A Gay–Berne potential for dissimilar biaxial particles

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Abstract

We present a generalized biaxial Gay–Berne potential describing the interaction between two arbitrary, not necessarily identical, (AB) ellipsoidal particles. The model does not rely on approximate combination rules like that of Berthelot, but the pair energy is nevertheless computed efficiently using molecular parameters, optimized for the homogeneous cases (AA) and (BB), such as their respective shape and interaction biaxialities. © 1998 Elsevier Science B.V. All rights reserved.

The Gay–Berne (GB) pair potential [1] is a simple one-site attractive–repulsive interaction that represents an anisotropic generalization of a shifted 6–12 Lennard–Jones potential. The GB potential between two identical particles 1, 2 of a certain type A can be written as

$$
U_{AA}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \mathbf{r}_{12})
$$
$$
= 4\varepsilon_0 \, \varepsilon_{AA}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}_{12})
$$
$$
\times \left\{ \left[\frac{\sigma_s}{r_{12} - \sigma_{AA}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}_{12}) + \sigma_s} \right]^{12} \right.
$$
$$
\left. - \left[\frac{\sigma_s}{r_{12} - \sigma_{AA}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}_{12}) + \sigma_s} \right]^{6} \right\}, \quad (1)
$$

where $\mathbf{r}_i \equiv (x_i, y_i, z_i)$ is the position of particle i in the laboratory frame, $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1 \equiv (r_x, r_y, r_z)$ is the intermolecular vector $(\mathbf{r}_{12} \equiv r_{12}\hat{\mathbf{r}}_{12})$ and the unit vector $\hat{\mathbf{u}}_i \equiv (u_{ix}, u_{iy}, u_{iz})$ describes the orientation of the axis of particle i. σ_s and ε_0 are taken as units for distances and energies. The zero energy contour

surface around a GB particle interacting with another parallel one has an essentially ellipsoidal shape and it is convenient to think of particles interacting via the GB potential simply as soft attractive–repulsive ellipsoids. Computer simulations have shown that the GB potential is sufficiently rich to yield a number of the bulk phases experimentally observed: isotropic, nematic, and smectic [2–6] for elongated molecules and nematic and columnar [7] for discotic. Nematic–vapour [8,9] and nematic–isotropic [10] interfaces have also been simulated.

The potential depends on the molecular shape and well depth through the anisotropic terms $\sigma_{AA}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}_{12})$ and $\varepsilon_{AA}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}_{12})$ and on two additional parameters μ_{AA} and ν_{AA}, where we have added the chemical identity AA subscript which is usually omitted when only one type of molecule is dealt with. Given molecular length and breadth σ_e, σ_s and well depth ε_e, ε_s for an end-to-end and side-by-side approach, μ and ν can be used to tune the potential and, ultimately, to modify the phase diagram of the system. For instance, using $\mu = 2$ and $\nu = 1$, a smectic B phase and a narrow nematic is obtained with $\sigma_e/\sigma_s = 3$ and $\varepsilon_e/\varepsilon_s = 0.2$ at a number density $\rho^* = 0.3$, but using $\mu = 1$ and $\nu = 3$

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a smectic A is also obtained together with a much wider nematic.

Despite its usefulness, two important limitations of the GB potential are its uniaxiality and the fact that it applies to identical molecules. The first limitation is quite severe, in view of the fact that practically all mesogenic molecules are devoid of cylindrical symmetry. A biaxial version of the GB potential has been developed by us [11] and then by other groups [12,13] and is now being used to examine the possibility of forming biaxial phases. As for the second limitation, a heterogeneous version has been developed for uniaxial molecules [13], but to our knowledge a GB potential for dissimilar biaxial particles does not exist, although an ellipsoid contact potential has recently been worked out [14]. On the other hand, such a potential would be quite useful: first for the possibility of modelling mixtures, which are often used in practical applications, to tune specific liquid crystal properties not only with uniaxial [15,16] but also with biaxial molecular models. Moreover, many experimental investigations of anisotropic forces and of the mechanism of ordering are based on the investigation of suitable biaxial solutes in liquid crystals [17,18] and a heterogeneous interaction would allow their modelling.

