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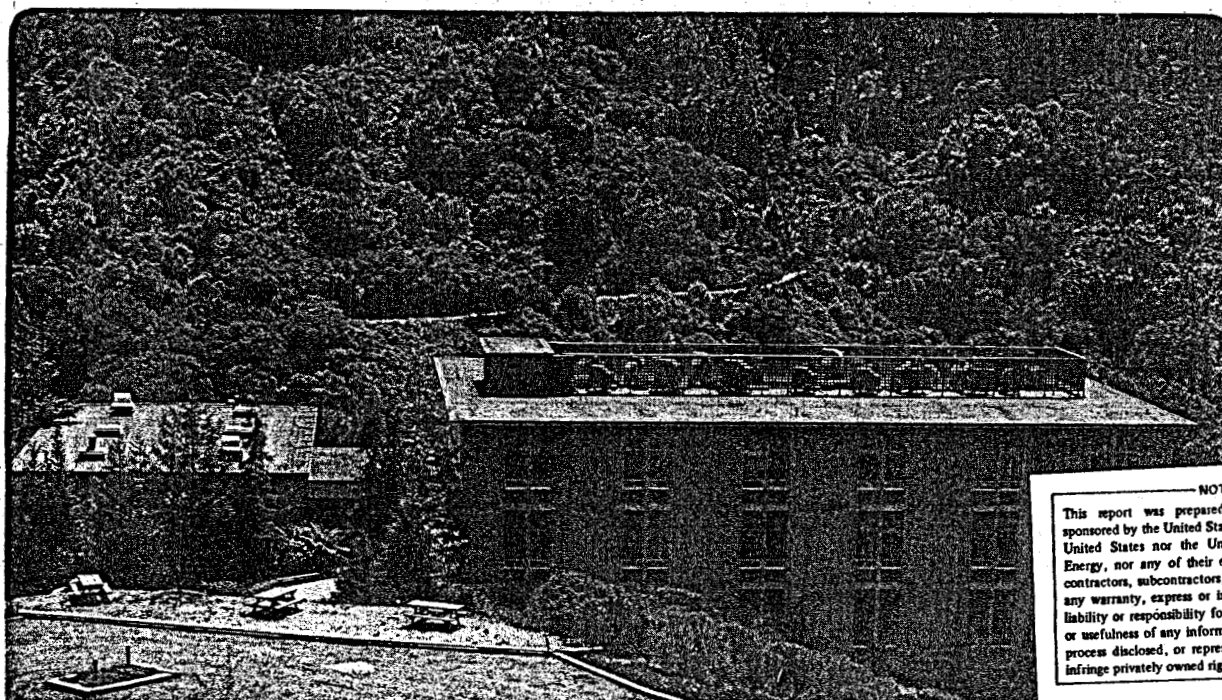
To be presented at the 9th International Conference
on the Properties of Steam, Munich, Germany,
September 10-14, 1979

A NEW EQUATION OF STATE FOR FLUID WATER BASED ON
HARD-SPHERE PERTURBATION THEORY AND DIMERIZATION
EQUILIBRIA

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August 1979

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Prepared for the U. S. Department of Energy
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A NEW EQUATION OF STATE FOR FLUID WATER BASED ON
HARD-SPHERE PERTURBATION THEORY AND DIMERIZATION EQUILIBRIA

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ABSTRACT

The perturbation theory of Barker, Henderson, Alder, and others has been extended to gaseous and liquid water first by inclusion of Prigogine's parameter c to account for external degrees of freedom due to rotation and vibration and second by including chemical and hydrogen bonding. Water molecules are assumed to form dimers in chemical equilibrium with monomers in both liquid and vapor phases. Using our equation of state, which contains only two parameters characterizing the water molecule and a temperature-dependent dimerization constant, we fit the saturation pressure of water to within 0.1% (from the triple point to just below the critical point) and the saturated liquid and vapor volumes to within 1.8 and 3.2%, respectively. Superheated-steam and compressed-water volumes and enthalpies (to 800°C, 1000 bars) agree with experiment to within 1.2 and 5.4%, respectively. Consideration is also given to the effect of multiple associations (trimers, tetramers, etc.). Our equation may be useful for engineering applications where the above-quoted accuracy is adequate and where a relatively simple analytic equation of state is desirable for computational efficiency.

