Ellipsoid contact potential: Theory and relation to overlap potentials

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We propose and analyze the properties of a simple, computationally efficient pair potential for nonpolar molecules based on the contact function for ellipsoidal cores. We discuss the relation of this potential to the Gaussian overlap potential and show that the present potential gives the correct extension of the ideas of the Gaussian overlap potential to mixtures. We show that this potential obeys a form of the principle of corresponding states and derive an expression for the second virial coefficient. As this potential has an incorrect symmetry at large separations, we derive another contact potential that behaves isotropically at infinite separation. Unfortunately, this potential does not have the good computational features of the one investigated here. [S1063-651X(96)05412-8]

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I. INTRODUCTION

There is now a considerable amount of literature in which models of soft potentials [1] between nonspherical molecules are used for simulating the behavior of simple molecules and liquid crystals [2–4]. A number of these models [5,6] are extensions of the original Gaussian overlap potential (GOP) originally proposed in Ref. [7]. Our interest in this potential became aroused by a work by Singh *et al.* [8] reporting the implementation of a perturbation theory for a model fluid described by it, ascribing to the GOP a geometric significance that it does not have. We therefore thought it important to report the theory of a more general potential, the ellipsoid contact potential (ECP), based on the contact function [9,10] for hard ellipsoids, to which the GOP is an approximation. In the body of the article, we will demonstrate that although the GOP is a reasonable approximation for not too eccentric identical particles, it has serious problems when extended in an obvious way to mixtures.

It should be remarked that a preliminary version of this work has circulated around for some time. Some of the results have been stated and used in a recent article [11], but there is no full report in the literature of the complete formulation of the ECP, nor does Ref. [11] stress the problems associated with naively applying Gay-Berne potentials to nonidentical particles.

The genesis of the GOP is to consider the joint probability distribution for two three-dimensional asymmetric Gaussian distributions centered around two points, which are the molecular centroids. This is itself a Gaussian distribution of the components of the vector connecting the molecular centers. If $\mathbf{R}$ denotes this vector, then the distribution function is proportional to

$$\exp(-\mathbf{R}^T\mathbf{G}'^{-1}\mathbf{R}), \tag{1.1}$$

where $\mathbf{G}'$ is a matrix whose elements have the units of length squared and depend on the lengths and orientations of the three principal semiaxes for the shape ellipsoid of each molecule.

The (simplest version of) GOP is then obtained by replacing the square of the scaled length of a spherically symmetric potential by the negative of the argument of the exponential in the joint probability distribution. For example, if we write the Lennard-Jones potential as

$$4\epsilon[(r^2/\sigma^2)^{-6}-(r^2/\sigma^2)^{-3}], \tag{1.2}$$

then the constant energy GOP is

$$4\epsilon[(\mathbf{R}^T\mathbf{G}'^{-1}\mathbf{R})^{-6}-(\mathbf{R}^T\mathbf{G}'^{-1}\mathbf{R})^{-3}]. \tag{1.3}$$

In the original version, the parameter ϵ is also orientation dependent, but this is rather weak. We will retain the orientation independence of ϵ partly because it entails certain computational advantages, partly because potentials of the form (1.3) satisfy a form of the principle of corresponding states, and partly because the physical interpretation of the angle dependence of the ϵ is more obscure than that of the separation parameter.

Even though the idea behind the GOP is physically attractive, the argument $\mathbf{R}^T\mathbf{G}'^{-1}\mathbf{R}$ of the probability function does not have a clear *geometric* interpretation. This lack of interpretation has led Singh *et al.* [8] into the trap of giving it one anyway. If we write $\mathbf{R}=R\hat{\mathbf{R}}$, where $\hat{\mathbf{R}}$ is a unit vector, then

$$\mathbf{R}^T\mathbf{G}'^{-1}\mathbf{R}=R^2\hat{\mathbf{R}}^T\mathbf{G}'^{-1}\hat{\mathbf{R}}. \tag{1.4}$$

In constructing a perturbation theory with a nonspherical reference system, these authors mistakenly interpret the distance

$$\sigma=(\hat{\mathbf{R}}^T\mathbf{G}'^{-1}\hat{\mathbf{R}})^{-1/2} \tag{1.5}$$

as the distance of closest approach of two ellipsoids with fixed orientations. In the main body of this article, we show that $\mathbf{R}^T\mathbf{G}'^{-1}\mathbf{R}$ is an *approximation* to the *contact function* for ellipsoids, which has been discussed elsewhere. Whereas it is a good approximation in the case of two not too asymmetric ellipsoids with equal dimensions, we show that it is not in other cases. More explicitly, we show that the contact function $F(A,B)$ for two ellipsoids labeled A and B, which is given by

$$F(A,B) = \{\max S(\lambda) | \lambda \in [0,1]\}, \qquad (1.6)$$

where $S(\lambda)$ is a non-negative function of the ellipsoid coordinates derived by Perram and Wertheim [9], is related to the Berne-Pechukas function by the relation

$$\mathbf{R}^T\mathbf{G}'^{-1}\mathbf{R} = S(1/2). \qquad (1.7)$$

The object function in the maximization (1.6) has the form

$$S(\lambda) = 4\lambda(1-\lambda)\mathbf{R}^T\mathbf{G}(\lambda)^{-1}\mathbf{R}, \qquad (1.8)$$

so that the distance scaling of the contact function is the same as that of the GOP function, as shown in Eq. (1.4). Note that $\mathbf{G}(1/2) = \mathbf{G}'$.

Thus the function $\mathbf{R}^T\mathbf{G}'^{-1}\mathbf{R}$ is always an *underestimate* of the contact function and hence the estimate (1.5) of the intercenter distance at the tangency of the ellipsoidal cores is an *overestimate*, as has been noted in [12]. The accuracy of this estimate declines dramatically in the case when the two ellipsoids have different sizes or shapes.

