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Gaussian Model Potentials for Molecular Interactions*

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Simple analytical forms for the orientation dependence of the potential between two molecules are derived from a Gaussian overlap model. Orientation-dependent range and energy parameters are determined, which can be used with any two-parameter atomic potential to give simple and reasonable polyatomic potentials.

INTRODUCTION

Until recently, an accurate intermolecular potential for any system with a respectable complement of electrons was just a gleam in the theorist's eye, or a noncommittal "V" on his paper. Accordingly, statistical mechanical studies were done with model potentials.[1] The structure and dynamics of monatomic solids or fluids were calculated on the basis of simple, convenient, and "reasonable" pair potentials, and often enough the results were surprisingly good; for example, molecular dynamics studies have shown that the Lennard-Jones (12–6) potential accounts quite adequately for the thermodynamic and transport properties of liquid argon.[2] Even cruder model potentials have been used to explore fundamental questions of statistical mechanics, concerning ergodicity, the nature of phase transitions, the long-time behavior of correlation functions, and so on.

A good model potential, then, is a useful object. The potential must have two characteristics: It must be mathematically simple, involving only functions which are easy to calculate; and it must not violate too strongly our sense of what is physically correct. As our ignorance recedes, of course, it becomes more difficult to satisfy both criteria; however, short range interactions of polyatomic molecules are still sufficiently mysterious that the chief criterion for a good model potential is simplicity. It is in this spirit that we offer here a variety of model potentials defined by Gaussians, the functions of choice when one has to work with many variables. We try to model the repulsive part of the intermolecular potential—that is, the shape of the molecule—and Gaussians are sufficiently flexible to represent easily molecules which are spherical or flat or thin or warped. In the body of the paper we specify the basic model, discuss special cases, describe a number of variations on it, and comment on the relation to other commonly used model potentials for polyatomic systems.

THE MODEL

We think of a space-filling model of a molecule, constructed from the little balls and bonds available from companies specializing in chemical education. Regarded under low resolution, as produced for example by squinting, the molecule may look like an ellipsoid, or like several ellipsoids partially intersecting one another (Fig. 1). We shall think of a molecule, then, as a rigid union of a set of ellipsoids; to simplify the model further we shall specify that each ellipsoid is rotationally symmetric about a principal axis—that is, an ellipsoid of revolution.

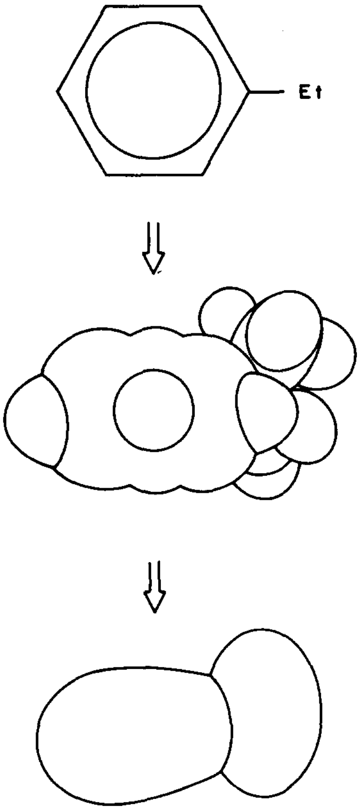

Fig. 1. Modeling of ethylbenzene.

Now consider the Gaussian function of a three-dimensional vector $\mathbf{x}$ defined by

$$G(\mathbf{x}) = \exp(-\mathbf{x}\cdot\boldsymbol{\gamma}^{-1}\cdot\mathbf{x}),$$
$$\boldsymbol{\gamma} = (\sigma_{\parallel}^2 - \sigma_{\perp}^2)\mathbf{u}\mathbf{u} + \sigma_{\perp}^2\mathbf{I} \qquad (1)$$

where $\mathbf{u}$ is a unit vector along the principal axis and $\mathbf{I}$ is the unit matrix. The surfaces of constant G are

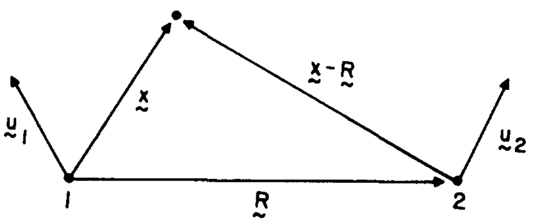

FIG. 2. Geometry for the overlap model.

