Effective Pair Interactions in Liquids.   Water

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A variational principle is proposed to determine an optimal "effective pair potential" v in liquids whose molecules actually experience nonadditive interactions. A formal perturbation method is outlined which in principle determines v iteratively. On account of the temperature and density dependence of v, and because this function contains a weak "tail" of macroscopic range, the usual statistical-mechanical expressions for energy, pressure, and isothermal compressibility suffer fundamental changes. The theory is applied to water, and tentative conclusions are offered about the way that the bare two-molecule potential differs from the liquid phase v for this substance.

I.   Introduction

It is conventional to use pairwise-additive potentials in developing the formal theory of the liquid state.[1] This tactic apparently preserves most qualitative features of the observed properties of real liquids. It is also justified by the remarkable simplicity of expressions for thermodynamic energy and pressure that result from the pair potential assumption. Nowadays, electronic computer simulation of liquids[2,3] has become routine, and in that context pairwise-additive potentials again prove convenient.

Unfortunately, there is evidence that the pairwise-additivity assumption commits significant quantitative errors even for nonpolar substances.[4] Surely the situation is even worse for polar materials and ionic fluids in which large fluctuating electric fields exist. It is therefore clear in the strict sense that precise statistical-mechanical theory of real liquids requires inclusion of many-body forces.

We shall demonstrate nevertheless that a rational procedure exists for selection of a "best" approximate pair potential which incorporates the average effects of nonadditive potentials. This "effective pair potential" satisfies a variational principle that has been selected by the requirement that the sum of effective pair interactions preserves all local order as well as possible. Our effective pair potential therefore differs in a fundamental way from the one advocated by Sinanoğlu,[5-7] which was designed previously to reproduce the thermodynamic energy.

The next section, II, introduces the fundamental variational principle, and displays a few general results that may be derived therefrom. Section III provides details of a formal perturbative method of constructing the effective pair potential. The modifications of standard statistical-mechanical formulas for energy, pressure, and compressibility that result from temperature and density dependence of the effective pair potential are listed in section IV.

On account of its fundamental importance in the physical and biological sciences, water has been selected here to illustrate the application of the effective potential concept. Section V is devoted to this one liquid, and conclusions are offered there about the way that the

(1) S. A. Rice and P. Gray, "The Statistical Mechanics of Simple Liquids," Interscience, New York, N. Y., 1965.

(2) W. W. Wood, *J. Chem. Phys.*, **48**, 415 (1968).

(3) B. J. Alder and T. E. Wainwright, *ibid.*, **33**, 1439 (1960).

(4) N. R. Kestner and O. Sinanoğlu, *ibid.*, **38**, 1730 (1963).

(5) O. Sinanoğlu, *Chem. Phys. Lett.*, **1**, 340 (1967).

(6) O. Sinanoğlu, *Advan. Chem. Phys.*, **12**, 283 (1967).

(7) T. Halcioğlu and O. Sinanoğlu, *J. Chem. Phys.*, **49**, 996 (1968).

effective interaction differs at both large and small distances from the "bare" pair potential for two molecules *in vacuo*.

The final discussion in section VI outlines other important substances to which the present concepts could fruitfully be applied. Also we mention there possible conditions under which the effective pair potential method would have substantial shortcomings.

II. General Relations

Although the quantum-mechanical generalization is straightforward, we shall use classical statistics throughout the following analysis.

For any liquid of interest, we suppose that N molecules are confined to the interior of a large, but finite, vessel with volume $\mathcal{V}$. The configuration of each molecule will be described by a vector $\mathbf{x}$ whose components comprise coordinates of the molecular center, and a set of angles to fix the molecular orientation. The free energy F for the liquid may in principle be obtained from the canonical partition function

$$\exp(-\beta F) = \frac{1}{N!}\left(\frac{\mathcal{V}Q_{\text{int}}(\beta)}{\Omega}\right)^N Z_N(\beta)$$

$$\beta = 1/kT; \quad \Omega = \int dx \qquad (2.1)$$

Here, Q_{int} is essentially the rotational–vibrational partition function for an isolated molecule, and Z_N is the N-molecule configuration integral.

We shall let $V_N(\mathbf{x}_1 \ldots \mathbf{x}_N)$ stand for the total potential of interaction among the N molecules in the specified configuration $\mathbf{x}_1 \ldots \mathbf{x}_N$. The classical configuration integral Z_N appearing in eq 2.1 hence may be written

$$Z_N(\beta) = \int dx \ldots \int dx_N \exp[-\beta V_N(\mathbf{x}_1 \ldots \mathbf{x}_N)] \quad (2.2)$$

Although we do not explicitly indicate them, the integration limits on the $\mathbf{x}_j$ are all finite, and depend upon the volume $\mathcal{V}$ for molecular center positions, and upon the specific choice of orientation angles. It is convenient to introduce now an inner product of two functions, $f(\mathbf{x}_1 \ldots \mathbf{x}_N)$ and $h(\mathbf{x}_1 \ldots \mathbf{x}_N)$, as the integral of their product with the same finite limits as used in eq 2.2.

$$\{f,h\} = \int dx_1 \ldots \int dx_N f(\mathbf{x}_1 \ldots \mathbf{x}_N) h(\mathbf{x}_1 \ldots \mathbf{x}_N) \quad (2.3)$$

In concordance with this definition, we can express Z_N as the inner product of a function with itself

$$Z_N(\beta) = \{\exp(-\tfrac{1}{2}\beta V_N), \exp(-\tfrac{1}{2}\beta V_N)\} \quad (2.4)$$

The generic functions and their inner product in eq 2.3 are quite analogous to ordinary vectors and the scalar product for pairs of such vectors. Indeed it is valid to regard functions f and h as infinite-dimensional vectors whose scalar product is given in eq 2.3. By the same token, eq 2.4 exhibits Z_N as the square of an infinite-dimensional vector. The square of the dis-

tance between two vectors (functions) f and h may also be expressed as an inner product

$$D^2(f,h) = \{f - h, f - h\} =$$

$$\int dx_1 \ldots \int dx_N [f(\mathbf{x}_1 \ldots \mathbf{x}_N) - h(\mathbf{x}_1 \ldots \mathbf{x}_N)]^2 \quad (2.5)$$

in complete analogy with ordinary vectors.

Our central problem in this paper consists in finding an optimal effective pair interaction $v(\mathbf{x}_i, \mathbf{x}_j)$ to represent the liquid which is actually subject to the very complicated nonadditive potential V_N. In the convention of eq 2.4, we seek to approximate Z_N by an inner product of the form

$$\left\{\exp\left[-\frac{1}{2}\beta \sum_{i<j=1}^N v(ij)\right], \ \exp\left[-\frac{1}{2}\beta \sum_{i<j=1}^N v(ij)\right]\right\} \quad (2.6)$$

The effective pair potential v clearly should be chosen to minimize the distance between the function–space vectors appearing in eq 2.4 and 2.6

$$D^2\{\exp[-\tfrac{1}{2}\beta V_N],$$

$$\exp[-\tfrac{1}{2}\beta \sum v(ij)]\} = \text{minimum} \quad (2.7)$$

or

$$\min = \int dx_1 \ldots \int dx_N \left\{\exp\left[-\frac{\beta}{2}V_N(1 \ldots N)\right] - \exp\left[-\frac{1}{2}\beta \sum v(ij)\right]\right\}^2 \quad (2.8)$$

This constitutes the basic variational principle of our effective potential theory.

