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A generalized Gay–Berne intermolecular potential for biaxial particles

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Abstract

A biaxial version of the Gay–Berne potential used to model uniaxial anisotropic molecules is developed. This novel biaxial potential can be used to deal with molecules with different attractive and repulsive contributions along their three axes.

The Gay–Berne (GB) [1] potential can be regarded as an anisotropic and shifted version of the Lennard-Jones 6–12 (LJ) interaction suitable for uniaxial molecules, where the strength ϵ and the range parameter σ depend on the orientations of the two particles and their intermolecular vector. An explicit expression for ϵ and σ has been obtained by Berne and Pechukas [2] by representing each molecule with a uniaxial ellipsoidal Gaussian and their interaction as related to their overlap integral. This integral can in turn be written down as a Gaussian whose pre-exponential and width are taken to be proportional to ϵ and σ. Gay and Berne [1] then modified the Gaussian-overlap potential in order to introduce a parametric angular dependence on the well depth and width. In the case of uniaxial particles the analytic form of the potential can be written down explicitly [1]. Other slightly different potentials based on the same ϵ and σ have been put forward [3]. The GB potential presents several useful features, in particular: (i) it uses less (albeit anisotropic) centres than atomic site models, e.g., one GB site with suitable parameters can model benzene with results similar to those of six united atom centres [3]; (ii) its parameters can be interpreted and altered as the shape of the molecule changes; (iii) it can be easily differentiated analytically with respect to the positional variables avoiding the discontinuities of purely hard core models.

More importantly, the Gay–Berne potential [1] has proved to be successful in modelling the various condensed phases resulting from a collection of prolate or oblate uniaxial particles. Various simulations [4–10] have now shown that a GB system exhibits the most important liquid crystalline phases, namely nematic, smectic A and B for prolate and, respectively, nematic and columnar for oblate particles.

On the other hand the current version of the potential is only appropriate for uniaxial molecules, while the need to generalize the GB potential to biaxial particles is rather pressing because, for instance: (a) practically all mesogenic molecules are not uniaxial; (b) the effects of molecular biaxiality are essential for understanding the detailed temperature dependence of ordering in liquid crystals; (c) biaxial contributions to the potential will be essential for obtaining biaxial phases; (d) there is widespread interest in studying the behaviour of biaxial solutes.

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The aim of this Letter is thus to propose a generalization of the Gay–Berne potential suitable for the description of the interaction of biaxial ellipsoids. We start with an overlap model for fully asymmetric ellipsoidal Gaussians and show how this can be used to obtain a generalized biaxial potential. We then parametrize this potential using the interaction of two rigid oligophenyls as a reference.

A particle i at position $\boldsymbol{r}_i$ and orientation ω with respect to the laboratory frame is represented by a Gaussian function $G_i(\omega_i, \boldsymbol{r})$ that, apart from a normalization factor, can be written as [11,12]

$$G_i(\omega_i, \boldsymbol{r}) = \exp[-\tfrac{1}{2}(\boldsymbol{r} - \boldsymbol{r}_i)^{\mathrm{T}}\mathbf{M}_i^{\mathrm{T}}\mathbf{S}_i^{-2}\mathbf{M}_i(\boldsymbol{r} - \boldsymbol{r}_i)], \tag{1}$$

where $\mathbf{S}$ is a diagonal '*shape*' matrix with elements σ_x, σ_y, σ_z, the axes of the ellipsoid representing the molecule measured with respect to a unit length σ_0, and $\mathbf{M}_i$ is the rotation matrix transforming from laboratory to molecular frame. A molecular shape biaxiality can be defined from the matrix $\mathbf{S}$ as [13]

$$\lambda_{\mathrm{S}} = \sqrt{3/2}\frac{\sigma_x - \sigma_y}{2\sigma_z - \sigma_x - \sigma_y}. \tag{2}$$

To make the definition of the orientation of a biaxial object unambiguous, we conventionally assign the axes $\boldsymbol{x}$, $\boldsymbol{y}$ and $\boldsymbol{z}$ so as to obtain the lowest biaxiality. In practice for a prolate object we choose $\sigma_z > \sigma_x \geqslant \sigma_y$ while for an oblate particle we adopt $\sigma_y \geqslant \sigma_x > \sigma_z$. Using this prescription λ_{S} can vary from 0, corresponding to a uniaxial object to $1/\sqrt{6}$ for an object of spherical symmetry, i.e. when all three σ_i tend to σ with the ordering above.