ellipsoids of revolution about the $\mathbf{u}$ axis, and we can think of G as representing, in some sense, the distribution of matter in one of our molecular ellipsoids, the spatial extent of the distribution being of order $2\sigma_{\parallel}$ along the principal axis $\mathbf{u}$ and of order $2\sigma_{\perp}$ perpendicular to it. With every molecular ellipsoid we associate the corresponding Gaussian; with every pair of ellipsoids, one each from adjoining molecules, we associate a potential of interaction proportional to the mathematical overlap of their Gaussians; and we say that the total potential between two molecules is the sum of the pairwise interactions of their respective ellipsoids. We refer to this as the "overlap model," or OM, with apologies to Allen Ginsberg. It is a mathematically tractable model of the dependence of short-range repulsive forces on the shapes of the molecules involved.[3]

Our problem is to calculate the potential of interaction between two ellipsoids of revolution as a function of the relative orientation of their axial unit vectors $\mathbf{u}_1$, $\mathbf{u}_2$ and of the vector $\mathbf{R}$ joining their centers. Referring to Fig. 2 for the overlap model, we have

$$V(\mathbf{u}_1, \mathbf{u}_2, \mathbf{R}) \sim |\boldsymbol{\gamma}_1|^{-1/2} |\boldsymbol{\gamma}_2|^{-1/2} \int d\mathbf{x} \times \exp[-\mathbf{x}\cdot\boldsymbol{\gamma}_1^{-1}\cdot\mathbf{x} - (\mathbf{x}-\mathbf{R})\cdot\boldsymbol{\gamma}_2^{-1}\cdot(\mathbf{x}-\mathbf{R})], \tag{2a}$$

where $|\boldsymbol{\gamma}_i|$ denotes the determinant of the range matrix $\boldsymbol{\gamma}_i$ and

$$\boldsymbol{\gamma}_i = (\sigma_{i\parallel}^2 - \sigma_{i\perp}^2)\mathbf{u}_i\mathbf{u}_i + \sigma_{i\perp}^2 \mathbf{I}. \tag{2b}$$

As with any Gaussian integral, we get the exponential of a quadratic form, divided by a determinant,

$$V(\mathbf{u}_1, \mathbf{u}_2, \mathbf{R}) \sim |\boldsymbol{\gamma}_1+\boldsymbol{\gamma}_2|^{-1/2} \exp[-\mathbf{R}\cdot(\boldsymbol{\gamma}_1+\boldsymbol{\gamma}_2)^{-1}\cdot\mathbf{R}] \tag{3}$$

The dependence on $\mathbf{R}$ is entirely in the exponent. For fixed $\mathbf{u}_1$ and $\mathbf{u}_2$ the equipotentials are ellipsoids in $\mathbf{R}$, with principal axes along the eigenvectors of $(\boldsymbol{\gamma}_1+\boldsymbol{\gamma}_2)$. The shape of these equipotentials depends on the relative orientation of $\mathbf{u}_1$ and $\mathbf{u}_2$, through the eigenvalues of $(\boldsymbol{\gamma}_1+\boldsymbol{\gamma}_2)$, as does the strength of the potential, through the determinant $|\boldsymbol{\gamma}_1+\boldsymbol{\gamma}_2|$.

The overlap model is a five-parameter model: Two parameters $(\sigma_{\parallel}, \sigma_{\perp})$ characterize each molecular ellipsoid, and we need in addition a strength parameter to define the potential (3) completely. It is clear from Eq. (3), however, that the overlap model generates only a four-parameter set of potentials: V is completely determined by the strength parameter and by the three parameters—$(\sigma_{1\perp}^2+\sigma_{2\perp}^2)$, $(\sigma_{1\parallel}^2-\sigma_{1\perp}^2)$, $(\sigma_{2\parallel}^2-\sigma_{2\perp}^2)$—that define $(\boldsymbol{\gamma}_1+\boldsymbol{\gamma}_2)$.

