

Modification of the overlap potential to mimic a linear site-site potential

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A modification of the overlap potential of Berne and Pechukas is proposed. The overlap strength and range parameters are used in a new functional form resulting in a single-site potential which closely resembles a linear site-site potential.

I. INTRODUCTION

In computer simulations of aspherical molecules a popular and effective representation of the short-ranged attractive and repulsive interaction consists of designating several sites in each molecule between which Lennard-Jones (LJ) 6-12 potentials act.¹⁻⁸ When longer-ranged electrostatic forces are important, they may be represented by multipole interactions.³

The collection of LJ potentials may be termed a site-site potential since its contribution to the intermolecular pair interaction involves a double sum over the respective sites of the two molecules. For larger molecules it may be necessary to employ many sites, typically one at each atom position, to adequately represent the short-ranged interactions. For these larger molecules, the fact that the time to evaluate the potential (and its derivatives for simulations requiring forces) goes as the square of the number of sites leads to computational inefficiency.

A way to avoid this problem is to model the site-site potential with a single-site potential. In the following, we propose such a potential to model the site-site potential for a linear array of atoms.

II. A MODIFIED OVERLAP POTENTIAL

Several single-site potentials have been proposed previously⁹⁻¹² to represent aspherical molecules. The first to be tractable mathematically is the *overlap* potential of Berne and Pechukas.¹¹ In its simplest form this potential is obtained by considering the overlap integral between two identical ellipsoidal Gaussians

$$G(\mathbf{r}) = \exp[-(x^2 + y^2)/\sigma_{\parallel}^2 - z^2/\sigma_{\perp}^2] \quad (1)$$

for arbitrary relative orientations of the Gaussians. If $\hat{\mathbf{u}}_1$ and $\hat{\mathbf{u}}_2$ are unit vectors specifying the axes of symmetry of the two Gaussians and \mathbf{r} the vector between their centers, this overlap is

$$S(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \mathbf{r}) = \epsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) \exp[-r^2/\sigma^2(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})] \quad (2)$$

The strength and range parameters in Eq. (2) are

$$\epsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = \epsilon_0 [1 - \chi^2(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)^2]^{-1/2}, \quad (3)$$

$$\sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) = \sigma_0 \left(1 - \frac{1}{2}\chi \left\{ \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_1 + \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_2)^2}{1 + \chi(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)} + \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_1 - \hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_2)^2}{1 - \chi(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)} \right\} \right)^{-1/2}. \quad (4)$$

The anisotropy parameter χ is determined by the parameters of the ellipsoidal Gaussians

$$\chi = (\sigma_{\parallel}^2 - \sigma_{\perp}^2)/(\sigma_{\parallel}^2 + \sigma_{\perp}^2), \quad (5)$$

and ϵ_0 and σ_0 are constants.

The overlap potential is obtained by using the orientation dependent strength and range parameters in the Lennard-Jones potential, i.e.,

$$V(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \mathbf{r}) = 4\epsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) \left\{ \left[\frac{\sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})}{r} \right]^{12} - \left[\frac{\sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})}{r} \right]^6 \right\}. \quad (6)$$

The distance $r = \sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})$ is, to good accuracy, the separation at which two ellipsoids of major and minor axes σ_{\parallel} and σ_{\perp} and relative orientation specified by $\hat{\mathbf{u}}_1$, $\hat{\mathbf{u}}_2$, and $\hat{\mathbf{r}}$ touch. It is exactly that separation for some orientations. It is also the separation at which the repulsive and attractive components of the potential (6) exactly balance. Thus this potential may be viewed as an interaction between molecules whose repulsive cores are basically ellipsoids of revolution.

The overlap potential is readily differentiated to obtain forces and torques and allows molecules of any axial ratio to be treated with equal ease. The potential is thus well suited to a study of nematic ordering of fluids of rodlike molecules, and, in fact, was employed in the first such study by computer simulated molecular dynamics.¹³

However, in certain aspects, the overlap potential is unrealistic. These aspects may be identified by comparing an overlap potential for ellipsoids at axial ratio $\sigma_{\parallel}/\sigma_{\perp} = 3$ with the potential of the four-site molecule sketched in Fig. 1. This molecule effectively has an axial ratio of 3 and a bond length/atom diameter ratio of $\frac{2}{3}$. This latter value is at the upper end of the range of values employed in site-site models of diatomic molecules.³