The overlap integral corresponding to the interaction between two identical particles, with shape $\mathbf{S}$, can be written as a convolution integral. When the first molecule is centred at the origin, $\boldsymbol{r}_1 = 0$, and the second at $\boldsymbol{r}_2 = \boldsymbol{r}_{12} + \boldsymbol{r}_1 = \boldsymbol{r}_{12}$ we have

$$Q_{12}(\omega_1, \omega_2, \boldsymbol{r}_{12}) = \int_0^\infty \mathrm{d}\boldsymbol{r}\, G_1(\omega_1, \boldsymbol{r}) G_2(\omega_2, \boldsymbol{r}) \tag{3a}$$

$$= \int_0^\infty \mathrm{d}\boldsymbol{r}\, \exp\{-\tfrac{1}{2}[\boldsymbol{r}^{\mathrm{T}}\mathbf{M}_1^{\mathrm{T}}\mathbf{S}^{-2}\mathbf{M}_1\boldsymbol{r} - (\boldsymbol{r}_{12} - \boldsymbol{r})^{\mathrm{T}} \times \mathbf{M}_2^{\mathrm{T}}\mathbf{S}^{-2}\mathbf{M}_2(\boldsymbol{r}_{12} - \boldsymbol{r})]\}. \tag{3b}$$

This convolution integral can be calculated as the inverse Fourier transform of the product of Fourier transforms of G_1 and G_2 (see, e.g., Ref. [14]). We find in this way

$$Q_{12}(\omega_1, \omega_2, \boldsymbol{r}_{12}) = \det[\mathbf{S}^2]\left(\frac{\pi^3}{8\det[\mathbf{A}]}\right)^{1/2} \times \exp(-\tfrac{1}{2}\boldsymbol{r}_{12}^{\mathrm{T}}\mathbf{A}^{-1}\boldsymbol{r}_{12}), \tag{4}$$

where $\det[\mathbf{S}^2] = (\sigma_x\sigma_y\sigma_z)^2$ and the symmetric overlap matrix $\mathbf{A}$ is defined as

$$\mathbf{A} = \mathbf{M}_1^{\mathrm{T}}\mathbf{S}^2\mathbf{M}_1 + \mathbf{M}_2^{\mathrm{T}}\mathbf{S}^2\mathbf{M}_2. \tag{5}$$

For uniaxial molecules (with $\sigma_x = \sigma_y \neq \sigma_z$) both $\det[\mathbf{A}]$ and $\mathbf{A}^{-1}$ can be calculated analytically [1,2]. When $\sigma_x \neq \sigma_y \neq \sigma_z$ the matrix $\mathbf{A}$ can be inverted using an algebraic manipulation language such as Mathematica [15] and an explicit expression for the elements of $\mathbf{A}^{-1}$ is given in the Appendix. Although the resulting elements are a bit unwieldy and we shall continue to employ the matrix notation, the availability of an explicit form for the inverse matrix elements makes the actual evaluation of the potential not unduly slow. In any case we can still write the overlap integral in a form similar to that of Refs. [1,2] and employ the resulting coefficients to write a generalized anisotropic LJ potential as

$$U_{\mathrm{BX}}(\omega_1, \omega_2, \boldsymbol{r}_{12}) = 4\epsilon_0\epsilon(\omega_1, \omega_2, \hat{\boldsymbol{r}}_{12}) \times \left[\left(\frac{\sigma_{\mathrm{c}}}{r_{12} - \sigma(\omega_1, \omega_2, \hat{\boldsymbol{r}}_{12}) + \sigma_{\mathrm{c}}}\right)^{12} - \left(\frac{\sigma_{\mathrm{c}}}{r_{12} - \sigma(\omega_1, \omega_2, \hat{\boldsymbol{r}}_{12}) + \sigma_{\mathrm{c}}}\right)^{6}\right], \tag{6}$$