The geometry of the contact function can be understood by performing the following thought experiment. Focus on one of the ellipsoidal bodies and consider one of the family of similar ellipsoids obtained from it. For this member of the family, there will be a single member of the family of similar ellipsoids obtained from the other ellipsoidal body that is tangent to it. The locus of points obtained by repeating this operation for every member of the first family is a curve connecting the centers of the two ellipsoidal bodies. The object function (1.8) is a weighted sum of the quadratic forms describing the two ellipsoids evaluated on this curve. In [9] it is shown that this object function has a maximum value at some point on the curve. This maximum value is the contact function, which, although it is a measure of the proximity of the two ellipsoidal bodies, cannot be related in any simple way to a collision diameter unless the axes of the two ellipsoids are parallel.

This leads us to propose a variant of the GOP, which we call the ellipsoid contact potential, in which we replace the square of the scaled distance in the Lennard-Jones potential by the *contact function of ellipsoidal cores*

$$4\epsilon[(F(A,B))^{-6} - (F(A,B))^{-3}]. \qquad (1.9)$$

Potentials of the form (1.3) or (1.9) have a couple of interesting properties. The first is that the second virial coefficient obeys a type of principle of corresponding states. For Eq. (1.9), the value of the second virial coefficient is

$$B_2^{\text{ECP}} = B_2^{\text{HE}}B_2^{\text{LJ}}(k_BT/\epsilon), \qquad (1.10)$$

i.e., the product of the (temperature-independent) second virial coefficient B_2^{HE} for hard ellipsoids with the same semi-axes as that of the ellipsoidal core and the reduced second virial coefficient $B_2^{\text{LJ}}(k_BT/\epsilon)$ for the Lennard-Jones potential. Many real molecular gases satisfy a relation of the form (1.10) and hence the principle of corresponding states. A word of caution is in order: the second virial coefficient for a model fluid consisting of two-center Lennard-Jones molecules very closely satisfies a formula of the form (1.10).

The scaling of the contact function, which we may write in the form

$$F(A,B) = R^2 f(A,B), \qquad (1.11)$$

where $f(A,B)$ depends only on orientations, means that orientational averages of the ECP can be written in the form

$$4\epsilon[R^{-12}\langle(f(A,B))^{-6}\rangle - R^{-6}\langle(f(A,B))^{-3}\rangle], \quad (1.12)$$

where $\langle F(A,B)\rangle$ denotes an average over the orientations of A and B. The orientation averages in Eq. (1.12) are *independent of separation* R. These orientation averages are a major computational overhead in the implementation of the perturbation theory with a nonspherical reference system. For this potential, the three-dimensional integrals they imply need only be performed once instead of at each separation, as is the case with potentials such as the two-center Lennard-Jones (2CLJ) model for homonuclear diatomic molecules.

This useful property has its downside. We would expect that the interaction of two nonpolar molecules would become isotropic at large separation, meaning that the ratio of the (numerically) largest and smallest energy should tend to 1. This is the case with the 2CLJ model, but not, for example, with either the GOP or the ECP. As the contribution to thermodynamic functions from values of short-ranged potential functions at large distances is negligible, this is something we can live with, especially if the potential better models the forces between molecules in close proximity to each other. However, for the sake of completeness, we present the derivation of another contact function for hard ellipsoids that leads to a potential isotropic at large separations.

The only real test of empirical effective two-body potentials is whether they work. In this context, ''work'' means that we are able to find constant (or almost constant) values of the potential parameters that are able to reproduce the properties of real substances over large ranges of temperature and pressure. An even more stringent test is whether the potential parameters can then reproduce the properties of mixtures.

This potential should be well suited to a variant [13] of the Kohler-Quirke-Perram perturbation theory [14] for nonpolar molecular fluids. We are currently using this theory to extract ECP potential parameters from equation of state data for simple molecular fluids such as nitrogen. The results of these investigations will be reported elsewhere.

II. THE CONTACT FUNCTION FOR ELLIPSOIDS REVISITED

Although the contact function for ellipsoids has been derived elsewhere [9], we sketch here some of its principal

properties, as well as generalize and simplify some of its consequences.

A. Definition of the contact function

Consider two ellipsoids labeled A and B with semiaxes a_1, a_2, a_3 and b_1, b_2, b_3, respectively. Let us suppose for the time being that all six of these semiaxes are positive. The rotational state of the ellipsoids is conveniently expressed by giving the sets $\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3$ and $\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3$ of orthonormal unit vectors along the principal axes of the two ellipsoids. If the centers are at $\mathbf{r}_a, \mathbf{r}_b$, respectively, we define the intercenter vector

$$\mathbf{R} = \mathbf{r}_b - \mathbf{r}_a. \tag{2.1}$$

Let us define the matrices

$$\mathbf{A} = \sum_k a_k^{-2} \mathbf{u}_k \mathbf{u}_k^T, \tag{2.2a}$$

$$\mathbf{B} = \sum_k b_k^{-2} \mathbf{v}_k \mathbf{v}_k^T. \tag{2.2b}$$

In the case where none of the semiaxes vanish, these matrices have the inverses

$$\mathbf{A}^{-1} = \sum_k a_k^2 \mathbf{u}_k \mathbf{u}_k^T, \tag{2.3a}$$

$$\mathbf{B}^{-1} = \sum_k b_k^2 \mathbf{v}_k \mathbf{v}_k^T. \tag{2.3b}$$

Perram and Wertheim [9] then derived the object function

$$S(\lambda) = \lambda(1-\lambda)\mathbf{R}^T[(1-\lambda)\mathbf{A}^{-1} + \lambda\mathbf{B}^{-1}]^{-1}\mathbf{R} \tag{2.4}$$

$$= \lambda(1-\lambda)\hat{\mathbf{R}}^T[(1-\lambda)\mathbf{A}^{-1} + \lambda\mathbf{B}^{-1}]^{-1}\hat{\mathbf{R}}R^2, \tag{2.4'}$$

where λ is a parameter. It may be easily seen that $S(\lambda)$ is non-negative for $\lambda \in [0,1]$. Then a contact function $F(A,B)$ for the two ellipsoids is

$$F(A,B) = \{\max S(\lambda) | \lambda \in [0,1]\}. \tag{2.5}$$

If $F(A,B) < 1$ the two ellipsoids overlap, if $F(A,B) > 1$ they do not, and if $F(A,B) = 1$ they are externally tangent. In Ref. [9], it was proved that the function $S(\lambda)$ is concave down for $\lambda \in [0,1]$. Taken with the property that $S(\lambda)$ is non-negative in $[0,1]$ and zero at both end points, this has the important consequence that the object function $S(\lambda)$ has a single maximum in the interval $[0,1]$.