KEYWORDS

Association; dimerization; perturbed-hard-chain theory; vapor pressure; equation of state; water; van der Waals-type equation of state.

INTRODUCTION

Since extensive experimental measurements of the thermodynamic properties of water exist, it is tempting to construct an analytical equation of state to represent these properties over the entire range of fluid densities at subcritical and supercritical temperatures. Such attempts have been made previously using an empirical equation with a very large number of adjustable parameters that have essentially no physical significance. In this work we report an equation of state that uses some theoretical ideas as a point of departure and that, consequently, requires only a few adjustable parameters with clearly-identifiable physical significance. The resulting equation of state does not have very high accuracy, although, except for the critical region, it can reproduce volumetric properties and vapor pressures to within about 1-2% and enthalpies to within about 6% over a remarkably wide range of temperature and pressure.

VAN DER WAALS-TYPE PARTITION FUNCTION

The equation of state follows from a partition function of the extended van der Waals form:

$$Q = \frac{1}{N!} \left(\frac{V}{\Lambda^3}\right)^N \left(\frac{V_f}{V}\right)^{Nc} \left[\exp \frac{-\phi}{2kT}\right]^{Nc} [q_{int}]^N, \quad (1)$$

where N is the number of molecules in total volume V at temperature T , V_f is the free volume, k is Boltzmann's constant, Λ is the de Broglie wavelength, and $\phi/2$ is the potential energy per molecule. The number of external degrees of freedom per molecule is $3c$, and q_{int} is the molecular partition function for all internal degrees of freedom. The equation of state is related to Q through

$$P = kT(\partial \ln Q / \partial V)_{T,N} \quad (2)$$

Equation (1), proposed by Beret and Prausnitz (1975) and by Donohue and Prausnitz (1978) for polyatomic nonpolar (or slightly polar) fluids, is an extension of the van der Waals form to complex molecules through use of parameter $3c$ (Prigogine, 1957). The major assumption here is that all external degrees of freedom (e.g., density-dependent rotations and vibrations) are considered to be equivalent translational degrees of freedom. A more proper definition of $3c$ is the number of equivalent translational degrees of freedom. Parameter c is unity for monatomic fluids like argon; it is larger than unity for polyatomic fluids.

For the free volume we use the expression of Carnahan and Starling (1969):

$$\ln\left(\frac{V_f}{V}\right) = \frac{3(\tau/\tilde{v})^2 - 4(\tau/\tilde{v})}{(1 - \tau/\tilde{v})^2}, \quad (3)$$

where the reduced volume $\tilde{v} \equiv v/v^*$, $\tau \equiv \pi/\sqrt{18}$, $v \equiv$ molar volume, $v^* \equiv r\sigma^3 N_A/\sqrt{2}$. The number of segments per molecule is r , and σ is the diameter of a segment. Avogadro's number is N_A .

For the potential we use the molecular dynamics results of Alder, Young, and Mark (1972), who use a square-well potential:

$$\frac{\phi}{2kT} = \sum_{n=1}^2 \sum_{m=1}^5 \frac{A_{nm}}{\tilde{T}^n \tilde{v}^m}, \quad (4)$$

where reduced temperature $\tilde{T} \equiv T/T^*$, $T^* \equiv \epsilon q / ck$. The potential energy per unit of external surface area is ϵ , and q is the external surface area per molecule. For pure fluids, parameters ϵ and q and parameters r and σ^3 always appear as products; therefore, Eq. (1) requires only three adjustable parameters: v^* , T^* , and c . Universal coefficients A_{nm} are given in Table 1.