where σ_{c} is a distance, ϵ_0 defines the energy scale and $\omega \equiv \{\alpha, \beta, \gamma\}$ are Euler angles [16]. The anisotropic contact distance is

$$\sigma(\omega_1, \omega_2, \hat{\boldsymbol{r}}_{12}) = (2\hat{\boldsymbol{r}}_{12}^{\mathrm{T}}\mathbf{A}^{-1}\hat{\boldsymbol{r}}_{12})^{-1/2} \tag{7}$$

and, similarly to the uniaxial case [1], the anisotropic interaction term is written as

$$\epsilon(\omega_1, \omega_2, \hat{\boldsymbol{r}}_{12}) = \epsilon^{\nu}(\omega_1, \omega_2)\epsilon'^{\mu}(\omega_1, \omega_2, \hat{\boldsymbol{r}}_{12}), \tag{8}$$

where μ and ν are empirical exponents and the proposed form of the dimensionless strength coefficient is now

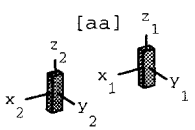
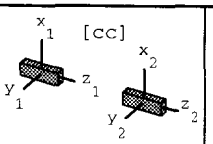
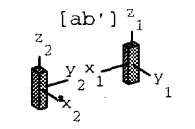
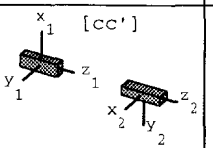
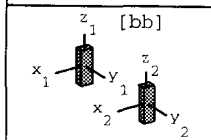
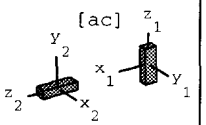
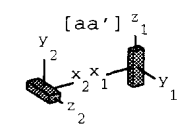
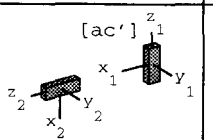
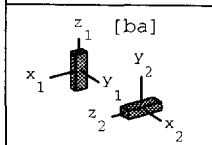
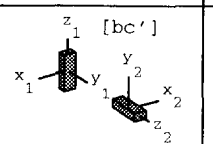
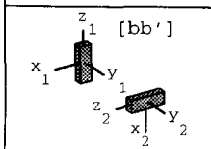
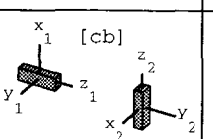
	$\sigma = \sigma_x$ $\epsilon = (\sigma_x^2 + \sigma_z^2)/(2\sigma_z(\sigma_x\sigma_y)^{1/2})$ $\epsilon' = (\epsilon_x/\epsilon_0)^{1/\mu}$		$\sigma = \sigma_z$ $\epsilon = (\sigma_x^2 + \sigma_z^2)/(2\sigma_z(\sigma_x\sigma_y)^{1/2})$ $\epsilon' = (\epsilon_z/\epsilon_0)^{1/\mu}$
	$\sigma = [(\sigma_x^2 + \sigma_y^2)/2]^{1/2}$ $\epsilon = (\sigma_x\sigma_y)^{1/2}(\sigma_x^2 + \sigma_z^2)/((\sigma_x^2 + \sigma_y^2)\sigma_z)$ $\epsilon' = 2/[(\epsilon_0/\epsilon_x)^{1/\mu} + (\epsilon_0/\epsilon_y)^{1/\mu}]$		$\sigma = \sigma_z$ $\epsilon = (\sigma_x\sigma_y)^{1/2}(\sigma_x^2 + \sigma_z^2)/((\sigma_x^2 + \sigma_y^2)\sigma_z)$ $\epsilon' = (\epsilon_z/\epsilon_0)^{1/\mu}$
	$\sigma = \sigma_y$ $\epsilon = (\sigma_x^2 + \sigma_z^2)/(2\sigma_z(\sigma_x\sigma_y)^{1/2})$ $\epsilon' = (\epsilon_y/\epsilon_0)^{1/\mu}$		$\sigma = [(\sigma_x^2 + \sigma_z^2)/2]^{1/2}$ $\epsilon = (\sigma_x\sigma_y)^{1/2}(\sigma_x^2 + \sigma_z^2)\tau$ $\epsilon' = 2/[(\epsilon_0/\epsilon_x)^{1/\mu} + (\epsilon_0/\epsilon_z)^{1/\mu}]$
	$\sigma = \sigma_x$ $\epsilon = (\sigma_y/\sigma_x)^{1/2}(\sigma_x^2 + \sigma_z^2)/(\sigma_y^2 + \sigma_z^2)$ $\epsilon' = (\epsilon_x/\epsilon_0)^{1/\mu}$		$\sigma = [(\sigma_x^2 + \sigma_z^2)/2]^{1/2}$ $\epsilon = (\sigma_x/\sigma_y)^{1/2}$ $\epsilon' = 2/[(\epsilon_0/\epsilon_x)^{1/\mu} + (\epsilon_0/\epsilon_z)^{1/\mu}]$
	$\sigma = [(\sigma_x^2 + \sigma_y^2)/2]^{1/2}$ $\epsilon = (\sigma_x\sigma_y)^{1/2}(\sigma_x^2 + \sigma_z^2)\tau$ $\epsilon' = 2/[(\epsilon_0/\epsilon_x)^{1/\mu} + (\epsilon_0/\epsilon_y)^{1/\mu}]$		$\sigma = [(\sigma_y^2 + \sigma_z^2)/2]^{1/2}$ $\epsilon = (\sigma_y/\sigma_x)^{1/2}(\sigma_x^2 + \sigma_z^2)/(\sigma_y^2 + \sigma_z^2)$ $\epsilon' = 2/[(\epsilon_0/\epsilon_y)^{1/\mu} + (\epsilon_0/\epsilon_z)^{1/\mu}]$
	$\sigma = \sigma_y$ $\epsilon = (\sigma_x/\sigma_y)^{1/2}$ $\epsilon' = (\epsilon_y/\epsilon_0)^{1/\mu}$		$\sigma = [(\sigma_y^2 + \sigma_z^2)/2]^{1/2}$ $\epsilon = (\sigma_x\sigma_y)^{1/2}(\sigma_x^2 + \sigma_z^2)\tau$ $\epsilon' = 2/[(\epsilon_0/\epsilon_y)^{1/\mu} + (\epsilon_0/\epsilon_z)^{1/\mu}]$