If it were to happen that

$$V_N(\mathbf{x}_1 \ldots \mathbf{x}_N) = \sum_{i<j=1}^N V_2(\mathbf{x}_i, \mathbf{x}_j) \quad (2.9)$$

in other words that the exact N-molecule potential were a pairwise sum of exact 2-molecule potentials, then certainly the variational principle (2.8) would force v to equal V_2 identically, and the distance D would be reduced to zero. However under the more realistic circumstance that V_N contains three-body, four-body, $\ldots$ contributions, the minimum attainable D in eq 2.7 presumably is still greater than zero. We must bear in mind that the effective pair potential v which produces that minimum D can be both temperature and density dependent.

The functional equation which determines v may be obtained by setting equal to zero the first functional derivative of the right member of (2.8) with respect to $v(\mathbf{x}_i, \mathbf{x}_j)$. One finds

$$\int dx_3 \ldots \int dx_N \exp\{-\tfrac{1}{2}\beta[V_N + \sum v(ij)]\} =$$

$$\int dx_3 \ldots \int dx_N \exp\{-\beta \sum v(ij)\} \quad (2.10)$$

which must be obeyed for all $\mathbf{x}_1, \mathbf{x}_2$. We will suppose for convenience that periodic boundary conditions apply to $\mathcal{V}$; since V_N then possesses full translation in-

variance, so too will v. If $\mathcal{V}$ is macroscopically large and the system is in a fluid phase exclusively, then v will also possess the rotational invariance expected of a pair of rigid bodies in space.

In view of the multidimensional integrals it contains, nonlinear integral eq 2.10 is not trivial to solve for v (though we outline an iterative method in the next section). Nevertheless, some general characteristics of v may be deduced directly from eq 2.10. If both sides of that equation are integrated with respect to $\mathbf{x}_1$ and $\mathbf{x}_2$, one finds

$$Z_N\{\textstyle\sum v(ij)\} = Z_N\{{}^1/_2 V_N + {}^1/_2 \textstyle\sum v(ij)\} \quad (2.11)$$

in other words the configuration integrals are equal for two hypothetical assemblies of N molecules, the first of which interacts with the additive effective potential, and the second of which interacts with the *average* of V_N and the additive effective potential. Of course neither of the two Z_N in eq 2.11 necessarily equals the liquid's correct configuration integral, $Z_N\{V_N\}$, but still we can use the Schwartz inequality[8] to establish

$$Z_N\{V_N\}Z_N\{\textstyle\sum v(ij)\} \geq$$
$$Z_N{}^2\{{}^1/_2 V_N + {}^1/_2\textstyle\sum v(ij)\} \quad (2.12)$$

By referring to eq 2.11, we conclude that

$$Z_N\{V_N\} \geq Z_N\{\textstyle\sum v(ij)\} \quad (2.13)$$

In view of eq 2.1 therefore, it is clear that replacement of an actual V_N by its optimal effective pairwise potential approximation never lowers the free energy

$$F\{V_N\} \leq F\{\textstyle\sum v(ij)\} \quad (2.14)$$

A somewhat more general result follows from Hölder's inequality,[8] namely

$$Z_N{}^{1/p}\{{}^1/_2 p V_N\}Z_N{}^{1/q}\{{}^1/_2 q\textstyle\sum v(ij)\} \geq$$
$$Z_N\{{}^1/_2 V_N + {}^1/_2\textstyle\sum v(ij)\}$$
$$p,q > 1; \quad (1/p) + (1/q) = 1 \quad (2.15)$$

The previous eq 2.12 corresponds to $p = q = 2$. In terms of free energies all computed at the same temperature and density

$$\frac{1}{p}F\left\{\frac{p}{2}V_N\right\} + \frac{1}{q}F\left\{\frac{q}{2}\textstyle\sum v(ij)\right\} \leq$$
$$F\left\{\frac{1}{2}V_N + \frac{1}{2}\textstyle\sum v(ij)\right\} \quad (2.16)$$

The set of n-molecule correlation functions for the liquid is defined as

$$g^{(n)}(\mathbf{x}_1 \ldots \mathbf{x}_n) =$$
$$\frac{\Omega^n\int d\mathbf{x}_{n+1}\ldots\int d\mathbf{x}_N \exp[-\beta V_N(\mathbf{x}_1\ldots\mathbf{x}_N)]}{\int d\mathbf{x}_1\ldots\int d\mathbf{x}_N \exp[-\beta V_N(\mathbf{x}_1\ldots\mathbf{x}_N)]} \quad (2.17)$$

In the large $\mathcal{V}$ limit, and as the n molecules mutually separate from one another, $g^{(n)}$ approaches unity. With

obvious modifications, definition 2.17 applies equally for other intermolecular potentials besides V_N. Equations 2.10 and 2.11 allow us to conclude

$$g^{(2)}(\mathbf{x}_1,\mathbf{x}_2|\textstyle\sum v(ij)) =$$
$$g^{(2)}(\mathbf{x}_1,\mathbf{x}_2|{}^1/_2 V_N + {}^1/_2\textstyle\sum v(ij)) \quad (2.18)$$

so that like Z_N, the pair correlation function is identically the same for the additive effect potential, and for the average of V_N with this additive effective potential. Unfortunately it is not possible to obtain $g^{(2)}$ inequalities analogous to eq 2.12–2.16.

III. Perturbation Expansion

It is always possible to separate V_N into a part attributable strictly to bare pair interactions V_2 and a remainder $V^\dagger$ comprising all many-body effects

$$V_N(\mathbf{x}_1\ldots\mathbf{x}_N) = \sum_{i<j=1}^{N} V_2(\mathbf{x}_i,\mathbf{x}_j) + \lambda V^\dagger(\mathbf{x}_1\ldots\mathbf{x}_N) \quad (3.1)$$

The "coupling constant" λ introduced here has no fundamental significance, and will be used only to generate an iterative construction for v. At the end of that construction, we will set $\lambda = 1$. Corresponding to 3.1, there will be a formal λ series for v

$$v(\mathbf{x}_i,\mathbf{x}_j) = \sum_{n=0}^{\infty} \lambda^n v_n(\mathbf{x}_i,\mathbf{x}_j) \quad (3.2)$$

where of course

$$v_0(\mathbf{x}_i,\mathbf{x}_j) \equiv V_2(\mathbf{x}_i,\mathbf{x}_j) \quad (3.3)$$

Insert expressions 3.1 and 3.2 into the basic v eq 2.10, and expand the exponential functions into λ power series. The result appears as

$$0 = \int d\mathbf{x}_3\ldots\int d\mathbf{x}_N \exp\left[-\beta\sum_{i<j=1}^{N}V_2(ij)\right] \times$$
$$\left\{\lambda\left[\sum_{i<j=1}^{N}v_1(ij) - V^\dagger(1\ldots N)\right] + \right.$$
$$\lambda^2\left[\sum_{i<j=1}^{N}v_2(ij) + \frac{\beta}{4}\left(V^\dagger + \sum_{i<j=1}^{N}v_1(ij)\right)^2 - \right.$$
$$\left.\beta\left(\sum_{i<j=1}^{N}v_1(ij)\right)^2\right] + \lambda^3\left[\sum_{i<j=1}^{N}v_3(ij) + \right.$$
$$\beta\left(V^\dagger - 3\sum_{i<j=1}^{N}v_1(ij)\right)\sum_{k<l=1}^{N}v_2(kl) - \frac{\beta^2}{24} \times$$
$$\left(V^\dagger + \sum_{i<j=1}^{N}v_1(ij)\right)^3 + \frac{\beta^2}{3}\left(\sum_{i<j=1}^{N}v_1(ij)\right)^3\right] + 0(\lambda^4)\right\}$$
$$\quad (3.4)$$

Since λ may be regarded at this stage as an arbitrary parameter, the terms of different order in λ in eq 3.4 must separately vanish. The first-order equation

