

Estimate of the intermolecular polarization contribution to the static dielectric constant of water

James W. Kress[†] and John J. Kozak

Department of Chemistry and Radiation Laboratory,* University of Notre Dame, Notre Dame, Indiana 46556
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In this paper, molecular-structure data derived from recent quantum-chemical studies are used in conjunction with the Mandel-Mazur theory of the static dielectric constant to estimate the importance of intermolecular polarization contributions to the static dielectric constant of water. A scalar expression for the static dielectric constant is identified and then investigated via a multibody decomposition in which the effects of 2-, 3-, ... n -body interactions are displayed and then analyzed numerically. Our main conclusion is that the intermolecular polarization contribution is of crucial importance in determining the static dielectric constant of water. Further, our calculations show that the predicted dielectric constant is extraordinarily sensitive to the geometry of the first hydration shell; thus, the use of a slightly inaccurate potential function may lead to a predicted dielectric constant in significant disagreement with the experimental value.

I. INTRODUCTION

For many years, the coupling of rigid dipoles has been held to be of primary importance in the determination of the static dielectric constant of a dipolar fluid. On the other hand, the probable importance of the intermolecular polarization contribution to the static dielectric constant has never really been assessed, at least at the microscopic level. Accordingly, the purpose of the present study is to estimate the intermolecular polarization contribution to the static dielectric constant of the fluid, water.

The importance of dipole-dipole coupling in determining the static dielectric constant of water was first pointed out by Kirkwood¹ in his classic paper on the dielectric polarization of polar liquids. Using a simple model of water, he carried out a semiexact analysis of the rigid-dipole contribution to the polarization of the sample, and by estimating the intermolecular polarization contribution via essentially macroscopic arguments, was able to describe qualitatively the behavior of the static dielectric constant of water. Somewhat later, Pople² using his "bent bond" model of water was able to obtain a better numerical estimate of the rigid-dipole contribution as derived by Kirkwood, and by opting for the same intermolecular polarization contribution as used by Kirkwood, was able to obtain a better, though still qualitative, estimate of the static dielectric constant of water.

In a more recent study, Mandel and Mazur³ have presented a formally exact, molecular theory of the dielectric constant. These authors used their theory specifically to examine the mathematical structure and properties of a generalized Clausius-Mossotti function. Mandel^{4,5} later used the approach developed in Ref. 3 to examine the approximations implicit in the Kirkwood theory of the dielectric constant. The cornerstone of the present contribution is the observation that the Mandel-Mazur theory provides the means for determining from first principles the intermolecular polarization contribution to the static dielectric constant. In this paper, we shall cast the Mandel-Mazur theory into a form suitable for an in-depth analysis of the intermolecular polarization contribution. Practical-

ly, this involves identifying a scalar relationship for the dielectric constant, rather than the vector relationship laid down in Ref. 4.

In Sec. II we review those aspects of the Mandel-Mazur theory relevant to the problem discussed in this paper. Then we identify a field-independent scalar relationship for the dielectric constant which involves averages over canonical distributions of molecules. In Sec. III we show how this expression for the static dielectric constant may be partitioned in such a way as to give some insight into the multibody contributions to the intermolecular polarization contribution; our analysis is facilitated by developing a diagrammatic representation for the result obtained. In Sec. IV we present the results of numerical studies in which the importance of the intermolecular polarization contribution to the static dielectric constant of water is assessed. Finally, in Sec. V, we discuss the results obtained, present our conclusions, and describe the relevance of our study to some recent work on computer-simulated water.

II. FORMAL RESULTS

We consider a macroscopic, spherical sample of volume V containing N identical molecules located at positions \mathbf{r}_i ($i = 1, 2, \dots, N$). Each molecule is characterized by a permanent point dipole of magnitude μ and a polarizability tensor A . In this study, the tensor A is represented by the unit tensor $\mathbf{1}$ times a scalar α , where the scalar α is taken to be the experimentally determined, rotationally averaged molecular polarizability. The approximation of introducing an isotropic molecular polarizability to characterize the substance water will be discussed in Sec. V. The orientation of the permanent moment \mathbf{m}_i of a molecule with respect to a fixed coordinate system is represented by the unit vector ω_i (\mathbf{m}_i , then, is defined as $\mu \omega_i$). We define the total dipole moment \mathbf{p}_i of a given molecule in the sample in the presence of a weak, static, external field \mathbf{E}_0 as

$$\mathbf{p}_i = \mathbf{m}_i + \alpha \mathbf{1} \cdot \left(\mathbf{E}_0 - \sum_{j \neq i} \Upsilon_{ij} \cdot \mathbf{p}_j \right). \quad (1a)$$

In this definition, $-\sum_{j \neq i} \Upsilon_{ij} \cdot \mathbf{p}_j$ is the field at the i th

molecule due to the dipole moments of all other molecules in the sample, and Υ_{ij} is the dipolar interaction tensor defined as

$$\Upsilon_{ij} = (1/r_{ij}^3)[1 - 3\mathbf{r} \cdot \mathbf{r}/r_{ij}^2], \quad (1b)$$

where r_{ij} is the scalar distance between the i th and j th dipoles. We also define the total dipole moment \mathbf{p}_i^0 of the i th molecule in the sample in the absence of an external field as

$$\mathbf{p}_i^0 = \mathbf{m}_i - \alpha \mathbf{1} \cdot \left(\sum_{j \neq i} \Upsilon_{ij} \cdot \mathbf{p}_j^0 \right). \quad (2)$$

The total potential energy U_N of the system is given by Mandel and Mazur as

$$U_N = U_0 + \sum_{1 \leq i < j \leq N} \mathbf{m}_i \cdot \Upsilon_{ij} \cdot \mathbf{p}_j^0 - \sum_{s=1}^N \mathbf{p}_s^0 \cdot \mathbf{E}_0 + \mathcal{O}(E_0^2), \quad (3)$$

where U_0 is the non-Coulombic part of the potential energy. If one defines

$$U_{0,N} = U_0 + \sum_{1 \leq i < j \leq N} \mathbf{m}_i \cdot \Upsilon_{ij} \cdot \mathbf{p}_j^0 \quad (4)$$

and neglects terms of order E_0^2 (since, by assumption, \mathbf{E}_0 is a weak field), Eq. (3) can be rewritten as

$$U_N = U_{0,N} - \sum_{s=1}^N \mathbf{p}_s^0 \cdot \mathbf{E}_0. \quad (5)$$

We now recall that the polarization \mathbf{P} of a system due to the presence of an external field can be written formally as

$$\mathbf{P} = \rho \frac{\int \dots \int \mathbf{p}_i \exp(-\beta U_N) d\mathbf{R}_1 \dots d\mathbf{R}_N d\Omega_1 \dots d\Omega_N}{\int \dots \int \exp(-\beta U_N) d\mathbf{R}_1 \dots d\mathbf{R}_N d\Omega_1 \dots d\Omega_N} \quad (6a)$$

$$= \rho \langle \mathbf{p}_i \rangle, \quad (6b)$$

where ρ is the number density (N/V), β is $(kT)^{-1}$, and $\langle \dots \rangle$ designates an average over the full $6N$ -dimensional configuration space (or, $5N$ -dimensional configuration space if the molecules are spherical) of the system. Utilizing Eq. (5) and expanding the exponential in Eq. (6a) in powers of \mathbf{E}_0 we obtain, to first order in \mathbf{E}_0 ,

$$\mathbf{P} = \rho \frac{\int \dots \int \mathbf{p}_i \exp(-\beta U_{0,N}) d\mathbf{R} d\Omega + \beta \int \dots \int \sum_{s=1}^N \mathbf{p}_i \mathbf{p}_s^0 \cdot \mathbf{E}_0 \exp(-\beta U_{0,N}) d\mathbf{R} d\Omega}{\int \dots \int \exp(-\beta U_{0,N}) d\mathbf{R} d\Omega + \beta \int \dots \int \sum_{s=1}^N \mathbf{p}_s^0 \cdot \mathbf{E}_0 \exp(-\beta U_{0,N}) d\mathbf{R} d\Omega}. \quad (7a)$$

Inasmuch as

$$\langle \mathbf{p}_i^0 \rangle_0 = \frac{\int \dots \int \mathbf{p}_i^0 \exp(-\beta U_{0,N}) d\mathbf{R} d\Omega}{\int \dots \int \exp(-\beta U_{0,N}) d\mathbf{R} d\Omega} = 0,$$

where $\langle \dots \rangle_0$ denotes an average over the full configuration space of the system in the absence of an external field, Eq. (7a) reduces to

$$\mathbf{P} = \rho \frac{\int \dots \int \mathbf{p}_i \exp(-\beta U_{0,N}) d\mathbf{R} d\Omega + \beta \int \dots \int \sum_{s=1}^N \mathbf{p}_i \mathbf{p}_s^0 \cdot \mathbf{E}_0 \exp(-\beta U_{0,N}) d\mathbf{R} d\Omega}{\int \dots \int \exp(-\beta U_{0,N}) d\mathbf{R} d\Omega},$$

or

$$\mathbf{P} = \rho \left\{ \langle \mathbf{p}_i \rangle_0 + \beta \left\langle \mathbf{p}_i \sum_{s=1}^N \mathbf{p}_s^0 \cdot \mathbf{E}_0 \right\rangle_0 \right\}. \quad (7b)$$

If the applied external field (\mathbf{E}_0) is assumed to be small, the moments ($\alpha \mathbf{1} \cdot \mathbf{E}_0$) induced by the external field will also be small. Thus, the moments induced in the other molecules, by the moment induced in the i th molecule due to the external field, may be neglected. Accordingly, in the regime of small \mathbf{E}_0 , we can rewrite Eq. (1a) as

$$\mathbf{p}_i = \mathbf{m}_i + \alpha \mathbf{1} \cdot \left(\mathbf{E}_0 - \sum_{j \neq i} \Upsilon_{ij} \cdot \mathbf{p}_j^0 \right)$$

which implies, using Eq. (2), that

$$\mathbf{p}_i = \mathbf{p}_i^0 + \alpha \mathbf{1} \cdot \mathbf{E}_0.$$

This last result, when used in conjunction with Eq. (7b), yields the following expression for the polarization \mathbf{P} :

$$\mathbf{P} = \rho \left\{ \langle \mathbf{p}_i^0 \rangle_0 + \left\langle \alpha \mathbf{1} \cdot \mathbf{E}_0 \right\rangle_0 + \beta \left\langle \mathbf{p}_i \sum_{s=1}^N \mathbf{p}_s^0 \cdot \mathbf{E}_0 \right\rangle_0 \right\}$$

or

$$\mathbf{P} = \rho \left\{ \alpha \mathbf{1} + \beta \left\langle \mathbf{p}_i \sum_{s=1}^N \mathbf{p}_s^0 \right\rangle_0 \right\} \cdot \mathbf{E}_0, \quad (8)$$

an expression valid to first order in \mathbf{E}_0 .