Fig. 1. The twelve independent '*orthogonal*' configurations for a pair of biaxial molecules (shown as parallelepipeds) with their respective expressions for the coefficients $\sigma(\omega_1, \omega_2, \hat{r}_{12})$, $\epsilon(\omega_1, \omega_2)$ and $\epsilon'(\omega_1, \omega_2, \hat{r}_{12})$ of the biaxial GB potential defined in the text. The symbol τ is used as shorthand for $\{2/[(\sigma_x^2 + \sigma_y^2)(\sigma_y^2 + \sigma_z^2)(\sigma_z^2 + \sigma_x^2)]\}^{1/2}$.

$$\epsilon(\omega_1, \omega_2) = (\sigma_x\sigma_y + \sigma_z^2)\left(\frac{2\sigma_x\sigma_y}{\det[\mathbf{A}]}\right)^{1/2}. \quad (9)$$

We can also proceed to define a dimensionless interaction parameter ϵ' similar to that in Ref. [1] as

$$\epsilon'(\omega_1, \omega_2, \hat{r}_{12}) = 2\,\hat{r}_{12}^{\mathrm{T}}\mathbf{B}^{-1}\hat{r}_{12}, \quad (10)$$

where the matrix $\mathbf{B}$ is defined as

$$\mathbf{B} = \mathbf{M}_1^{\mathrm{T}}\mathbf{E}\mathbf{M}_1 + \mathbf{M}_2^{\mathrm{T}}\mathbf{E}\mathbf{M}_2 \quad (11)$$

in terms of the auxiliary diagonal interaction matrix $\mathbf{E}$ with elements $E_{ij} = \delta_{i,j}(\epsilon_0/\epsilon_i)^{1/\mu}$. The coefficients ϵ_x, ϵ_y and ϵ_z are related to the well depths for the *side-by-side*, *width-to-width* and *end-to-end* interactions.

