An Adaptation of the Lattice Gas to the Water Problem

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The lattice-gas approach is generalized to incorporate features of the configurational problem posed by the randomly hydrogen-bonded "gel" model for liquid water. Because it possesses sublattices characterized by tetrahedral angles associated with triads of sites, a body-centered cubic (bcc) lattice is used. Each water molecule is allowed 12 orientations with respect to the bcc lattice. When two nearest neighbors have relative orientations which permit hydrogen bonding, they are assigned a hydrogen bond energy. When hydrogen bonding is not permitted the pair is assigned one of two weaker interaction energies. Like the simple lattice gas, this model displays a "vapor–liquid" phase transition. The critical site density proves to be less than $\frac{1}{2}$. The model should also exhibit a transition to a solid phase as a result of the possibility of complete hydrogen bonding associated with exclusive occupation of one sublattice. Excellent agreement is obtained with the observed temperature dependence of the second virial coefficient. The agreement in the case of the third virial coefficient is poor, however. The mean field approximation is shown to be inadequate for quantitative description of the vapor–liquid transition and the properties of the liquid phase.

KEY WORDS: Water; lattice gas; liquid–vapor phase transition; hydrogen bond; "gel"; tetrahedral; body-centered cubic; virial coefficients.

1. INTRODUCTION

The lattice-gas model was used by Lee and Yang[1] as an aid to comprehension of the liquid–gas phase transition and its critical point. These authors demonstrated the mathematical equivalence of this model and the magnetic Ising model, an equivalence which suggests a similarity between real magnetic transitions and real gas–liquid transitions. The putative similarity of these and other critical phenomena has contributed significantly to our understanding and classification of critical behavior.

Unfortunately, the lattice-gas model appears not to be a very good model for calculation of many quantitative features of gas–liquid behavior of simple fluids such as argon. Much of this unsuitability can be attributed to the existence in the model of preferred directions, as well as distances, for the positions of molecules which may reside in the first coordination shell around a given molecule.

It seems reasonable to anticipate that the lattice-gas model should prove more appropriate for treatment of the gas–liquid transition in fluids composed of molecules that interact through strongly directional forces. An example of such a substance is water, for which the notion of the hydrogen bond has proven extremely useful in qualitative discussion.

These observations naturally suggest the exploration of a lattice-gas model with internal degrees of freedom as a basis for more quantitative discussion of water (and other "associated" liquids). As we shall see, this model can be provided with at least two breakable symmetries, one of which corresponds to the gas–liquid transition, the other to a liquid–solid transition.

In another article[2] we have presented a discussion of the physical essence of the phase transitions which bound and define the liquid state of water. This discussion of the melting of ice and the condensation of water vapor has led to an interpretation of the nature of liquid water which attributes to the latter at any instant the "structure" of a randomly polymerized (via hydrogen bonds), three-dimensional network of macroscopic extent (in high-polymer parlance, a "gel"). The detailed structure of this "gel" is constantly and rapidly changing by virtue of the very rapid breaking and forming of hydrogen bonds (hydrogen bond lifetime $\sim 10^{-11}$ sec).

In this "gel" the often postulated tetrahedral "structure" of liquid water is presumably present in the limited sense that the equilibrium angle between any two hydrogen bonds emanating from a common participant water molecule is probably not greatly different from the tetrahedral angle. This tetrahedral character is also expected to be present in the somewhat fuller sense that some of the water molecules participate simultaneously in four (nearly tetrahedrally disposed) hydrogen bonds. Others, however, participate in only three, two, or one hydrogen bonds.

The proposition that a macroscopic "gel" phase (liquid) is related to the corresponding depolymerized "sol" phase (vapor) via a first-order phase transition has been posed (long ago) by Stockmayer,[3] applied to water in Ref. 2 and clarified in a more recent article.[4]

One way of characterizing the difference between a "gel" structure and a crystalline structure is to note that such ring closures as exist in the "gel" are random in both location and size, whereas the ring closures in the crystal are highly organized in a fashion that permits an especially large number of rings of a particular size (hexagonal rings in the case of ice). That the breakup of a structure composed of ordered, interconnected small rings (crystal) to yield a "gel" structure (liquid) is highly cooperative and should be a first-order phase transition, even if unaccompanied by the breakup of the resulting "gel" structure, is illustrated in Ref. 2.