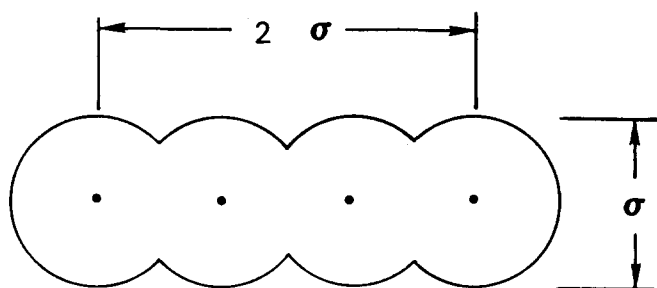


FIG. 1. A four-site molecule. LJ potentials with range parameter σ act between sites on neighboring molecules which are located on the axes of the molecules $2\sigma/3$ apart.

Two properties of this potential with which the overlap potential is at variance are illustrated in Fig. 2 in which the site-site potential is plotted as a function of separation for a side-by-side orientation and an end-to-end orientation of two molecules. The first property is that the side-by-side potential well is approximately 5 times deeper than the end-to-end. The other is that well widths are sensibly independent of orientation as is evidenced in Fig. 2 by the approximately equal well widths for the two orientations. The overlap potential, on the other hand, has well depths which are the same for both orientations since $\epsilon(\hat{u}_1, \hat{u}_2) = \epsilon_0$ for both. Further, since well width is proportional to $\sigma(\hat{u}_1, \hat{u}_2, \hat{r})$, the well width of the overlap potential is wider by the axial ratio for the end-to-end as compared to the side-by-side configuration.

Despite these unrealistic aspects, we have been able to use the basic idea of the overlap model which leads to the strength and range parameters of Eqs. (3) and (4) to construct a modified single site potential which reproduces the subject site-site potential quite well.

The first modification is to use the overlap range parameter to displace the LJ potential rather than dilate

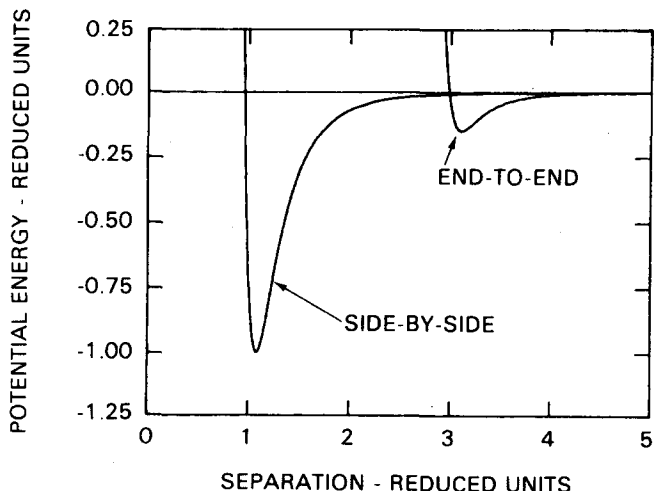


FIG. 2. Potential energy of two four-site molecules as a function of separation for a side-by-side and an end-to-end configuration. The potential is normalized so that the well depth is unity for the side-by-side configuration. Separation is measured in units of σ .

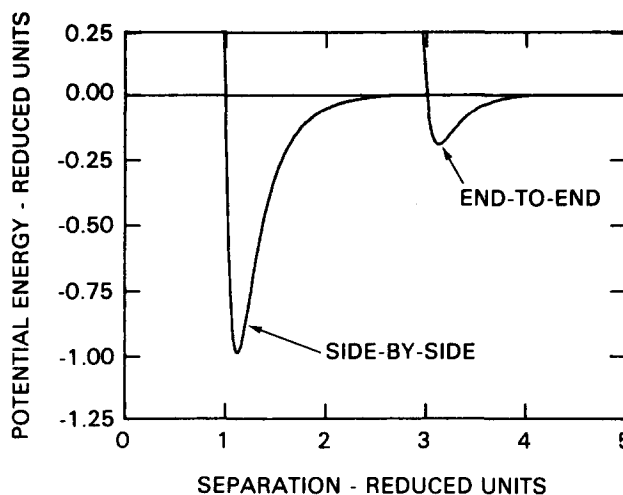


FIG. 3. Energy of the modified overlap potential as a function of separation for a side-by-side and an end-to-end configuration. Energy is measured in units of ϵ_0 and separation in units of q_0 .