The static dielectric constant ϵ of the sample is defined by the expression

$$(\epsilon - 1)\mathbf{E} = 4\pi\mathbf{P}, \quad (9)$$

where \mathbf{E} is the average (Maxwellian) field inside the sample. Combining Eqs. (8) and (9), and noting that for a macroscopic, spherical sample

$$\mathbf{E}_0 = \frac{1}{3}(\epsilon + 2)\mathbf{E},$$

we obtain

$$\mathbf{E} = \frac{\epsilon + 2}{\epsilon - 1} \frac{4\pi\rho}{3} \left\{ \alpha \mathbf{1} + \beta \left\langle \mathbf{p}_i \sum_{s=1}^N \mathbf{p}_s^0 \right\rangle_0 \right\} \cdot \mathbf{E} \quad (10)$$

which, for nonpolarizable dipoles, collapses to the result obtained previously by Mandel.⁴ Equation (10) leads directly to the following relationship:

$$\frac{\epsilon + 2}{\epsilon - 1} \frac{4\pi\rho}{3} \left\{ \alpha \mathbf{1} + \beta \left\langle \mathbf{p}_i^0 \sum_{s=1}^N \mathbf{p}_s^0 \right\rangle_0 \right\} = 1. \quad (11)$$

Since the off-diagonal elements of the unit tensor $\mathbf{1}$ are zero, we need consider only the three diagonal components of the tensor on the left-hand side of Eq. (11); each of these components satisfies the relation

$$\frac{\epsilon + 2}{\epsilon - 1} \frac{4\pi\rho}{3} \left\{ a_{\kappa\kappa} + \beta \left\langle p_{i\kappa}^0 \sum_{s=1}^N p_{s\kappa}^0 \right\rangle_0 \right\} = 1. \quad (12)$$

Summing the three diagonal components, and using explicitly the assumption of isotropic molecular polarizability (viz., $a_{xx} = a_{yy} = a_{zz} = \alpha$), we obtain the following result:

$$\frac{\epsilon + 2}{\epsilon - 1} \frac{4\pi\rho}{3} \left\{ 3\alpha + \beta \left\langle \mathbf{p}_i^0 \cdot \sum_{s=1}^N \mathbf{p}_s^0 \right\rangle_0 \right\} = 3 \quad (13)$$

or, upon rearrangement,

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho}{3} \left\{ \alpha + \beta \left\langle \mathbf{p}_i^0 \cdot \sum_{s=1}^N \mathbf{p}_s^0 \right\rangle_0 \right\}. \quad (14)$$

For a system of molecules with *no* permanent moments, Eq. (14) collapses to the Clausius-Mossotti equation. If the molecules do possess permanent moments, but the molecules themselves are assumed to be non-interacting and there are no contributions to \mathbf{p}_i due to terms of the form $\sum_{i \neq j} \Upsilon_{ij} \cdot \mathbf{p}_j$, then Eq. (14) collapses to the Debye equation. Finally for $\alpha = 0$, Eq. (14) is precisely Kirkwood's nonpolarizable-dipole result prior to his imposition of any approximations, other

than that the external field is small, and the sample is spherical. The full expression, Eq. (14), will now be studied to estimate the possible importance of intermolecular polarization contributions to the static dielectric constant, starting from a microscopic point of view.

III. THE MULTIBODY DECOMPOSITION

The total dipole moment \mathbf{p}_i^0 of the *i*th molecule of the sample in the absence of an external field was defined earlier [Eq. (2)]. We note that the second term in Eq. (2) can be written as $-\alpha(\sum_{i \neq j} \Upsilon_{ij} \cdot \mathbf{p}_j^0)$, so that \mathbf{p}_i^0 assumes the form

$$\mathbf{p}_i^0 = \mathbf{m}_i - \alpha \left(\sum_{i \neq j} \Upsilon_{ij} \cdot \mathbf{p}_j^0 \right);$$

one notices that this relation is a cyclic definition in the sense that the moment of one molecule is defined in terms of its permanent moment and the moments of the remaining $N-1$ molecules. We can use this feature of Eq. (2) to develop, via the method of successive substitution, a series expansion for the molecular moment of the *i*th molecule in terms of the polarizability α . Thus, to second order in α we obtain

$$\mathbf{p}_i^0 = \mathbf{m}_i - \alpha \sum_{i \neq j} \Upsilon_{ij} \cdot \mathbf{m}_j + \alpha^2 \sum_{i \neq j} \Upsilon_{ij} \cdot \left(\sum_{k \neq j} \Upsilon_{jk} \cdot \mathbf{m}_k \right)$$

and for \mathbf{p}_s^0 ,

$$\mathbf{p}_s^0 = \mathbf{m}_s - \alpha \sum_{s \neq q} \Upsilon_{sq} \cdot \mathbf{m}_q + \alpha^2 \sum_{s \neq q} \Upsilon_{sq} \cdot \left(\sum_{r \neq q} \Upsilon_{qr} \cdot \mathbf{m}_r \right).$$

Substitution of these expressions into Eq. (14) yields (again to order α^2),

$$\begin{aligned} \frac{\epsilon - 1}{\epsilon + 2} - \frac{4\pi\rho\alpha}{3} = \frac{4\pi\rho\beta}{9} \sum_{s=1}^N \left\{ \left\langle \mathbf{m}_i \cdot \mathbf{m}_s - \alpha \left[\sum_{s \neq q} \mathbf{m}_i \cdot \Upsilon_{sq} \cdot \mathbf{m}_q + \sum_{i \neq j} \mathbf{m}_s \cdot \Upsilon_{ij} \cdot \mathbf{m}_j \right] \right. \right. \\ \left. \left. + \alpha^2 \left[\sum_{s \neq q} \mathbf{m}_i \cdot \Upsilon_{sq} \cdot \left(\sum_{r \neq q} \Upsilon_{qr} \cdot \mathbf{m}_r \right) + \sum_{i \neq j} \mathbf{m}_s \cdot \Upsilon_{ij} \cdot \left(\sum_{k \neq j} \Upsilon_{jk} \cdot \mathbf{m}_k \right) + \left(\sum_{i \neq j} \Upsilon_{ij} \cdot \mathbf{m}_j \right) \cdot \left(\sum_{s \neq q} \Upsilon_{sq} \cdot \mathbf{m}_q \right) \right] \right\rangle_0 \right\}. \end{aligned} \quad (15)$$

Thus, by taking advantage of the cyclic property of Eq. (2), the static dielectric constant can be represented in terms of a series expansion in the polarizability α .

Before proceeding with an analysis of Eq. (15), a few remarks are in order. First, we note that the first term in Eq. (15), the rigid-dipole (RD) term, can be written (apart from constants) as

$$\text{RD} \equiv \sum_{s=1}^N \langle \mathbf{m}_i \cdot \mathbf{m}_s \rangle_0 = \mu^2 \sum_{s=1}^N \langle \omega_i \cdot \omega_s \rangle_0. \quad (16)$$

Since

$$\langle \omega_i \cdot \omega_i \rangle_0 = \langle 1 \rangle_0 = 1 \quad (17a)$$

and

$$\langle \omega_i \cdot \omega_s \rangle_0 = \langle \omega_i \cdot \omega_t \rangle_0 \quad (s \neq t), \quad (17b)$$

Eq. (16) may be written as

$$(1/\mu^2) \text{RD} = 1 + (N-1) \langle \omega_i \cdot \omega_s \rangle_0. \quad (18)$$

Now, if we define

$$\mathbf{M} \equiv \sum_{i=1}^N \omega_i \quad (19)$$

and examine

$$\left\langle \frac{M^2}{N} \right\rangle_0 = \left\langle \frac{\mathbf{M} \cdot \mathbf{M}}{N} \right\rangle_0 = \frac{1}{N} \left\langle \left(\sum_{i=1}^N \omega_i \right) \cdot \left(\sum_{s=1}^N \omega_s \right) \right\rangle_0, \quad (20)$$

we find that

$$\left\langle \frac{M^2}{N} \right\rangle_0 = \frac{1}{N} \left[\sum_{i=1}^N \langle \omega_i \cdot \omega_i \rangle_0 + \sum_{i \neq s=1}^N \langle \omega_i \cdot \omega_s \rangle_0 \right]. \quad (21)$$

Using Eqs. (17), we then have that

$$\begin{aligned} \langle M^2/N \rangle_0 &= (1/N) [N + N(N-1) \langle \omega_i \cdot \omega_s \rangle_0] \\ &= 1 + (N-1) \langle \omega_i \cdot \omega_s \rangle_0 \end{aligned} \quad (22)$$

which, in turn, gives that

$$\text{RD} = \mu^2 \langle M^2/N \rangle_0. \quad (23)$$

We note that Stillinger and Rahman have calculated the

quantity $\langle M^2/N \rangle$ for pure water via a molecular-dynamics simulation; we shall return to this point in a later paragraph.

The second remark concerns notation; for convenience, the various components of the intermolecular polarization contribution will be denoted by $\alpha^n A_n$, where n refers to the power of α considered. Thus, the first-order contribution is written

$$\alpha A_1 = \alpha \sum_s \left\{ \sum_{s \neq q} \omega_i \cdot \mathbf{T}_{sq} \cdot \omega_q + \sum_{i \neq j} \omega_s \cdot \mathbf{T}_{ij} \cdot \omega_j \right\}. \quad (24)$$

In this way, we can rewrite Eq. (15) conveniently as

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{4\pi\rho\alpha}{3} = \frac{4\pi\rho\beta}{9} \mu^2 \left\langle \frac{M^2}{N} - \alpha A_1 + \alpha^2 A_2 - \alpha^3 A_3 + \alpha^4 A_4 - \dots \right\rangle_0 \quad (25)$$

to order α^4 .

Turning now to an explicit discussion of Eq. (15), we note that the leading term,

$$\sum_{s=1}^N \mathbf{m}_i \cdot \mathbf{m}_s, \quad (26)$$

corresponds to the rigid-dipole-rigid-dipole coupling term and, for $i \neq s$, represents a two-body interaction term; for $i = s$, this term reduces to a one-body (or self-interaction) term. The next term in Eq. (15), $-\alpha(\sum_s \sum_{q \neq i} \mathbf{m}_i \cdot \mathbf{T}_{sq} \cdot \mathbf{m}_q)$, for $s = i$ or $q = i$, is seen to correspond to another two-body term. For the case $i = s$, this term represents the permanent dipole moment of the i th molecule interacting with the field generated at the i th molecule by the q th molecule. For the case $i = q$, this term represents the permanent dipole moment of the i th molecule interacting with the field generated by itself at the position of the s th molecule. Finally, if $i \neq s$, $q \neq s$ this term describes a three-body effect: the i th molecule interacting with the field generated at the s th molecule by the q th molecule. Similar interpretations can be provided for the term $-\alpha(\sum_s \sum_{i \neq j} \mathbf{m}_s \cdot \mathbf{T}_{ij} \cdot \mathbf{m}_j)$, or indeed for any higher-order term in the representation being studied. For example, the term $\alpha^2[\sum_s \sum_{q \neq i} \mathbf{m}_i \cdot \mathbf{T}_{sq} \cdot (\sum_{r \neq q} \mathbf{T}_{qr} \cdot \mathbf{m}_r)]$ for $i = s = r$ can be classified as a two-body term, since only two of the four indices are distinct; such a term is interpreted as the interaction of the permanent moment of the i th molecule with the field generated by the moment of the q th molecule which, in turn, is influenced by the presence of the i th molecular moment. By analyzing relations among the various indices we can achieve an overall partitioning of each term in terms of two-body, three-body, ..., n -body interactions. All contributions to Eq. (15) involving 2-body interactions can then be collected, with a similar resummation being effected for the 3-body, 4-body, ..., n -body terms. Thus, the static dielectric constant ϵ can be represented as a sum of increasingly complex, n -body interactions, with the various terms in this representation being themselves series expansions in α .