That these two phase transitions, identified with boiling and melting, would be expected under conditions of sufficiently low pressure to coalesce to one transition, identified with sublimation, is also argued in Ref. 2.

The interpretation in Ref. 2 of melting as a randomization of the sizes and interconnections of rings of interaction (at the price of a small net loss of total bonding) supports the "gel" model of the liquid and suggests that Stockmayer's observation of the similarity between sol–gel and vapor–liquid transitions should be viewed as an identification of more than an analogy. This latter proposition is justified in Ref. 4.

Now the "vapor–liquid" transition afforded by the "lattice-gas" version of the Ising model can also be interpreted as a gelation, as can the ferromagnetic transition of the Ising model itself (in the sense of the formation of macroscopically large "spongy" domains of correlated spins). These considerations lend further support for the idea that a lattice-gas model (with internal degrees of freedom) may not be inappropriate for calculation of the properties of both liquid water and its condensation from the vapor.

Ideally, one hopes to avoid the use of a lattice model. Since the modification of conventional gelation theory (given in Ref. 2) for treatment of cases involving reversible bonding so easily provides an interpretation of the condensation of water vapor, one would perhaps be tempted to try to pursue this approach further into the liquid range. Unfortunately, however, three complications ensue. First, the modified gelation theory itself required introduction of a (Flory–Huggins[2]) lattice as a device to account for the effects of intermolecular repulsions (just as in a lattice gas). With allowance only for attractive interactions modified gelation theory yielded condensation in the form of total system collapse and provided no termination of the liquid–vapor equilibrium curve at a critical point. Second, allowance for

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[2] See Ref. 5. The DiMarzio–Gibbs[6] modification was used in Refs. 2 and 4.

ring closures (even at random) is very difficult to achieve in the context of gelation theory. Without allowance for these one has an unrealistic type of "gel" model for a liquid (i.e., a Cayley tree cannot be contained in space). Third, various summations arising in gelation theory are divergent on the liquid side of the vapor–liquid transition (just as in the case of the closely related Mayer[7] cluster integral theory for simpler substances). This third complication is closely related to the second.

Accordingly, we here invoke at the outset full use of an Ising lattice, purely as a computational device. A body-centered cubic[3] lattice is chosen, because the tetrahedral angles formed by triads of sites in each of its two tetrahedral sublattices correspond nicely to the tetrahedral angles presumed to exist between adjacent hydrogen bonds. Although this choice of bcc lattice may thus be expected to introduce less computational error than a less natural choice, it should be borne in mind that over distances stretching out beyond second nearest neighbors neither the real vapor nor the real liquid possesses crystalline order. That is, although the angles between adjacent hydrogen bonds may be nearly tetrahedral, the rotation around these H bonds effectively destroys longer range spatial order of the crystalline type.

Indeed, the calculations presented here show, even more clearly than those performed with the Lee–Yang lattice-gas model for a monatomic liquid as argued in Ref. 4, that the essence of the gas–liquid transition is not the appearance of a short-range manifestation of that type of order which a crystal possesses fully, but is rather the onset in long range of the type of ordering associated with gelation (aggregation to form randomly organized clusters, or "spongy" domains, of macroscopic extent.) Thus the network which will be found to exist on the low-temperature side of the (gas–liquid) phase transition exhibited by this lattice model (described more fully in Section 2) will be seen to be random in the fullest sense permitted by the lattice. That is, the network "domains" will not only prove to be "spongy" (as in the monatomic case) but also will be seen to wander randomly over both sublattices.