(8) F. Riesz and B. Sz.-Nagy, "Functional Analysis," Frederick Ungar Publishing Co., New York, N. Y., 1955, pp 40–43.

$$0 = \int d\mathbf{x}_3 \ldots \int d\mathbf{x}_N \exp\left[-\beta \sum_{i<j=1}^{N} V_2(ij) \right] \times$$

$$\left[\sum_{i<j=1}^{N} v_1(ij) - V^\dagger(1\ldots N) \right] \quad (3.5)$$

is a linear integral equation for determining v_1 in terms of $V^\dagger$. Once v_1 has been obtained, the second-order equation

$$0 = \int d\mathbf{x}_3 \ldots \int d\mathbf{x}_N \exp\left[-\beta \sum_{i<j=1}^{N} V_2(ij) \right] \times$$

$$\left[\sum_{i<j=1}^{N} v_2(ij) + \frac{\beta}{4}\left(V^\dagger(1\ldots N) + \sum_{i<j=1}^{N} v_1(ij) \right)^2 - \right.$$

$$\left. \beta\left(\sum_{i<j=1}^{N} v_1(ij) \right)^2 \right] \quad (3.6)$$

similarly determines v_2, once $V^\dagger$ and the previously calculated v_1 are inserted. This trend persists to all succeeding orders; the λ^n-order linear integral equation requires knowledge of $V^\dagger$ and each of the previously determined $v_1 \ldots v_{n-1}$. Hence one has in principle an iterative technique for constructing the effective pair interaction v.

We now examine the first-order integral eq 3.5 in depth. The average value of $V^\dagger$ in the assembly of N molecules interacting only *via* direct pair potentials V_2 may be written thus

$$N\epsilon_1{}^\dagger = [Z_N\{\textstyle\sum V_2(ij)\}]^{-1} \times$$

$$\int d\mathbf{x}_1 \ldots \int d\mathbf{x}_N V^\dagger(1\ldots N) \exp\left[-\beta \sum_{i<j=1}^{N} V_2(ij) \right] \quad (3.7)$$

where the average value per molecule, $\epsilon_1{}^\dagger$, clearly depends on both temperature and density. The analogous average of $V^\dagger$ when molecules 1 and 2 are constrained to preassigned configurations $\mathbf{x}_1$ and $\mathbf{x}_2$ may next be expressed as

$$[N\epsilon_1{}^\dagger + f_1{}^\dagger(\mathbf{x}_1,\mathbf{x}_2)]g^{(2,0)}(\mathbf{x}_1,\mathbf{x}_2) =$$

$$\frac{\Omega^2}{Z_N\{\textstyle\sum V_2(ij)\}} \int d\mathbf{x}_3 \ldots \int d\mathbf{x}_N V^\dagger(1\ldots N) \times$$

$$\exp\left[-\beta \sum_{i<j=1}^{N} V_2(ij) \right] \quad (3.8)$$

Here and in the following, the $g^{(n,0)}$ stand for correlation functions

$$g^{(n,0)} \equiv g^{(n)}\left(\mathbf{x}_1 \ldots \mathbf{x}_n \middle| \sum_{i<j=1}^{N} V_2(ij) \right) \quad (3.9)$$

for molecules interacting only through the V_2 sum. The quantity $f_1{}^\dagger$ in eq 3.8 represents the variation in the $V^\dagger$ average at small distances between 1 and 2 due to local order in the liquid. We expect $f_1{}^\dagger$ to decay rapidly to zero with increasing separation.

If eq 3.5 is multiplied throughout by $\Omega^2/Z_N\{\sum V_2\}$, the result may be transformed to yield

$$N\epsilon_1{}^\dagger + f_1{}^\dagger(12) = v_1(12) +$$

$$\frac{N-2}{\Omega}\int d\mathbf{x}_3 [v_1(13) + v_1(23)]\frac{g^{(3,0)}(123)}{g^{(2,0)}(12)} +$$

$$\frac{(N-2)(N-3)}{2\Omega^2}\int d\mathbf{x}_3 \int d\mathbf{x}_4 v_1(34)\frac{g^{(4,0)}(1234)}{g^{(2,0)}(12)} \quad (3.10)$$

Set

$$v_1(\mathbf{x}_1,\mathbf{x}_2) = \frac{2\epsilon_1{}^\dagger}{N-1} + \vartheta_1(\mathbf{x}_1,\mathbf{x}_2) \quad (3.11)$$

when this expression is inserted in eq 3.10, the quantity $\epsilon_1{}^\dagger$ drops out entirely to leave a linear integral equation for ϑ_1

$$f_1{}^\dagger(12) = \vartheta_1(12) + \frac{N-2}{\Omega}\int d\mathbf{x}_3 [\vartheta_1(13) +$$

$$\vartheta_1(23)]\frac{g^{(3,0)}(123)}{g^{(2,0)}(12)} + \frac{(N-2)(N-3)}{2\Omega^2} \times$$

$$\int d\mathbf{x}_3 \int d\mathbf{x}_4 \vartheta_1(34)\frac{g^{(4,0)}(1234)}{g^{(2,0)}(12)} \quad (3.12)$$

Had the many-body potential $V^\dagger$ been at the outset a constant independent of molecular configurations, then $f_1{}^\dagger$ would have vanished identically and the implied v_1 would have been equal precisely to $2\epsilon_1{}^\dagger/(N-1)$ for all pairs. Evidently ϑ_1 for more general $V^\dagger$ will be confined primarily to small pair distances, as dictated by the nonvanishing of $f_1{}^\dagger$ there.

Although one normally is concerned with very large systems and hence large N, it is extremely important not to drop the very small constant term proportional to $(N-1)^{-1}$ in the right member of eq 3.11. After all, this is a very long-ranged contribution to the effective potential, and acts on all $N(N-1)/2$ molecular pairs at once. The totality of these long-range effective interactions consequently is proportional to N, and therefore provides a nonvanishing effect on the free energy in the conventional large-system limit.

A comparison of eq 3.7 and 3.8 allows one to conclude

$$0 = \frac{1}{\Omega}\int d\mathbf{x}_1 \int d\mathbf{x}_2 f_1{}^\dagger(\mathbf{x}_1,\mathbf{x}_2)g^{(2,0)}(\mathbf{x}_1,\mathbf{x}_2) \quad (3.13)$$

Next multiply both sides of eq 3.12 by $\Omega^{-1}g^{(2,0)}(12)$ and integrate with respect to $\mathbf{x}_1$ and $\mathbf{x}_2$ to obtain (for the finite system function ϑ_1)

$$0 = \frac{1}{\Omega}\int d\mathbf{x}_1 \int d\mathbf{x}_2 \vartheta_1(\mathbf{x}_1,\mathbf{x}_2)g^{(2,0)}(\mathbf{x}_1,\mathbf{x}_2) \quad (3.14)$$

This last relation allows us to put integral eq 3.12 into a form most suitable for passage to the conventional large-system limit

$$f_1{}^\dagger(12) = \vartheta_1(12) + \frac{N-2}{\Omega} \int d\mathbf{x}_3 [\vartheta_1(13) +$$

$$\vartheta_1(23)] \frac{g^{(3,0)}(123)}{g^{(2,0)}(12)} + \frac{(N-2)(N-3)}{2\Omega^2} \int d\mathbf{x}_3 \int d\mathbf{x}_4 \vartheta_1(34) \times$$

$$\left[\frac{g^{(4,0)}(1234)}{g^{(2,0)}(12)} - g^{(2,0)}(34) \right] \quad (3.15)$$

Now the integrals will become strictly confined to regions of molecular size. Of course

$$\frac{N-2}{\Omega} \longrightarrow \rho^{(1)}, \quad \frac{(N-2)(N-3)}{2\Omega} \longrightarrow \frac{(\rho^{(1)})^2}{2} \quad (3.16)$$

in that large-system limit, where $\rho^{(1)}$ is the fixed singlet density N/Ω.