it. That is, we replace Eq. (6) by

$$V(\hat{u}_1, \hat{u}_2, \hat{r}) = \epsilon(\hat{u}_1, \hat{u}_2, \hat{r}) \left[\left(\frac{1}{r - \sigma(\hat{u}_1, \hat{u}_2, \hat{r}) + 1} \right)^{12} - \left(\frac{1}{r - \sigma(\hat{u}_1, \hat{u}_2, \hat{r}) + 1} \right)^6 \right]. \quad (7)$$

In this modified form the positive and negative terms still cancel at $r = \sigma(\hat{u}_1, \hat{u}_2, \hat{r})$ so the ellipsoidal repulsive core is retained.¹⁴ However, the well width is now independent of orientation.

The second modification is to define a new strength parameter which, as is indicated in Eq. (7), is a function of \hat{r} as well as \hat{u}_1 and \hat{u}_2 . The parameter has the form

$$\epsilon(\hat{u}_1, \hat{u}_2, \hat{r}) = \epsilon'(\hat{u}_1, \hat{u}_2) \epsilon''(\hat{u}_1, \hat{u}_2, \hat{r}), \quad (8)$$

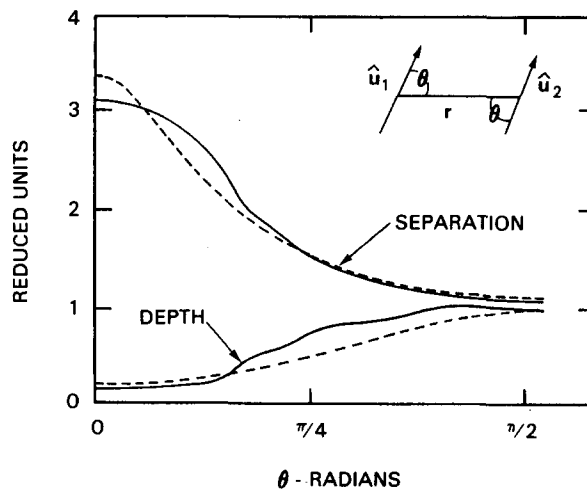


FIG. 4. Comparison of the maximum well depth and separation at maximum well depth of the modified potential (dashed lines) with those of the site-site potential (solid lines) as a function of angle for the planar configuration shown in the inset.

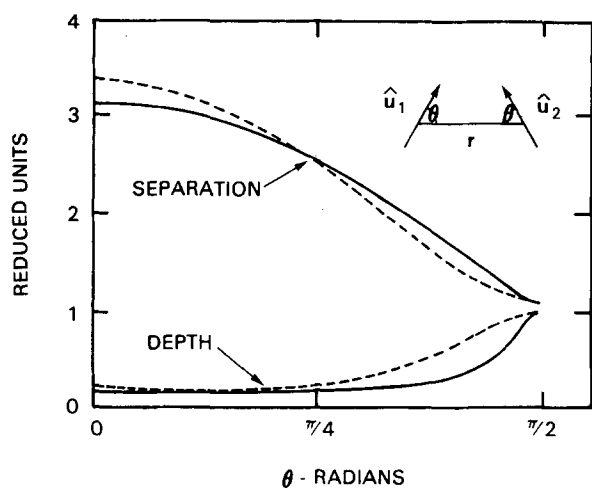


FIG. 5. Comparison of the maximum well depth and separation at maximum well depth of the modified potential (dashed lines) with those of the site-site potential (solid lines) as a function of angle for the planar configuration shown in the inset.

where $\epsilon(\hat{u}_1, \hat{u}_2)$ is the original strength parameter (3) and $\epsilon'(\hat{u}_1, \hat{u}_2, \hat{r})$ is basically $1/\sigma^2$ but with a new parameter χ' which is used to adjust the ratio of side-by-side to end-to-end well depths. That is,

$$\epsilon'(\hat{u}_1, \hat{u}_2, \hat{r}) = 1 - \frac{\chi'}{2} \left[\frac{(\hat{r} \cdot \hat{u}_1 + \hat{r} \cdot \hat{u}_2)^2}{1 + \chi' \hat{u}_1 \cdot \hat{u}_2} + \frac{(\hat{r} \cdot \hat{u}_1 - \hat{r} \cdot \hat{u}_2)^2}{1 - \chi' \hat{u}_1 \cdot \hat{u}_2} \right]. \quad (9)$$