The potential reduces to the standard Gay–Berne one when the molecules become uniaxial except for the fact that a tunable σ_c is used instead of $\sigma_\perp$, following a suggestion of Kabadi [17]. The need for introducing σ_c also stems from an examination of the form of U_{BX}. For a given interparticle configuration $\{\omega_1, \omega_2, \hat{r}_{12}\}$, the potential has two minima located at $r_{12}^{\pm} = \sigma(\omega_1, \omega_2, \hat{\mathbf{r}}_{12}) - \sigma_c(1 \pm 2^{1/6})$ and is zero at $r_{12} = \sigma(\omega_1, \omega_2, \hat{r}_{12})$ and $r_{12} = \sigma(\omega_1, \omega_2, \hat{r}_{12}) - 2\sigma_c$, thus σ_c is related to the width of the potential well. The minimum at r_{12}^{+} is not physically meaningful, but if $\sigma(\omega_1, \omega_2, \hat{r}_{12}) > 2\sigma_c$ part of its branch of the curve could be found at positive (and thus potentially occurring) values of r_{12}. This spurious branch should be avoided in MC simulations, where the molecules are moved with discrete jumps, since they would lead to unphysical and possibly unlockable configurations. It is also worth realizing that when $\sigma_c >> \sigma(\omega_1, \omega_2, \hat{r}_{12})$, as could be the case if σ_c is taken close to the in plane dimensions for two oblate molecules approaching face to face, $U_{BX}(0)$ can be finite and even small rather than tending to ∞ as desired. The introduction of the parameter σ_c, with $0 < \sigma_c \leqslant \min(\sigma_x, \sigma_y, \sigma_z)$, allows the generalization of the potential to the interaction of arbitrary shaped objects.

We now wish to consider special cases of the interaction for well defined configurations and for the purpose of representation we consider the biaxial ellipsoids introduced in the previous sections as parallelepipeds with the faces orthogonal to $\boldsymbol{x}$, $\boldsymbol{y}$ and $\boldsymbol{z}$ labelled as a, b and c. In other words face a is parallel to the yz plane, b to the xz plane and c to the xy one. Given two identical molecules with a fixed mutual orientation we then consider their interaction energy as a function of separation r. In particular we choose the twelve configurations (Fig. 1) where every axis of the second frame is parallel (antiparallel) or perpendicular to those of the first one. Each of these is identified with a two-letter code formed by the names of the faces coming in contact so that axes perpendicular to both faces define the intermolecular vector. All the mutual '*orthogonal*' orientations can be generated starting with the two molecules aligned, i.e. $\boldsymbol{x}_1 \| \boldsymbol{x}_2$, $\boldsymbol{y}_1 \| \boldsymbol{y}_2$, $\boldsymbol{z}_1 \| \boldsymbol{z}_2$ and performing a rotation of the second molecule of Euler angles $\omega = \{\alpha, \beta, \gamma\}$. Every rotation generates three approaching configurations, each of them along one axis of the first molecule. In Table 1 we list in boldface the independent configurations (twelve out of fifteen) obtained rotating the frame of the second molecule with the given angles α, β and γ equal to 0 or $\pi/2$. In Fig. 1 we sketch these twelve configurations with their codes and the respective analytic expressions for σ, ϵ and ϵ'. For a uniaxial object there are only four unique configurations of this type: **aa** ≡ ab′ ≡ bb ≡ (side-by-side), **cc** ≡ cc′ ≡ (end-to-end), **ac** ≡ ac′ ≡ cb′ ≡ bc′ ≡ cb ≡ (tee), **aa′** ≡ ba ≡ bb′ ≡ (cross), underlined in Table 1.