TABLE 1 Universal Coefficients A_{nm}^\dagger

$n \setminus m$	1	2	3	4	5
1	-7.04677	-7.22636	-3.16538	14.34352	-1.26227
2	-3.56999	11.35209	-10.85375	-3.6131	7.34334

[†] These coefficients are based on the molecular dynamics calculations of Alder, Young, and Mark (1972) with small empirical modifications to fit experimental data for methane and n-hexane better.

DIMERIZATION HYPOTHESIS

Since water is a strongly polar, hydrogen-bonded substance, we must account for orientational forces that are strongly temperature- and volume-dependent. Following Gmehling, Liu, and Prausnitz (1979), we do so by assuming that water is an equivalent mixture of monomers and dimers. (Equivalent does *not* mean that water is, in fact, a mixture of monomers and dimers but rather that the thermodynamic properties of real water can be represented by a hypothetical mixture of monomers and dimers.) For the dimerization equilibrium constant, we use

$$\underline{K} = (\zeta_D \phi_D) / (\zeta_M^2 \phi_M^2 P) \quad , \quad (5)$$

where ζ is the mole fraction and ϕ is the fugacity coefficient. Subscript M stands for monomer and subscript D for dimer. The effect of density is accounted for through the fugacity coefficients, which are calculated from the equation of state. Equilibrium constant \underline{K} is a function of temperature only:

$$\ln(\underline{K}) = \Delta S^\circ / R - \Delta H^\circ / (RT) \quad , \quad (6)$$

where R is the gas constant, ΔS° and ΔH° are, respectively, the entropy and enthalpy of dimerization in the standard state.

In this approximation, water is considered to be an equivalent mixture of monomers and dimers at chemical equilibrium. The properties of this mixture are given by the equation of state [Eqs. (1-4)] extended to a binary mixture. This extension is given by a one-fluid theory wherein the characteristic constants are given as a function of composition by mixing rules, summarized in Appendix I. To reduce the number of adjustable parameters, we set $c(\text{monomer}) = 1$ and also set some ratios at arbitrary but physically reasonable values: $r_D/r_M = 1.75$; $\sigma_D/\sigma_M = 1$; $q_D/q_M = 1.75$; $\epsilon_M/\epsilon_D = 1$; $c_D/c_M = 1.3$.

This theory for water is based on a superposition of a chemical equilibrium [Eq. (5)] on a perturbed-hard-chain equation of state [Eqs. (1-4)]. Because of the simplification introduced above, there are only four adjustable parameters. Upon reducing experimental data for water in the region 273-1073 K and 0-1000 bars (Bain, 1964), we obtain the following parameters: $v_M^* = 12.227 \text{ cm}^3/\text{mol}$; $T_M^* = 466.73 \text{ K}$; $\Delta H^\circ = -36.35 \text{ kJ/mol}$; $\Delta S^\circ = -121.8 \text{ J/mol}\cdot\text{K}$. All these parameters are physically reasonable. In particular, the values for ΔH° and ΔS° are close to those reported for hydrogen bonding of water dimers (Eisenberg and Kauzmann, 1969).

Using these parameters, we calculate a pressure-volume diagram (Fig. 1). Except for the critical region, agreement with experiment is good. It is remarkable that, with just four adjustable parameters, one can obtain a nearly quantitative representation of the thermodynamic properties of water, including the two-phase region. Figure 2 shows excellent agreement between calculated and experimental vapor pressures. Figure 3, using a logarithmic ordinate, compares calculated with experimental configurational enthalpies; agreement is good. The average and maximum deviations from experimental data are summarized in Table 2.