One may anticipate, therefore, that this model should display a liquid–solid transition in addition to the aforementioned gas–liquid transition. The liquid–solid transition would be characterized by assemblage of the molecules exclusively on one sublattice with the formation of ordered interconnected small rings and concomitant saturation of H-bonding capabilities.

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[3] This lattice is especially useful, because it allows the possibility of some non-hydrogen-bonded nearest neighbors even for a molecule which is hydrogen-bonded to four nearest neighbors. That this lattice is useful for discussion of tetrahedrally coordinated molecules with nonbonded neighbors was pointed out by Gibbs and DiMarzio.[8] It has been utilized in a discussion of water by Porosoff.[9] It has also been used in models of water by Bell and by Weres and Rice.[10]

In Section 2 the details of the model are introduced and discussed. In Section 3 the mean (molecular) field approximation (MFA) to the model is invoked. There it is seen that, while there is a liquid–vapor coexistence curve with a corresponding critical point, there is no stable crystalline phase in this order of approximation. It is also seen that since the strong directional dependence of the forces in the model is only treated in an average way in the MFA, the thermodynamic properties calculated with this approximation are not sufficiently accurate to be identified with those of real water. In Section 4 the second and third virial coefficients are calculated exactly for the model. It is seen that for appropriate choices of the interaction parameters the second virial coefficient for water can be fitted very well. The agreement with the third virial coefficient is even worse than that obtained with more realistic continuum calculations.[11] The absence from all these calculations of any allowance for "cooperative" H-bond interaction[12] (three-body attractive potential term) is probably responsible for this disagreement with the third virial coefficient.

The mean field approximation is known to correspond to the leading term in an expansion of the exact result in terms of the intermolecular potential. In a subsequent paper[13] we shall show that dramatic improvement is obtained by incorporation of the next higher term in this expansion. Inclusion of this quadratic term in the potential is sufficient to give the experimentally observed density maximum (as a function of temperature) in the liquid phase.

2. MODEL

We construct the model by dividing position space into cells each of which is a Wigner–Seitz cell of a body-centered cubic (bcc) lattice. Each tetrahedral sublattice of this bcc lattice is isomorphic with a diamond lattice, the lattice corresponding to cubic ice[14] (ice Ic). We assume that each cell may or may not be occupied by one water molecule. The center of mass of the water molecule in an occupied cell is assumed to reside at the corresponding lattice site at the center of the cell. A water molecule in an occupied cell is assumed to have any one of the 12 distinct orientations each of which points both of its OH groups and both of its lone pairs of electrons toward the nearest vertices of one of the tetrahedral sublattices (see Fig. 1).

