbol{\sigma})$
- 2: $\mathbf{p} \leftarrow \mathbf{\Lambda} \hat{\mathbf{r}}_{12}$

- 3: $\delta_R \sigma_2 \leftarrow -\sigma_2^3 \mathbf{p}^T \mathbf{v}_2$
- 4: $\delta_R \mathbf{H}_{12} \leftarrow (\mathbf{A}_2^T \mathbf{S}_2^2 \mathbf{A} + \mathbf{A}^T \mathbf{S}_2^2 \mathbf{A}_2) / \sigma_2 - (\delta_R \sigma_2 / \sigma_2^2) \mathbf{\Gamma}_2$
- 5: $\delta_R d_H \leftarrow 0$
- 6: **for** $i = 1$ to 3 **do**
- 7: $\mathbf{J} \leftarrow \mathbf{H}_{12}^{(i)}$ {Defined in the corresponding section}
- 8: $\delta_R d_H \leftarrow \delta_R d_H + \det \mathbf{J}$
- 9: **end for**
- 10: $\delta_R \eta_{12} \leftarrow \frac{\eta_{12} \delta_R \sigma_2}{2(\sigma_1 + \sigma_2)} - \frac{\eta_{12} \delta_R d_H}{2d_H} - \frac{2\eta_{12} d_{S2} \delta_R \sigma_2}{\lambda \sigma_2^3}$
- 11: $\delta_R \chi_{12} \leftarrow -4\mathbf{w}^T \mathbf{A}_2^T \mathbf{E}_2 \mathbf{A} \mathbf{w}$
- 12: $\delta_R h_{12} \leftarrow -\frac{1}{2} \sigma_{12}^3 \mathbf{s}^T \mathbf{\Gamma}_2 \mathbf{s}$
- 13: Evaluate $\delta_R U_\alpha$ using Eq. (17)

Routine 3: Evaluation of $\delta_T U_\alpha$

Require: Evaluated variable space of Routine (1)

- 1: $\gamma \leftarrow \hat{\rho}^T \hat{\mathbf{r}}_{12}$
- 2: $\mathbf{u} \leftarrow (\hat{\rho} - \gamma \hat{\mathbf{r}}_{12}) / \|\mathbf{r}_{12}\|$
- 3: $\mathbf{u}_1 \leftarrow \mathbf{A}_1 \mathbf{u}$
- 4: $\mathbf{u}_2 \leftarrow \mathbf{A}_2 \mathbf{u}$
- 5: $\delta_T \sigma_1 \leftarrow -\sigma_1^3 \mathbf{u}_1^T \mathbf{v}_1$
- 6: $\delta_T \sigma_2 \leftarrow -\sigma_2^3 \mathbf{u}_2^T \mathbf{v}_2$
- 7: $\delta_T \mathbf{H}_{12} \leftarrow -\frac{\delta_T \sigma_1}{\sigma_1^2} \mathbf{\Gamma}_1 - \frac{\delta_T \sigma_2}{\sigma_2^2} \mathbf{\Gamma}_2$
- 8: $\delta_T d_H \leftarrow 0$
- 9: **for** $i = 1$ to 3 **do**
- 10: $\mathbf{J} \leftarrow \mathbf{H}_{12}^{(i)}$ {Defined in the corresponding section}
- 11: $\delta_T d_H \leftarrow \delta_T d_H + \det \mathbf{J}$
- 12: **end for**
- 13: $\delta_T \eta_{12} \leftarrow \eta_{12} \frac{\delta_T \sigma_1 + \delta_T \sigma_2}{2(\sigma_1 + \sigma_2)} - \frac{\eta_{12} \delta_T d_H}{2d_H} - \frac{2\eta_{12}}{\lambda} \left(\frac{d_{S1} \delta_T \sigma_1}{\sigma_1^3} + \frac{d_{S1} \delta_T \sigma_1}{\sigma_1^3} \right)$
- 14: $\delta_T \chi_{12} \leftarrow 4\mathbf{u}^T \mathbf{w}$
- 15: $\delta_T h_{12} \leftarrow \gamma + \frac{1}{2} \sigma_{12}^3 \mathbf{u}^T \mathbf{s}$
- 16: Evaluate $\delta_T U_\alpha$ using Eq. (17)

6. Conclusion

We have derived analytical expressions for the forces and torques exerted on two molecules interacting via the RE-squared potential. Moreover, efficient routines have been provided for molecular dynamics simulations. A numerical investigation reveals that the provided routines are 1.6 times faster than a two-point finite difference approach. The evaluation of energy derivatives is the most expensive element in a MD simulation. Using the provided analytic derivatives, a MD simulation will run almost as fast as a similar MC simulation (Eq. (46)). This speedup leads to the possibility of larger scale MD simulations of a wide range of materials such as liquid crystals and certain organic molecules.

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References

- [1] M. Allen, D. Tildesley, Computer Simulation of Liquids, Oxford University Press, Oxford, 1989.
- [2] D. Frenkel, B. Smit, Understanding Molecular Simulations, Academic Press, New York, 2002.
- [3] A.R. Leach, Molecular Modelling: Principles and Applications, Addison Wesley Longman Limited, 1996.
- [4] J.G. Gay, B.J. Berne, Modification of the overlap potential to mimic a linear sitesite potential, J. Chem. Phys. 74 (1981) 3316–3319.
- [5] R. Berardi, C. Fava, C. Zannoni, A gay-berne potential for dissimilar biaxial particles, Chem. Phys. Lett. 297 (1998) 8–14.

- [6] J.W. Perram, J. Rasmussen, E. Praestgaard, J.L. Lebowitz, Ellipsoid contact potential: Theory and relation to overlap potentials, *Phys. Rev. E* 54 (1996) 6565–6572.
- [7] R.J. Hunter, *Foundations of Colloid Science*, Oxford University Press, USA, 2001.
- [8] R. Everaers, M.R. Ejtehadi, Interaction potentials for soft and hard ellipsoids, *Phys. Rev. E* 67 (2003) 041710.
- [9] M. Babadi, R. Everaers, M.R. Ejtehadi, Coarse-grained interaction potentials for anisotropic molecules, *J. Chem. Phys.* 124 (2006) 174708.
- [10] B.V. Derjaguin, *Kolloid Z.* 69 (1934) 155.
- [11] The parameterization routine (MATLAB/Octave) along with an efficient set of C subroutines for the evaluation of RE-squared interaction potential and its analytic derivatives are freely available at: <http://mehr.sharif.edu/softmatter/RE-squared>.