In this Letter, we derive a Gay–Berne potential for dissimilar biaxial molecules and show how it can be calculated effectively and parametrized in practical applications. We start by considering two interacting molecules A and B each described by a 3-dimensional gaussian with ranges $\sigma_x^{(i)}$, $\sigma_y^{(i)}$ and $\sigma_z^{(i)}$, $i = A,B$, along the three axes. The overlap integral between two unlike gaussians with the given orientations ω_1, ω_2, parametrized in terms of Euler angles [19] (i.e., $\omega_i \equiv \{\alpha_i, \beta_i, \gamma_i\}$), or quaternions [20–23], and separation $\mathbf{r}_{12}$ can be computed analytically and is still a gaussian [11,14], and its range is used to define an anisotropic distance function $\sigma_{AB}(\omega_1, \omega_2, \hat{\mathbf{r}}_{12})$ and a pre-exponential term that gives an interaction strength at zero separation $\varepsilon_{AB}(\omega_1, \omega_2)$. Both depend explicitly on the set of coefficients $\sigma_a^{(i)}$ for the two molecules. The anisotropic distance function is

$$\sigma_{AB}(\omega_1, \omega_2, \hat{\mathbf{r}}_{12}) = \left[2\hat{\mathbf{r}}_{12}^{T} \mathbf{A}_{AB}^{-1}(\omega_1, \omega_2) \hat{\mathbf{r}}_{12} \right]^{-1/2}$$

(2)

where molecule 1 (2) is of type A (B), the dimensionless pre-exponential strength coefficient is

$$\varepsilon_{AB}(\omega_1, \omega_2) = \left[\frac{2\sigma_e^{(A)} \sigma_e^{(B)}}{\det[\mathbf{A}_{AB}(\omega_1, \omega_2)]} \right]^{1/2}$$

(3)

and the geometrical scaling constants $\sigma_e^{(i)}$ are

$$\sigma_e^{(i)} = \left[\sigma_x^{(i)} \sigma_y^{(i)} + \sigma_z^{(i)} \sigma_z^{(i)} \right] \left[\sigma_x^{(i)} \sigma_y^{(i)} \right]^{1/2},$$
$$i = A, B.$$

(4)

The symmetric overlap matrix $\mathbf{A}_{AB}(\omega_1, \omega_2)$ is defined explicitly in terms of the dimensions of the two molecular ellipsoids and their orientations

$$\mathbf{A}_{AB}(\omega_1, \omega_2) = \mathbf{M}^{T}(\omega_1) \mathbf{S}^{(A)2} \mathbf{M}(\omega_1)$$
$$+ \mathbf{M}^{T}(\omega_2) \mathbf{S}^{(B)2} \mathbf{M}(\omega_2).$$

(5)

The cartesian rotation matrices $\mathbf{M}(\omega_i)$, defined in terms of the orientation ω_i, rotate a vector from the laboratory to the molecular frame i [19]. The range matrices $\mathbf{S}^{(i)}$ have principal elements $S_{a,b}^{(i)} = \delta_{a,b} \sigma_a^{(i)}$ with $a, b = x, y, z$ that effectively describe the shape of a molecule.

The GB heterogeneous interaction energy is obtained, similarly to that for the homogeneous case, by transplanting the overlap σ_{AB} and strength ε_{AB} in a shifted LJ potential with the further inclusion of an ad-hoc interaction term ε'_{AB} [1,11]

$$U_{AB}(\omega_1, \omega_2, \mathbf{r}_{AB})$$
$$= 4\varepsilon_0 \varepsilon_{AB}^{\nu}(\omega_1, \omega_2) \varepsilon'^{\mu}_{AB}(\omega_1, \omega_2, \hat{\mathbf{r}}_{12})$$
$$\times \left\{ \left[\frac{\sigma_c}{r_{AB} - \sigma_{AB}(\omega_1, \omega_2, \hat{\mathbf{r}}_{12}) + \sigma_c} \right]^{12} \right.$$
$$\times \left. \left[\frac{\sigma_c}{r_{AB} - \sigma_{AB}(\omega_1, \omega_2, \hat{\mathbf{r}}_{12}) + \sigma_c} \right]^{6} \right\}$$