For simplicity we restrict this discussion to the case in which only nearest neighbors interact, although this restriction is not required in principle. We assume that two nearest neighbors form a hydrogen bond (H bond) if their relative orientations are appropriate, i.e., one OH group of one pointing toward a lone pair of electrons of the other (see Fig. 1). If their relative orientations do not permit H bonding, the molecules are assumed to interact
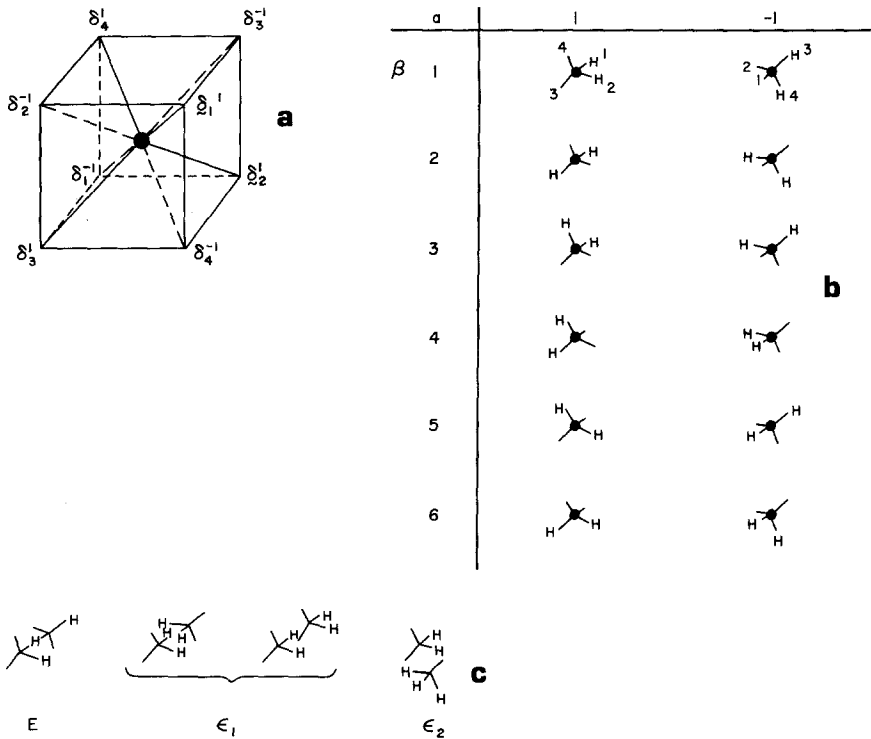
Fig. 1. (a) Lattice site and nearest neighbors for bcc lattice. The two possible orientations
$a = \pm 1$ of a tetrahedron are shown. Solid lines denote the $a = +1$ tetrahedron, while
dashed lines indicate the $a = -1$ tetrahedron. (b) The different possible orientations of
a water molecule with respect to a given tetrahedron ($a = \pm 1$) with their label β. (c)
Examples of the three types of interactions involved. The interaction is E for the relative
orientation that permits H bonding, ϵ_1 for relative orientations in which rotation of a
single member of the pair will permit H bonding, and ϵ_2 for relative orientations that
require rotation of both members of the pair to permit H bonding.

more weakly. We find it convenient to allow this non-H-bond interaction
to depend on the possibility that the pair can be readjusted to an orientation
favorable to H bonding by rotation of just one of the molecules of the pair.
We assign a repulsive (or less attractive) interaction to those orientations
that require rotation of both members of the pair for readjustment to an
H-bonded configuration. This results in an effective repulsion between the
two ice Ic sublattices. This repulsion seems required to account for the fact
that ice VIII, which is composed of two interpenetrating ice Ic sublattices
(bcc), has a larger nearest-neighbor distance than ice Ic and requires the
application of high pressures for its formation.

These arguments imply a model Hamiltonian of the form

$$H - \mu N = \text{K.E.} + \sum_{\mathbf{R},\alpha} (U^{\text{int}} - \mu)n_\alpha(\mathbf{R}) + \tfrac{1}{2} \sum_{\substack{\mathbf{R} \neq \mathbf{R}' \\ \alpha, \alpha'}} V_{\alpha\alpha'}(\mathbf{R} - \mathbf{R}')n_\alpha(\mathbf{R})n_{\alpha'}(\mathbf{R}')$$

(1)

where $\mathbf{R}$ labels the lattice site; α labels each of the 12 orientations of the water molecule; $n_\alpha(\mathbf{R})$, which possesses only the values zero or one, is the number of molecules at lattice site $\mathbf{R}$ in orientation α; the "one-body potential" U^{int} is assumed to consist of an "internal kinetic energy"[4] (of rotation, vibration, etc.); μ is the chemical potential; $V_{\alpha\alpha'}(\mathbf{R} - \mathbf{R}')$ is the potential energy associated with the two-body interaction between molecules in orientations α and α' separated by the distance vector $\mathbf{R} - \mathbf{R}'$.

The variables $n_\alpha(\mathbf{R})$ are constrained by the condition

$$\sum_\alpha n_\alpha(\mathbf{R}) \leqslant 1$$

(2)

That is, multiple occupation of a lattice site (cell) is forbidden.