In Fig. 2 we see a representation of the potential surface for two molecules approaching side by side for uniaxial and biaxial particles ($\lambda_S = 0$ and $\lambda_S = 0.111$). Switching on the biaxiality allows different approach distances and interaction strengths for the two shorter axes of the molecules. The potential contains various parameters μ, ν, ϵ_x, ϵ_y, ϵ_z and σ_c that, together with the shape parameters σ_x, σ_y, σ_z should allow a certain flexibility in modelling intermolecular

Table 1
The orthogonal configurations defined in the text for orientation $\omega \equiv \{\alpha, \beta, \gamma\}$ of the second molecule with respect to the first one and $\boldsymbol{r}_{12} \| \boldsymbol{x}_1$, or $\boldsymbol{y}_1$ or $\boldsymbol{z}_1$. For biaxial molecules the independent configurations are printed in boldface while they are underlined for the uniaxial case

α	β	γ	$r_{12} \| x_1$	$r_{12} \| y_1$	$r_{12} \| z_1$
0	0	0	**aa**	**bb**	**cc**
0	0	$\pi/2$	**ab′**	ba′	**cc′**
0	$\pi/2$	0	**ac′**	**bb′**	ca′
0	$\pi/2$	$\pi/2$	**ac**	**ba**	**cb**
$\pi/2$	$\pi/2$	$\pi/2$	**aa′**	**bc′**	cb′