One could, of course, write the expression derived via this partitioning procedure in terms of m 's and \mathbf{T} 's, but this would result in an overly complex expres-

sion from which it would be difficult to extract much meaningful information. Accordingly, we opt for a diagrammatic representation of the series generated. In this representation we use vertices to represent molecules and bonds to represent the \mathbf{T}_{ij} 's. In the single case where no \mathbf{T}_{ij} appears, i.e., the leading term in Eq. (15), the vertices are defined to be connected. Examining Eq. (15), then, we find that we have essentially three types of terms,

(1) dipole-dipole

An example here is the term $\mathbf{m}_i \cdot \mathbf{m}_s$, representing the interaction of two dipoles.

(2) dipole-field

An example is $\mathbf{m}_i \cdot \mathbf{T}_{js} \cdot \mathbf{m}_s$, which represents the i th dipole interacting with the field generated by the s th dipole at the j th dipole.

(3) field-field

Here, for example, $(\mathbf{T}_{jk} \cdot \mathbf{m}_k) \cdot (\mathbf{T}_{sr} \cdot \mathbf{m}_r)$ denotes the field generated at the j th dipole by the k th dipole interacting with the field generated at the s th dipole by the r th dipole.

We note further that in (1), $i = s$ is a vertex, while $i \neq s$ is a direct bond; in (2), $i = j$ is a direct (or sequential) bond, while $i \neq j$ is an indirect (or nonsequential) bond; and in (3) $j = s$ is a direct bond, whereas $j \neq s$ is an indirect bond. Denoting vertices by dots, direct bonds by solid lines, and indirect bonds by dashed lines, the above diagrammatic scheme is specified completely. In this scheme, Eq. (15) may be written explicitly as shown in Fig. 1. Further we note that the resummation of Eq. (15) into two-body, three-body, ..., n -body interaction terms is straightforward (see Fig. 2). In the resummed expression, each n -body term is itself a power series in α , and we note that the expression derived closely resembles the more conventional multibody expansion of the total energy of a system. The usefulness of the multibody decomposition presented here will be apparent in the discussion presented in Sec. V.

IV. ESTIMATE OF THE INTERMOLECULAR POLARIZATION CONTRIBUTION

To make optimal use of the available molecular-structure calculations on water, we have chosen to represent the local equilibrium geometry of a water cluster in terms of an average dimer structure (ADS). In particular, after identifying the ADS, we generate the local structure of the fluid by appropriate symmetry transformations on the ADS, assuming the hydration number of a given water molecule to be four. (See the remarks below and those in Appendix I for details of this procedure.)

The structural parameters⁶ relevant to the problem at hand can be identified via an examination of Eq. (15). The first term on the right-hand side of Eq. (15) is

$$\mathbf{m}_i \cdot \mathbf{m}_s = \mu^2 \omega_i \cdot \omega_s = \mu^2 \cos \gamma_{is}. \quad (27)$$

Here, γ_{is} is the angle between the dipole moment vec-

$$\frac{\epsilon-1}{\epsilon+2} - \frac{4\pi\rho\alpha}{3} = \frac{4\pi\rho\beta}{9} \left\langle \left\{ \begin{array}{c} \bullet \\ i \end{array} + \sum_{s=1}^N \begin{array}{c} \bullet \quad \bullet \\ i \quad s \\ | \quad | \\ \text{---} \end{array} \right\} \right.$$

$$- \alpha \left\{ \sum_s \left[\sum_{q \neq s} \left(\begin{array}{c} \bullet \quad \bullet \\ s(i) \quad q \\ | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \\ s \quad q(i) \\ | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \\ s \quad q \\ | \quad | \\ \text{---} \end{array} \right) + \sum_{j \neq i} \left(\begin{array}{c} \bullet \quad \bullet \\ i(s) \quad j \\ | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \\ i \quad j(s) \\ | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \\ i \quad j \\ | \quad | \\ \text{---} \end{array} \right) \right] \right\}$$

$$+ \alpha^2 \left\{ \sum_s \left[\sum_{q \neq s} \sum_{r \neq s} \left(\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i(q) \quad s(r) \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ s \quad r(s,i) \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad r(i) \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad r(s) \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ s \quad r \quad s(i) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ q \quad r \quad i \\ | \quad | \quad | \\ \text{---} \end{array} \right) \right.$$

$$+ \sum_{j \neq i} \sum_{k \neq j} \left(\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i(k) \quad s(j) \quad (s,i)k \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ (s,i)k \quad j \quad (s)k \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad k(i) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad k \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i(s) \quad j \quad k(j,s) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ s \quad j \quad k \\ | \quad | \quad | \\ \text{---} \end{array} \right) \right.$$

$$\left. + \sum_{j \neq i} \sum_{q \neq s} \left(\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i(q) \quad s(j) \quad i(s) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i(s) \quad j(q) \quad j \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad s \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i(q) \quad s \quad i \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad s(j) \quad s \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad s \quad j \\ | \quad | \quad | \\ \text{---} \end{array} \right) \right\} \rangle_0$$

FIG. 1. The diagrammatic expansion of the expression $(\epsilon-1)/(\epsilon+2) - \frac{4}{3}\pi\rho\alpha$ in terms of the polarizability α , to order α^2 .

tors of molecules i and s ; thus, γ_{is} fixes the relative orientation of the permanent dipoles of the two molecules, i and s . Subsequent terms in the expansion, Eq. (15), also involve parameters which specify the relative orientation of molecules, with the influence of one molecule on another modulated by the T_{ij} ; however, since T_{ij} depends only on r_{ij} [cf. Eq. (1b)], one notices here that the parameters that must be specified are the γ_{ij} and the r_{ij} . Now, recent work by Clementi *et al.*⁷ has indicated that the most stable form of the water dimer is that in which the oxygen of the first hydrogen-bonded water molecule is located in the plane defined by the second water molecule. We display a representative, average-dimer structure in Fig. 3.

In this figure, R_{OH} corresponds to the equilibrium OH bond length in water (fixed here at 0.957 Å), and ϕ_{HOH} corresponds to the equilibrium HOH angle (fixed at 104.52°). The angle γ_{12} is then determined as

$$\gamma_{12} = \phi_{HOH}/2 - \theta + \xi, \quad (28)$$

where θ is defined to be less than zero for the case in which the second water molecule lies above the line defined by O_1 and H_{12} (as displayed in Fig. 3), greater than zero for the case where the second water molecule is below the line defined by O_1 and H_{12} , and equal to zero if O_2 , O_1 , and H_{12} are colinear. We note that the xy plane bisects the HOH angle of the second water molecule, and that the dipole moment vector ω_2 is

$$\frac{\epsilon-1}{\epsilon+2} - \frac{4\pi\rho\alpha}{3} = \frac{4\pi\rho\beta}{9} \left\langle \left\{ \begin{array}{c} \bullet \\ i \end{array} \right\} \right.$$

$$+ \left\{ \left[\sum_{s=1}^N \begin{array}{c} \bullet \quad \bullet \\ i \quad s \\ | \quad | \\ \text{---} \end{array} \right] - \alpha \left[\sum_s \left(\sum_{q \neq s} \left[\begin{array}{c} \bullet \quad \bullet \\ s(i) \quad q \\ | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \\ s \quad q(i) \\ | \quad | \\ \text{---} \end{array} \right] + \sum_{j \neq i} \left[\begin{array}{c} \bullet \quad \bullet \\ i(s) \quad j \\ | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \\ i \quad j(s) \\ | \quad | \\ \text{---} \end{array} \right] \right) \right] \right\}$$

$$+ \alpha^2 \left\{ \sum_s \left(\sum_{q \neq s} \sum_{r \neq q} \left[\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i(q) \quad s(r) \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ s \quad r(s,i) \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad r(i) \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad r(s) \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ s \quad r \quad s(i) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ q \quad r \quad i \\ | \quad | \quad | \\ \text{---} \end{array} \right) \right.$$

$$+ \sum_{j \neq i} \sum_{k \neq j} \left[\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i(k) \quad s(j) \quad (s,i)k \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ (s,i)k \quad j \quad (s)k \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad k(i) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad k \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i(s) \quad j \quad k(j,s) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ s \quad j \quad k \\ | \quad | \quad | \\ \text{---} \end{array} \right] \right.$$

$$+ \left\{ -\alpha \left[\sum_s \left(\sum_{q \neq s} \left[\begin{array}{c} \bullet \quad \bullet \\ s \quad q \\ | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \\ i \quad j \\ | \quad | \\ \text{---} \end{array} \right] \right) + \alpha^2 \left[\sum_s \left(\sum_{q \neq s} \sum_{r \neq q} \left[\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ q \quad r(i) \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ q \quad r(s) \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ q \quad r \quad s(i) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad r(i) \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad r(s) \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ s \quad r \quad s(i) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ q \quad r \quad i \\ | \quad | \quad | \\ \text{---} \end{array} \right) \right.$$

$$+ \sum_{j \neq i} \sum_{q \neq s} \left[\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad s \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad s \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad s \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad q \\ | \quad | \quad | \\ \text{---} \end{array} \right] \right\} \right.$$

$$+ \left\{ \alpha^2 \left[\sum_s \left(\sum_{q \neq s} \sum_{r \neq q} \left[\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ s \quad r \quad s(i) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ q \quad r \quad i \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad r(i) \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad r(s) \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ s \quad r \quad s(i) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ q \quad r \quad i \\ | \quad | \quad | \\ \text{---} \end{array} \right) \right.$$

$$+ \sum_{j \neq i} \sum_{k \neq j} \left[\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad k \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad k \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad k \\ | \quad | \quad | \\ \text{---} \end{array} \right] + \sum_{j \neq i} \sum_{q \neq s} \left[\begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad s \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad s \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad q \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad s \quad i(q) \\ | \quad | \quad | \\ \text{---} \end{array} + \begin{array}{c} \bullet \quad \bullet \quad \bullet \\ i \quad j \quad q \\ | \quad | \quad | \\ \text{---} \end{array} \right] \right\} \right\} \rangle_0$$

FIG. 2. The resummed diagrammatic expansion of the expression $(\epsilon-1)/(\epsilon+2) - \frac{4}{3}\pi\rho\alpha$ in terms of the polarizability α , organized in terms of 1-, 2-, 3-, ..., n -body contributions.