The potential energy is such that for a nearest-neighbor separation

$$V_{\alpha\alpha'}(\boldsymbol{\delta}) = \begin{cases} -E & \text{if } \alpha, \alpha' \text{ correspond to orientations which permit H} \\ & \text{bonding} \\ -\epsilon_1 & \text{if rotation of a single molecule permits H bonding} \\ -\epsilon_2 & \text{if rotations of both members of the pair are neces-} \\ & \text{sary to permit H bonding} \end{cases}$$

(3)

V is assumed to vanish at separations other than nearest-neighbor separations. The explicit form of the potential matrix is given in Appendix A. The parameters E, ϵ_1, and ϵ_2 are kept adjustable, but we expect $|\epsilon_1|$ and $|\epsilon_2|$ to be of order 0.5 kcal/mole and E of order 2–6 kcal/mole. In Section 4 we shall see that a choice of $\epsilon_1 = \epsilon_2 = 7.2 \times 10^{-2}$ kcal/mole and $E = 4.65$ kcal/mole gives the correct critical temperature for water in the MFA.

The somewhat similar model considered by Bell[10] also employs three parameters: (1) an H-bond energy which is identical to ours, (2) a non-H-bonded energy which in this model corresponds to setting $\epsilon_2 = \epsilon_1$, and (3) a three-body repulsive energy assigned to configurations of three molecules in which two molecules on different sublattices share a common nearest neighbor. Bell's repulsive energy was introduced, as was our ϵ_2, to favor local occupation of a single ice Ic sublattice and to provide a density maximum in the results.[13] The attractive "cooperative H-bond" three-body energy,

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[4] Actually, to be more correct, this energy should be treated as an internal free energy of a water molecule.

which has been thought to be important in water,[12] is neglected in both Bell's treatment and ours.

We are interested in the grand partition function

$$\Xi(\beta, \mu) = \exp W(\beta, \mu)$$
$$= \text{Tr} \exp \left\{ -\beta \left[\sum_{\mathbf{R}_1, \alpha_1} (U^{\text{int}} - \bar{\mu}) n_{\alpha_1}(\mathbf{R}_1) + \frac{1}{2} \sum_{\substack{\mathbf{R}_1 \neq \mathbf{R}_2 \\ \alpha_1, \alpha_2}} V_{\alpha_1 \alpha_2}(\mathbf{R}_1 - \mathbf{R}_2) \right. \right.$$
$$\left. \left. \times n_{\alpha_1}(\mathbf{R}_1) n_{\alpha_2}(\mathbf{R}_2) \right] \right\} \tag{4}$$

where $\bar{\mu} = \mu + (1/\beta) \ln(v_c/\lambda^3)$, v_c is the volume of the unit cell, and $\lambda = (\beta h^2/2m\pi)^{1/2}$ is the thermal wavelength (β and m have their usual meanings). The factor λ arises via treatment of the translational kinetic energy and assures that the translational kinetic energy is always $\frac{3}{2}kT$ per molecule. The symbol Tr denotes a sum over all allowed states of the system, i.e., over all the sets of values of the variables $n_\alpha(\mathbf{R})$ that are consistent with (2).

Considering the similarity of our model to the ordinary lattice-gas model, we expect a system described by Hamiltonian (1) to exhibit a second-order phase transition at some critical temperature T_c. At temperatures below T_c the system should be separated into two phases of different densities, the lower density phase being identified with the vapor and the higher density phase with the liquid.
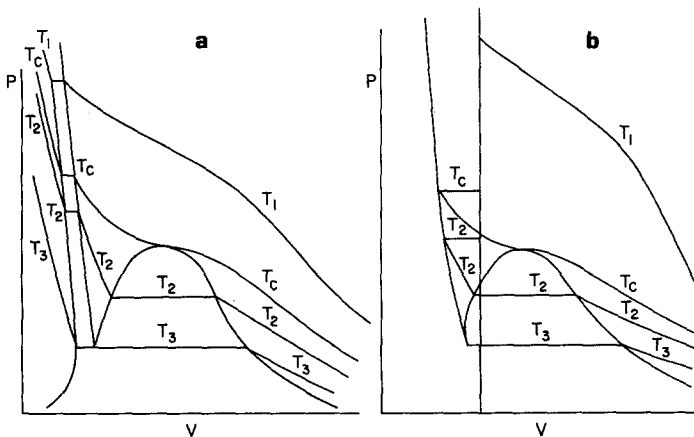