If ϵ_s is the value desired for the strength parameter for a side-by-side configuration and ϵ_e the value for an end-to-end configuration, then

$$\chi' = (\epsilon_s^{1/\mu} - \epsilon_e^{1/\mu}) / (\epsilon_s^{1/\mu} + \epsilon_e^{1/\mu}). \quad (10)$$

We have found a satisfactory fit to the site-site potential of the molecules of Fig. 1 if we use an axial ratio of 3 and set $\nu=1$, $\mu=2$, and $\epsilon_e/\epsilon_s=0.2$. Figure 3 is a plot similar to Fig. 2 showing the behavior of the new

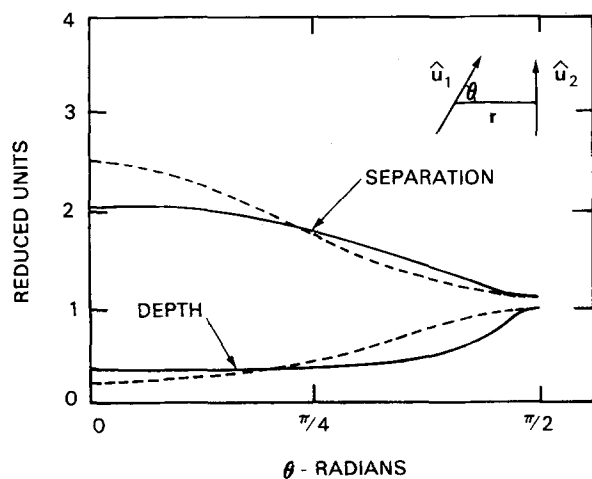


FIG. 6. Comparison of the maximum well depth and separation at maximum well depth of the modified potential (dashed lines) with those of the site-site potential (solid lines) as a function of angle for the planar configuration shown in the inset.

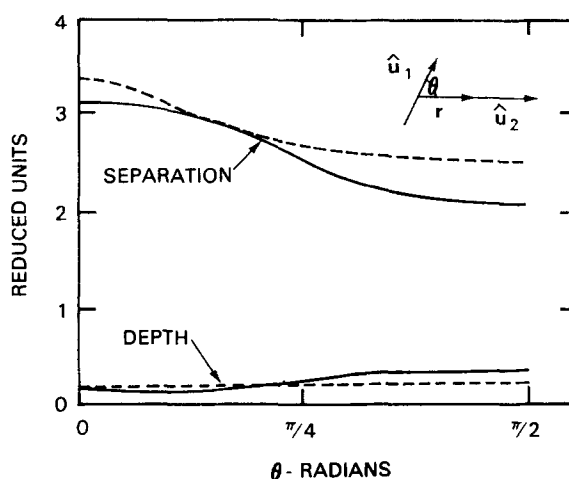


FIG. 7. Comparison of the maximum well depth and separation at maximum well depth of the modified potential (dashed lines) with those of the site-site potential (solid lines) as a function of angle for the planar configuration shown in the inset.

potential. Comparison shows that, in the properties discussed above, the new potential accurately models the site-site potential.

To assess the new potential further, we have compared it to the site-site potential for 5 ranges of configurations obtained by rotation from an initial to a final configuration. The ranges include: rotation from side-by-side to end-to-end maintaining the molecules parallel, rotation from side-by-side to end-to-end through a Vee configuration, rotation from side-by-side to a Tee configuration, rotation from end-to-end to a Tee configuration, and finally rotation from side-by-side to a crossed configuration. The comparisons are shown in Figs. 4-8 as plots of maximum well depth and separation at maximum well depth. It is clear that the new single-site potential reproduces the behavior of the site-site potential rather well in these comparisons.

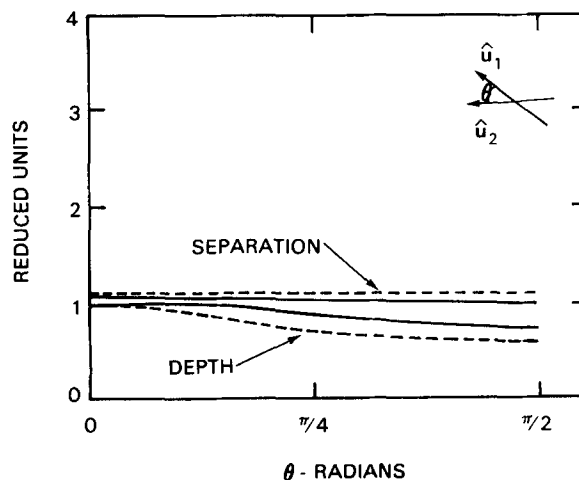


FIG. 8. Comparison of the maximum well depth and separation at maximum well depth of the modified potential (dashed lines) with those of the site-site potential (solid lines) as a function of angle for the configuration shown in the inset in which \hat{u}_1 and \hat{u}_2 are perpendicular to \hat{r} .