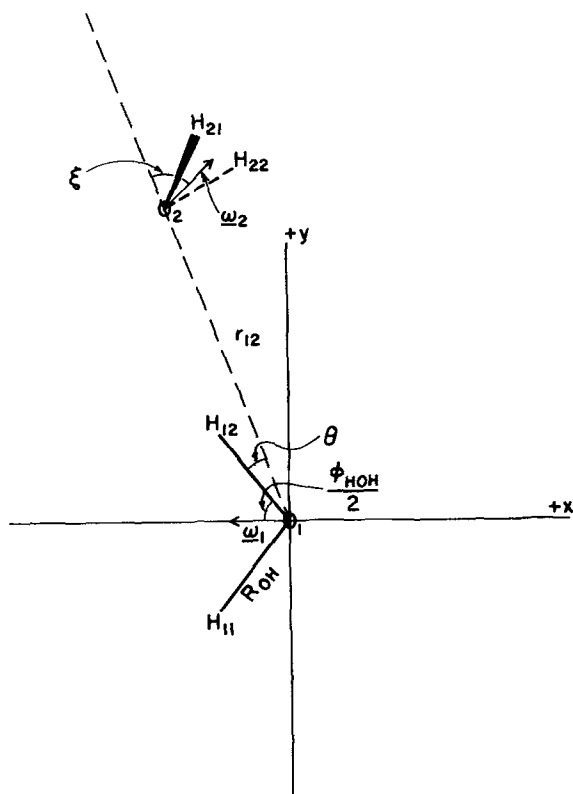


FIG. 3. The average-dimer structure (ADS) of water.

wholly contained within this plane. The plane of the second water molecule is aligned perpendicular to the plane of the first one; this fixes the angle of rotation about ω_2 . Finally, ξ is the angle between the line defined by O_1 and O_2 , and the vector ω_2 , and is positive always, as is evident from Fig. 3.

At a given temperature, we construct the ADS in the following way. First, we fix r_{12} by examining the position of the first maximum of the oxygen-oxygen pair-correlation function g_{OO} . Then, by examining the positions of the first and second maxima of the oxygen-hydrogen pair correlation function g_{OH} , we can determine the radii $R_{O_2H_{12}}$ and $R_{O_2H_{11}}$. The location of O_2 (and hence the angle θ) can be determined by finding the common point of intersection of these three radii, in particular, the first with origin at O_1 with length r_{12} , the second with origin at H_{12} with length $R_{O_2H_{12}}$, and the third with origin at H_{11} with length $R_{O_2H_{11}}$. Finally, using the positions of the first maximum of the hydrogen-hydrogen pair-correlation function g_{HH} , the second maximum in g_{OH} , and the value of R_{OH} (all in projection on the xy plane), the angle ξ can be determined in the same manner as the angle θ .

An examination of the correlation functions g_{OO} , g_{OH} , and g_{HH} reveals that the various maxima cannot be located with absolute certainty. Hence, we identify a range of probable θ and ξ values, and then determine an angle γ_{12} consistent with these choices of θ and ξ .⁸ For a given γ_{12} and a specific choice of θ and ξ , the angles γ_{12} , θ , ξ are used to generate, starting from the ADS, the local structure of a water cluster containing five water molecules. (In this study, only a central water molecule and four nearest neighbors are considered explicitly—see the remarks in Sec. V). We then utilize Eq. (15), developed to fourth order in α , to construct a [2, 2]-Padé approximant to the infinite series,⁹ Eq. (15). The above procedure is repeated (different choices of the angles θ and ξ are assumed), until for a specific choice of γ_{12} , the dielectric constant calculated via the [2, 2]-Padé approximant is in agreement with the value determined experimentally at the given temperature. It is for this resultant, optimized geometry of a five water molecule cluster, that we estimate the intermolecular polarization contribution to the static dielectric constant.

Using the pair-correlation function data of Clementi *et al.*¹⁰ (generated using the HFK potential function), we find that at a temperature of 298 °K, the most probable θ values are in the range $-7.5^\circ \pm 2^\circ$, and the most probable ξ values are in the range $64^\circ \pm 14^\circ$; the most probable values of the angle γ_{12} , determined using the above estimates of θ and ξ , are in the range $123^\circ \pm 16^\circ$. The optimal values of γ_{12} have been determined for several choices of θ ; these values are listed in Table I, along with the attendant values of M^2/N , αA_1 , $\alpha^2 A_2$, $\alpha^3 A_3$ and $\alpha^4 A_4$. These results indicate that the optimal values of γ_{12} as well as the rest of the tabulated quantities are not very sensitive to variations in θ over the range of θ considered. It can be noted further that for the range of θ and ξ considered, the series representation of Eq. (15) seems to be converging very rapidly. The magnitude of successive terms in Eq. (15) decreases sequentially by (at least) a factor of three; thus, the $\alpha^4 A_4$ term is only 0.8% as large as the leading term in the expansion.

The results described in the preceding paragraph are displayed graphically in Figs. 4–10. Figure 4 illustrates the sensitivity of the rigid-dipole contribution to Eq. (15) to variations in θ and ξ . We note that this contribution is relatively insensitive to changes in θ , but changes dramatically with changes in the angle ξ (a value of -2.0 for large ξ , to about -0.4 for small ξ). Figures 5–8 illustrate the sensitivity of αA_1 , $\alpha^2 A_2$, $\alpha^3 A_3$, and $\alpha^4 A_4$ to variations in θ and ξ , and

TABLE I. ^aOptimal angles and the corresponding components of the static dielectric constant.

θ	ξ	γ_{12}	αA_1	$\alpha^2 A_2$	$\alpha^3 A_3$	$\alpha^4 A_4$	M^2/N
-5.5	56.265410	114.025405	-0.594010	0.187407	-0.031860	0.004755	-0.628567
-6.5	55.251470	114.011465	-0.593548	0.187009	-0.031843	0.004747	-0.627678
-7.5	54.226150	113.986145	-0.592710	0.186287	-0.031812	0.004732	-0.626063
-8.5	53.189300	113.949295	-0.591485	0.185239	-0.031768	0.004710	-0.623712
-9.5	52.140750	113.900745	-0.589867	0.183865	-0.031708	0.004682	-0.620614

^a $\epsilon = 78.54$.

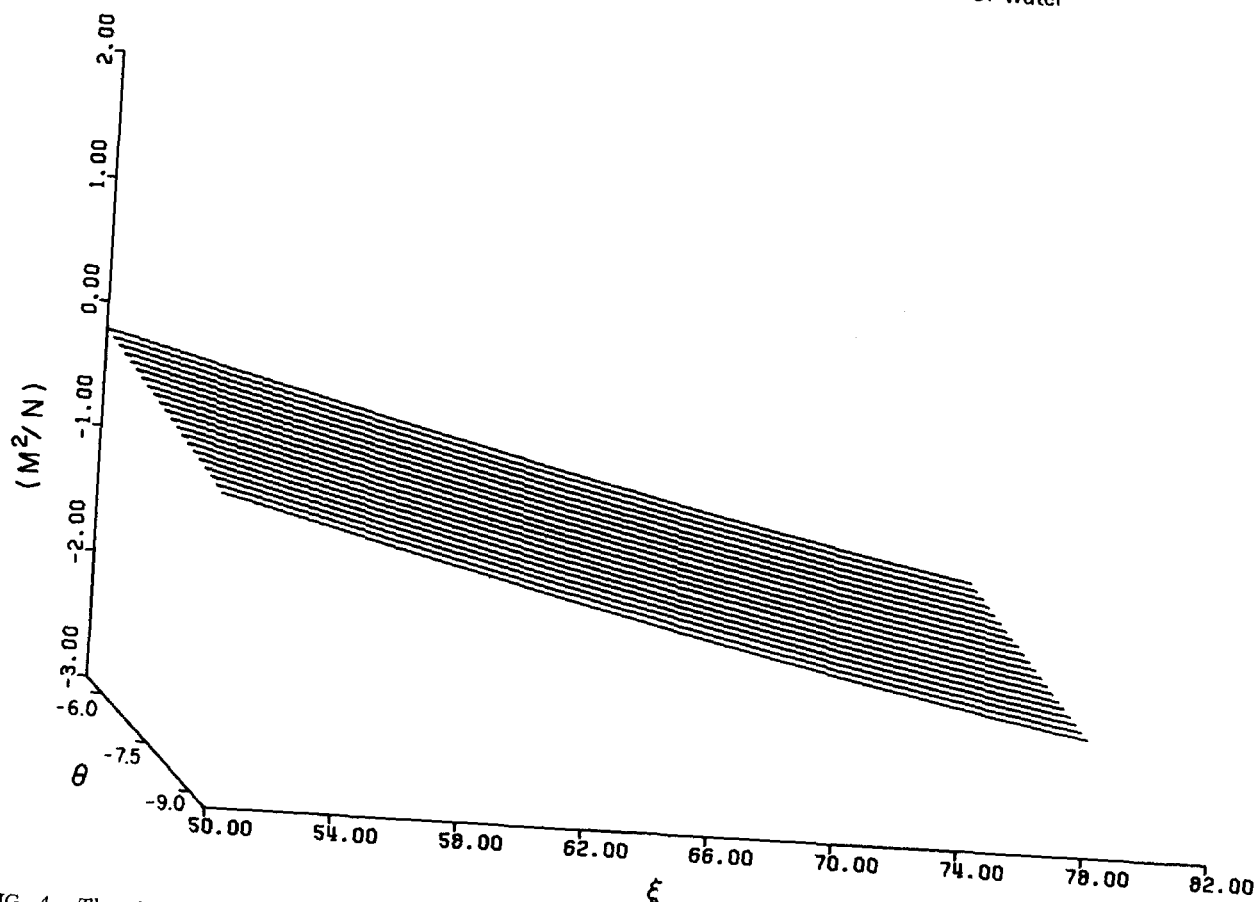


FIG. 4. The rigid-dipole contribution (M^2/N) as a function of θ and ξ .