The concavity property of $S(\lambda)$ guarantees that Brent's method [15] will converge superlinearly to the unique maximum. However, optimization schemes can sometimes be speeded up if the derivative of the object function can be computed quickly, although this was not our experience. The value of $f'(\lambda)$ may be computed as follows. Let us define the matrix

$$\mathbf{G} = (1-\lambda)\mathbf{A}^{-1} + \lambda\mathbf{B}^{-1}, \tag{2.6}$$

so that

$$S(\lambda) = \lambda(1-\lambda)\mathbf{R}^T\mathbf{G}^{-1}\mathbf{R} = \lambda(1-\lambda)(\mathbf{G}^{-1}\mathbf{R})^T\mathbf{R}. \tag{2.7}$$

After a certain amount of algebra, the result of differentiating equation (2.7) is

$$f'(\lambda) = (\mathbf{G}^{-1}\mathbf{R})^T\{(1-\lambda)^2\mathbf{A}^{-1} - \lambda^2\mathbf{B}^{-1}\}\mathbf{G}^{-1}\mathbf{R}. \tag{2.8}$$

The only computational task of any complexity is to compute $\mathbf{G}^{-1}\mathbf{R}$, which is most simply calculated as $\mathbf{X}$, the solution of the 3×3 system of linear equations

$$\mathbf{GX} = \mathbf{R}, \tag{2.9}$$

so that

$$S(\lambda) = \lambda(1-\lambda)\mathbf{R}^T\mathbf{X}.$$

Although the form of the object function is complicated, its calculation proceeds quite rapidly. An alternative algorithm for rapid computation of the contact function is given in [12].

If we denote by λ_m the value of λ for which the maximum of Eq. (2.5) occurs and use the form (2.4a), then the contact function is

$$F(A,B) = \lambda_m(1-\lambda_m)\hat{\mathbf{R}}^T[(1-\lambda_m)\mathbf{A}^{-1} + \lambda_m\mathbf{B}^{-1}]^{-1}\hat{\mathbf{R}}R^2. \tag{2.10}$$

Note that the value of λ_m is independent of the separation R. This has the computationally useful property that the orientational average of any power of $F(A,B)$ is a function of R times the orientational average of a single function of orientations, which therefore need only be performed once. Other potentials, such as the 2CLJ, do not have this property [14], so that the implementation of perturbation theories for them are much more time consuming. Setting the contact function in Eq. (2.10) to unity and solving for the value R^* of R at which this occurs, we have for the separation of the cores at contact

$$R^* = \{\lambda_m(1-\lambda_m)\hat{\mathbf{R}}^T[(1-\lambda_m)\mathbf{A}^{-1} + \lambda_m\mathbf{B}^{-1}]^{-1}\hat{\mathbf{R}}\}^{-1/2}. \tag{2.11}$$

To establish the relationship between the contact function and the function (1.4) appearing the GOP, we need to generalize the original derivation of Berne and Pechukas. We wish to derive a general algorithm for the computation of the Gaussian overlap potential in the case when (i) the ellipsoids are not necessarily identical and (ii) the ellipsoids do not necessarily have a symmetry axis. We have also taken the liberty of employing the notation we use for the discussion of the ellipsoid contact function. Consider the quadratic form

$$P(\mathbf{s}) = \tfrac{1}{2}[\mathbf{s}^T\mathbf{As} + (\mathbf{s} - \mathbf{R})^T\mathbf{B}(\mathbf{s} - \mathbf{R})] \tag{2.12}$$

of the vector $\mathbf{s}$. The derivation of the GOP involves computing the integral

$$I(\mathbf{R}, \mathbf{u}, \mathbf{v}) = C \int \int \int d\mathbf{s} \exp\{-\tfrac{1}{2}[\mathbf{s}^T\mathbf{As} + (\mathbf{s} - \mathbf{R})^T\mathbf{B}(\mathbf{s} - \mathbf{R})]\}, \tag{2.13}$$

where $\mathbf{u}, \mathbf{v}$ stand for the two triplets of unit vectors defining the principal axes and C is the normalization constant of the

probability distribution represented by the integrand in Eq. (2.13). To evaluate this integral we write

$$s^T\mathbf{A}s + (s - \mathbf{R})^T\mathbf{B}(s - \mathbf{R}) = (s - \mathbf{R}^*)^T\mathbf{E}(s - \mathbf{R}^*) + g \qquad (2.14)$$

and attempt to find values of the matrix $\mathbf{E}$, the vector $\mathbf{R}^*$, and the scalar $\mathbf{g}$. Clearly

$$\mathbf{E} = \mathbf{A} + \mathbf{B}. \qquad (2.15)$$

Expanding and equating coefficients, we find that

$$s^T\mathbf{E}\mathbf{R}^* = s^T\mathbf{B}\mathbf{R},$$

giving

$$\mathbf{R}^* = \mathbf{E}^{-1}\mathbf{B}\mathbf{R}. \qquad (2.16)$$

Finally,

$$g = \mathbf{R}^T\{\mathbf{A}^{-1} + \mathbf{B}^{-1}\}^{-1}\mathbf{R}. \qquad (2.17)$$

The value of the integral (2.13) is then

$$I(\mathbf{R}, \mathbf{u}, \mathbf{v}) = Ce^{-(1/2)\mathbf{R}^T\{\mathbf{A}^{-1} + \mathbf{B}^{-1}\}^{-1}\mathbf{R}}$$

$$\times \int\int\int ds\, e^{-(1/2)(s - \mathbf{R}^*)^T\mathbf{E}(s - \mathbf{R}^*)}.$$