Equation 3.15 is the basic first-order equation that must in principle be solved for ϑ_1. In a practical sense that would be very difficult, though nowadays evaluation of integrals of the type it contains is becoming increasingly more feasible with rapid electronic computers. As section V below will illustrate, however, that equation may be used (without being fully solved) to infer important features of the effective potential for specific substances.

There may well exist applications in which the many-body potential $V^\dagger$ has significant magnitude, but for which the error incurred in the first-order estimate $v(ij) \cong V_2 + v_1(ij)$ is quite small. In this connection it should be realized that the free energy F is unchanged to linear order in λ by replacement of $V^\dagger$ by the effective pair-potential sum, due to the extremum character of our variational principle. Likewise, the pair correlation function will be unchanged through first order in λ upon making that potential replacement.

The concepts involved in the first-order equation which generates v_1 (i.e., $\epsilon_1{}^\dagger$ and ϑ_1) from a given $V^\dagger$ may readily be applied in succeeding orders. To do so, it is useful to recognize that the first-order calculation amounts to a linear projection operation $\mathbf{P}$

$$\mathbf{P}V^\dagger(1\ldots N) = \sum_{i<j=1}^{N} v_1(ij) \quad (3.17)$$

$$\mathbf{P}^2 = \mathbf{P} \quad (3.18)$$

The second of these relations is required for all projections, and states in the present case that any potential $V^\dagger$ already in pairwise additive form is carried identically into the effective potential.

By comparing the second-order eq 3.6 with the first-order eq 3.5 we see that

$$\mathbf{P}\left\{ \beta \left[\sum_{i<j=1}^{N} v_1(ij) \right]^2 - \frac{\beta}{4} \left[V^\dagger(1\ldots N) + \right.\right.$$

$$\left.\left. \sum_{i<j=1}^{N} v_1(ij) \right]^2 \right\} = \sum_{i<j=1}^{N} v_2(ij) \quad (3.19)$$

in other words, the second-order effective pair potential

v_2 is projected out of a combination of $V^\dagger$ and v_1 just as v_1 before was projected out of $V^\dagger$. Equation 3.19 may be rewritten thus

$$\mathbf{P}V_2{}^\dagger(1\ldots N) = \sum_{i<j=1}^{N} v_2(ij)$$

$$V_2{}^\dagger(1\ldots N) = \frac{\beta}{4}\left[3\sum_{i<j=1}^{N} v_1(ij) + V^\dagger(1\ldots N) \right] \times$$

$$\left[\sum_{k<l=1}^{N} v_1(kl) - V^\dagger(1\ldots N) \right] \quad (3.20)$$

which shows directly that if $V^\dagger$ is a pairwise additive function (which becomes identified in first order as $\Sigma v_1(ij)$), then v_2 vanishes identically. One incidentally sees here from the factor β in $V_2{}^\dagger$ that v_2 will tend toward zero as the temperature is raised at fixed density.

The detailed procedure of carrying out the projection in second order is entirely the same as before. The new "many-body potential" $V_2{}^\dagger$ takes the place of $V^\dagger$, and by the same strategy as shown by eq 3.7 and 3.8 with $V_2{}^\dagger$ inserted for $V^\dagger$, one first computes $\epsilon_2{}^\dagger$ and $f_2{}^\dagger(\mathbf{x}_1,\mathbf{x}_2)$. Then after writing

$$v_2(\mathbf{x}_1,\mathbf{x}_2) = \frac{2\epsilon_2{}^\dagger}{N-1} + \vartheta_2(\mathbf{x}_1,\mathbf{x}_2) \quad (3.21)$$

in direct correspondence with eq 3.11 for v_1, we will have a linear integral equation for determination of the short-range second-order function ϑ_2 which is isomorphous with eq 3.12 above. Second-order analogs of integral conditions 3.13 and 3.14 are also available, and they lead finally to the second-order version of eq 3.15

$$f_2{}^\dagger(2) = \vartheta_2(12) + \frac{N-2}{\Omega} \int d\mathbf{x}_3 \times$$

$$[\vartheta_2(13) + \vartheta_2(23)] \frac{g^{(3,0)}(123)}{g^{(2,0)}(12)} + \frac{(N-2)(N-3)}{2\Omega^2} \times$$

$$\int d\mathbf{x}_3 \int d\mathbf{x}_4 \vartheta_2(34) \left[\frac{g^{(4,0)}(1234)}{g^{(2,0)}(12)} - g^{(2,0)}(34) \right] \quad (3.22)$$

In the projection-operator terminology, the third-order equation is

$$\mathbf{P}\left\{ \frac{\beta^2}{24} [V^\dagger - \sum v_1(ij)] [(V^\dagger)^2 + \right.$$

$$4V^\dagger \sum v_1(ij) + 7(\sum v_1(ij))^2] -$$

$$\left. \beta[V^\dagger - 3\sum v_1(ij)] \sum v_2(ij) \right\} = \sum v_3(ij) \quad (3.23)$$

If $V^\dagger$ is pairwise additive, this relation shows that v_3 would vanish as v_2 would. In the high temperature regime, v_3 will be proportional to β^2.

By continuation of the procedure we have outlined,

we would eventually obtain (appropriate to the large-system limit functions ϑ_n and $g^{(n,0)}$)

$$\epsilon = \sum_{n=1}^{\infty} \left[\epsilon_n{}^\dagger - \frac{\rho^{(1)}}{2} \int dx_2 \vartheta_n(x_1,x_2) g^{(2,0)}(x_1,x_2) \right]$$

$$\vartheta(x_1,x_2) = V_2(x_1,x_2) + \sum_{n=1}^{\infty} \vartheta_n(x_1,x_2) \quad (3.24)$$

after having set λ equal to unity. The corresponding effective pair potential approximation to the partition function thereupon becomes

$$\exp(-\beta F) \cong \frac{1}{N!} \left(\frac{\mathcal{V} Q_{int}(\beta)}{\Omega} \right)^N \exp(-N\beta\epsilon) \times$$

$$\int dx_1 \ldots \int dx_N \exp\left[-\beta \sum_{i<j=1}^{N} \vartheta(x_i,x_j) \right] \quad (3.25)$$

IV. Effective Pair Potential Formulas

A criterion has now been advanced for representing a given substance by a "model substance," whose hypothetical molecules interact by the effective pairwise-additive potential which optimally preserves the original local order. The next step must be deduction of the thermodynamic properties of this model substance, and to that end we shall now derive statistical-mechanical expressions for mean energy, pressure, and compressibility. This task is rendered nontrivial by the density and temperature dependence of the effective pair potential. In this section we shall denote correlation functions in the model system by an extra superscript "m"

$$g^{(n,m)}(1 \ldots n) \equiv g^{(n)}(1 \ldots n | \sum v(ij)) \quad (4.1)$$

and ϑ will be strictly the infinite-system limit function.