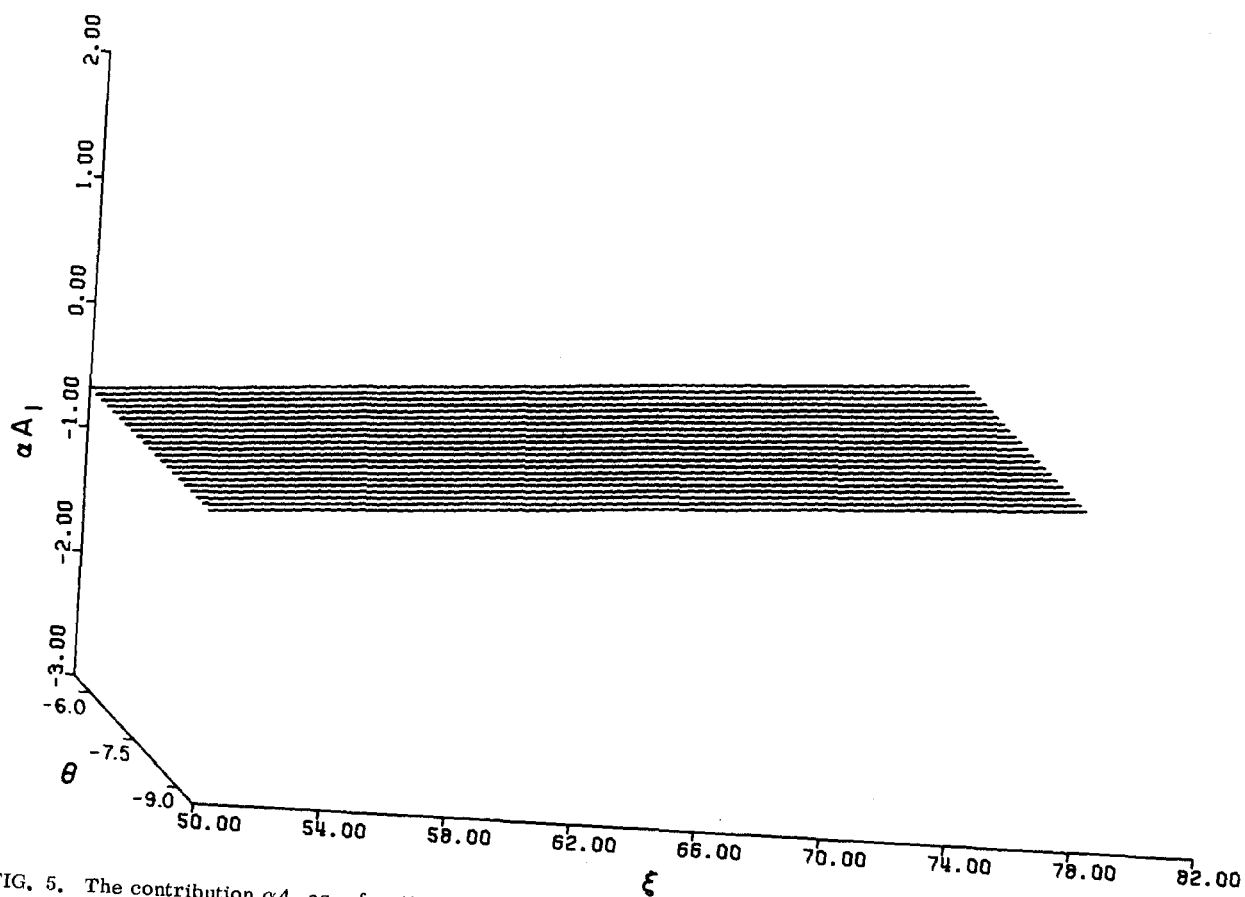


FIG. 5. The contribution αA_1 as a function of θ and ξ .

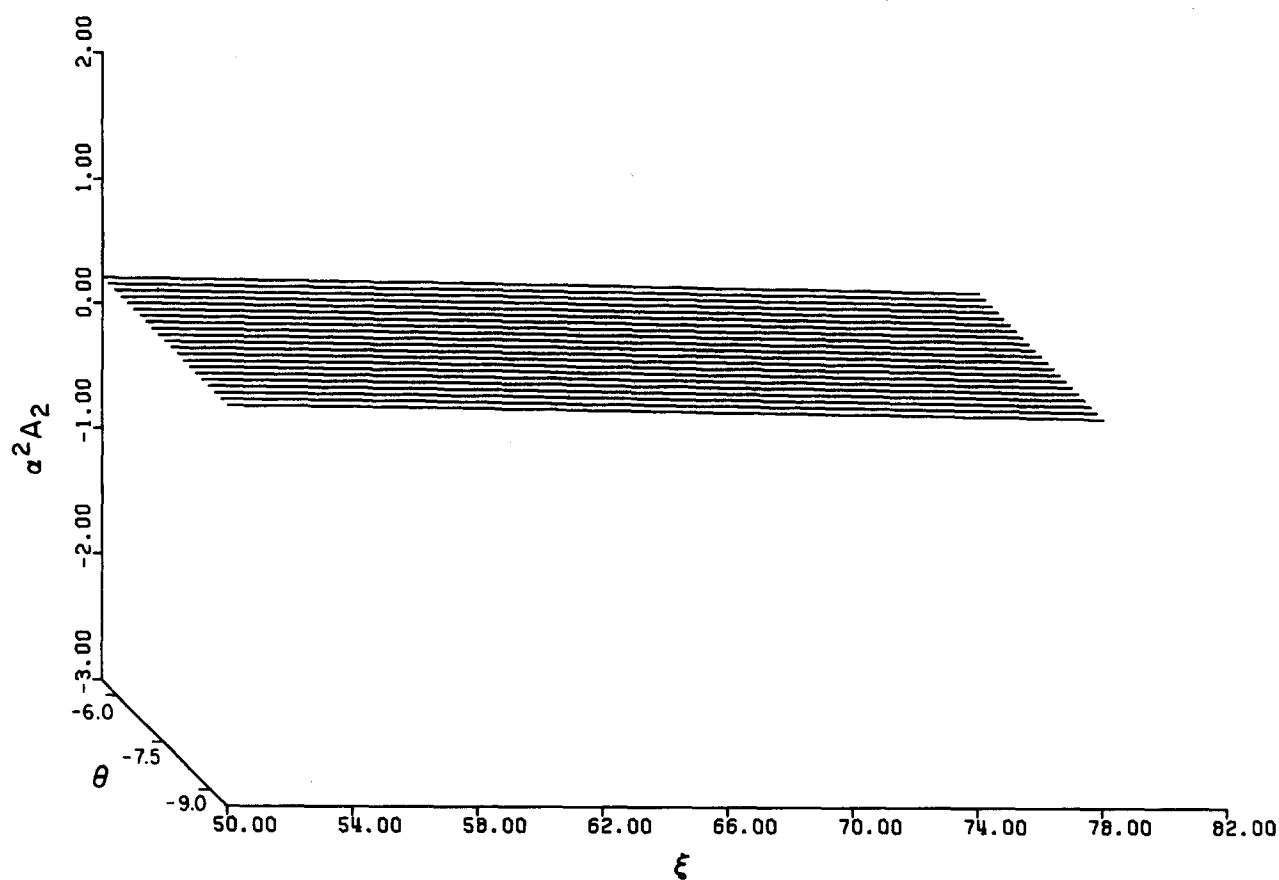


FIG. 6. The contribution $\alpha^2 A_2$ as a function of θ and ξ .

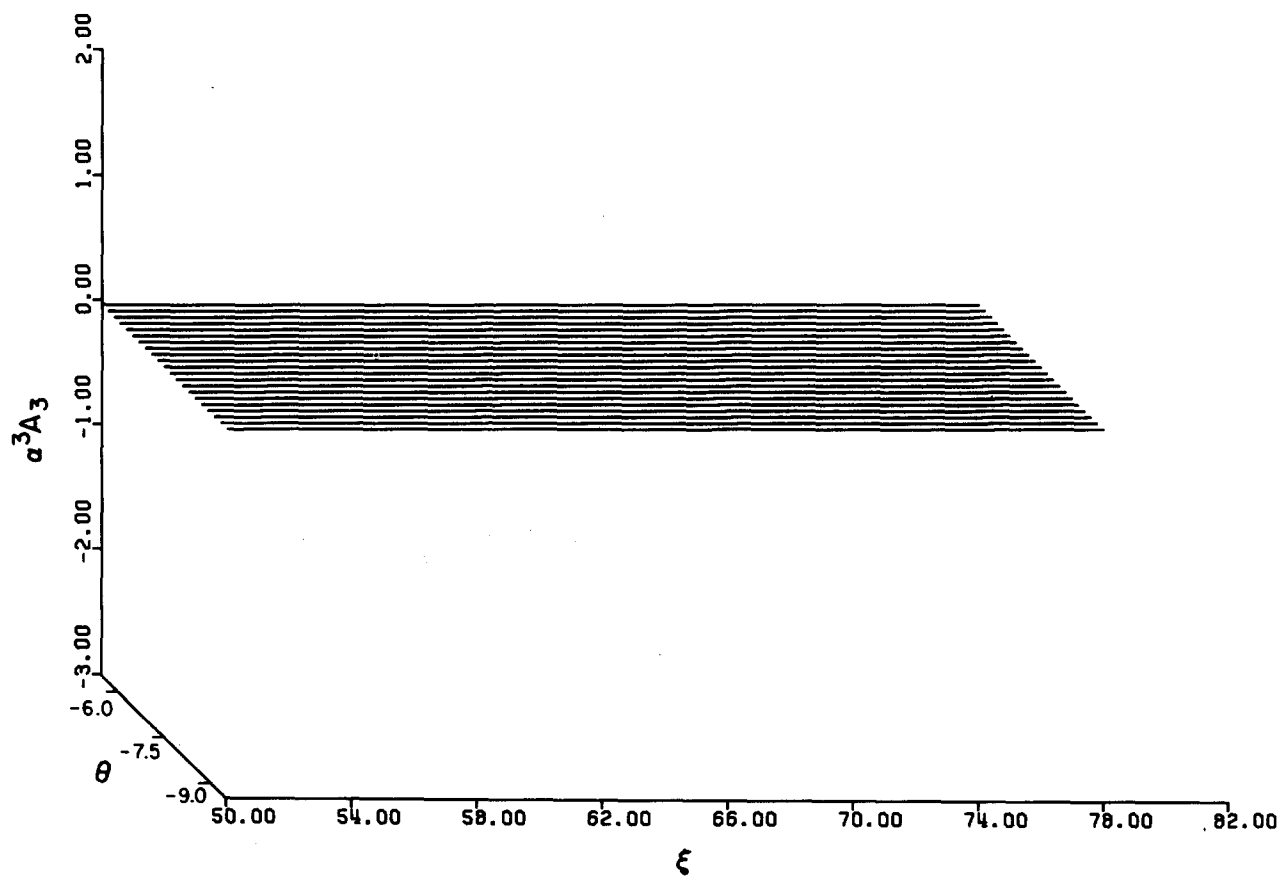


FIG. 7. The contribution $\alpha^3 A_3$ as a function of θ and ξ .