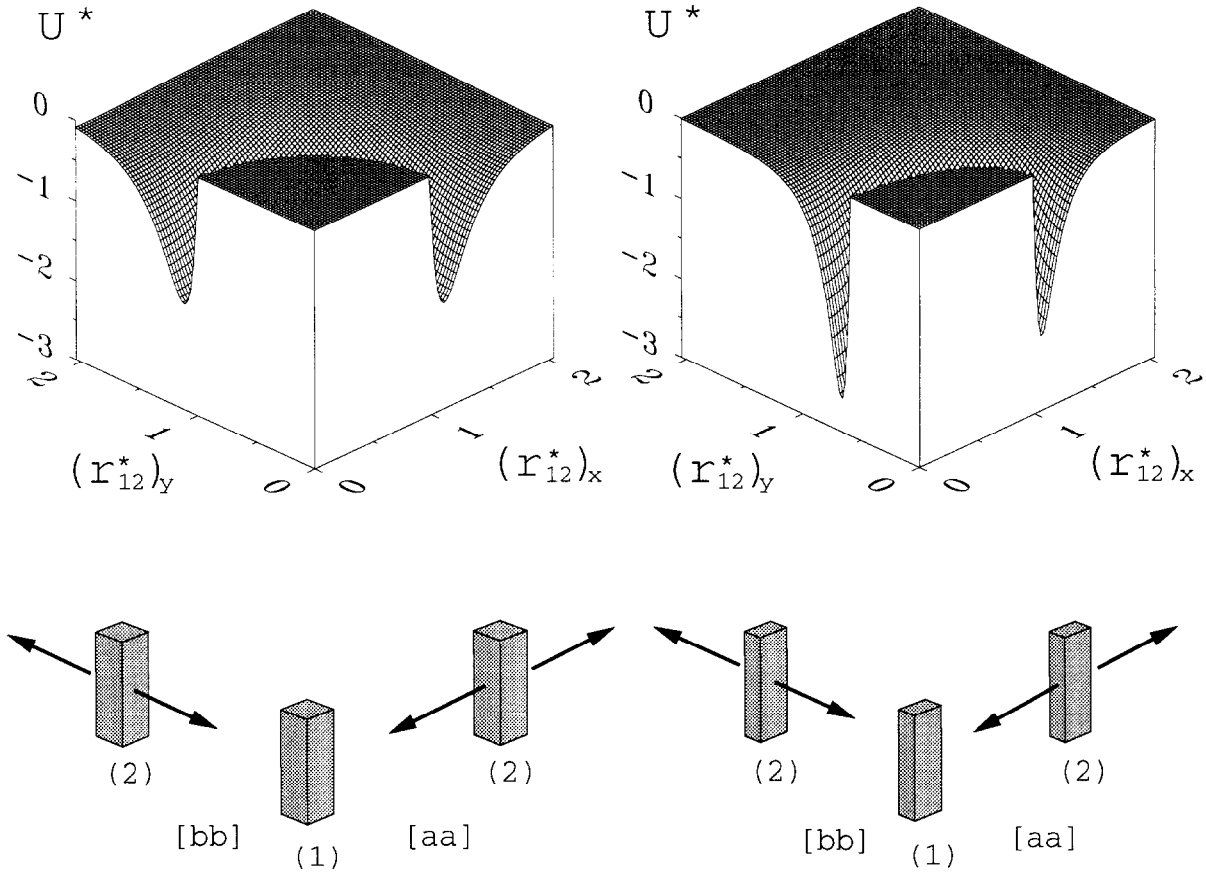


Fig. 2. Uniaxial (left) and biaxial (right) interaction energy U^* for two GB particles ($\mu = 2$, $\nu = 1$) with fixed orientation ($\omega_i = \{0, 0, 0\}$) and located on the xy plane ($r^*_{12} \perp Z$). The approach along the x, y axes corresponds to the aa, bb configurations described in Fig. 1. On the left we consider uniaxial molecules with $\sigma_x = \sigma_y = \sigma_c = 1$, $\sigma_z = 3$ ($\lambda_S = 0$), and $\epsilon_x = \epsilon_y = 1$, $\epsilon_z = 0.2$. On the right we show a biaxial case with $\sigma_y = \sigma_c = 0.6$ ($\lambda_S = 0.111$), and $\epsilon_y = 1.25$. All distances are expressed in σ_0 units and energies in ϵ_0 units.

potentials. Here we have taken as an example the series of p-polyphenyls from biphenyl to quinquephenyl. A parametrization based on terphenyl has previously been used (Luckhurst and Simmonds [5]). Since the aim here is mainly that of seeing how the parameters in our potential vary upon regular changes in a molecular structure, we have arbitrarily assumed these oligophenyls to be planar, setting to zero the dihedral angles of the optimized geometry obtained using the molecular mechanics package MacroModel [18] and the MM2 force field [19]. For each configuration listed in Fig. 1 we have used MacroModel to compute the potential energy curves as a function of intermolecular distance. Then we have fitted the biaxial potential for these twelve approach directions, optimizing contact distance, position of the minimum, depth and width of the well. The minimization of a sum of mean square normalized residuals was performed with Simplex [20] in a first stage, followed by a conjugate gradient method [21] near the minimum.

For this series of molecules (although not in general) the parameters μ, ν proved to be relatively insensitive when changing molecule and after a preliminary investigation of their effect we then set them to 2 and 1 as in the standard uniaxial GB [1], leaving 7 parameters to be fitted. In Table 2 we show the fit results together with the biaxiality calculated from the fitted shape matrix. The sum of normalized squared residuals is typically 0.02 for all molecules even if the quality of the fit as such should be considered with care in view of the limited number of parameters employed. In any case it is interesting to see that the

Table 2
The biaxial GB parameters for the planar p-polyphenyls, from biphenyl to quinquephenyl, obtained as described in the text. Here $\mu = 2$ and $\nu = 1$ has been used