The thermodynamic energy E may be obtained from the Helmholtz free energy F by means of the thermodynamic relation

$$E = \left(\frac{\partial \beta F}{\partial \beta} \right)_{N,\mathcal{V}} \quad (4.2)$$

By applying this operation to the logarithm of the model partition function (3.25), one finds the energy per particle to be

$$\frac{E}{N} = \frac{E_0}{N} + \left(\frac{\partial \beta\epsilon}{\partial \beta} \right)_{N,\mathcal{V}} + \frac{N-1}{2\Omega^2} \times$$

$$\int dx_1 \int dx_2 \left(\frac{\partial \beta\vartheta(12)}{\partial \beta} \right)_{N,\mathcal{V}} g^{(2,m)}(12) \quad (4.3)$$

where E_0 is the zero-density energy for N widely separated molecules. This general result is equally applicable to all phases, fluid or crystalline. If the model system is in the liquid state and is macroscopically large, then both ϑ and $g^{(2,m)}$ depend only on *relative* configuration coordinates so that eq 4.3 may be simplified somewhat to

$$\frac{E}{N} = \frac{E_0}{N} + \left(\frac{\partial \beta\epsilon}{\partial \beta} \right)_{N,\mathcal{V}} + \frac{\rho^{(1)}}{2} \int dx_2 \left(\frac{\partial \beta\vartheta(12)}{\partial \beta} \right)_{N,\mathcal{V}} g^{(2,m)}(12)$$

$$\rho^{(1)} = \frac{N}{\Omega} \quad (4.4)$$

The pressure in the model system may be computed from

$$p = -\left(\frac{\partial F}{\partial \mathcal{V}} \right)_{N,\beta} \quad (4.5)$$

If once again we utilize eq 3.25 for F, the result may be expressed in terms of a $g^{(2,m)}$ integral by using Green's technique for volume differentiation of configuration integrals.[9] One finds for the fluid phases

$$\frac{\beta p}{\rho} = 1 + \beta\rho \left(\frac{\partial \epsilon}{\partial \rho} \right)_\beta - \frac{\beta \mathcal{V} \rho}{2\Omega} \int dx_2 \left\{ \frac{1}{3} r_{12} \cdot \nabla_{r_{12}} \vartheta(12) - \right.$$

$$\left. \rho \left(\frac{\partial \vartheta(12)}{\partial \rho} \right)_\beta \right\} g^{(2,m)}(12), \quad \rho = \frac{N}{\mathcal{V}} = \frac{\Omega \rho^{(1)}}{\mathcal{V}} \quad (4.6)$$

The vector r_{12} is the spatial separation between the centers of molecules 1 and 2, and the gradient operator following it in eq 4.6 acts only on those position coordinates.

The isothermal compressibility κ_T is defined as

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_\beta \quad (4.7)$$

or equivalently

$$\left(\frac{\partial \beta p}{\partial \rho} \right)_\beta = \frac{\beta}{\rho \kappa_T} \quad (4.8)$$

Now set

$$\frac{\beta}{\rho \hat{\kappa}_T} = 1 - \frac{\beta \mathcal{V} \rho}{6\Omega} \int dx_2 r_{12} \cdot \nabla_{r_{12}} \vartheta(12) \times$$

$$\left[2g^{(2,m)}(12) + \rho \left(\frac{\partial g^{(2,m)}(12)}{\partial \rho} \right)_{\beta,\hat{v}} \right] \quad (4.9)$$

by indicating that ϑ is held fixed in the partial derivative of $g^{(2,m)}$, we mean to include *only* the contribution due to the explicit variation in density, and not the implicit variation occurring through variation of the effective potential. We can verify from eq 4.6 and 4.8 that $\hat{\kappa}_T$ is the isothermal compressibility for a system of molecules that interact at *all* temperatures and densities with a short-range potential that coincidentally equals ϑ when the latter is evaluated at the actual temperature and density of interest. The general fluctuation-compressibility theorem[10] applies in the case of such temperature and density independent interactions of short range, and allows us to write

(9) H. S. Green, "The Molecular Theory of Fluids," North-Holland Publishing Co., Amsterdam, 1952, p 51.

(10) T. L. Hill, "Statistical Mechanics," McGraw-Hill, New York, N. Y., 1956, p 236.

$$\frac{\rho \hat{k}_T}{\beta} = 1 + \frac{\mathcal{V}\rho}{\Omega} \int d\mathbf{x}_2 [g^{(2,m)}(12) - 1] \quad (4.10)$$

The pair correlation function occurring here must strictly be taken as the infinite-system limit function, before the integration is carried out.

After eq 4.6 is multiplied throughout by ρ, the application of an isothermal density derivative leads to the following compressibility formula

$$\frac{\beta}{\rho \kappa_T} = \frac{\beta}{\rho \hat{k}_T} + \beta \frac{\partial}{\partial \rho} \rho^2 \left(\frac{\partial \epsilon}{\partial \rho}\right)_\beta +$$

$$\frac{\beta \mathcal{V}\rho^3}{2\Omega} \int d\mathbf{x}_2 \left(\frac{\partial \hat{v}(12)}{\partial \rho}\right)_\beta \left(\frac{\partial g^{(2,m)}(12)}{\partial \rho}\right)_{\beta,\hat{v}} -$$

$$\frac{\beta \mathcal{V}\rho^2}{2\Omega} \int d\mathbf{x}_2 \left\{\frac{1}{3} \mathbf{r}_{12} \cdot \nabla_{12}\left(\frac{\partial \hat{v}(12)}{\partial \rho}\right)_\beta - 3\left(\frac{\partial \hat{v}(12)}{\partial \rho}\right)_\beta - \right.$$

$$\left. \rho\left(\frac{\partial^2 \hat{v}(12)}{\partial \rho^2}\right)_\beta\right\} g^{(2,m)}(12) - \frac{\beta \mathcal{V}\rho^2}{2\Omega} \times$$

$$\int d\mathbf{x}_2 \int d\mathbf{x}_3 \int d\mathbf{x}_4 \left\{\frac{1}{3} \mathbf{r}_{12} \cdot \nabla_{r_{12}} \hat{v}(12) - \rho\left(\frac{\partial \hat{v}(12)}{\partial \rho}\right)_\beta\right\} \times$$

$$\frac{\delta g^{(2,m)}(12)}{\delta \hat{v}(34)}\left(\frac{\partial \hat{v}(34)}{\partial \rho}\right)_\beta \quad (4.11)$$

The implicit density variation of $g^{(2,m)}$ through $\hat{v}$ enters this last expression via the functional derivative

$$\frac{\delta g^{(2,m)}(12)}{\delta \hat{v}(34)} = -\frac{1}{2}\beta(\rho^{(1)})^2 [g^{(4,m)}(1234) -$$

$$g^{(2,m)}(12)g^{(2,m)}(34)] - \beta\rho^{(1)}[g^{(3,m)}(124) \times$$

$$\delta(\mathbf{x}_1 - \mathbf{x}_3) + g^{(3,m)}(123)\delta(\mathbf{x}_2 - \mathbf{x}_4)] -$$

$$\beta g^{(2,m)}(12)\delta(\mathbf{x}_1 - \mathbf{x}_3)\delta(\mathbf{x}_2 - \mathbf{x}_4) \quad (4.12)$$

Under conventional circumstances one expects an expression of type 4.10 to yield the isothermal compressibility of a fluid system. Indeed that is invariably true with interactions of limited range, whether those interactions are pairwise additive or not. However the model system effective pair potential has essentially infinite range. This infinite range is clear enough in the constant "tail" $2\epsilon/(N-1)$ of $\hat{v}(\mathbf{x}_1,\mathbf{x}_2)$, but it is also manifest in the density dependence of $v(\mathbf{x}_1,\mathbf{x}_2)$ as extra particles are placed into the volume $\mathcal{V}$ macroscopically far from molecules 1 and 2. The terms in κ_T expression 4.11 following the one containing $\hat{k}_T$ are the direct result of these long-ranged contributions.