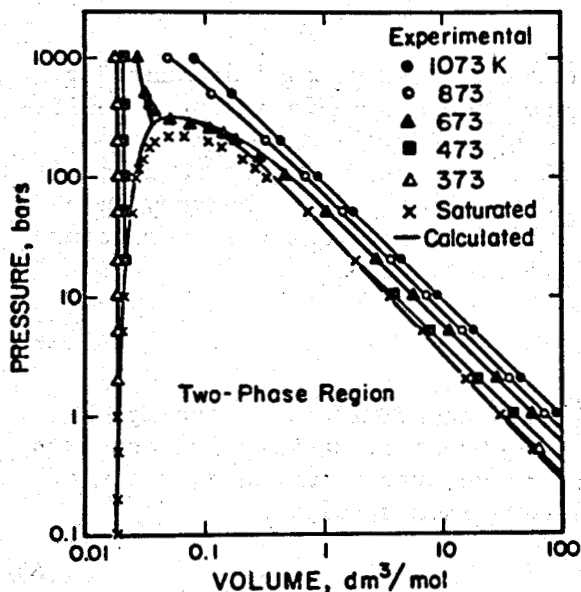


Fig. 1. Pressure-volume diagram for water.

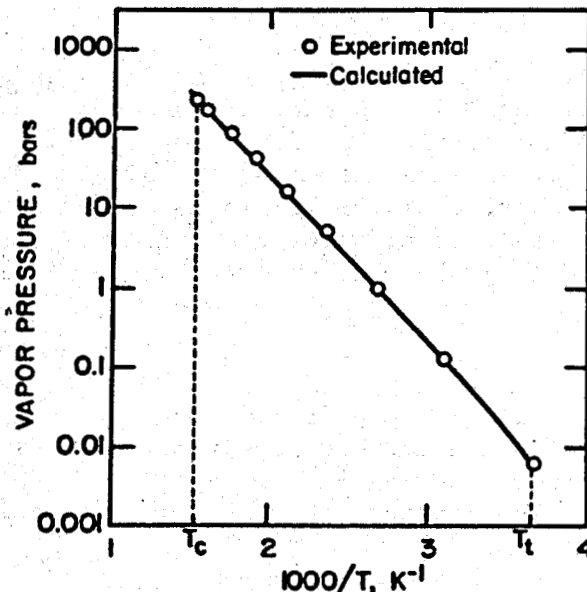


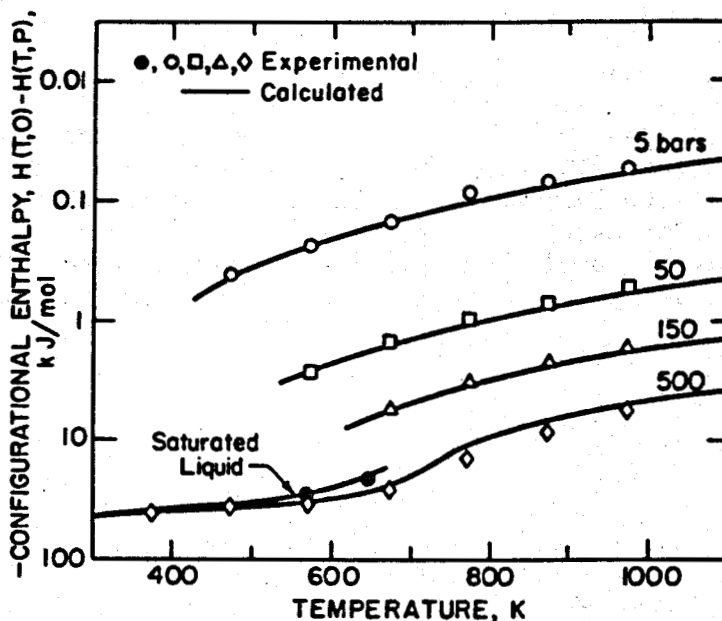
Fig. 2. Vapor pressure for water.