(6)

where μ and ν are empirical exponents and, as usual, ε_0 determines the energy scale. Molecular lengths are measured in σ_0 units. The 'minimum contact distance' parameter σ_c determines the width of the potential wells and lies in the range $0 < \sigma_c \leq (\min[\{\sigma_a^{(A)}\}] + \min[\{\sigma_a^{(B)}\}])/2$. We employ here

$$\sigma_c = \tfrac{1}{2}\left[\sigma_c^{(A)} + \sigma_c^{(B)} \right],$$

(7)

the average of the parameters $\sigma_c^{(i)}$ relative to the like interactions [11]. By analogy with the standard
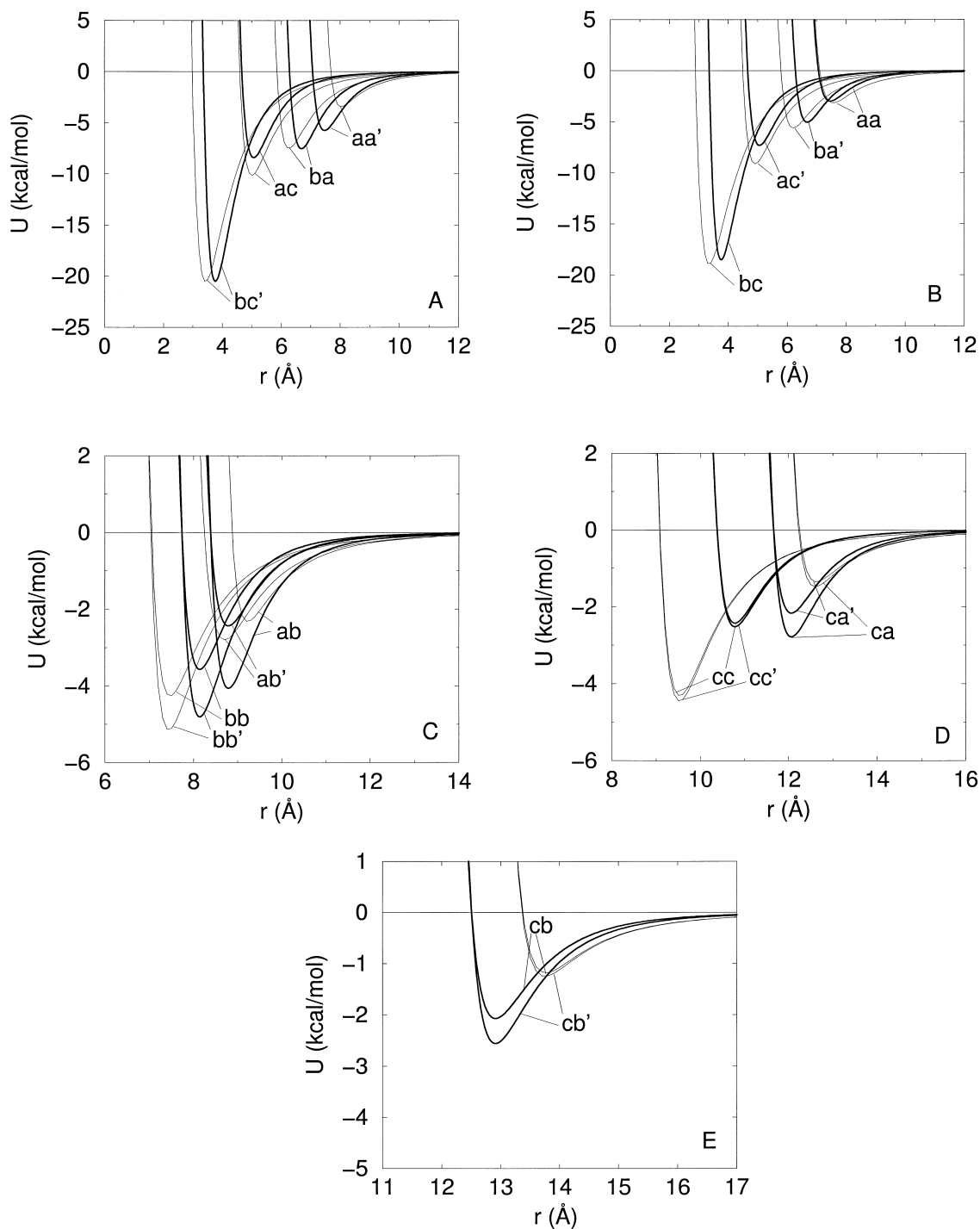
Fig. 1. Biaxial GB U_{AB} (thick line) and UFF [28,29]–MM (thin line) energy $\mathscr{U}_{AB}$ profiles of the pair perylene (oblate) and planar *p*-terphenyl (prolate) for the 18 'orthogonal' configurations described in the text. To aid comparison, the curves are grouped in five plates as: side-by-side (A), cross (B), tee-1 (C), tee-2 (D) and end-to-end (E).