Fig. 2. (a) Typical P–V phase diagram for a simple substance which contracts on freezing. (b) Expected P–V phase diagram for the lattice model. The coexistence curve should show a volume minimum (density maximum) similar to the corresponding minimum (maximum) at constant pressure. The solid side of the coexistence curve and all isotherms in the solid phase would lie on a single vertical straight line when the lattice size is kept fixed. The density of this solid phase would be smaller than that of the liquid, since the solid (ice Ic) only fills half the bcc lattice.

However, the additional structure of the model suggests the existence of a third phase under appropriate conditions of temperature and pressure. Since the ice Ic lattice is a sublattice of the bcc lattice, we expect the presence of a transition to ice Ic, this configuration being favored energetically. In more formal terms, we may state this as the recognition that our model Hamiltonian has two breakable symmetries. One is a kind of "particle–hole" symmetry, the breaking of which is usually associated with the vapor–liquid transition. The other is the translational symmetry of the bcc lattice, which is broken by the transition to ice Ic (either tetrahedral sublattice is of lower symmetry than the whole bcc lattice). These considerations lead to the expectation that this model should give rise to a phase diagram similar to that depicted in Fig. 2.

3. MEAN FIELD APPROXIMATION

In this section we explore the thermodynamic consequences of the MFA. This approximation is best motivated by consideration of the particular situation in which the two-body potential V vanishes. It is easy to show that for $V = 0$ the thermodynamic potential is given by

$$W_0(\beta, \mu) = N_0 \ln\{1 + 12\bar{Z} \exp [\beta(U^{\text{int}} - \mu)]\} \tag{5}$$

where $\bar{Z} = v_c/\lambda^3$ and N_0 is the number of lattice sites. The average density of particles per lattice site is obtained by differentiation:

$$n = \frac{\langle N \rangle_0}{N_0} = \frac{\partial}{\partial \beta \mu} \left(\frac{W_0(\beta, \mu)}{N_0} \right) = \frac{12\bar{Z} \exp [\beta(U^{\text{int}} - \mu)]}{1 + 12\bar{Z} \exp [\beta(U_{\text{int}} - \mu)]} \tag{6}$$

The mean field approximation to the more general case which allows for interaction is obtained by making the following replacement in (6):

$$U^{\text{int}} \to U^{\text{int}} + \sum_{\alpha', \mathbf{R}'} V_{\alpha\alpha'}(\mathbf{R} - \mathbf{R}')\langle n_{\alpha'}(\mathbf{R}') \rangle = U^{\text{int}} + (1/12) \sum_{\alpha', \mathbf{R}'} V_{\alpha\alpha'}(\mathbf{R} - \mathbf{R}')n \tag{7}$$

That is, we assume that the effective energy experienced by a particular molecule is just its intrinsic energy plus its average potential energy. It is easy to verify that the sum over $\mathbf{R}'$ and α' in (7) is independent of α and $\mathbf{R}$. Thus the generalization of (7) becomes

$$n = \frac{12\bar{Z} \exp [-\beta(U^{\text{int}} - \mu + \bar{V}n)]}{1 + 12\bar{Z} \exp [-\beta(U^{\text{int}} - \mu + \bar{V}n)]} \tag{8}$$

where

$$\bar{V} = (1/144) \sum_{\alpha, \alpha' \mathbf{R}} V_{\alpha\alpha'}(\mathbf{R}) = -5\epsilon_1 - 2\epsilon_2 - E$$

