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Shape matters: The case for Ellipsoids and Ellipsoidal Water¹

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Abstract. We describe the shape potentials used for the van der Waals interactions between soft-ellipsoids used to coarse-grain molecular moieties in Metropolis Monte-Carlo simulation software. The morphologies resulting from different expressions for these van der Waals interaction potentials are discussed for the case of a prolate spheroid system with a strong dipole at the center. We also show that the calculation of ellipsoids is, at worst, only about fivefold more expensive computationally when compared to a simple Lennard-Jones sphere. Finally, as an application of the ellipsoidal shape we parametrize water from the original SPC water model and observe – just through the difference in shape alone – a significant improvement of the O-O radial distribution function when compared to experimental data.

1. Introduction

In the development of coarse-grained force fields based on all atom force fields, the reduction of a set of charges is a reasonably well understood process. Using multipole expansions about centers (or clusters of centers within molecules) one knows how to express many point charges with higher order moments or even fewer partial charges. Additionally, with the use of methods such as CHELPG [1] or RESP [2,3] *ab-initio* quantum mechanical electrostatic potentials can be reduced to a discrete set of point charges (often placed on the atom centers) that well describe most molecules. However, for descriptions of molecular shapes, generally at the all atom level, only spheres are used to represent the van der Waals interactions. Typically, the Lennard-Jones (LJ) type potential is the avatar of van der Waals interactions.

A widely used coarse-grained alternative to a spherical molecular shape is the Gay-Berne formulation of a LJ-like potential energy function implementing spheroidal [4] as well as ellipsoidal shapes [5]. The parameterization of this energy function has proved challenging and there has not been a systematic, bottom-up approach to understanding the parameters needed. We have recently published a method, called the Level-of-Detail method [6], to envision ellipsoids replacing specific units within a molecule, and even the entire molecule. In this work, we described how to calculate the ellipsoid shapes and associated potential parameters directly from an underlying all atom force field such as OPLSAA [7] or GAFF [8]. The results suggest that the ellipsoids and associated parameters that describe the Lennard-Jones energies well reproduce the results of the underlying all atom force field.

This proceedings paper serves as an illustration that ellipsoidal shapes allow for a nuanced representation of the dispersion interactions of molecules. The first part of this paper presents insights

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into how small tweaks to the potential energy function can lead to dramatic changes in the resulting morphology. Secondly, we report on an ellipsoidal water model based on the original SPC [9] model.

2. Gay-Berne-like Lennard Jones Potential for Ellipsoids

Table 1. Model parameters used in this work

Model	Semi axes [Å] (LJ width σ_0 [Å]) [*]	LJ energy [kcal/mol]	Charges; (Locations) [e; Å]	Dipole [Debye]
Prolate Spheroid	12.15x3.14x3.14 (3.0) [*]	3.515	-	(15,0,0)
SPC Water [9]	1.583x1.583x1.583	0.155	-0.82; (0,0,0)	-
Water Ellipsoid	1.973x1.642x1.224	0.159	0.41; (0.8165,0.5774,0) 0.41; (-0.8165,0.5774,0) ^{**}	-

^{*} If “Adjusted Width” LJ potential, eq. 4, is used. ^{**} Charge locations are the same for both models.

Ellipsoids are promising shapes to add to the simulation toolbox [6,10–12]. They enable the description of large, coarse-grained molecular moieties without the need to introduce further corrective terms to the simulation Hamiltonian to account for shape anisotropy [13–15]. Additionally, a physically intuitive understanding of the resulting shapes from simulation parameters is retained. The shape potential used is derived from a generalized Lennard-Jones (LJ) potential similar to the Gay-Berne description [4]:

$$V_{AB}(\vec{r}_{AB}, \Omega_{AB}) = 4\epsilon_{AB} \left\{ \left(\frac{\sigma_0}{r_{AB} - \delta_{AB}} \right)^{12} - \left(\frac{\sigma_0}{r_{AB} - \delta_{AB}} \right)^6 \right\} \quad (1)$$

