

Analytical first derivatives of the RE-squared interaction potential

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Received 31 January 2006; received in revised form 10 April 2006; accepted 12 April 2006

Available online 13 June 2006

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.

Keywords: Lennard–Jones(6–12) potential; Coarse-grained model; Biaxial ellipsoidal potential; Analytical derivatives; Rigid-body MD simulation

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]:

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

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