TABLE 2 Summary of Agreement with Experiment

T(K)	Vapor pressure	Average Deviations (%)		Volume (overall)	Enthalpy
		Saturated volume Liquid	Vapor		
273	0.01	4.5	2.2	2.0	1.0
373	0.1	1.2	3.0	1.4	0.5
473	0.1	0.8	3.1	1.1	2.7
573	0.02	0.7	4.6	1.3	3.3
673	-	-	-	1.9	3.4
773	-	-	-	2.2	11.6
873	-	-	-	0.8	8.9
973	-	-	-	0.3	8.6
1073	-	-	-	0.2	8.5

Pressure range: 0-1000 bars

Fig. 3. Configurational enthalpy for water.



SECOND-VIRIAL-COEFFICIENT CORRECTION

The van der Waals-type partition function described here is valid at high temperatures. The assumption of a homogeneous potential is worst at low densities and low temperatures. Therefore, all van der Waals-type partition functions give poor second virial coefficients, especially at low temperatures. To correct for this deficiency, we include a second-virial-coefficient correction (SV) according to

$$\ln Q = \ln Q^{\text{vdW}} + \ln (q^{\text{sv}})^N, \quad (7)$$

where Q^{vdW} is given by Eqs. (1-4). For $\ln(q^{\text{sv}})$ we propose a simple function of density ρ and reduced temperature T_r :

$$\ln q^{\text{sv}} = (d/T_r^n) \rho \exp(-\lambda \rho), \quad (8)$$

where $T_r \equiv T/T_c$, and T_c is the critical temperature. Constants d and n are determined from second-virial-coefficient data and positive constant λ is fixed so that the partition function gives a reasonable third virial coefficient. It is a property of Eq. (8) that $\ln(q^{\text{sv}})^N$ makes a negligible contribution to the total partition function at high densities; vapor pressures and liquid volumes are affected only slightly. For water we use $d = 38.2 \text{ cm}^3/\text{mol}$, $n = 3.71$, and $\lambda = 177.2 \text{ cm}^3/\text{mol}$. Figure 4 shows that calculated and observed second virial coefficients are in excellent agreement.

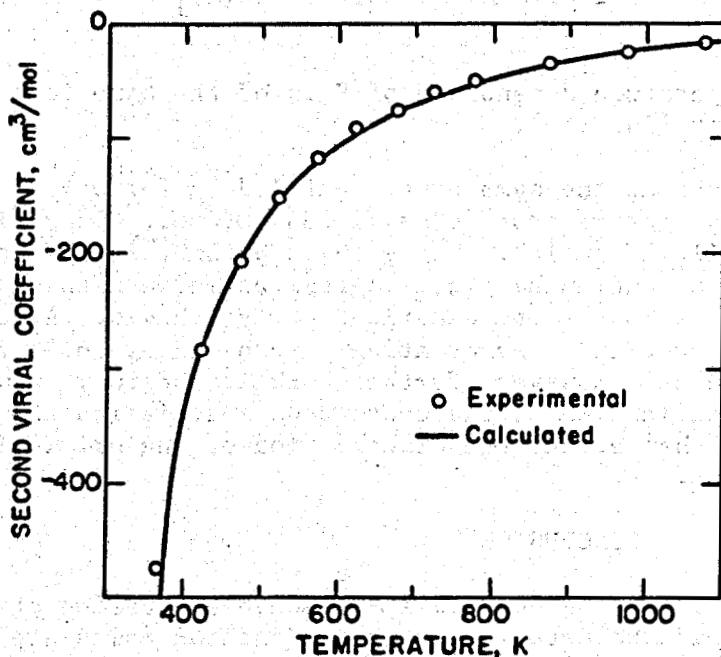


Fig. 4. Second virial coefficient for water.