We can calculate the isothermal compressibility from Eq. (8), since

$$n\left(\frac{\partial n}{\partial \beta P}\right)_T = \left(\frac{\partial n}{\partial \beta \mu}\right)_T = \frac{n(1-n)}{1 + n(1-n)\beta \bar{V}} \tag{9}$$

(We have used the unit cell volume v_c as our unit of volume.) We obtain the critical temperature in this approximation as the highest temperature at which the compressibility diverges. It is seen that this occurs at

$$n_c = \tfrac{1}{2} \quad \text{and} \quad kT_c = -\tfrac{1}{4}\bar{V} = \tfrac{1}{4}E + \tfrac{5}{4}\epsilon_1 + \tfrac{1}{2}\epsilon_2 \tag{10}$$

If we choose $\epsilon_1 = \epsilon_2 = 7.2 \times 10^{-2}$ kcal/mole (36°K) (this is the value of ϵ used in the Lennard-Jones formula applied to neon, which is isoelectronic with water), then we obtain the correct critical temperature, $T_c = 647°$K, for water if we choose $E = 4.65$ kcal/mole (2336°K). The important point here is that, with the simplest approximation to the model, we fit T_c with a reasonable value for the hydrogen bond energy. According to the Ben-Naim–Stillinger potential,[11] the "fully formed hydrogen bond configuration" corresponds to a potential energy of 6.5 kcal/mole (3270°K).

If we assume that the nearest-neighbor distance is a linear function of the temperature, we obtain a value of 0.688 g/cm³ for the critical density ρ_c, a value of 783 atm for the critical pressure P_c, and a value of 0.386 for the critical ratio $Z_c = P_c \rho_c v_c / n_c$. These values are to be compared with experimental values $\rho_c = 0.325$ g/cm³, $P_c = 218$ atm, and $Z_c = 0.230$.[15] The discrepancies in the cases of the critical density and pressure are serious. Thus the MFA calculation only serves to demonstrate the reasonableness of the choice of important energy values required to relate the model to real water.

It is easily seen that the MFA is a poor approximation to the model because Eqs. (8)–(10) contain no reference to the details of the interaction matrix $V_{\alpha\alpha'}$. Equation (8) shows that MFA reduces the theory to the status of a single-parameter theory. The same results could have been obtained from an ordinary lattice gas with a single interaction parameter. In a subsequent paper[13] we will consider the next simplest approximation to the model. There we show that better quantitative agreement with critical and other equilibrium properties can be obtained.

Next we derive the equation of state which is thermodynamically consistent with (10). This equation is easily obtained by integrating (9). We have

$$\partial(\beta P/\partial n)_T = [1/(1-n)] + n\beta\bar{V} \tag{11}$$

This equation can be immediately integrated to give

$$p\beta = -\ln(1-n) + n^2\beta\bar{V} \tag{12}$$

Equation (12) is identical to the equation of state of the simple (argon type) ordinary lattice-gas model in MFA. Quantitative comparison with PVT properties of water would be pointless, since (12) is totally insensitive to the special nature of the interaction between water molecules. It is also obvious that the MFA will not yield a transition to the ice Ic phase, the mean potential in (7) being linear in the density.

In order to obtain properties of the model of sufficient accuracy to warrant comparison with water, we must employ an approximation which is more sensitive to the dependence of the interaction potential on the relative orientations of neighboring molecules. The approximation treated in a subsequent paper[13] is such an approximation. It yields a correction to (12) which is of the order of the potential squared. This second-order approximation (SOA) proves to be strongly sensitive to the details of the interaction.