It is obvious from Eq. (3) that the potential can be expressed in the simple form

$$V(\mathbf{u}_1, \mathbf{u}_2, \mathbf{R}) = \epsilon(\mathbf{u}_1, \mathbf{u}_2) \exp[-R^2/\sigma^2(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{R}})], \tag{4}$$

where $\epsilon(\mathbf{u}_1, \mathbf{u}_2)$ and $\sigma(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{R}})$ are angle dependent strength and range parameters, respectively, and $\hat{\mathbf{R}}$ is the unit vector in the $\mathbf{R}$ direction. In general one calculates these parameters from Eq. (3) by first finding the eigenvectors and eigenvalues of $(\boldsymbol{\gamma}_1+\boldsymbol{\gamma}_2)$. This amounts to diagonalizing a 2×2, since a vector perpendicular to $\mathbf{u}_1$ and $\mathbf{u}_2$ is automatically an eigenvector of $(\boldsymbol{\gamma}_1+\boldsymbol{\gamma}_2)$, and we leave the general calculation to the reader. In the important special case that the molecular ellipsoids have identical parallel and perpendicular range parameters, we find

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

$$\sigma(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{R}}) = \sigma\left(1-\tfrac{1}{2}\chi\left\{\frac{(\hat{\mathbf{R}}\cdot\mathbf{u}_1+\hat{\mathbf{R}}\cdot\mathbf{u}_2)^2}{[1+\chi(\mathbf{u}_1\cdot\mathbf{u}_2)]}+\frac{(\hat{\mathbf{R}}\cdot\mathbf{u}_1-\hat{\mathbf{R}}\cdot\mathbf{u}_2)^2}{[1-\chi(\mathbf{u}_1\cdot\mathbf{u}_2)]}\right\}\right)^{-1/2} \tag{5a}$$

where ϵ, σ, and χ are strength, range, and anisotropy parameters, respectively. In terms of the range parameters $\sigma_{\parallel}$ and $\sigma_{\perp}$ characterizing each molecular ellipsoid, we find

$$\sigma = \sqrt{2}\sigma_{\perp}, \qquad \chi = (\sigma_{\parallel}^2-\sigma_{\perp}^2)/(\sigma_{\parallel}^2+\sigma_{\perp}^2). \tag{5b}$$

Notice that to first order in the anisotropy the potential depends on $\hat{\mathbf{R}}\cdot\mathbf{u}_1$ and on $\hat{\mathbf{R}}\cdot\mathbf{u}_2$ but not on $\mathbf{u}_1\cdot\mathbf{u}_2$; in other words, the potential between weakly anisotropic ellipsoids is virtually unchanged by rotation of one ellipsoid with respect to the other about the line joining their centers.

Equations (5) confirm that the strength of the interaction, which is measured by the overlap of the molecular ellipsoids when their centers coincide, is a maximum when the ellipsoidal axes are parallel, and a minimum when they are perpendicular, as it should be. We also find from Eq. (5) that the interaction is most anisotropic when the ellipsoidal axes are parallel, the equipotentials in $\mathbf{R}$ space being ellipsoids of revolution about the molecular axis with range parameters $\sqrt{2}\sigma_{\parallel}$ and $\sqrt{2}\sigma_{\perp}$. The interaction is most isotropic when the ellipsoidal axes are perpendicular, the equipotentials in $\mathbf{R}$ space being ellipsoids of revolution about $\mathbf{u}_1\times\mathbf{u}_2$, with range parameters $\sqrt{2}\sigma_{\perp}$ (along $\mathbf{u}_1\times\mathbf{u}_2$) and $(\sigma_{\parallel}^2+\sigma_{\perp}^2)^{1/2}$ (transverse to $\mathbf{u}_1\times\mathbf{u}_2$).

There is a second special case of Eq. (4) which is worth discussing: When one or both of the molecular ellipsoids degenerates to a sphere, we have a model potential for atom–molecule or atom–atom interactions.

The energy parameter is angle independent. We find

$$\sigma(\mathbf{u}, \hat{\mathbf{R}}) = (\sigma_\perp^2+\sigma_2^2)^{1/2} \times \{1-[(\sigma_{\|}^2-\sigma_\perp^2)/(\sigma_{\|}^2+\sigma_2^2)](\hat{\mathbf{R}}\cdot\mathbf{u})^2\}^{-1/2}, \quad (6a)$$

for atom–molecule interactions and

$$\sigma = (\sigma_1^2+\sigma_2^2)^{1/2} \quad (6b)$$

for atom–atom interactions, where σ_1, σ_2 denote the atomic range parameters. Notice that for atom–molecule interactions the surface $R=\sigma(\mathbf{u}, \hat{\mathbf{R}})$ is an ellipsoid of revolution about the $\mathbf{u}$ axis. For atom–molecule interactions we have a four-parameter model—strength, $\sigma_{\|}$, $\sigma_\perp$, σ_2 which generates a three-parameter family of potentials; for atom–atom interactions we have a three-parameter model—strength, σ_1, σ_2—which generates a two-parameter family of potentials.