Shifting the origin of coordinates, this is

$$I(\mathbf{R}, \mathbf{u}, \mathbf{v}) = Ce^{-(1/2)\mathbf{R}^T\{\mathbf{A}^{-1} + \mathbf{B}^{-1}\}^{-1}\mathbf{R}}\int\int\int ds\, e^{-(1/2)s^T\mathbf{E}s}. \qquad (2.18)$$

Let $\mathbf{w}_1, \mathbf{w}_2, \mathbf{w}_3$ be the eigenvectors of the (positive definite) matrix $\mathbf{E}$ with corresponding (positive) eigenvalues $\lambda_1, \lambda_2, \lambda_3$. If we denote by $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ the corresponding unit vectors in the laboratory frame, then the unitary matrix

$$\mathbf{D} = \sum \mathbf{w}_i\mathbf{e}_i^T$$

diagonalizes $\mathbf{E}$. Performing standard manipulations, the value of the integral can be evaluated to give the result

$$I(\mathbf{R}, \mathbf{u}, \mathbf{v}) = Ce^{-(1/2)\mathbf{R}^T\{\mathbf{A}^{-1} + \mathbf{B}^{-1}\}^{-1}\mathbf{R}}[8\pi^3/\det(\mathbf{E})]^{1/2}. \qquad (2.19)$$

The negative

$$\tfrac{1}{2}\mathbf{R}^T\{\mathbf{A}^{-1} + \mathbf{B}^{-1}\}^{-1}\mathbf{R} \qquad (2.20)$$

of the argument of the exponential function in Eq. (2.19) is precisely equal to the right-hand side of Eq. (2.4) evaluated with $\lambda = 1/2$. By the maximal property of the contact function, the quantity (2.20) is always bounded above by the contact function. Alternatively, we can write Eq. (2.20) in the form

$$\tfrac{1}{2}\mathbf{R}^T\{\mathbf{A}^{-1} + \mathbf{B}^{-1}\}^{-1}\mathbf{R} = \tfrac{1}{2}\hat{\mathbf{R}}^T\{\mathbf{A}^{-1} + \mathbf{B}^{-1}\}^{-1}\hat{\mathbf{R}}R^2 \qquad (2.21)$$

and interpret the quantity

$$\sigma(\hat{\mathbf{R}}, \mathbf{u}, \mathbf{v})^{-2} = \tfrac{1}{2}\hat{\mathbf{R}}^T\{\mathbf{A}^{-1} + \mathbf{B}^{-1}\}^{-1}\hat{\mathbf{R}} \qquad (2.22)$$

as the inverse square of an orientation-dependent collision parameter or proximity measure. In fact, σ is only the distance of closest approach when the axes of the two ellipsoids are parallel

$$a_i = b_i$$

and the shape ellipsoids are not too eccentric. Then the value of λ at which the maximum of occurs will lie close to 1/2 for many configurations, so that the quantity $\sigma(\hat{\mathbf{R}}, \mathbf{u}, \mathbf{v})^{-2}$ will not be too different from the contact function. This is, of course, generally not the case, so that no geometrical interpretation should be put on $\sigma(\hat{\mathbf{R}}, \mathbf{u}, \mathbf{v})^{-2}$. In Sec. II B, we give an example illustrating this point.

B. Degenerate cases

We achieve a couple of interesting results for special values of the axis ratios.

1. Spheres

If all the semiaxes of A are equal to a and all those of B are equal to b, then the matrices $\mathbf{A}, \mathbf{B}$ have the form

$$\mathbf{A} = a^{-2}\sum_k \mathbf{u}_k\mathbf{u}_k^T = a^{-2}\mathbf{I},$$

$$\mathbf{B} = b^{-2}\sum_k \mathbf{v}_k\mathbf{v}_k^T = b^{-2}\mathbf{I},$$

so that the matrix $\mathbf{G}$ is given by

$$\mathbf{G} = [(1 - \lambda)a^2 + \lambda b^2]\mathbf{I}.$$

The object function $S(\lambda)$ is then given simply by

$$S(\lambda) = \lambda(1 - \lambda)[(1 - \lambda)a^2 + \lambda b^2]^{-1}\mathbf{R}^T\mathbf{R}. \qquad (2.23)$$

The maximum value of this function occurs when

$$\lambda = a/(a + b)$$

and is is easily calculated to be

$$\mathbf{R}^T\mathbf{R}[a + b]^{-2},$$

which is the square of the intercenter distance divided by the square of the sum of the radii. This is, of course, a natural contact function for spheres. This should be compared with the value of the GOP collision parameter

$$(1/2)(a^2 + b^2)^{-1}. \qquad (2.24)$$

This value is, of course, unphysical. Thus the GOP, as it stands, has no natural generalization to mixtures.

2. Ellipses

The results of this section cease to be valid when one or more of the ellipsoid semiaxes becomes zero. In this event

the matrix $\mathbf{G}$ will become singular at $\lambda = 0$ and/or $\lambda = 1$. This case has been analyzed in detail elsewhere [16] and we give the principal results here.