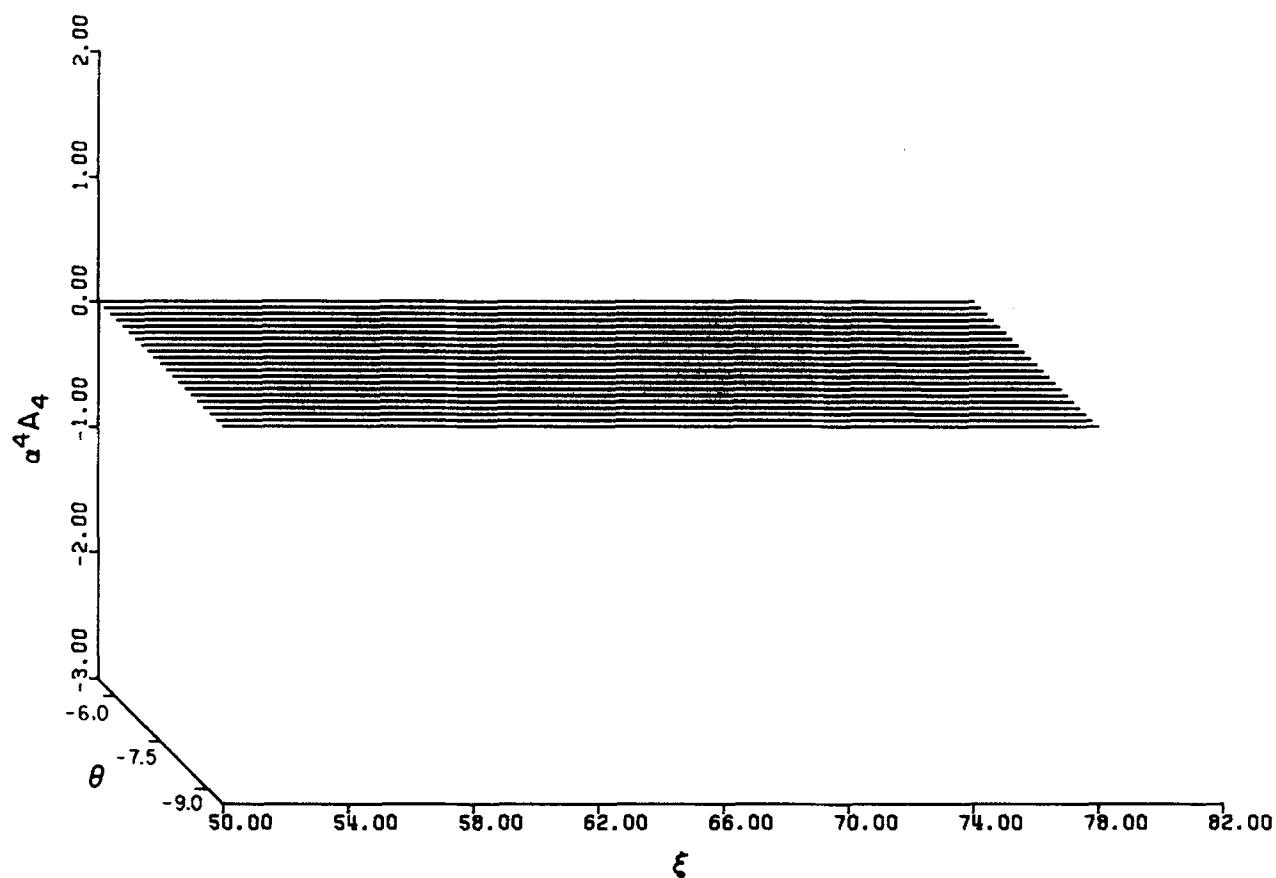


FIG. 8. The contribution $\alpha^4 A_4$ as a function of θ and ξ .

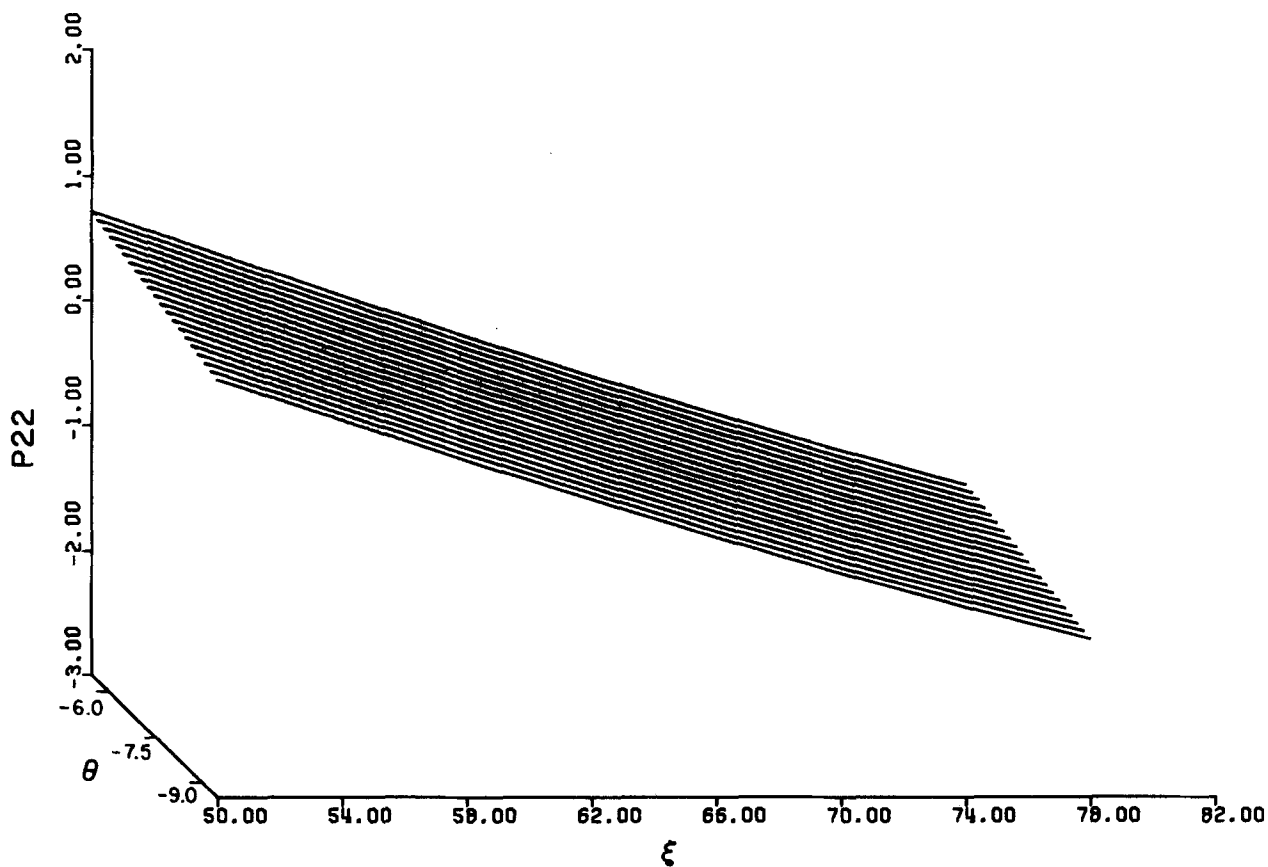
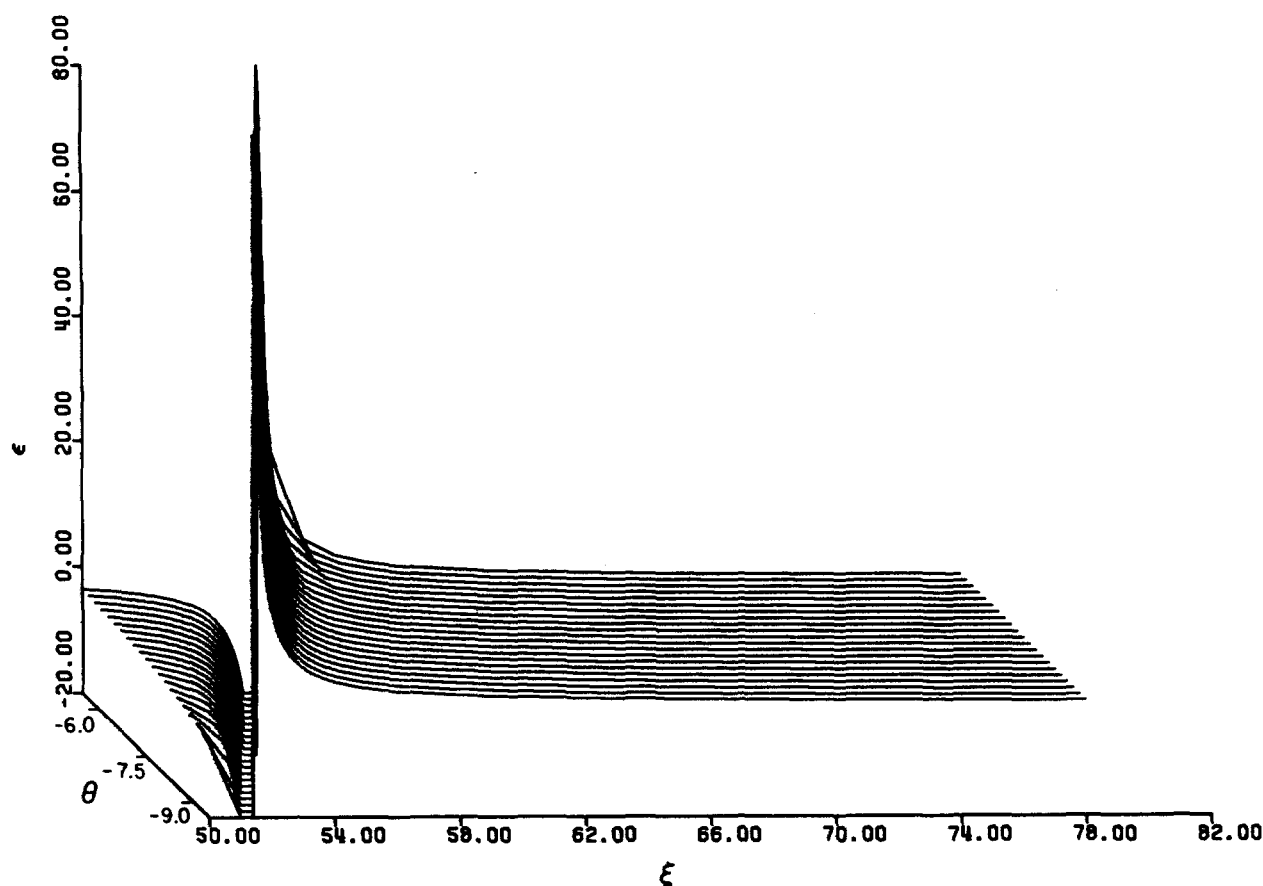


FIG. 9. The 2,2-Padé approximant to Eq. (15) as a function of θ and ξ .