We close this section with a remark on the total interaction between molecules composed of several ellipsoids. Here one wants the interaction as a function of the molecular centers of mass and of the relative orientation of body-fixed coordinate systems attached to these centers of mass. This is a simple problem in vector addition. The distinguished axis of each ellipsoid and the vector from the center of mass to the center of each ellipsoid, are both body-fixed vectors. They have accordingly a definite expansion in a body-fixed basis attached to the center of mass. We simply substitute these expansions into the formulas above for the interaction of two ellipsoids.

DISCUSSION

Model potentials have a long history in statistical mechanics,[1,4–6] and ours is by no means the first proposal for modeling anisotropic molecular interactions. One can make a rough division of models into two classes, according to whether a geometric or analytic interpretation is more appropriate. The hard sphere model of monatomic fluids is the canonical example of a geometric model; the appealing physical and mathematical simplicity of this model have made it a favorite for both equilibrium and dynamical studies. For molecular fluids, the spherocylinder, hard ellipsoid, and loaded and rough sphere models are very much in the same spirit; the Kihara potential,[5] although making use of a Lennard-Jones for distance dependence, also introduces anisotropy through a fundamentally geometric construction. Unfortunately, the intuitive geometric simplicity of these various models is not matched by analytic simplicity of the potentials to which they give rise, and in fact only the loaded and rough sphere models are at all suited for dynamical calculations. Our Gaussian potential is also basically geometric in flavor, yet at the same time sufficiently simple in analytic form—in particular, susceptible to differentiation—that dynamical calculations with it should present no problem.

An intuitive geometric interpretation is sacrificed in the second class of model potentials, where one starts with the observation that a general anisotropic potential can be expanded in Wigner rotation matrices, with expansion coefficients that are functions of the separation between the centers of mass of the molecules. Model potentials are generated by truncating the expansion and assuming functional forms for the coefficients. There are two difficulties with this approach. First, it is difficult to visualize the change in the shape of the potential which one produces by changing a given expansion parameter. Second, if the potential between two polyatomics is represented even roughly by a sum of pairwise interactions between the constituent atoms, one anticipates that many terms will be needed to give an adequate representation of the potential between distinctly anisotropic molecules: Roughly, the greater the spread in force centers, the more slowly convergent will be the expansion in Wigner matrices. These model potentials, therefore, should be used primarily for weakly anisotropic molecules. The Gaussian model above, on the other hand, can represent with equal ease the nearly spherical and the extremely anisotropic.

We end with a suggestion for increasing substantially the flexibility of the Gaussian model. The model was devised primarily to give simple expressions for the orientation dependence of molecular interactions; it is not expected to mimic closely the distance dependence of realistic potentials. However, as we see from Eq. (4), every Gaussian potential is characterized by orientation-dependent strength and range parameters. This suggests that we simply use these expressions in any two-parameter atomic potential, such as a Lennard-Jones (12, 6), obtaining a simple intermolecular potential with what is, presumably, a more realistic distance dependence,

$$V(\mathbf{u}_1, \mathbf{u}_2, \mathbf{R}) = \epsilon(\mathbf{u}_1, \mathbf{u}_2)\phi[R/\sigma(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{R}})]. \quad (7)$$

This approach recalls a suggestion made by Corner[4] several years ago. Corner proposed a potential between linear molecules in which force centers placed along the molecular axis of one molecule interact through Lennard-Jones (12, 6) potentials with force centers on the axis of the other molecule. One gets a complicated superposition of potentials; to simplify the mess, Corner numerically fit it to a single Lennard-Jones (12, 6) potential, obtaining angle-dependent range and energy parameters. Our approach is much simpler in that it gives analytical—not numerical—formulas for these parameters, and our anisotropy parameter can be readily varied, making possible the study of varying degrees of anisotropy without necessitating a new numerical computation for each case.

We believe that the Gaussian model should prove very useful for molecular dynamics and for Monte Carlo studies of liquid crystals, the Kerr effect, and other fluid manifestations of molecular anisotropy.