GB potential, we define the dimensionless interaction term ε' as

$$\varepsilon'_{AB}(\omega_1, \omega_2, \hat{\mathbf{r}}_{12}) = 2\hat{\mathbf{r}}_{12}^T \mathbf{B}_{AB}^{-1}(\omega_1, \omega_2)\hat{\mathbf{r}}_{12} \qquad (8)$$

where the matrix $\mathbf{B}_{AB}$ is defined in terms of two diagonal interaction matrices $\mathbf{E}^{(A)}, \mathbf{E}^{(B)}$, one for each molecule, with elements $E_{a,b}^{(i)} = \delta_{a,b}(\varepsilon_0/\varepsilon_a^{(i)})^{1/\mu}$.

$$\mathbf{B}_{AB}(\omega_1, \omega_2) = \mathbf{M}^T(\omega_1)\mathbf{E}^{(A)}\mathbf{M}(\omega_1)$$
$$+ \mathbf{M}^T(\omega_2)\mathbf{E}^{(B)}\mathbf{M}(\omega_2) \qquad (9)$$

The coefficients $\varepsilon_x^{(i)}$, $\varepsilon_y^{(i)}$ and $\varepsilon_z^{(i)}$ are related to the well depths for the homogeneous interactions for the *aa*, *bb* and *cc orthogonal* configurations defined in Ref. [11]. In particular their ratios are equal to those of the corresponding well depths. The potential reduces to the standard Gay–Berne [1] when the molecules become uniaxial, identical and the parameter $\sigma_c = \sigma_0$. Similarly, the potential reduces to that in Ref. [11] when the two biaxial molecules are equal. In the case of unlike uniaxial molecules, a similar potential but with a different interaction strength term ε' to that in Ref. [13], is obtained.

A relevant feature of the mixed potential (Eq. (6)) is that the parameters in U_{AB} can be computed on the fly using the molecular dimensions $\sigma_a^{(i)}$ and interaction terms $\varepsilon_a^{(i)}$ relative to the (AA) and (BB) interactions. Indeed, for a given pair configuration ω_1, ω_2 and $\hat{\mathbf{r}}_{12}$, these coefficients determine the matrices $\mathbf{A}_{AB}$, $\mathbf{B}_{AB}$ and implicitly the GB parameters σ_{AB}, ε_{AB} and ε'_{AB}. There is no need to invoke any more or less arbitrary application [15] of the Lorentz linear average rule for the contacts σ and of the Berthelot geometric mean rule for the well depths [24] for these non-spherical particles. To see how effective this is, we have chosen a pair of molecules A,B from a set with various aspect ratios and we have calculated $\mathscr{U}_{AB}$, $\mathscr{U}_{AA}$, $\mathscr{U}_{BB}$ using a molecular mechanics (MM) approach. We determined the principal frame of each molecule diagonalizing its inertia tensor. We then fitted the (AA), (BB) pairs to a biaxial GB as discussed in Ref. [11] and we have used these parameters to construct a heterogeneous GB potential U_{AB}. This is compared with $\mathscr{U}_{AB}$ in Fig. 1 without any further optimization, in particular of μ, ν.