CONTINUOUS ASSOCIATION HYPOTHESIS

Since the dimerization hypothesis appears to be at least moderately successful, it is tempting to inquire if allowing for higher linear aggregates (trimers, tetramers, etc.) might improve agreement with experiment. To investigate this possibility without, however, increasing the number of adjustable parameters, we postulate chemical equilibria of the type



where X_j is the j -mer of water. The equilibrium constant is given by

$$K_{j+1} = (\zeta_{j+1} \phi_{j+1}) / (\zeta_j \zeta_1 \phi_j \phi_1 P). \quad (10)$$

We now make the strong assumption that K_{j+1} is independent of j where $j=1,2,\dots,\infty$.

All fugacity coefficients ϕ are found from the equation of state. Our subsequent treatment is similar to that of Heidemann and Prausnitz (1976). We first adopt the mixing rules:

$$\langle c \rangle = 0.7 + 0.3(n_0/n_T); \quad \langle v^* \rangle = (n_0/n_T)v_M^*; \quad \langle T^* \rangle = (n_0/n_T)T_M^* \langle c \rangle^{-1}. \quad (11)$$

Here n_T is the total number of moles, and n_0 is the number of moles if there were no association ($n_0/n_T > 1$). Subscript M again stands for monomer. The equation of state for this multi-associated system is

$$z \equiv \frac{Pv}{RT} = \frac{n_T}{n_0} + \left(0.3 + 0.7 \frac{n_T}{n_0}\right) \frac{4(\tau/\tilde{v}) - 2(\tau/\tilde{v})^2}{(1 - \tau/\tilde{v})^3} + \sum_{n=1}^2 \sum_{m=1}^5 m \frac{A_{nm}}{\tilde{T}^n \tilde{v}^m} \left(\frac{n_T}{n_0} \langle c \rangle\right)^{1-n}, \quad (12)$$

where $\tilde{T} \equiv T/T_M^*$, $\tilde{v} \equiv v/v_M^*$, and $v \equiv V/n_0$. We show in Appendix II that

$$\frac{n_T}{n_0} = 2 \left[1 + \sqrt{1 + (4KRT/v) \exp(h)}\right]^{-1}; \quad h \equiv 0.7 \left[\frac{4(\tau/\tilde{v}) - 3(\tau/\tilde{v})^2}{(1 - \tau/\tilde{v})^2}\right]. \quad (13)$$

The temperature dependence of K is of the same form as that in the dimerization treatment [Eq. (6)].

Upon reducing the same experimental data for water as before, we obtain the following parameters: $v_M^* = 11.684 \text{ cm}^3/\text{mol}$; $T_M^* = 514.54 \text{ K}$; $\Delta H^0 = -18.04 \text{ kJ/mol}$; $\Delta S^0 = -113.1 \text{ J/mol}\cdot\text{K}$. Using these parameters, we calculate volumes, vapor pressures, and enthalpies. Agreement between theory and experiment is not as good as it is for the dimerization hypothesis. Average deviations from experiment for the continuous association hypothesis are 6.4% for vapor pressures and 2.5% for volumes. However, further work is underway in which we assume $K_2 \neq K_3 = K_4 = \dots$. This modification of the continuous association treatment should give better results than either the dimerization or the original continuous association treatment.

CONCLUSION

We have derived a physically-reasonable equation of state, with only a few adjustable parameters, with which one can calculate accurately the vapor pressures, volumes, and enthalpies of fluid water. The assumptions inherent in our equation are:

- (1) The water-water potential consists of a hard sphere surrounded by an attractive square well;
- (2) The effect of hydrogen bonding and other orientational forces is equivalent to the formation of water dimers (and j-mers, in general);
- (3) Density-dependent rotational and vibrational motions contribute to the equation of state through equivalent translational motions.

Our equation, based on the dimerization hypothesis, may be useful for engineering applications where the accuracy shown in Table 2 is adequate and where a relatively simple analytic equation of state is desirable for computational efficiency.

ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Science, U.S. Department of Energy.