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[3] There is a second Gaussian model which at first glance looks somewhat different from the overlap model. We suppose that along the principal axis of each ellipsoid there are distributed centers of force; we assume that the density of centers of force along the axis is a Gaussian function of distance from the center of the ellipsoid; and we say that a center of force in one ellipsoid repels a center of force in another ellipsoid according to a potential which is a Gaussian in the distance between the two centers of force. The total interaction of two ellipsoids is the "sum" (actually, integral) of the interactions between the centers of force on their two axes, and we calculate the total potential between two molecules as before. This we call the "line interaction model potential" or LIMP. However, with every LIMP we can associate an OM giving the same potential, for a spherically symmetric Gaussian repulsion can be regarded as the overlap of two spherically symmetric Gaussians [see Eq. (6b)] centered on the centers of force. Accordingly, the total interaction between two Gaussian distributions of centers of force is proportional to the overlap of two Gaussian distributions of spherically symmetric Gaussians. But a Gaussian distribution of spherically symmetric Gaussians is a Gaussian in its own right, and we are back to OM.

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Raman Spectral Studies of HTO in H_2O*

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Argon-ion laser Raman spectra have been recorded photoelectrically from a 10 volume % solution of T_2O in H_2O at temperatures from 26 to 94°C and from a 3.6*M* ternary solution of $NaClO_4$ in 5 volume % T_2O in H_2O at 25°C. Laser-Raman spectra were also obtained from a 10 volume % solution of H_2O in D_2O at temperatures from ∼23 to 96°C. At 26°C, a Raman intensity maximum was observed in the OT stretching region from HTO near $\Delta\bar{\nu}=2130\pm5\ \mathrm{cm}^{-1}$, and a shoulder was apparent near $\Delta\bar{\nu}=2225$–$2250\ \mathrm{cm}^{-1}$. An isosbestic frequency was also indicated for HTO near $\Delta\bar{\nu}=2164\pm7\ \mathrm{cm}^{-1}$ from 26 to 70°C and for HDO near 3450 cm^{-1} from ∼23 to 63°C. The shapes of the OT and OH stretching contours from HTO and HDO were approximated by two broad Gaussian components using an analog computer, and the resulting plots of $\log_{10}(I_{\mathrm{NHB}}/I_{\mathrm{HB}})$ vs $1/T$, where I_{NHB} refers to the high-frequency nonhydrogen-bonded Gaussian component intensity (the shoulder), and I_{HB} refers to the low-frequency hydrogen-bonded intensity (the peak), were characterized by values of about 2.5±0.2 kcal/mole OTO and 2.2±0.3 kcal/mole OHO in resonable agreement with a previous two-Gaussian value of 2.5±0.6 kcal/mole ODO. Two pronounced intensity maxima were also observed in the OT stretching region from the ternary $NaClO_4$ solution near $\Delta\bar{\nu}=2150\pm5\ \mathrm{cm}^{-1}$ and $\Delta\bar{\nu}=2225\pm5\ \mathrm{cm}^{-1}$ in general support of the two-Gaussian analysis of the binary solution stretching contours. The $\Delta H°$ values corresponding to the disruption of O–T···O, O–D···O, and O–H···O bonds agree despite the facts that the three contour shapes are different and that the nonhydrogen-bonded OT stretching component is, relative to the hydrogen-bonded component, roughly 2 times more intense than the corresponding OD and OH components. The value of ∼2.5 kcal/mole hydrogen bond was also found to agree with numerous other experimental $\Delta H°$ values, as well as with a recent value from molecular dynamics calculations.

INTRODUCTION

Raman spectral investigations of solutions of HDO in H_2O at temperatures from 16 to 97°C [1,2] and of HDO in D_2O [3,4] have been conducted, and the studies have been extended to include effects of electrolytes[5,6] and of pressure.[6,7] In addition, stimulated Raman spectra from solutions containing HDO have been obtained.[8,9] Raman spectral investigations of solutions of HTO in H_2O, however, have not been reported, although information relating to the fundamental vibrations of gaseous HTO, DTO, and T_2O is available from infrared studies,[10,11] see also Refs. 12 and 13.

Raman data from solutions of HTO in H_2O are of value in several respects. The intramolecular vibrational coupling between OT and OH stretching vibrations is minimal for HTO, and thus intermolecular interactions at the OT or OH groups should be more distinct spectroscopically. Some experimental advantages should also result from the greater frequency separation of the OT and OH stretching vibrations. In addition, experience with HDO [1–7] suggests that the hydrogen-bonded OT stretching components should be narrower than those corresponding to the OD and OH vibrations. Narrowing of the hydrogen-bonded OT stretching component would tend to make certain spectral features more pronounced relative to HDO, and this expectation was verified by the observation