Suppose that one of the semiaxes, a_i say, of the ellipsoid A is zero. Then the matrix $\mathbf{G}$ is singular when $\lambda = 0$. In this event the value of $f(0)$ may be shown to be [16]

$$f(0) = (\mathbf{u}_i^T \mathbf{R})^2 / \mathbf{u}_i^T \mathbf{B}^{-1} \mathbf{u}_i, \qquad (2.25)$$

whereas if A is nondegenerate but one of the semiaxes of B, b_i say, is zero, then $\mathbf{G}$ is singular when $\lambda = 1$ and the value of $f(1)$ is

$$f(1) = (\mathbf{v}_i^T \mathbf{R})^2 / \mathbf{v}_i^T \mathbf{A}^{-1} \mathbf{v}_i. \qquad (2.26)$$

The cases when two semiaxes of A or B (but not both) are zero and the ellipsoid degenerates to a line segment are also discussed in Ref. [16]. If $a_i = a_j = 0$, then

$$f(0) = \alpha_i \mathbf{R}^T \mathbf{u}_j + \alpha_j \mathbf{R}^T \mathbf{u}_i, \qquad (2.27)$$

where α_i, α_j are given as the solution of the linear equations

$$[\mathbf{u}_i^T \mathbf{B}^{-1} \mathbf{u}_i] \alpha_i + [\mathbf{u}_i^T \mathbf{B}^{-1} \mathbf{u}_j] \alpha_j = \mathbf{u}_i^T \mathbf{R},$$

$$[\mathbf{u}_j^T \mathbf{B}^{-1} \mathbf{u}_i] \alpha_i + [\mathbf{u}_j^T \mathbf{B}^{-1} \mathbf{u}_j] \alpha_j = \mathbf{u}_j^T \mathbf{R}.$$

The corresponding result when the ellipsoid B is doubly degenerate and $\mathbf{G}$ is singular when $\lambda = 1$ may be obtained by symmetry considerations. The case when each ellipsoid has a degenerate axis will not generally occur in practice and we do not discuss it here.

C. Computation of the contact function

The most convenient numerical method for finding the contact function is the obvious one. We begin by computing the elements of the matrices

$$\mathbf{A}^{-1} = \sum_k a_k^2 \mathbf{u}_k \mathbf{u}_k^T,$$

$$\mathbf{B}^{-1} = \sum_k b_k^2 \mathbf{v}_k \mathbf{v}_k^T,$$

noting that they are symmetric, so that only six elements of each are required. For each value of λ in the open interval $[0,1]$, compute the six necessary elements of the symmetric matrix $\mathbf{G}$ and compute the solution $\mathbf{X}$ of the linear equations (2.9). It does not seem to make very much difference to the time required whether we use the explicit solution or use a Gauss-Jordan elimination routine. A systematic method for locating the maximum is then given by Brent's method [15]. Alternatively, we may iterate towards the maximum by applying a root finding technique to the equation (2.8) for $f'(\lambda)$, written as

$$f'(\lambda) = \mathbf{X}^T \{ (1-\lambda)^2 \mathbf{A}^{-1} - \lambda^2 \mathbf{B}^{-1} \} \mathbf{X}. \qquad (2.28)$$

We conclude this section by noting that when one of the ellipsoids is degenerate, the object function can be monotonic and its maximum may occur at an end point. We also note that the method of obtaining the ellipsoid contact func-

tion relies on the fact that the Cartesian equation of the surface of an ellipsoid is a quadratic form, so there are no other closed surfaces apart from ellipsoids for which this type of contact function can be derived.

A contact function that is isotropic at large separations

Another contact function may be obtained by considering the point $\mathbf{r}$ on the surface of ellipsoid B for which the value of the quadratic form

$$S_A = (\mathbf{r} - \mathbf{r}_A)^T \mathbf{A} (\mathbf{r} - \mathbf{r}_A) \qquad (2.29)$$

is a minimum. That is, we seek to minimize the right-hand side of Eq. (2.29) subject to the constraint

$$S_B = (\mathbf{r} - \mathbf{r}_B)^T \mathbf{B} (\mathbf{r} - \mathbf{r}_B) = 1. \qquad (2.30)$$

This problem may be solved using the method of Lagrange multipliers by taking the gradient with respect to $\mathbf{r}$ of the function

$$S^* = (\mathbf{r} - \mathbf{r}_A)^T \mathbf{A} (\mathbf{r} - \mathbf{r}_A) + \mu \{ (\mathbf{r} - \mathbf{r}_B)^T \mathbf{B} (\mathbf{r} - \mathbf{r}_B) - 1 \}. \qquad (2.31)$$

The minimizing value $\mathbf{r}$ for fixed μ is given by the solution of the linear equations

$$\mathbf{A} (\mathbf{r} - \mathbf{r}_A) + \mu \mathbf{B} (\mathbf{r} - \mathbf{r}_B) = 0. \qquad (2.32)$$

Writing this as

$$\mathbf{A} (\mathbf{r} - \mathbf{r}_A) + \mu \mathbf{B} (\mathbf{r} - \mathbf{r}_A + \mathbf{r}_A - \mathbf{r}_B) = 0,$$

we have that

$$\{ \mathbf{A} + \mu \mathbf{B} \} (\mathbf{r} - \mathbf{r}_A) = \mu \mathbf{B} (\mathbf{r}_B - \mathbf{r}_A). \qquad (2.33)$$

We also have that

$$\{ \mathbf{A} + \mu \mathbf{B} \} (\mathbf{r} - \mathbf{r}_B) = - \mathbf{A} (\mathbf{r}_B - \mathbf{r}_A). \qquad (2.34)$$

As the multiplier μ must be positive, the matrix $\{ \mathbf{A} + \mu \mathbf{B} \}$ must be positive definite and hence nonsingular. Thus

$$\mathbf{r} - \mathbf{r}_A = \mu \{ \mathbf{A} + \mu \mathbf{B} \}^{-1} \mathbf{B} (\mathbf{r}_B - \mathbf{r}_A) \qquad (2.35)$$

and

$$\mathbf{r} - \mathbf{r}_B = - \{ \mathbf{A} + \mu \mathbf{B} \}^{-1} \mathbf{A} (\mathbf{r}_B - \mathbf{r}_A). \qquad (2.36)$$

We can derive an equation for μ by substituting Eq. (2.36) into the constraint (2.30) to obtain

$$(\mathbf{r}_B - \mathbf{r}_A)^T \mathbf{A} \{ \mathbf{A} + \mu \mathbf{B} \}^{-1} \mathbf{B} \{ \mathbf{A} + \mu \mathbf{B} \}^{-1} \mathbf{A} (\mathbf{r}_B - \mathbf{r}_A) = 1. \qquad (2.37)$$