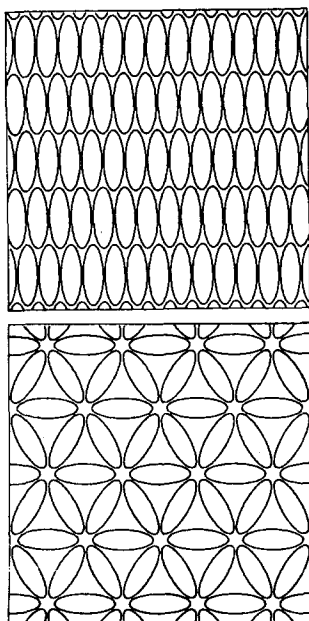


FIG. 9. The top panel is the close-packed nematically ordered crystal structure into which a layer of molecules interacting via the modified overlap potential condenses at zero temperature and pressure. The bottom panel is the low density structure into which the layer will condense if the original overlap potential for ellipsoids of axial ratio 3 is used. In the figure, the ellipsoids are sized to delineate the repulsive cores of the molecules. They will touch when $r \approx \sigma(\hat{u}_1, \hat{u}_2, \hat{r})$.

There are two chief consequences when the number of sites in the site-site potential is increased while keeping the same distance between extreme sites. First, the ratio ϵ_s/ϵ_s decreases, becoming 0.073 in the limit of a continuous uniform distribution of sites. Second, the "waisted" shape of the potential (see Fig. 1), which is responsible for the bumpy curves in Fig. 4, diminishes. To model such potentials with the modified overlap potential requires only that χ' be adjusted to account for the ratio change. Because of the increased smoothness of the site-site potential as the number of sites increases, the modified potential is an even more faithful representation. We believe there is sufficient flexibility in the modified potential that any reasonable linear site-site potential can be adequately modeled.

Walmsley¹² has proposed a modification of the overlap potential which may be described as follows. The original LJ form (6) is used and the strength parameter is given by (8) with $\nu=2$, $\mu=\frac{1}{2}$, and $\chi'=\chi$. This potential would not accurately model a site-site potential.

III. DISCUSSION

The modified overlap potential was developed to study orientational ordering in systems of aspherical molecules. We note, for nonpolar molecules, that it is the relatively short-ranged overlap and dispersion forces modeled by this potential which produce nematic order-

ing since electric quadrupole forces favor a Tee configuration rather than configurations in which the axes of the molecules are aligned parallel.³

The differences between the modified and original overlap potentials will manifest themselves principally in simulation at low pressure. At sufficiently high pressure the two potentials are expected to give similar results since there the phase behavior is dominated by the steric effects of the ellipsoidal cores which are similar for both potentials.

At low pressure, however, the attractive parts of the potentials dominate so the two potentials can exhibit entirely different phase behavior. As an example, consider a situation in which a layer of molecules is constrained to lie in a plane. The crystal structure into which the two potentials cause this system to condense at zero temperature and pressure are shown in Fig. 9. The modified potential forms the anticipated close-packed structure of the upper panel which has complete nematic order. On the other hand, the original potential for ellipsoids of axial ratio 3 forms the curious low density structure of the lower panel in which the molecules become the legs of the triangles of a lattice of equilateral triangles. The triangular structure occurs for the following reason. In the triangular structure each molecule has four nearest neighbors whereas in the close-packed structure each molecule has only two. It happens with the original potential that each nearest neighbor in the triangular lattice contributes slightly more than one-half as much binding energy as does a nearest neighbor in the close packed configuration so that the triangular lattice is favored. The modified overlap potential and the site-site potential do not show this behavior since they bind weakly in the triangular configuration ($\theta = \pi/3$ in Fig. 5).

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¹⁴When $\sigma > 2$, the potential (7) has an "interior" well for $r < \sigma - 2$. This may be removed by having (7) apply only for $r > \sigma - 1$, but, in practice, does not pose a problem since the inner and outer wells are separated by an infinite barrier.