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APPENDIX I. Partition Function for a Binary Mixture

For a mixture of two components containing N_1 molecules of species 1 and N_2 molecules of species 2, the partition function is

$$Q = \frac{V^N}{N_1! N_2!} \left(\frac{1}{\Lambda_1^3}\right)^{N_1} \left(\frac{1}{\Lambda_2^3}\right)^{N_2} \left(\frac{\langle v_f \rangle}{V}\right)^{N_c} \left(\exp - \frac{\langle \phi \rangle}{2kT}\right)^{N_c} (q_{int,1})^{N_1} (q_{int,2})^{N_2}, \quad (I.1)$$

where $N = N_1 + N_2$ and $N_c = N_1 c_1 + N_2 c_2$. The brackets $\langle \rangle$ indicate a composition average. The equation of state is given by:

$$P = kT(\partial \ln Q / \partial V)_{T, N_1, N_2} \quad (I.2)$$

The mixing rules are:

$$\ln \langle v_f \rangle / V = \frac{3(\tau/\tilde{v})^2 - 4(\tau/\tilde{v})}{(1 - \tau/\tilde{v})^2}; \quad \langle v^* \rangle = (\sigma^3 N_A / \sqrt{2}) (N_1 r_1 + N_2 r_2) / N; \quad \tilde{v} \equiv v / \langle v^* \rangle; \quad (I.3)$$

$$\frac{c \langle \phi \rangle}{2kT} = \sum_{n=1}^2 \sum_{m=1}^5 \frac{A_{nm} \langle cT^* \rangle \langle T^* \rangle^{(n)}}{T^n \langle \tilde{v} \rangle^m}; \quad (I.4)$$

$$\langle cT^* \rangle = \frac{\epsilon}{k} \frac{[N_1^2 q_1 r_1 + N_1 N_2 (q_1 r_2 + q_2 r_1) + N_2^2 q_2 r_2]}{N(N_1 r_1 + N_2 r_2)}; \quad \langle T^* \rangle^{(1)} = 1; \quad (I.5)$$

$$\langle T^* \rangle^{(2)} = \frac{\epsilon}{k} \frac{\left[\frac{N_1^2 q_1^2 r_1}{c_1} + N_1 N_2 \left(\frac{q_1^2 r_2}{c_1} + \frac{q_2^2 r_1}{c_2} \right) + \frac{N_2^2 q_2^2 r_2}{c_2} \right]}{[N_1^2 q_1 r_1 + N_1 N_2 (q_1 r_2 + q_2 r_1) + N_2^2 q_2 r_2]} \quad (I.6)$$

APPENDIX II. Total Number of Moles for Continuous Association

We use the equation of state [Eqs. (11-12)] and standard thermodynamic relations to calculate the fugacity coefficient of a j-mer:

$$(P\phi_j\phi_1)/(\phi_{j+1}) = (n_T/n_O)(RT/v) \exp(h) \quad ; \quad (II.1)$$

$$h \equiv (0.7) \frac{4(\tau/\tilde{v}) - 3(\tau/\tilde{v})^2}{(1 - \tau/\tilde{v})^2} + \frac{0.7}{\tilde{T}^2} \sum_{m=1}^5 A_{2m} \int_{\infty}^{\tilde{v}} \frac{d\tilde{v}}{v^{m+1}} \left(0.7 \frac{n_T}{n_O} + 0.3 \right)^{-2} \quad (II.2)$$

We find that the second term in h is small; therefore, we neglect it. It is important to note that $(P\phi_j\phi_1)/(\phi_{j+1})$ is independent of j. Mass balances for water molecules and for j-mers give

$$\sum_j j\zeta_j = n_O/n_T \quad ; \quad \sum_j \zeta_j = 1 \quad . \quad (II.3)$$

Upon substituting the expression for ζ_{j+1} given in Eq. (10) into Eqs. (II.3) and solving these two equations and Eq. (II.1) simultaneously, we obtain:

$$n_T/n_O = 2/[1 + \sqrt{1 + (4KRT/v) \exp(h)}] \quad . \quad (II.4)$$