We can simplify the matrix product

$$\mathbf{H} = \mathbf{A} \{ \mathbf{A} + \mu \mathbf{B} \}^{-1} \mathbf{B} \{ \mathbf{A} + \mu \mathbf{B} \}^{-1} \mathbf{A}$$

by computing its inverse as

$$\mathbf{H}^{-1} = \mathbf{A}^{-1} \{ \mathbf{A} + \mu \mathbf{B} \} \mathbf{B}^{-1} \mathbf{B} \mathbf{B}^{-1} \{ \mathbf{A} + \mu \mathbf{B} \} \mathbf{A}^{-1}$$

or

$$\mathbf{H}^{-1} = \{ \mathbf{B}^{-1} + \mu \mathbf{A}^{-1} \} \mathbf{B} \{ \mathbf{B}^{-1} + \mu \mathbf{A}^{-1} \}, \qquad (2.38)$$

so that the constraint (2.37) simplifies to

$$[\{\mathbf{B}^{-1}+\mu\mathbf{A}^{-1}\}^{-1}(\mathbf{r}_B-\mathbf{r}_A)]^T\mathbf{B}^{-1}[\{\mathbf{B}^{-1}+\mu\mathbf{A}^{-1}\}^{-1}$$

$$\times(\mathbf{r}_B-\mathbf{r}_A)]=1, \tag{2.39}$$

which we may write as

$$\mathbf{X}^T\mathbf{B}^{-1}\mathbf{X}=1, \tag{2.40}$$

where the vector $\mathbf{X}$ is the solution of the linear equations

$$\{\mathbf{B}^{-1}+\mu\mathbf{A}^{-1}\}\mathbf{X}=(\mathbf{r}_B-\mathbf{r}_A). \tag{2.41}$$

The value of the object function (2.29) is then given by

$$S_A=\mu^2(\mathbf{r}_B-\mathbf{r}_A)^T\mathbf{B}\{\mathbf{A}+\mu\mathbf{B}\}^{-1}\mathbf{A}\{\mathbf{A}+\mu\mathbf{B}\}^{-1}\mathbf{B}(\mathbf{r}_B-\mathbf{r}_A),$$

which may be simplified by computing the inverse of the matrix product

$$\mathbf{B}\{\mathbf{A}+\mu\mathbf{B}\}^{-1}\mathbf{A}\{\mathbf{A}+\mu\mathbf{B}\}^{-1}\mathbf{B}$$

$$\text{as } \{\mathbf{B}^{-1}+\mu\mathbf{A}^{-1}\}\mathbf{A}\{\mathbf{B}^{-1}+\mu\mathbf{A}^{-1}\}.$$

The value of the object function is then

$$S_A=\mu^2\mathbf{X}^T\mathbf{A}^{-1}\mathbf{X}. \tag{2.42}$$

This quantity also represents a measure of the proximity of the two surfaces of the two ellipsoids. The computational problem involved in calculating it consists of solving the nonlinear algebraic equation (2.40) for the parameter μ, where the vector $\mathbf{X}$ is given by the linear equations (2.41). When this has been solved, the value of μ thus found and the components of the vector $\mathbf{X}$ are inserted into Eq. (2.42).

III. PROPERTIES OF THE ECP AND THE GOP

The nature of the contact function discussed in the preceding section enables us to define a set of potentials analogous to the Gaussian overlap potential. In this section, we give this definition and deduce some consequences of it.

A. Definition

The potential function for the interaction of structureless particles situated at two points $\mathbf{r}_b,\mathbf{r}_a$ is a function of the scalar separation

$$R=(\mathbf{R}^T\mathbf{R})^{1/2}=\{(\mathbf{r}_b-\mathbf{r}_a)^T(\mathbf{r}_b-\mathbf{r}_a)\}^{1/2} \tag{3.1}$$

or better still of its square R^2. We write this potential as

$$\phi(R^2/\sigma^2). \tag{3.2}$$

Here ϕ is any scalar function and σ is a scalar length parameter expressing the extent of the particle cores. If we evaluate the ellipsoid contact function in the limit where the lengths of all semiaxes become equal, then we have seen in Sec. II B 1 that the contact function takes the form

$$R^2/(2a)^2. \tag{3.3}$$

This suggests that we can derive a family of nonspherical potentials for particles with ellipsoidal cores analogous to the

GOP by replacing R^2/σ^2 in Eq. (3.1) with the contact function $F(A,B)$. Thus our nonspherical potentials are of the form $\phi(F(A,B))$. If we choose for ϕ the Lennard-Jones potential $\phi^{LJ}(r^2/\sigma^2)$, then the explicit form of the contact potential is

$$\phi^{ECP}(A,B)=4\epsilon[F(A,B)^{-6}-F(A,B)^{-3}]. \tag{3.4}$$

As remarked in the Introduction, this potential is analogous to the Gaussian overlap potential, the difference being that it has the correct additive collision parameters for dissimilar particles.

B. Computation of forces between ECP molecules

It is relatively straightforward to compute partial derivatives of these functions with respect to the coordinates representing the positions and orientations of the ellipsoids to obtain the corresponding generalized forces. We note the derivatives

$$\phi_{\mathbf{R}}(F(A,B))=\phi'(F(A,B))F_{\mathbf{R}}(A,B),$$

$$\phi_{\mathbf{u}_i}(F(A,B))=\phi'(F(A,B))F_{\mathbf{u}_i}(A,B),$$

where

$$F_{\mathbf{R}}(A,B)=2\lambda(1-\lambda)\mathbf{X} \tag{3.5}$$

and

$$F_{\mathbf{u}_i}(A,B)=2\lambda(1-\lambda)(\mathbf{X}^T\mathbf{u}_i)\mathbf{X}, \tag{3.6}$$

where we have used the extremal property of the contact function F with respect to λ.