The compressibility $\hat{k}_T$ measures the local (but large-dimension) density fluctuations in the effective potential model system. It is this local compressibility which determines the intensity of X-ray scattering extrapolated to zero scattering angle. Conventionally this would be identical with the thermodynamic compressibility for an overall compression of the entire system, but the long-range interactions induce a difference. The magnitude of $\kappa_T - \hat{k}_T$ hence measures the
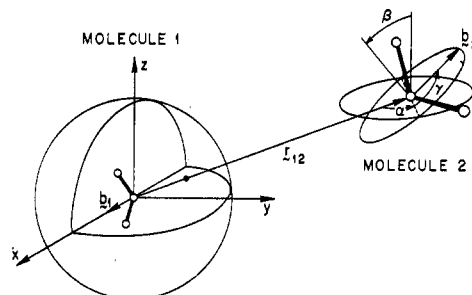

Figure 1. Relative configuration variables for a pair of water molecules. r_{12} is the separation between the oxygen nuclei, and $\mathbf{b}_1$ and $\mathbf{b}_2$ are unit vectors along the molecular symmetry axes. Euler angles α, β, γ are an ordered set of rotations which carry the orientation of molecule 1 into that of molecule 2. Configurations for which r_{12} does not pierce the sphere quadrant as shown may be generated by reflection in symmetry planes xy or xz or both.

inability of the model system to mimic the local density fluctuations of the initial real liquid. If the effective potential approximation has validity, this difference should be small.

V. Application to Water

The water molecule possesses C_{2v} symmetry. Measurements indicate[11] that an isolated molecule incorporates O–H bonds of length 0.957 Å, and an angle between these bonds at the oxygen nucleus of 104.5°. Consequently we treat each molecule in the liquid as a rigid asymmetric rotor with the same symmetry. Each configuration vector $\mathbf{x}_i$ will involve six components: three to specify the Cartesian coordinates of the oxygen nucleus, plus three Euler angles to fix the molecule's orientation in space.

The three normal modes of vibration, ν_1, ν_2, and ν_3, for the water molecule occur at 3656.65, 1594.59, and 3755.79 cm^{-1}.[12] At room temperature these vibrations are virtually all unexcited, so the partition function for internal degrees of freedom will contain the factor

$$\exp[-\frac{1}{2}\beta h(\nu_1 + \nu_2 + \nu_3)] \quad (5.1)$$

The potential energy V_2 for an isolated pair of water molecules depends irreducibly upon six relative configuration variables. Figure 1 shows that these variables may be taken to be the polar coordinates of the second oxygen nucleus relative to the first, and Euler angles for the rotation which would carry the first molecule into the orientation of the second. Figure 1 also demonstrates that the O–O polar coordinates need only be considered in one quadrant, since the other configurations differ only by symmetry operations permitted by the molecular C_{2v} symmetry. For fluid phases, the functions $\hat{v}$ and $g^{(2,m)}$ depend on the same

(11) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford University Press, New York, N. Y., 1969, p 4.

(12) Reference 11, p 7.

relative configuration variables as V_2, and exhibit the same symmetry properties.

The many-body potential $V^\dagger(1\ldots N)$ is surely significant in liquid water. Since the isolated molecules have a large permanent dipole moment (1.84 D), there must be large local fluctuating electric fields in the liquid. These fields polarize the molecules, and the correspondingly modified molecular moments in turn affect the fluctuating fields.

At small distances, hydrogen bonding is the most important aspect of water molecule interactions. This type of interaction is already manifest in V_2, which would plunge to about -5 kcal/mol for a fully formed, essentially linear, hydrogen bond.[13] However it has been suggested[14,15] that the energy of hydrogen bonding is not additive, and detailed quantum-mechanical calculations support this hypothesis. Although energy nonadditivity is found to be nonuniform in sign,[16] the predominant influence of sequential sets of hydrogen bonds in any condensed phase appears to amount to an effective strengthening of each hydrogen bond.[16,17]

Thus it appears that $V^\dagger$ is negative for most configurations of interest in liquid water. The quantity $\epsilon(\beta,\rho)$ is most likely dominated by $\epsilon_1{}^\dagger(\beta,\rho)$, and since eq 3.7 shows this latter to be a canonical average of $V^\dagger$, we tentatively conclude that

$$\epsilon(\beta,\rho) \leq 0 \qquad (5.2)$$

for liquid water. Although ϵ provides an important contribution to the water model-system chemical potential (and therefore affects that model system's phase changes), it has the same numerical value for all molecular configurations. Consequently it has no effect whatever upon the local order established by the molecules in the model system.

On the other hand it is clear that the difference between the bare two-molecule potential V_2 and the short-range effective pair potential ϑ is directly reflected in the local molecular arrangements. Without having to solve the sequence of linear ϑ_n integral equations derived in the previous section, we can with some confidence infer the major features of the difference between V_2 and ϑ, by keeping in mind that this difference must be selected to produce substantially the same structural shifts as $V^\dagger$.

The best currently available *ab initio* Hartree–Fock calculations of V_2 indicate that the lowest energy for a pair of water molecules is achieved in the configuration shown in Figure 2. The O–O distance is 3.00 Å, and the energy of the hydrogen bond at that nuclear configuration is -4.72 kcal/mol.[16]

Within the regular hexagonal ice lattice one can identify sequences of hydrogen bonds of any length passing from oxygen to oxygen. As already pointed out, these sequential groupings (the most common type for a given large number of molecules) produce extra energy stabilization beyond that for just V_2 interac-
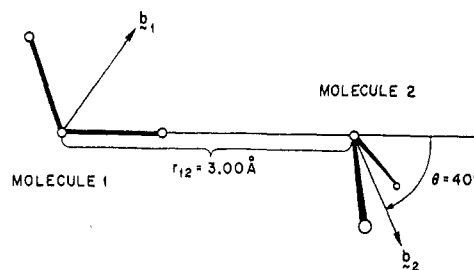
Figure 2. Stable water-molecule pair configuration according to Hartree-Fock calculations (ref 16). Molecules 1 and 2 lie in perpendicular planes.

tions. It has also been established (at least for sequential triplets) that this hydrogen-bond nonadditivity contribution to $V^\dagger$ acts to compress distances in the crystal.

The melting of ice to produce liquid water obviously adds configurational disorder: the new phase lacks long-range periodicity and exhibits fluidity. Still, the melting energy only amounts to about one-eighth of the crystal's sublimation energy, so the liquid presumably consists of a random space-filling network of strained hydrogen bonds, incorporating occasional broken bonds and interstitials. Indeed the X-ray scattering from water[18] shows that this network is spatially quite homogeneous (not broken up into disconnected "clusters"), and retains the local propensity for tetrahedral coordination that always appears in the ices and clathrates.[19]

Although hydrogen-bond sequences may be somewhat fewer in number and shorter in average length in the liquid compared to ice, they should still exert the same stabilizing and compressing effects. The short-range effective potential ϑ can produce the same result by exhibiting a deeper hydrogen-bond energy minimum than V_2, at a somewhat smaller O–O distance. Figure 3 illustrates this presumption by comparing schematic V_2 and ϑ curves for r_{12} variation in the configuration shown in Figure 2. One must keep in mind here that a deepening of the hydrogen-bond part of the pair potential must be compensated by a rise for some other configurations, since eq 3.14 and its analogs for $\vartheta_2, \vartheta_3, \ldots$ imply for liquid water that in a finite system

$$0 = \int d\mathbf{x}_2[V_2(\mathbf{x}_1,\mathbf{x}_2) - \vartheta(\mathbf{x}_1,\mathbf{x}_2)]g^{(2,0)}(\mathbf{x}_1,\mathbf{x}_2) \qquad (5.3)$$

But in any event the primary structural effect here is a strengthening of the hydrogen bonds in the random

(13) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969).

(14) H. S. Frank and W. Y. Wen, *Disc. Faraday Soc.*, **24**, 133 (1957).

(15) H. S. Frank, *Proc. Roy. Soc.*, **A247**, 481 (1958).