Here, \vec{r}_{AB} is the distance vector (with r_{AB} its magnitude), Ω_{AB} is the set of relative orientations of the two ellipsoids, ϵ_{AB} is the potential well depth, σ_0 determines the width of the potential well, and δ_{AB} can be used to adjust the zero-crossing of the potential. Note that this reduces to the original LJ potential with $\sigma_0 = \text{const.}$ and $\delta_{AB} = 0$. The interaction between two arbitrarily oriented ellipsoids, A and B, is given by $\sigma_{AB}(\vec{r}_{AB}, \Omega_{AB})$, as the distance at which the ellipsoids would touch when moved along the distance vector \vec{r}_{AB} from the contact function (CF), F_{AB} , described by Perram and Wertheim [16]:

$$\sigma_{AB}(\vec{r}_{AB}, \Omega_{AB}) = r_{AB} \cdot F_{AB}(\vec{r}_{AB}, \Omega_{AB})^{-\frac{1}{2}} \quad (2)$$

When this expression is used as σ_0 in conjunction with $\delta_{AB} = 0$ in eq. 1, one obtains a simple, LJ-like potential, called the “Simple Touch” potential [6]:

$$V_{AB}^{CF}(\vec{r}_{AB}, \Omega_{AB}) = 4\epsilon_{AB} \left\{ \left(\frac{\sigma_{AB}(\vec{r}_{AB}, \Omega_{AB})}{r_{AB}} \right)^{12} - \left(\frac{\sigma_{AB}(\vec{r}_{AB}, \Omega_{AB})}{r_{AB}} \right)^6 \right\} = 4\epsilon_{AB} \{ F_{AB}^{-6} - F_{AB}^{-3} \} \quad (3)$$

Figure 1a) shows the resulting morphology of identical ellipsoids with a point dipole at their center in a two- and three-dimensional simulation box. The florid, micellar arrangement observed is caused by the wider potential well in the long direction of the ellipsoids. It is a direct consequence of the numerator, $\sigma_{AB}(\vec{r}_{AB}, \Omega_{AB})$, in eq. 3 affecting both the zero-crossing as well as the potential well.

Holding the potential well width constant, $\sigma_0 = \text{const.}$, and adjusting the zero-crossing such that the ellipsoids cannot overlap, $\delta_{AB} = \sigma_{AB}(\vec{r}_{AB}, \Omega_{AB}) - \sigma_0$, leads to the “Adjusted Width” potential:

$$V_{AB}(\vec{r}_{AB}, \Omega_{AB}) = 4\epsilon_{AB} \left\{ \left(\frac{\sigma_0}{r_{AB} - \sigma_{AB}(\vec{r}_{AB}, \Omega_{AB}) + \sigma_0} \right)^{12} - \left(\frac{\sigma_0}{r_{AB} - \sigma_{AB}(\vec{r}_{AB}, \Omega_{AB}) + \sigma_0} \right)^6 \right\} \quad (4)$$

The resulting morphologies are displayed in Figure 1b). This corrects the micellar behavior observed when using the “Simple Touch” potential in three dimensions.

The remaining, visible ordering behavior in the two-dimensional box is caused by the strong dipole at the center of each ellipsoid as well as by the width of the ellipsoids (in the short direction) and the relative potential well depths. A liquid crystalline arrangement as seen in Figure 1c) would eventually be favored if the circumference of the spheroid were further reduced (increasing dipole-dipole interaction). In the case of Figure 1c) we used the “Interaction Area” orientation dependent potential

well depth, $\epsilon_{AB}(\vec{r}_{AB}, \Omega_{AB})$, described in Tillack et al. [6] to favor the side-side interaction over the end-end interaction (by a factor of 3.87). This approach takes into account the dispersion interaction's proportionality to the surface areas of the interacting ellipsoids.