C. The formula for the second virial coefficient and the principle of corresponding states

The ECP has the interesting property that we may compute its second virial coefficient B_2^{ECP} analytically, at least for molecules with a symmetry axis. We define the Boltzmann factor $B^{ECP}(A,B)$ as

$$B^{ECP}(A,B)=\exp[-\phi^{ECP}(A,B)/(k_BT)], \tag{3.7}$$

$$B_2^{ECP}=\frac{1}{2}\int d\mathbf{R}\langle 1-\exp[-\phi^{ECP}(A,B)/k_BT]\rangle, \tag{3.8}$$

where $\langle\ \rangle$ denotes an average over the orientations of A,B. Now we note that the contact function can be written as

$$F(A,B)=R^2f(A,B), \tag{3.9}$$

where $f(A,B)$ can be computed from Eq. (2.12) as

$$f(A,B)=\lambda_m(1-\lambda_m)\mathbf{r}^T[(1-\lambda_m)\mathbf{A}^{-1}+\lambda_m\mathbf{B}^{-1}]^{-1}\mathbf{r}. \tag{3.10}$$

This depends only on orientations, so that

$$B_2^{ECP}=\frac{1}{2}\int d\mathbf{R}\langle 1-\exp[-\phi^{LJ}(R^2f(A,B))/k_BT]\rangle \tag{3.11}$$

We now choose a particular direction for $\mathbf{R}$ and interchange the order of integration and averaging to obtain

$$B_2^{\text{ECP}} = 2\pi \left\langle \int_0^\infty R^2 dR\{1 - \exp[-\phi^{\text{LJ}}(R^2 f(A,B))/k_B T]\} \right\rangle.$$

(3.12)

We now make the change of variable

$$z = Rf(A,b)^{1/2}$$

to obtain

$$B_2^{\text{ECP}} = 2\pi \langle f(A,B)^{-3/2} \rangle \int_0^\infty z^2 dz\{1 - \exp[-\phi^{\text{LJ}}(z^2)/k_B T]\}.$$

(3.13)

To compute the value of

$$2\pi \langle f(A,B)^{-3/2} \rangle$$

(3.14)

consider the problem of computing the second virial coefficient of hard ellipsoids, given by

$$B_2^{\text{HE}} = 2\pi \left\langle \int_0^\infty R^2 dR[1 - \Theta(R^2 f(A,B))] \right\rangle, \quad (3.15)$$

where $\Theta(x)$ is the usual Heaviside step function. This integral may be written as

$$B_2^{\text{HE}} = 2\pi \left\langle \int_0^{f(A,B)^{-3/2}} R^2 dR \right\rangle$$

(3.16)

$$= 2\pi \langle f(A,B)^{-3/2} \rangle / 3.$$

(3.17)

Now the quantity

$$\int_0^\infty z^2 dz\{1 - \exp[-\phi^{\text{LJ}}(z^2)/k_B T]\}$$

(3.18)

is usually written as $3B_2^{\text{LJ}}$, i.e., three times the reduced second virial coefficient for the Lennard-Jones potential. Thus

$$B_2^{\text{ECP}} = B_2^{\text{HE}} B_2^{\text{LJ}}.$$

(3.19)

Note that the first term on the right-hand side is a function of the core parameters only, whereas the second is a function of the reduced temperature $k_B T/\epsilon$ only. This implies that the second virial coefficient of the ECP satisfies a form of the law of corresponding states.

D. Perturbation theory for the ECP

We begin by splitting the intermolecular potential $\phi^{\text{ECP}}(A,B)$ at each orientation into a monotonic repulsive reference potential $\phi_R^{\text{ECP}}(A,B)$ and an attractive perturbation potential $\phi_A^{\text{ECP}}(A,B)$ according to the Weeks-Chandler-Andersen scheme [17]. We have that

$$\phi_R^{\text{ECP}}(A,B) = \begin{cases} \epsilon + \phi^{\text{ECP}}(A,B), & R < R^* = 2^{1/6} f(A,B)^{-1/2} \\ 0, & R > R^* \end{cases}$$

$$\phi_A^{\text{ECP}}(A,B) = \begin{cases} -\epsilon, & R < R^* = 2^{1/6} f(A,B)^{-1/2} \\ \phi^{\text{ECP}}(A,B), & R > R^*. \end{cases}$$

(3.20)

Then, to first order, the free energy F of the system is given by

$$F/Nk_B T = F_R/Nk_B T$$

$$+ 2\pi\rho\beta \int_0^\infty r^2 \langle g_R^{\text{ECP}}(A,B) \phi_A(A,B) \rangle_{A,B} dR,$$

(3.21)

where ρ is the number density, β is $1/k_B T$, R is the distance between the centers of the molecules, $g_R^{\text{ECP}}(A,B)$ is the pair correlation function for the reference system and the symbol $\langle \ \rangle_{A,B}$ denotes an average over the orientations of particles A,B. The evaluation of Eq. (2.1) requires a knowledge of the function $g_R^{\text{ECP}}(A,B)$.

1. Perturbation of the reference system about a system of hard ellipsoids

We now attempt to relate the reference free energy F_R to the free energy F_E of a suitably chosen assembly of hard ellipsoids. The natural choice is that the two axis ratios a_i/a_1 of the underlying hard ellipsoids should be the same as the corresponding quantities for the ECP. The energy of interaction of two such ellipsoids is infinite if they overlap and zero if they do not. We may write the Boltzmann factor for this potential as

$$B_{\text{HE}}(A,B) = \Theta(R - f(A,B)^{-1/2}),$$

(3.22)

where $\Theta(x)$ is the usual step function. Following Kohler *et al.* we have to first order

$$\beta F_R^{\text{ECP}} - \beta F_{\text{HE}} = 2\pi\rho \int_0^\infty R^2 \langle y_{\text{HE}}(A,B)\{B_{\text{HE}}(A,B)$$

$$- B_R^{\text{ECP}}(A,B)\} \rangle_{A,B} dR,$$

(3.23)

where $B_R^{\text{ECP}}(A,B)$ is the Boltzmann factor for the reference potential and $y_{\text{HE}}(A,B)$ is the so-called indirect correlation function for the ellipsoid system, defined as

$$g_{\text{HE}}(A,B) = y_{\text{HE}}(A,B) B_{\text{HE}}(A,B).$$

(3.24)