	$n = 2$	$n = 3$	$n = 4$	$n = 5$
σ_x/σ_0	5.99	5.72	5.45	5.21
σ_y/σ_0	3.24	3.27	3.32	3.34
σ_z/σ_0	10.67	14.67	18.56	22.11
σ_c/σ_0	2.98	2.88	2.94	3.11
λ_S	0.278	0.147	0.092	0.064
ϵ_x/ϵ_0	2.05	2.22	2.38	2.49
ϵ_y/ϵ_0	6.14	6.95	7.51	8.02
ϵ_z/ϵ_0	0.70	0.60	0.51	0.47

molecular dimensions are relatively well reproduced by the σ_i, with σ_z increasing regularly and σ_x, σ_y fairly constant. The parameter σ_c automatically comes out to be smaller than each σ_i. The shape biaxiality λ_S decreases as the molecules become longer as expected. The other parameters are quite similar for the various members of the series, with different values in the x, y, z directions. The biaxial potential, although simple, thus allows discrimination between interactions that would be degenerate with the usual uniaxial Gay–Berne. In conclusion, we have obtained a Gaussian overlap potential suitable for biaxial molecules that generalizes that developed by Gay and Berne for uniaxial molecules. The potential is designed to introduce an essential element, molecular biaxiality, in an already useful attractive–repulsive pair potential. Although this constitutes an important element of realism, the potential is not meant to reproduce molecular structures with atomic detail; rather the potential should be useful in a number of theoretical calculations and simulations, where the simplicity of a closed form for the interaction must be coupled with a representation of asymmetric molecular shape.

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Appendix

Here we write down explicitly the elements of the $\mathbf{A}^{-1}$ and $\mathbf{B}^{-1}$ matrices. The overlap matrix $\mathbf{A}$ was defined in the text (Eq. (5)) in terms of the Cartesian rotation matrices for two molecules i and j,

$$A_{a,b} = \sum_e \sigma_e^2 (M_{e,a}^{(i)} M_{e,b}^{(i)} + M_{e,a}^{(j)} M_{e,b}^{(j)}),$$

where a, b, e can be x, y or z. The determinant of $\mathbf{A}$ can be written explicitely as

$$\det[\mathbf{A}] = \sum_{a,b,c} \epsilon_{a,b,c} A_{x,a} A_{y,b} A_{z,c},$$

where $\epsilon_{a,b,c}$ is the Levi–Civita symbol (permutation symbol). It has value $+1$ if the subscripts $\{a, b, c\}$ correspond to any even permutation of $\{x, y, z\}$, -1 for any odd permutation and 0 if any of the indices are repeated. Using these definitions the three columns of the matrix $\mathbf{A}^{-1}$ can be written explicitely as

$$A_{a,x}^{-1} = \det[\mathbf{A}]^{-1} \times \sum_{b,c} \epsilon_{a,b,c} \sum_{d,e} \sigma_d^2 \sigma_e^2 \left(M_{d,y}^{(i)} M_{d,b}^{(i)} + M_{d,y}^{(j)} M_{d,b}^{(j)} \right) \times \left(M_{e,z}^{(i)} M_{e,c}^{(i)} + M_{e,z}^{(j)} M_{e,c}^{(j)} \right),$$

$$A_{b,y}^{-1} = \det[\mathbf{A}]^{-1} \times \sum_{a,c} \epsilon_{a,b,c} \sum_{d,e} \sigma_d^2 \sigma_e^2 \left(M_{d,x}^{(i)} M_{d,a}^{(i)} + M_{d,x}^{(j)} M_{d,a}^{(j)} \right) \times \left(M_{e,z}^{(i)} M_{e,c}^{(i)} + M_{e,z}^{(j)} M_{e,c}^{(j)} \right),$$

$$A_{c,z}^{-1} = \det[\mathbf{A}]^{-1} \times \sum_{a,b} \epsilon_{a,b,c} \sum_{d,e} \sigma_d^2 \sigma_e^2 \left(M_{d,x}^{(i)} M_{d,a}^{(i)} + M_{d,x}^{(j)} M_{d,a}^{(j)} \right) \times \left(M_{e,y}^{(i)} M_{e,b}^{(i)} + M_{e,y}^{(j)} M_{e,b}^{(j)} \right).$$

Since the matrices $\mathbf{A}$ and $\mathbf{B}$ were defined in a similar way (Eqs. (5) and (11)) the elements of $\mathbf{B}^{-1}$ can be found from the previous formulae replacing any term σ_a^2 with the corresponding ϵ_a.

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