(16) D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *Chem. Phys. Lett.*, **4**, 527 (1970).

(17) J. DelBene and J. A. Pople, *ibid.*, **4**, 426 (1969).

(18) A. H. Narten and H. A. Levy, *Science*, **165**, 447 (1969).

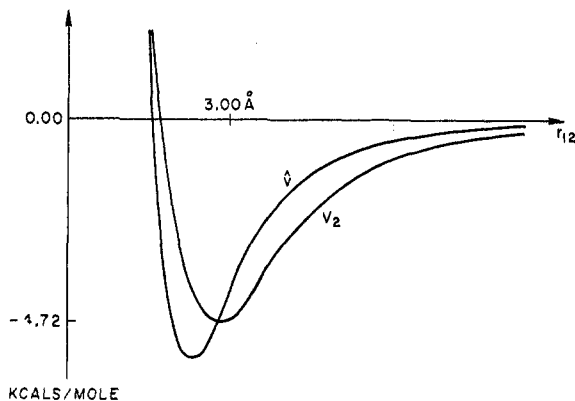(19) G. A. Jeffrey and R. K. McMullan, *Progr. Inorg. Chem.*, **8**, 43 (1967).

Figure 3. Qualitative shift expected between V_2 and ϑ. The hydrogen-bond nonaddivity effect of sequential groupings of molecules in the liquid deepen the minimum and move it to shorter O–O distance. The pair geometry is the one shown in Figure 2, except for the r_{12} variation. The V_2 minimum parameters shown are taken from ref 16.

Figure 4. Angular variation of V_2 and ϑ. Figure 2 gives the relevant configurations, with only θ varying. As a result of enhanced hybridization of oxygen orbitals in the liquid, one expects ϑ to be depressed relative to V_2 at the ideal tetrahedral angles indicated by arrows.

liquid network, so at a given temperature ϑ produces more hydrogen bonds on the average than V_2 alone would produce.

The quantity $V^{\dagger}$ very likely also affects the directionality of hydrogen bonding in liquid water. Hartree–Fock calculations[13,16,20] agree that the θ variation of V_2 in the pair arrangement shown in Figure 2 (with fixed r_{12} and maintaining the symmetry plane) gives a broad and flat featureless minimum. Consequently the lone pairs of electrons in the valence shell of the proton acceptor molecule must be quite delocalized. In particular this θ variation of V_2 fails to display relative minima localized about $\theta = +54°44'$ and $\theta = -54°44'$, the characteristic angles for perfect tetrahedral coordination about the acceptor molecule oxygen nucleus.

According to Coulson[21] the observed bond angle in water implies substantial hybridization of the oxygen 2s and 2p orbitals involved in the bonding. The lone pairs of electrons on the oxygen are therefore also partially hybridized. However it is clear that the hybridization is not of the full sp^3 type that obtains in methane,[22] so indeed the full set of tetrahedral coordination directions is not inherent in the electronic structure of an isolated water molecule.

Tetrahedral coordination however appears to occur with high probability in the liquid. Consistent with this presumption, consider a pair of water molecules in the configuration shown in Figure 2, but with θ equal to $\pm 54°44'$. The resulting hydrogen bond along one of these ideal tetrahedral directions surely will increase the degree of hybridization of the acceptor oxygen toward pure sp^3, and the lone pair of electrons not involved in that hydrogen bond will then be more localized along the remaining tetrahedral direction. Consequently the formation of a second hydrogen bond to the acceptor oxygen (right-hand molecule in Figure 2) will be confined to that remaining tetrahedral direction. This
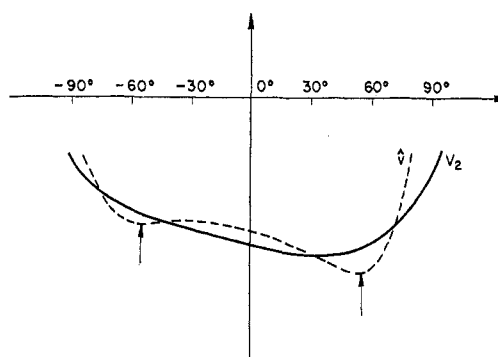
argues in favor of a cooperativity to tetrahedral geometry in that initial formation of tetrahedral hydrogen bonding facilitates extension of that local geometry in further hydrogen bonding. As advocated, this amounts to a three-molecule effect.

The effective pair potential ϑ consequently should manifest those tetrahedral angles more obviously than V_2. As Figure 4 indicates, we surmise that ϑ should be depressed relative to V_2 at the ideal tetrahedral angles. The model system would then exhibit the enhanced extent of local tetrahedral order that is possible in real water as a result of nonadditive contributions to the potential energy in the latter.

As a final aspect of the qualitative behavior of ϑ for water, we inquire about the large r_{12} regime. For these large distances it is known[23] that the pair correlation function behaves thus

$$g^{(2)}(\mathbf{x}_1,\mathbf{x}_2) - 1 \sim -\frac{9g_K(D-1)}{4\pi\rho(2D+1)}\,\mathbf{b}_1\cdot\mathbf{T}_{12}\cdot\mathbf{b}_2$$

$$\mathbf{T}_{12} = \frac{1}{r_{12}{}^3}\left[1 - \frac{3r_{12}r_{12}}{r_{12}{}^2}\right] \tag{5.4}$$

In this expression, the $\mathbf{b}$'s are unit vectors along the molecular symmetry axes, D is the static dielectric constant, and g_K is the Kirkwood[24] orientational correlation function

$$g_K = 1 + \frac{\rho}{8\pi^2}\int d\mathbf{x}_2(\mathbf{b}_1\cdot\mathbf{b}_2)g^{(2)}(\mathbf{x}_1,\mathbf{x}_2) \tag{5.5}$$

(20) K. Morokuma and L. Pedersen, *J. Chem. Phys.*, **48**, 3275 (1968).

(21) C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1961, p 221.

(22) R. F. W. Bader, *J. Amer. Chem. Soc.*, **86**, 5070 (1964).

(23) A. Ben-Naim and F. H. Stillinger, "Aspects of the Statistical Mechanical Theory of Water" in "Structure and Transport Processes in Water and Aqueous Solutions," R. A. Horne, Ed., Wiley, New York, N. Y., in press.

(24) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

We shall assume that the first-order perturbation estimate of ϑ as outlined in section III above predicts the correct qualitative trend at large r_{12}. In this order of approximation we know that $g^{(2)}$ and $g^{(2,m)}$ agree, so in fact g_K will be the same in the model system subject to ϑ as in the real liquid. Equation 5.4 then shows that the static dielectric constant D will also be the same in first order.

The true molecular pair interaction V_2 at large separation possesses dipole–dipole behavior

$$V_2(\mathbf{x}_1,\mathbf{x}_2) \sim \mu_v{}^2 \mathbf{b}_1 \cdot \mathbf{T}_{12} \cdot \mathbf{b}_2 \qquad (5.6)$$

appropriate for the dipole moment $\mu_v = 1.84$ D of an isolated molecule under vacuum. Two principal modifications of this form will be produced by many-body interactions in the liquid. (a) There will be an enhancement of the dipole moment μ_v to a larger average value μ_l due to charge transfer and polarization in hydrogen bonding with the molecule's immediate neighbors. (b) A form of dielectric shielding of $V_2(12)$ by intervening molecules will take place, even if these molecules are not permitted to reorient in the electric field of molecules 1 and 2. This polarization is partly electronic, but also involves nuclear displacement in the three normal vibrational modes at fixed molecular orientation. The appropriate dielectric constant D_{ir} refers experimentally to a wavelength range around 0.1–1.0 mm.