2. Perturbation of the hard ellipsoid system about a system of hard spheres

We complete the perturbation scheme by relating the properties of the hard ellipsoid system to those of an equivalent system of hard spheres. The compressibility of the hard ellipsoid system is given by

$$\left[k_B T \frac{\partial \rho}{\partial P} \right]_{\text{HE}} = 1 + 4\pi\rho \int_0^\infty \langle g_{\text{HE}}(A,B) - 1 \rangle_{A,B} R^2 dR.$$

(3.25)

A similar relation holds for a system of hard spheres, viz.,

$$\left[k_B T \frac{\partial \rho}{\partial P}\right]_S = 1 + 4\pi\rho \int_0^\infty [g_S(R) - 1]R^2 dR. \quad (3.26)$$

If we now make the approximation that

$$y_{HE}(A,B) = y_S(R) = y_R^{ECP}(A,B), \quad (3.27)$$

where y_S is the indirect correlation function for an equivalent hard sphere system, then we may subtract Eq. (3.26) from Eq. (3.25) to obtain

$$\left[k_B T \frac{\partial \rho}{\partial P}\right]_{HE} = \left[k_B T \frac{\partial \rho}{\partial P}\right]_S + 4\pi\rho \int_0^\infty y_S(r_{AB})$$
$$\times \{\langle B_{HE}(A,B)\rangle_{A,B} - B_S(R)\}R^2 dR. \quad (3.28)$$

The interested reader is referred to Ref. [13] for details of how the size parameters of the reference hard ellipsoid and sphere are to be chosen.

E. Computation of orientational averages

Implementation of the various formulas in Sec. III D requires the evaluation of a number of orientational averages. We describe how this may be done.

First we need to compute the expressions

$$\langle B_R^{ECP}(A,B)\rangle, \quad \langle B_R^{ECP}(A,B)\phi_A^{ECP}(A,B)\rangle.$$

The scaling property of the contact function can be exploited to reduce the potentially expensive computational overhead implied in calculating these averages, which are required for each separation R at the grid points needed for the computation of the integrals. This overhead is reduced by the scaling property of the contact function. The values of the angle-dependent parts need only be computed once at the orientations specified by the integration rule used to compute the integrals over orientations and can then be stored in a table.

Second we need to compute the expression

$$\langle \phi_A^{ECP}(A,B)\rangle.$$

For values of R greater than $2^{7/6}a_3$ in the case of prolate ellipsoids, where

$$\phi_A^{ECP}(A,B) = \phi^{ECP}(A,B),$$

the ECP may be written as

$$\phi^{ECP}(A,B) = 4\epsilon[R^{-12}f(A,B)^{-6} - R^{-6}f(A,B)^{-3}],$$

so that

$$\langle \phi_A^{ECP}(A,B)\rangle = 4\epsilon[R^{-12}\langle f(A,B)^{-6}\rangle - R^{-6}\langle f(A,B)^{-3}\rangle].$$

This is a very useful property, as the orientational averages $\langle f(A,B)^{-6}\rangle$ and $\langle f(A,B)^{-3}\rangle$ are independent of separation and need only be computed once. Thus the computational overhead for calculating contributions to the integral are asymptotically the same as those of the Lennard-Jones potential. Finally, the computation of $\langle B_{HE}(A,B)\rangle$ can be accomplished by approximating it as a tenth degree polynomial in R using the algorithm discussed in Ref. [13].

IV. CONCLUSION

We have thus shown that the contact function for ellipsoids gives a better physical basis for overlap potentials than the original probabilistic model, which leads to the incorrect collision diameter for mixtures of hard spheres. An analytic expression for the second virial coefficient for the improved overlap or ellipsoid contact potential is derived and shown to satisfy a principle of corresponding states.

[1] M. P. Allen and M. R. Wilson, J. Comput. Aided Mol. Des. **3**, 335 (1989).

[2] E. De Miguel, L.-F. Rull, N. K. Chalam, and K. E. Gubbins, Mol. Phys. **74**, 405 (1991).

[3] D. J. Adams, G. R. Luckhurst, and R. W. Phippen, Mol. Phys. **61**, 1575 (1987).

[4] J. Alejandre, J. W. Emsley, D. J. Tildesley, and P. Carlson, J. Chem. Phys. **101**, 7027 (1994).

[5] J. G. Gay and B. G. Berne, J. Chem. Phys. **75**, 3316 (1989).

[6] G. R. Luckhurst and P. S. J. Simmonds, Mol. Phys. **80**, 233 (1993).

[7] B. J. Berne and P. Pechukas, J. Chem. Phys. **64**, 4213 (1982).

[8] U. P. Singh, U. Mohanty, and K. S. Singh, Mol. Phys. **68**, 1047 (1989).

[9] J. W. Perram and M. S. Wertheim, J. Comput. Phys. **58**, 409 (1985).

[10] J. W. Perram, M. S. Wertheim, J. L. Lebowitz, and G. O. Williams, Chem. Phys. Lett. **105**, 277 (1984).

[11] D. J. Cleaver, C. M. Care, M. P. Allen, and M. P. Neal, Phys. Rev. E **54**, 559 (1996).

[12] M. P. Allen, G. T. Evans, D. Frenkel, and B. Mulder, Adv. Chem. Phys. **86**, 1 (1993).

[13] J. W. Perram and E. L. Præstgaard, Mol. Phys. **63**, 1103 (1988).

[14] F. Kohler, N. Quirke, and J. W. Perram, J. Chem. Phys. **71**, 4128 (1979).

[15] R. P. Brent, *Algorithms for Minimization Without Derivatives* (Prentice Hall, Englewood Cliffs, NJ, 1973).

[16] Lone Vad Jensen, M.Sc. thesis, Odense University, 1986 (unpublished).

[17] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).