In practice we calculate $\mathscr{U}_{AB}$ at a set of selected 'orthogonal' configurations [11] which we visualize representing a biaxial particle i as a box with the a,

b and c faces orthogonal to the $\mathbf{x}_i$, $\mathbf{y}_i$ and $\mathbf{z}_i$ molecular axes, respectively. For a pair of unlike molecules, these are the 18 configurations listed in Table 1, where we label each 'orthogonal' pair with a two-letter code [11] obtained from the names of the faces perpendicular to the intermolecular vector and coming in contact as illustrated with sketches in Ref. [11]. The label is unprimed if none or two axes of the first molecule are antiparallel to those of the second one and primed if one or three axes are antiparallel. We also choose the first molecule, A, using two rules in decreasing order of priority: (i) an oblate has priority over a prolate particle and (ii) the molecule with shortest axis has highest priority. Molecular axes are then assigned using the convention of lowest shape biaxiality of Ref. [11] and adopting right-handed reference frames. Since our mixed GB potential U_{AB} uses only the parameters relative to the (AA),(BB) pairs (and a chosen μ, ν) the parametrization problem reduces to that of homo-molecular interactions U_{AA}, U_{BB} already discussed by us in Ref. [11]. In practice, we optimize a selected number of characteristic features chosen on physical grounds from energy profiles obtained for the 18 'orthogonal' configurations, namely: (i) the well depth ($U_{AA}^\dagger = -\varepsilon_0 \, \varepsilon^\nu(\omega_1, \omega_2) \, \varepsilon'^\mu(\omega_1, \omega_2, \hat{\mathbf{r}}_{12})$); (ii) the distance corresponding to the well minimum ($r_{AA}^\dagger = \sigma(\omega_1, \omega_2, \hat{\mathbf{r}}_{12}) + \sigma_c(2^{1/6} - 1)$); (iii) the *soft contact* distance ($r_{AA}^0 = \sigma(\omega_1, \omega_2, \hat{\mathbf{r}}_{12})$); (iv) the width of the

Table 1

The 18 'orthogonal' approaching configurations for two dissimilar biaxial particles A,B. The angles $\omega \equiv (\alpha, \beta, \gamma)$ define the relative orientation of the second molecule with respect to the first one. Symmetry equivalent configurations are generated for successive rotations of an angle π of the molecular frame with respect to one of its axes or by inversion of the intermolecular vector. The correspondence rules between heterogeneous oblate–prolate (O–P) and homogeneous 'orthogonal' configurations (O–O), (P–P) as described in the text are given in brackets. Symmetry-independent homogeneous (AA) configurations are printed in boldface

α	β	γ	$\mathbf{r}_{AB}\|\mathbf{x}_A$	$\mathbf{r}_{AB}\|\mathbf{y}_A$	$\mathbf{r}_{AB}\|\mathbf{z}_A$
0	0	0	$\mathbf{aa}_{(aa';aa')}$	$\mathbf{bb}_{(bc';cb')}$	$\mathbf{cc}_{(cb';bc')}$
0	0	$\pi/2$	$\mathbf{ab}'_{(ac;ab)}$	$ba'_{(ba;ca)}$	$\mathbf{cc}'_{(cb;bc)}$
0	$\pi/2$	0	$\mathbf{ac}'_{(ab;ac)}$	$\mathbf{bb}'_{(bc;cb)}$	$cd'_{(ca;ba)}$
0	$\pi/2$	$\pi/2$	$ac_{(ab';ac')}$	$ba_{(ba';ca')}$	$cb_{(cc';bb')}$
$\pi/2$	$\pi/2$	$\pi/2$	$\mathbf{aa}'_{(aa;aa)}$	$bc'_{(bb;cc)}$	$\mathbf{cb}'_{(cc;bb)}$
$-\pi/2$	$-\pi/2$	0	$\mathbf{ab}_{(ac';ab')}$	$\mathbf{bc}_{(bb';cc')}$	$\mathbf{ca}_{(ca';ba')}$

potential well at half height ($w_{AA} = \sigma_c[(4 + 2\sqrt{2})^{1/6}$ $- (4 - 2\sqrt{2})^{1/6}]$). The *cost function* Φ we use in fitting is defined as

$$\Phi_{AA} = \frac{1}{4N_c} \sum_{i=1}^{N_c} \left\{ \left[\frac{\mathscr{U}_m^\dagger(i) - U_{AA}^\dagger(i)}{U_n} \right]^2 \right.$$