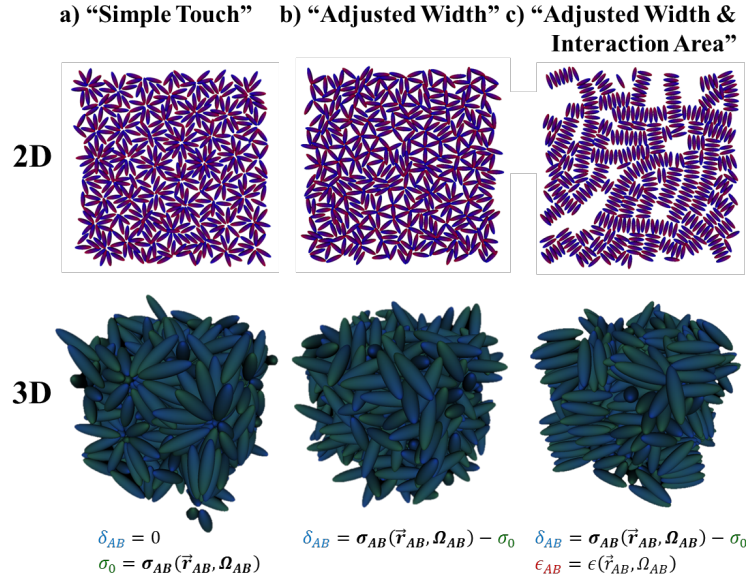


Figure 1. Effect of choice of Lennard-Jones Potential on resulting arrangement of ellipsoid-dipole system in two-dimensional (2D, top) and three-dimensional (3D, bottom; adapted with permission from [6]. Copyright 2016 American Chemical Society) simulation box. System consists of 432 prolate ellipsoids (see Table 1) in the the isothermal isobaric (NPT) ensemble under 1 atm at 400 K with periodic boundary conditions (PBCs). The 2D system was obtained by using a modified soft wall restoring potential [17]; walls separated by $L = \pm 2 \cdot 3.14 \text{ \AA}$ (matching the spheroid's short axis); a potential well depth of $6.6 \cdot 10^{-3} \frac{\text{kcal}}{\text{mol}}$; and PBCs in the y and z-direction.

An often thought downside to using ellipsoids and particularly when using Perram and Wertheim's contact function [16] is that the numerical implementation is done in an iterative fashion with no clearly specified end-condition, which implies an indeterminate computational cost. This naturally makes some feel uneasy because, theoretically, this could mean one ends up with an infinite loop in certain cases. However, if one fixes the precision of the answer (in our case to a variance of 10^{-6} in the scalar parameter λ of the contact function [16]) not only does the calculation typically converge within 5-6 loops, but also fewer iterations are needed the farther ellipsoids are from each other. The same lowered computational cost also applies for ellipsoids with smaller aspect ratios.

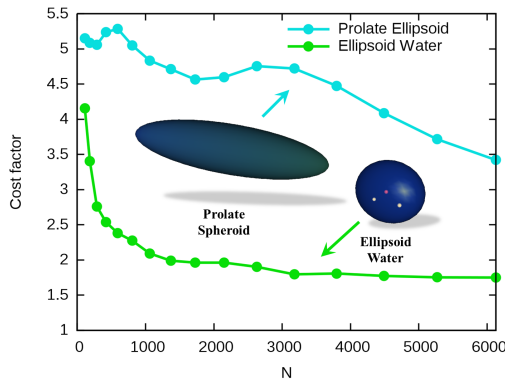


Figure 2. Cost factor of ellipsoids, from Table 1, is the cost (i.e. time) of computation relative to an equally sized system of a Lennard-Jones sphere. All calculations were run in the canonical (NVT) ensemble with potential cut off lengths fixed to half the box length.

Figure 2 shows the relative cost of using the ellipsoids from Table 1 with equation 2 but no electrostatics. For an ellipsoid of small aspect ratio (ellipsoidal water) the cost factor for increasing system sizes, N , decreases towards an asymptotic value of around 1.75. For the prolate ellipsoids, this drop in calculation cost is still ongoing for the largest system of 6000 ellipsoids. Overall, the maximum cost factor is about five, consistent with previous work [6], compared to the calculation of the spherical Lennard-Jones potential. Because the pairwise evaluation scales with the square of the number of entities involved, then when three or more Lennard-Jones spheres are replaced by one ellipsoid, the ellipsoid will be more computationally efficient ($\sqrt{5.5} < 3$, where 5.5 is the maximum observed ellipsoid cost factor). Ellipsoidal potentials may be adapted to an MD software package, because the contact function is analytic and could be used to evaluate forces and torques for both equations 3 and 4 [18].

3. Water: The Importance of Shape

To illustrate the utility of using an ellipsoidal shape, let us consider a simple, ellipsoidal water model based on the original SPC model [9]. By using the gyration tensor approach outlined in [6] an ellipsoid can be obtained from the SPC water model with oxygen, O, at the center of the ellipsoid.