The first-order perturbation eq 3.15 is designed to assure that the mean value of the many-body interactions $V^\dagger$ as a function of $\mathbf{x}_1,\mathbf{x}_2$ is the same as the mean of $N\epsilon_1 + \Sigma v_1(ij)$. In particular the right side of that equation has terms giving: (1) the effective interaction acting directly between molecules 1 and 2; (2) the effective interaction of 1 with 2's "correlation cloud" and of 2 with 1's correlation cloud; and (3) the effective potential between the two correlation clouds. Effects a and b above suggest that ϑ ($\cong V_2 + \vartheta_1$) at large r_{12} acts as the interaction of two point dipoles μ_l embedded in a dielectric medium with constant D_{ir}, and each (for computational simplicity) located centrally in an otherwise empty spherical cavity. An elementary computation then yields

$$\vartheta(\mathbf{x}_1,\mathbf{x}_2) \cong V_2(\mathbf{x}_1,\mathbf{x}_2) + \vartheta_1(\mathbf{x}_1,\mathbf{x}_2)$$

$$\sim \frac{9 D_{\mathrm{ir}}}{(2 D_{\mathrm{ir}} + 1)^2} \left(\frac{\mu_l}{\mu_v}\right)^2 V_2(\mathbf{x}_1,\mathbf{x}_2) \qquad (5.7)$$

When the liquid is at or near its melting point, μ_l is probably close to the molecular dipole moment in ice. This latter has been estimated[25] to be 2.95 D. Furthermore, the high-frequency dielectric constant has been reported to be 4.5.[26] Using these numbers we find

$$\frac{9 D_{\mathrm{ir}}}{(2 D_{\mathrm{ir}} + 1)^2} \left(\frac{\mu_l}{\mu_v}\right)^2 = 1.03 \qquad (5.8)$$

Considering the uncertainty of μ_l and D_{ir}, this factor

should be regarded as currently indistinguishable from unity. It is curious that in the large r_{12} regime apparently little modification of V_2 is required; effects a and b above essentially cancel each other.

VI. Discussion

(1) The N-molecule potential $V_N(\mathbf{x}_1 \ldots \mathbf{x}_N)$ was regarded above as temperature independent. In most applications (including water at ordinary temperatures) this assumption is correct. But neighboring molecules in interaction with each other tend to perturb their vibrational frequencies. If these internal vibrations are thermally excited under the ambient conditions, then the appropriate potential function, which includes a shift in vibrational free energy, becomes a function of temperature: $V_N(\mathbf{x}_1 \ldots \mathbf{x}_N;\beta)$. However this elaboration in no way changes the effective potential formalism presented above.

(2) Besides water, liquid metals provide an interesting class of fluids for application of the effective pair potential technique. The ions in a liquid metal move about under the influence of some potential function $V_N(\mathbf{r}_1 \ldots \mathbf{r}_N;\beta)$ that is strongly influenced by the presence of degenerate conduction electrons. Certainly this many-ion potential is not precisely resolvable into pair contributions, but for certain purposes it would be convenient to know the optimal effective pair potential approximation.[27,28] For these substances in particular it should be possible experimentally to detect a difference between the two isothermal compressibilities κ_T and $\hat{\kappa}_T$.

(3) No barrier exists in principal to the extension of the effective potential method to liquid mixtures. Of course a distinct temperature and composition dependent effective potential $v_{ab}(\mathbf{x}_a,\mathbf{x}_b)$ would have to be introduced for each different pair of molecular species. The multicomponent version of variational principle (2.8) then would require minimization over variation of all these v_{ab}. A particularly interesting application would be fused salts, where one would look for the dielectric shielding of the Coulomb interaction at large ion pair separation, and for the extent to which the ϵ_a for different ions could be identified as Born cavity energies.[29]

(4) The critical region for a fluid very likely will be more poorly described by the effective pair potential model than the liquid near the triple point. This does

(25) L. Onsager and M. Dupuis, "The Electrical Properties of Ice" in "Electrolytes," B. Pesce, Ed., Pergamon Press, New York, N. Y., 1962, p 27.

(26) E. H. Grant, T. J. Buchanan, and H. F. Cook, *J. Chem. Phys.*, **26**, 156 (1957).

(27) M. D. Johnson, P. Hutchinson, and N. H. March, *Proc. Roy. Soc.*, **A282**, 283 (1964).

(28) P. Ascarelli and R. J. Harrison, *Phys. Rev. Lett.*, **22**, 385 (1969).

(29) F. H. Stillinger, "Equilibrium Theory of Pure Fused Salts" in "Molten Salt Chemistry," M. Blander, Ed., Interscience, New York, N. Y., 1964.

not mean to say that the model fluid will necessarily fail to exhibit nonclassical critical exponents.[30] However, a fluid in the critical state has density fluctuations of large spatial extent and magnitude. The definition of $v(x_1, x_2; \beta, \rho)$ does not permit this function to adjust its density dependence to the local value of the density (which may be sensibly constant over many molecular diameters). Instead, only the overall density is recognized, and the average many-body structural effects built into v may be a significant misrepresentation. One possible outcome is a substantial displacement of the model system critical point from that of the real substance it attempts to imitate.

(5) In order to quantify our qualitative analysis of ϑ for water, an iterated series of quantum-mechanical and statistical-mechanical calculations should be carried out. One might start by guessing a reasonable approximation to ϑ, consistent with the few currently known facts about V_2 and the qualitative changes taking V_2 to ϑ.[31] By then using high-speed electronic computers to simulate the corresponding model liquid (via either a Monte Carlo or molecular dynamics technique), it would be possible to observe which local arrangements of molecules predominate in the liquid (at least as predicted by that approximate ϑ). These local arrangements of small groupings of, say, two to five molecules thereupon should be the ones examined by extensive and accurate quantum-mechanical calculations of V_2 and nonadditivity energies. With better estimates of the V_N, the computer liquid simulation could be used to refine ϑ (and estimate ϵ), and finally the entire procedure would be recycled until convergence obtained.

(30) M. E. Fisher, "Lectures in Theoretical Physics VII C," University of Colorado Press, Boulder, Colo., 1965, pp 1–159.

(31) One such choice for an analytic fit to $\hat{v}$ for water is suggested in ref 23.

Approximate Methods for Determining the Structure of

H₂O and HOD Using Near-Infrared Spectroscopy

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Approximate methods are described for determining the H-bonded state of liquid water to the critical region. It is shown that differences between spectra of solutions, and liquids in the bulk, indicate H bonds having different angles and distances. Spectra from water in solution in HF and NH₃ and in the gas-hydrate state are also presented.

Various theories of liquids have been advanced that assume lattice-like structures having cavity defects. A simple application of such liquid models can be demonstrated for densities under saturation conditions (Figure 1). The upper parts of the curves show the densities of different liquids. At low temperatures the densities of normal liquids decrease with increasing temperature in a linear fashion. (Increasing amplitudes of thermal motions.) The straight lines at high temperatures are the geometrical locus of the sum of densities of liquid and vapor in the saturated state. (One consequence of this is known as the rule of Cailletet and Mathias.) In a simple model the straight line gives the density of an ideal liquid. (Density decreases only as a result of thermal motions.) In addition the model assumes that the density of a real liquid depends upon the number of cavity defects. The number of these defects in our model is exactly equal to the number of molecules in the vapor state. In liquids with hydrogen bonds (H bonds) we must also take orientation defects into account, because the H bonds are dependent upon the angle between the proton axis and the axis of the free electron pair of the H-bond acceptor.[1] Therefore, a lattice-like model of liquids having H bonds must also involve the orientational defects of open H bonds. These orientational defects are especially important for water. The goal of our experiments has thus been to obtain information about the concentration of these orientational defects in water, CH₃OH, and C₂H₅OH.