$$+ \left[\frac{r_m^\dagger(i) - r_{AA}^\dagger(i)}{r_n} \right]^2$$

$$+ \left[\frac{r_m^0(i) - r_{AA}^0(i)}{r_n} \right]^2$$

$$\left. + \left[\frac{w_m(i) - w_{AA}(i)}{r_n} \right]^2 \right\} \qquad (10)$$

where all terms with a subscript m refer to the $\mathscr{U}_{AA}$ profiles to be reproduced. The quantities U_n and r_n render each term dimensionless and establish the relative weight of the interaction energy with respect to the molecular shape. We have arbitrarily chosen to

use $U_n = \min[\{\mathscr{U}_m^\dagger(i)\}]$ and $r_n = \max[\{r_m^\dagger(i)\}]$ and fixed $\mu = 2$ and $\nu = 1$. The sum is extended to the number N_c of energy profiles considered (here $N_c = 18$) even if some are degenerate.

The comparison between model and reference heterogeneous MM 'orthogonal' energy profiles $\mathscr{U}_{AB}$ is performed on curves U_{AB} with the same label. However, since we have 18 'orthogonal' configurations for (AB) pairs and 12 for (AA), (BB) a correspondence rule has to be established. If both particles are prolate (oblate) the comparison between heterogeneous and corresponding homogeneous orthogonal curves is still between configurations with the same name. For oblate–prolate interactions we use the following prescription, starting from 18 'orthogonal' configurations of two like prolate particles (P–P). For each configuration the label for the corresponding O–O case is found by exchanging $\mathbf{y}_i$ with $\mathbf{z}_i$ and reversing the $\mathbf{x}_i$ axes of each molecular frame. The corresponding configuration for the O–P case is obtained combining frame 1 from the O–O configuration with frame 2 from the P–P case. Each transformation does not affect the versor $\hat{\mathbf{r}}_{AB}$ in space

Table 2
Biaxial GB parameters for a selection of prolate and oblate molecules. The optimization was carried out using the procedure described in the text. The prolate molecules are: [1] sexithiophene; [2] planar quinquephenyl; [3] planar tetraphenyl; [4] planar terphenyl; [5] pentacene; [6] naphthacene; [7] planar biphenyl; [8] anthracene. The oblate molecules are: [9] porphine; [10] benzene; [11] perylene; [12] pyrene; [13] benzoquinone; [14] naphthalene; [15] anthraquinone; [16] tetrazine. Prolate (oblate) molecules labelled with a [*] have an oblate (prolate) interaction biaxiality λ_ε (i.e., the lowest λ_ε is that with ε_y and ε_z exchanged)

Mol #	λ_σ	λ_ε	σ_x	σ_y	σ_z	ε_x	ε_y	ε_z	σ_c	$10^3 \times \Phi$
Prolate molecules										
[1]	0.06	0.20	5.4	3.4	24.2	3.2	10.5	0.7	3.4	1.8
[2]	0.06	0.22	5.2	3.5	21.3	4.1	13.0	1.0	3.5	2.0
[3]	0.09	0.22	5.4	3.5	18.0	3.9	12.1	1.0	3.5	1.8
[4]	0.14	0.28	5.7	3.4	14.3	3.6	10.9	1.2	3.4	1.9
[5]	0.17	0.36	6.2	3.5	14.5	4.1	14.5	1.7	3.5	1.8
[6][*]	0.22	0.36[*]	6.2	3.5	12.4	3.7	13.4	1.9	3.5	1.9
[7]	0.27	0.28	5.9	3.3	10.5	3.2	9.3	1.1	3.3	2.1
[8][*]	0.36	0.29[*]	6.5	3.3	10.4	3.2	11.7	1.9	3.3	1.9
Oblate molecules										
[9]	0.00	0.02	11.4	11.4	3.2	2.2	2.1	13.6	3.2	4.9
[10]	0.04	0.12	6.3	6.5	3.1	1.2	1.0	4.1	3.1	1.6
[11]	0.22	0.25	8.2	10.4	3.3	3.7	2.3	15.7	3.2	2.3
[12]	0.24	0.32	8.1	10.5	3.2	2.5	1.3	11.6	3.2	2.3
[13][*]	0.24	0.38[*]	6.0	7.4	3.2	1.5	0.7	4.5	3.2	1.9
[14]	0.26	0.10	6.5	8.2	3.3	2.0	1.7	7.8	3.2	2.2
[15]	0.36	0.14	7.2	10.5	3.2	2.2	1.7	10.6	3.2	2.1
[16]	0.39	0.28	5.3	6.6	3.9	0.9	0.6	2.3	3.3	2.1

fixed frame. This leads to the correspondence sets reported in Table 1.