FIG. 10. The dielectric constant ϵ as a function of θ and ξ .

reveal clearly the insensitivity of these components to changes in θ . In fact, compared to the variations in the rigid-dipole contribution with change in angle, the components αA_1 , $\alpha^2 A_2$, $\alpha^3 A_3$, and $\alpha^4 A_4$ may be regarded as θ -independent. We note further that the components $\alpha^3 A_3$ and $\alpha^4 A_4$ are essentially constant over the range of θ and ξ considered, with the component $\alpha^2 A_2$ varying only slightly in this range. On the other hand, the component αA_1 has a definite dependence on ξ , although this dependence is not nearly as pronounced as the variation with ξ exhibited by the rigid-dipole term.

In Fig. 9 we illustrate the over-all sensitivity of the $[2, 2]$ -Padé approximant to variations in the angles θ and ξ over the range considered. In addition, results for intermediate and more extreme choices of θ and ξ are presented in Table II, and it is seen that the $[2, 2]$ -Padé approximant is well behaved for all choices of θ and ξ considered.

In Fig. 10 the sensitivity of the static dielectric constant ϵ per se to variations in the angles θ and ξ is presented,¹¹ and in Fig. 11 the sensitivity of the total polarization contribution to the static dielectric constant

TABLE II. ϵ components and corresponding Padé approximants for extreme choices of θ and ξ .

θ	ξ	γ_{12}	M^2/N	αA_1	$\alpha^2 A_2$	$\alpha^3 A_3$	$\alpha^4 A_4$	P22
-5.5	53.0	110.760	-0.41782	-0.64529	0.19948	-0.034304	0.0051554	0.46727
-5.5	63.0	120.760	-1.04577	-0.48810	0.16083	-0.026943	0.0039208	-0.36535
-5.5	73.0	130.760	-1.61157	-0.33870	0.11896	-0.020366	0.0027153	-1.13049
-6.5	53.0	111.760	-0.48288	-0.62828	0.19498	-0.033498	0.0050140	0.37972
-6.5	63.0	121.760	-1.10545	-0.47370	0.15762	-0.026278	0.0038160	-0.44342
-6.5	73.0	131.760	-1.66405	-0.32701	0.11701	-0.019834	0.0026448	-1.19722
-7.5	53.0	112.760	-0.54749	-0.61127	0.19044	-0.032696	0.0048725	0.29259
-7.5	63.0	122.760	-1.16449	-0.45934	0.15437	-0.025616	0.0037110	-0.52086
-7.5	73.0	132.760	-1.71572	-0.31536	0.11502	-0.019305	0.0025742	-1.26311
-8.5	53.0	113.760	-0.61163	-0.59430	0.18585	-0.031901	0.0047312	0.20592
-8.5	63.0	123.760	-1.22286	-0.44501	0.15107	-0.024960	0.0036060	-0.59764
-8.5	73.0	133.760	-1.76656	-0.30377	0.11301	-0.018780	0.0025038	-1.32816
-9.5	53.0	114.760	-0.67527	-0.57736	0.18123	-0.031113	0.0045900	0.11976
-9.5	63.0	124.760	-1.28056	-0.43073	0.14774	-0.024311	0.0035010	-0.67372
-9.5	73.0	134.760	-1.81655	-0.29225	0.11097	-0.018260	0.0024334	-1.39232

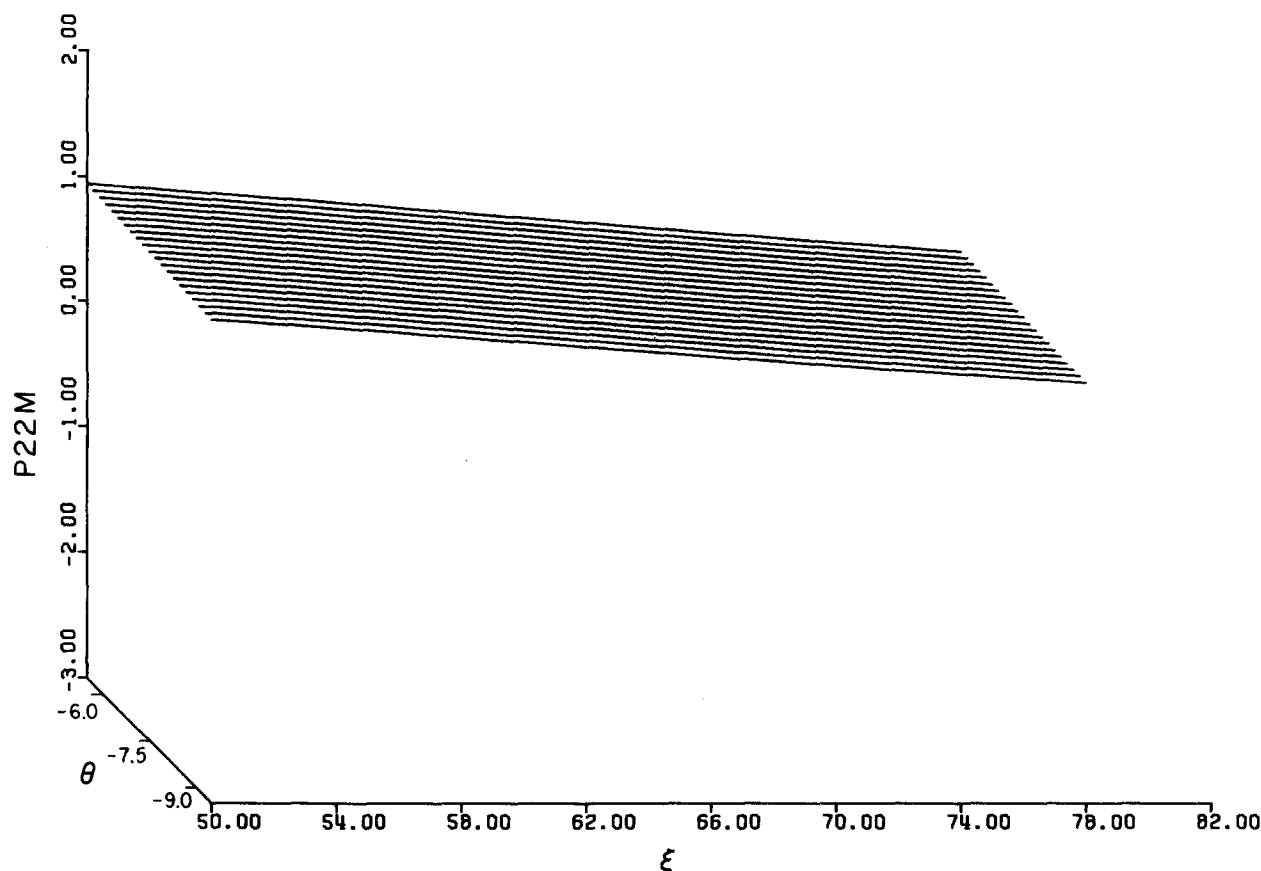


FIG. 11. The total intermolecular polarization contribution to the static dielectric constant (the full [2,2]-Padé, less the rigid-dipole contribution) as a function of θ and ξ .

(i. e., the full Padé value, less the rigid-dipole contribution) is displayed as a function of θ and ξ . In Table III we record the effect of more extreme choices of θ and ξ on the total intermolecular polarization contribution; once again the insensitivity of the intermolecular polarization with respect to variations in the angles θ and ξ is apparent (see also Fig. 11).

TABLE III. Rigid dipole and total intermolecular polarization contributions for extreme values of θ and ξ .

θ	ξ	γ_{12}	M^2/N	Sum ^a	$P22M^b$
-5.5	53.0	110.760	-0.41782	0.88423	0.88509
-5.5	63.0	120.760	-1.04577	0.67979	0.68042
-5.5	73.0	130.760	-1.61157	0.48074	0.48107
-6.5	53.0	111.760	-0.48288	0.86177	0.86260
-6.5	63.0	121.760	-1.10545	0.66142	0.66203
-6.5	73.0	131.760	-1.66405	0.46650	0.46683
-7.5	53.0	112.760	-0.54749	0.83928	0.84008
-7.5	63.0	122.760	-1.16449	0.64303	0.64363
-7.5	73.0	132.760	-1.71572	0.45227	0.45260
-8.5	53.0	113.760	-0.61163	0.81678	0.81755
-8.5	63.0	123.760	-1.22286	0.62464	0.62522
-8.5	73.0	133.760	-1.76656	0.43806	0.43840
-9.5	53.0	114.760	-0.67527	0.79429	0.79503
-9.5	63.0	124.760	-1.28056	0.60628	0.60684
-9.5	73.0	134.760	-1.81655	0.42391	0.42424

^aSum = $-\alpha A_1 + \alpha^2 A_2 - \alpha^3 A_3 + \alpha^4 A_4$.

^b $P22M = P22 - M^2/N$ = total intermolecular polarization contribution.

V. DISCUSSION

From the results of the numerical studies presented in the preceding section, it is clear that the intermolecular polarization contribution is of crucial importance in determining the static dielectric constant of water. To document this further, we have recorded in Table IV the rigid-dipole and intermolecular polarization contributions to the static dielectric constant for the optimal choices of γ_{12} deduced in our study. It is seen that the polarization contribution is larger in magnitude than the rigid-dipole contribution by a factor of ~ 1.5 . Also, over the entire range of θ and ξ considered, the intermolecular polarization contribution is always opposite in sign (it is always positive) relative to the rigid-dipole contribution. It is evident, then, that the *magnitude* of the static dielectric constant of pure water is the outcome of a competition be-

TABLE IV. Rigid dipole and total intermolecular polarization contributions for optimal values of θ and ξ .

θ	ξ	γ_{12}	M^2/N	$P22M^a$
-5.5	56.2654	114.0254	-0.6286	0.8188
-6.5	55.2515	114.0115	-0.6277	0.8179
-7.5	54.2262	113.9861	-0.6261	0.8163
-8.5	53.1893	113.9493	-0.6237	0.8140
-9.5	52.1408	113.9007	-0.6206	0.8109

^a $P22M = P22 - M^2/N$ = total intermolecular polarization contribution.

tween two contributions of approximately the same magnitude but opposite in sign.

We have also noted that the intermolecular polarization contribution is relatively insensitive to variations in θ and ξ , as compared to the rigid-dipole contribution (see Figs. 11 and 4, respectively). Thus, although the *magnitude* of the dielectric constant is determined by the relative magnitudes of the polarization and the rigid-dipole terms, any variation in the structure of the basic complex would seem to have a more significant effect on the rigid-dipole contribution than on the polarization contribution. This may be the reason why Pople obtained qualitative agreement for ϵ as a function of temperature but less good agreement for the value of ϵ at a given temperature.