With a Hamiltonian consisting of equation 3 for the LJ-like pair potential as well as a Coulomb interaction potential and a Barker-Watts type self-consistent reaction field [10,12,19] the resulting radial distribution function between oxygen centers for both the original SPC [9] and the ellipsoid water model in comparison to current experimental data from [20] is shown in Figure 3. It can be observed that while SPC generally matches the secondary peak locations well, it does overshoot the main peak by about 12% and generally shows slightly broader peaks than seen experimentally. The ellipsoid model improves the radial distribution function significantly in those regards.

Both models, using the NPT ensemble, give similar densities of $(0.98 \pm 0.01) \text{ g/cc}$. Interestingly, while the SPC model gave an overall dielectric of 60 ± 20 the ellipsoid model returned a dielectric of 23 ± 5 . This dramatic change of dielectric constants between the two models can be exclusively attributed to the difference in shape, spherical versus ellipsoidal. The ellipsoid breaks the high symmetry offered by the sphere used in the SPC water model. Combined with the strong dipole component of the interior charge distribution this leads the SPC water model (and by extension any water models using a spherical shape) to reach a larger dielectric constant than would be possible with a lower symmetry shape.

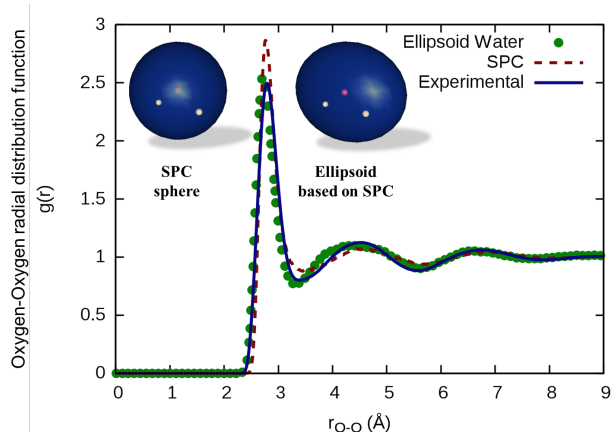


Figure 3. Shape effect demonstrated using O-O radial distribution function, $g(r)$, of water with spherical SPC water model (dashed red line), ellipsoidal model (green dots) based on SPC in comparison to experimental data [20] (solid blue line). Simulations consist of 216 water molecules (see Table 1) in the NPT ensemble under 1 atm at 298 K with periodic boundary conditions.

Our group has previously observed similarly inflated dielectric constants for a Stockmayer fluid (dipole in a sphere) when compared to an identical dipole inside of a prolate spheroid [10]. More importantly, prolate spheroids, with an aspect ratio larger than 1.3, agreed well with the Onsager value of the dielectric (quite close to the experimental dielectric for most organic solvents). Furthermore, using a simple dipolar expansions of charges and proper ellipsoids representing ethylene carbonate, we reported that analogous calculations obtained dielectric constants of 90, in agreement with experiment, using only a single or a two-ellipsoid coarse-grained model [6,14]. Therefore, it should be feasible to

obtain the experimental dielectric using the modified water shape, and position the charges to best describe the electrostatic potential of water, as recently suggested [21].

4. Conclusions

We have shown dramatic differences in the morphology of prolate spheroids with large dipoles, having a dipolar density on the order of water (5.42 for the prolate spheroid at 400 K vs 5.83 for SPC water at 298 K). The different morphologies shown for the prolate spheroids are caused by their large aspect ratio. Water however, has a much smaller aspect ratio but subtleties in close interactions can manifest in small changes in $g(r)$. In this case the simple substitution of an ellipsoid for the sphere in water definitely improved the SPC model of water with respect to the experimental $g(r)$. No further modifications of the model were performed.

The modification of the molecular shape to generate an ellipsoid for the Lennard-Jones interactions is based on an all atom transferable force field. Using well developed rules, one can automatically replace any simple set of atoms (within a molecule) with an ellipsoid. In the several cases we have tested [6] the agreement of the $g(r)$ of the ellipsoidal coarse-grained representation with the underlying all atom $g(r)$ has been excellent. We point out with water, that the ellipsoid we developed was consistent with the symmetry of the water molecule. The use of a sphere produces a system with a higher symmetry in its shape. The interaction of the point charges in the SPC Hamiltonian does respect the molecular symmetry of the molecule, but the same cannot be said for the intermolecular van der Waals energies. Replacing a sphere with an ellipsoid restores the underlying molecular dispersion symmetry of the water.

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