We have chosen to test the procedure using various elongated (prolate) and flat-like (oblate) aromatic molecules which are listed in Table 2. First, molecular geometries were optimized using Macromodel [25] with the MM2 force field [26,27]. Energy curves have instead been calculated using a simple MM potential based on the Universal Force Field (UFF) [28,29] which is expected to give a good estimate of the non-bonding interactions for aromatic hydrocarbons [30]. The optimized GB parameters for representative prolate and oblate molecules are listed in Table 2. We now show, as an example, the heterogeneous potential curves for an oblate and a prolate molecule, perylene and planar p-terphenyl. In Fig. 1A–E we plot the heterogeneous 'orthogonal' U_{AB} GB profiles against the reference molecular mechanics $\mathscr{U}_{AB}$ curves. We see that the heterogeneous GB curves are similar to the reference ones. This result is quite comforting, since it should be remembered that we are comparing curves where full atomic detail has been taken into account only with curves where a single interaction centre for each molecule has been used. The agreement is particularly good for the side-by-side and cross configurations. On the other hand, the end-to-end curves estimate the soft contact distance within a 10% error. This difference is acceptable, since these configurations usually contribute to a small extent to the global interaction in a bulk fluid phase.

An extremely important quantity in the study of biaxial solutes and mesogens is their molecular biaxiality [31] and its evaluation is seen to be critical, e.g., for designing mesogens that can yield biaxial phases. It is apparent, looking at our potential, that more than one biaxiality can be introduced for a molecule, e.g., in terms of the biaxiality of $\mathbf{S}^{(i)}$ and $\mathbf{E}^{(i)}$. In particular, the shape biaxiality [11] is

$$\lambda_\sigma^{(i)} = \sqrt{3/2}\ \frac{\sigma_x^{(i)} - \sigma_y^{(i)}}{2\,\sigma_z^{(i)} - \sigma_x^{(i)} - \sigma_y^{(i)}} \qquad (11)$$

and similarly, the interaction biaxiality

$$\lambda_\varepsilon^{(i)} = \sqrt{3/2}\ \frac{\varepsilon_x^{(i)-1/\mu} - \varepsilon_y^{(i)-1/\mu}}{2\,\varepsilon_z^{(i)-1/\mu} - \varepsilon_x^{(i)-1/\mu} - \varepsilon_y^{(i)-1/\mu}}\ . \tag{12}$$

For instance we see from Table 2 that some molecules have high shape but low interaction biaxialities or vice versa. Even more interestingly, we see that some molecules behave simultaneously as rods and disks when both shape and energy are considered. Thus, naphthacene and anthracene are rod-like molecules behaving as oblate particles form the interaction point of view. Benzoquinone is exactly the other way round. This model should then be able to reproduce excluded volume and attractive features and its detailed balance might be responsible for peculiar experimental properties. Similarly, we might try to define a shape (interaction) biaxiality for solute A when dissolved in solvent B. However, it is clear from the previous equations that such a $\lambda^{(AB)}$ is not separable in a product of $\lambda^{(A)}$ and $\lambda^{(B)}$.

In conclusion, we have developed a heterogeneous biaxial Gay–Berne potential that allows a direct and efficient computation of the anisotropic interaction energy between two single site biaxial particles. This heterogeneous potential has the correct symmetry and preserves the physical identity of both molecules. It is then able to distinguish all not equivalent configurations. There is a negligible additional computational effort in passing from the homogeneous to the heterogeneous case since the energy is computed using a combination of parameters optimized for the homogeneous case. All possible interaction schemes are then easily studied simply combining parameters from tables like those given in the text. This should make this novel potential particularly useful in computer simulation studies of mixtures and solute–solvent interactions.

Acknowledgements

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