From the preceding remarks it is clear that a successful calculation of the static dielectric constant of water depends on a rather delicate cancellation of two factors. To appreciate more fully the implications of this remark, consider the surface displayed in Fig. 10. In this figure it is seen that the static dielectric constant ϵ is *less* than zero for all values of ξ except those in the range $50^\circ \leq \xi \leq 58^\circ$. Moreover, for certain values of θ , even for ξ in the range $50^\circ \leq \xi \leq 58^\circ$, the static dielectric constant is negative—indeed, it appears to be tending to $-\infty$. Alternatively, for other choices of θ , but ξ in the range $50^\circ \leq \xi \leq 58^\circ$, ϵ appears to be tending to $+\infty$. This extreme sensitivity of ϵ to variations in θ and ξ can be traced back to Eq. (14). If we denote

$$R = \frac{4\pi\rho}{3} \left\{ \alpha + \frac{\beta}{3} \left\langle \mathbf{p}_i^0 \cdot \sum_{s=1}^N \mathbf{p}_s^0 \right\rangle_0 \right\}$$

then Eq. (14) can be rearranged to yield

$$\epsilon = (2R + 1)/(1 - R). \quad (29)$$

Note that if $R = 1 + \delta$ approaches unity from above (i. e., $\delta_+ \rightarrow 0$) then ϵ will tend to $-\infty$, whereas if R approaches unity from below ($\delta_- \rightarrow 0$) ϵ will tend to $+\infty$. Now, using the experimental value of ϵ , a simple calculation shows that $R = 0.9628$ at $T = 298^\circ\text{K}$ and, as our numerical studies show, even *trivial* departures from this value of R can lead to enormous discrepancies between calculated and observed values of ϵ . Two factors evidently contribute to this delicate dependence of ϵ on R : (i) our explicit use of the Lorentz field¹²

$$\mathbf{E}_0 = \frac{1}{3}(\epsilon + 2)\mathbf{E},$$

and (ii) the structure of the molecular complex assumed in the calculation of Eq. (29). If, however, one adopts the point of view that the static dielectric constant should be independent of the shape of the macroscopic sample (and hence that the assumption of spherical symmetry should not be crucial in developing a theory of the dielectric constant), it would appear that the success or failure of a theory of the dielectric constant hinges directly on an accurate determination of the basic cluster geometry.

We now consider the extent to which the above conclusions are dependent on the size of cluster assumed in our analysis—one central water molecule surrounded

by four neighboring water molecules. At first sight, the assumption of only first-shell coupling would seem to limit the usefulness of the analysis in that n -body effects ($n \geq 3$) are regarded as being negligible. In order that $\langle \omega_i \cdot \omega_s \rangle_0 \cong 0$ for an s molecule not contained in the first hydration sphere, there can be no significant angle-dependent interactions between the central molecule i and molecule s . In terms of our diagrammatic analysis, this approximation implies that all diagrams with three or more vertices can be ignored, along with all two-vertex diagrams for which the distance between molecular centers r_{is} is greater than r_{12} . Numerical calculations of several diagrams of this type indicate this approximation to be reasonable. The results reported in Fig. 12 indicate that the two-body (two-vertex) diagrams with $r_{is} \leq r_{12}$ are of primary importance in the multibody expansion of ϵ .

The above comments have direct bearing on some predictions derived from the recent molecular dynamics studies of Stillinger and Rahman on water.¹³ These authors simulated water using the ST2 potential. One result of these simulations was an estimate of $\langle M^2/N \rangle_0$; they determined a value of about 0.15 at 283°K and 0.16 at 303°K . Within the framework of our approach, we note that the ST2 value for $\langle M^2/N \rangle_0$ of about 0.15 implies that γ_{12} is about 102.26° . From an examination of the results presented in Table V, we find that for all choices of θ and ξ which yield a value of 102.26° , the intermolecular polarization contributions are positive (as is $\langle M^2/N \rangle_0$), and large relative to $\langle M^2/N \rangle_0$. Thus, the cancellation in terms necessary to produce the correct value of ϵ does not occur, and the predicted value of ϵ is in disagreement with the experimental value. This result suggests, at least for the problem under study, that the ST2 potential is not describing angular correlations adequately. The origin of the difficulty can be determined by examining the variation in energy as a function of the angle γ_{12} , as predicted by the ST2







DIAGRAM	VALUE / μ^2
	$-4.065 \times 10^{-1} \text{ a}$
	$-5.571 \times 10^{-2} \text{ b}$
	1.033×10^{-2}
	-3.404×10^{-3}
	-8.980×10^{-4}
	$1.536 \times 10^{-2} \text{ c}$

FIG. 12. Representative diagrams and their values for a geometry optimized at $\theta = -7.5^\circ$: (a) dipole-dipole bond, (b) dipole-field bond, (c) dipole-field bond for $r_{is} > r_{12}$.

TABLE V. ^aThe static dielectric constant and its components for the ST2 predicted structure.

θ	ξ	M^2/N	$P22M^b$	ϵ
-5.5	44.50	0.15061	1.04786	-9.483
-6.5	43.50	0.15061	1.04073	-9.618
-7.5	42.50	0.15061	1.03151	-9.801
-8.5	41.50	0.15061	1.02123	-10.015
-9.5	40.50	0.15061	1.00990	-10.265

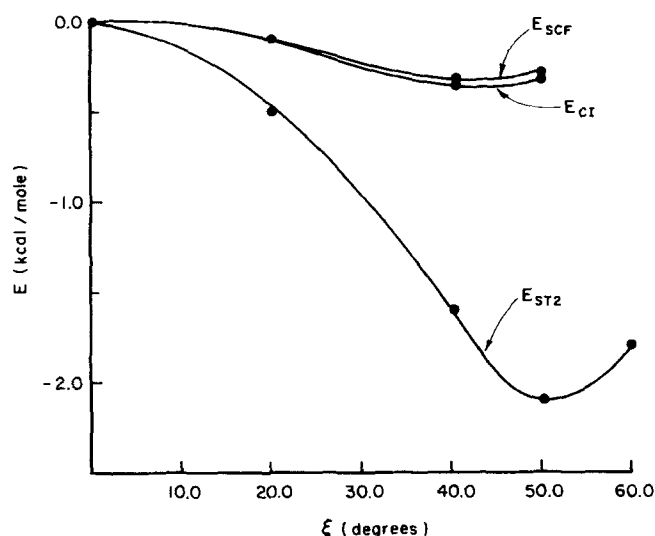
^a $\gamma_{12} = 102.26^\circ$.^b $P22M = P22 - M^2/N$ = total intermolecular polarization contribution.

potential. For convenience in our calculations, we choose $(\theta, \xi) = (0, 0)$ as defining the zero of energy. The results obtained in our variational study are recorded in Table VI and illustrated in Fig. 13. Also included in Table VI and Fig. 13 are some recent Hartree-Fock SCF calculations (designated E_{SCF}) and configuration interaction (CI) calculations (designated E_{CI}) on the water dimer by Dierksen *et al.*¹⁴ It is immediately apparent that the ST2 potential is much too binding for variations in γ_{12} , when compared to the "exact" results of the CI calculation. It is our belief that this augmented attractiveness in the ST2 potential is due to the absence of any angular-dependent, short-range repulsive potentials in the ST2 function (the *only* short-range repulsive potential in the ST2 function is the spherically symmetric, Lennard-Jones contribution), and that it is the absence of angular-dependent, short-range repulsive contributions which forces the ST2 potential to predict an angle γ_{12} of 102.26° . Further, we note that the minimum in the curve of energy versus ξ occurs at the value $\gamma_{12} \cong 102.7^\circ$ (a value not significantly displaced from the value $\gamma_{12} \cong 102.26^\circ$ computed above), whereas the CI studies indicate that such extreme localization of the angle ξ might not be possible. Apparently, allowing a certain flexibility in ξ ensures that the local structure defining a cluster will not be frozen into unfavorable angular configurations.

The main point to be drawn from the remarks presented in preceding paragraph, and indeed one of the

TABLE VI. ST2, SCF, and CI energies as functions of ξ .

ξ (Deg)	E_{ST2}^a	E_{SCF}^b	E_{CI}
0	0.0	0.0	0.0
20	-0.5	-0.19	-0.20
40	-1.6	-0.31	-0.35
50	-2.1	-0.28	-0.32
60	-1.8		

^aEnergies are in kcal/mole.^b $R_\infty = 2.85 \text{ \AA}$ and $\phi_{HOH} = 10.947^\circ$ for E_{ST2} while $R_\infty = 3.0 \text{ \AA}$ and $\phi_{HOH} = 104.52^\circ$ for E_{SCF} and E_{CI} . An examination of the data of Clementi *et al.*^{7a} indicates that these apparent inconsistencies do not significantly affect the results displayed in this table and in Fig. 13.FIG. 13. The variation with respect to ξ of the energy of the water dimer as determined from the ST2 potential (E_{ST2}), SCF calculations (E_{SCF}) and CI calculations (E_{CI}).

main conclusions of this paper, is that the static dielectric constant is an extremely sensitive measure of the reliability of a given potential energy function. One might go further here and suggest that although progress in the *theory* of the dielectric constant has advanced considerably in recent years, a successful application of the theory to the fluid water is dependent on the availability of reliable geometrical data derived from molecular-structure calculations. In a subsequent contribution we shall attempt to assess the extent to which this conclusion is dependent on the assumption that the molecular polarizability of water may be regarded as isotropic. In a preliminary way here, we can examine the polarizability tensor of water as calculated by Liebmann and Moskowitz.¹⁵ They obtained the result

$$A = \begin{vmatrix} 1.23 & 0 & 0 \\ 0 & 1.65 & 0 \\ 0 & 0 & 1.45 \end{vmatrix},$$

which can be represented as

$$A = \alpha \begin{vmatrix} 0.85 & 0 & 0 \\ 0 & 1.14 & 0 \\ 0 & 0 & 1.0 \end{vmatrix}$$

with $\alpha = 1.45 \text{ \AA}^3$. Although we believe, on the basis of this data, that the assumption of isotropic molecular polarizability for the substance water is not unreasonable, detailed calculations will be reported in the near future to assess the validity of this approximation.

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APPENDIX

The procedure used to generate the local water structure is as follows.

1. The Central Water Molecule and the First Neighbor

A choice of $(\theta, \xi, \gamma_{12})$ is used to generate the ADS.

2. The Second Neighbor

The ADS is reflected across the xz plane.

3. The Third Neighbor

The ADS is rotated clockwise about the x axis (looking down the positive axis toward the origin) by 90° . The rotated ADS is translated so that the O_2 is at the origin. Then, the resultant structure is rotated clockwise about the y axis (looking down the negative y axis toward the origin) through an angle of $(\gamma_{12} - \pi)$ degrees.

4. The Fourth Neighbor

The third molecule is reflected across the xy plane.

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¹¹In this figure, if ϵ is less than -20 , the ϵ is set equal to -20 ; if ϵ is greater than 80 , the ϵ is set equal to 80 . This convention is adopted for convenience in plotting and does not alter the basic structure of the surface.

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