4. VIRIAL COEFFICIENTS

The calculation of the second and third virial coefficients is facilitated by recognition that the "kinematic" elimination of multiple occupation of a lattice site is just a convenient method for treatment of the "dynamic" effects of the hard-core repulsion of two water molecules. It is well known[16] that lattice-gas models with restricted site occupation are isomorphic with "hard-core lattice-gas" models in which it is assumed that the intermolecular potential is infinite at zero separation (i.e., two molecules on the same site). For the model the statement is that

$$V_{\alpha\alpha'}(\mathbf{R} - \mathbf{R}') = \infty \qquad \text{if} \quad \mathbf{R} = \mathbf{R}' \tag{13}$$

The virial coefficients can then be obtained by conventional methods,[7,11] in which integrations over phase space are replaced by sums over lattice sites and orientations. The second virial coefficient is then simply given by

$$B_2 = -\tfrac{1}{2} \sum_{\mathbf{R}} \tilde{f}(\mathbf{R}) \tag{14}$$

where

$$\tilde{f}(\mathbf{R}) = (1/12^2) \sum_{\alpha,\alpha'} \{\exp\left[-\beta V_{\alpha\alpha'}(\mathbf{R})\right] - 1\}$$

We assume that the potential satisfies (13) at $\mathbf{R} = 0$ and coincides with the potential defined in the appendix when $\mathbf{R}$ is a nearest-neighbor vector. This enables us to rewrite (14) as

$$B_2 = \tfrac{1}{2} - \tfrac{1}{2} \sum_{\delta} \tilde{f}(\delta) \tag{15}$$

The leading term, $\tfrac{1}{2}$, is easily verified to be the coefficient of the quadratic term in the expansion of $-\ln(1 - n)$ in powers of n.

By direct calculation with our interaction potential we obtain

$$B_2 = \tfrac{1}{2} - \tfrac{1}{2}[5(e^{\beta \epsilon_1} - 1) + 2(e^{\beta \epsilon_2} - 1) + e^{\beta E} - 1]$$
$$= \tfrac{9}{2} - \tfrac{5}{2}e^{\beta \epsilon_1} - e^{\beta \epsilon_2} - \tfrac{1}{2}e^{\beta E} \tag{16}$$

In order to compare this expression with experimental measurements in water, we must express it in the proper units. The coefficient in units of volume per mole is just Nv_c times (16), N being Avogadro's number. v_c is calculated with the assumption that the nearest-neighbor distance is a linear function of the temperature. The correct nearest-neighbor distance is easily obtained from X-ray measurements of Narten et al.[17]

In Fig. 3 the calculated coefficient is plotted versus temperature for several different values of the energy parameters. These are compared with an empirical formula which is known to fit experiments by Keyes.[18] As we see, the agreement is excellent and is rather insensitive to ϵ_1 and ϵ_2. However, comparison with experimental points definitely suggests a value of the hydrogen bond energy of $E \simeq 2.88$ kcal/mole. This should be compared with the "spectroscopic" value of $E \simeq 2.5$ kcal/mole.
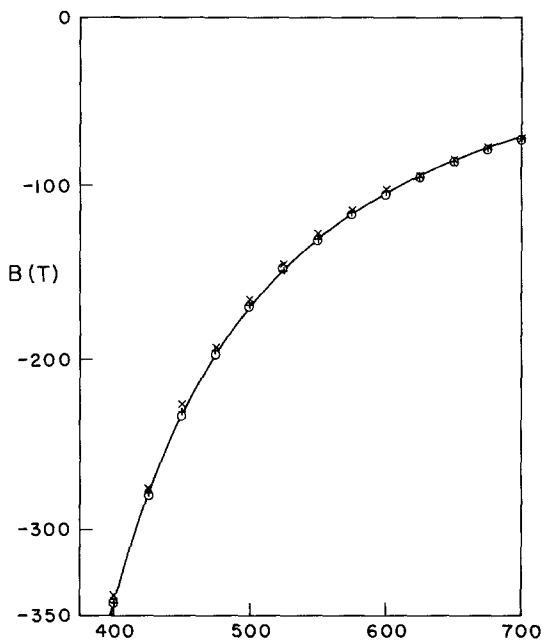

Fig. 3. Second virial coefficient $B(T)$ for water. The solid line is a plot of an empirical formula known to fit Keyes'[18] experiments. The points are calculated from the model using the following values of the parameters (in kcal/mole): $(+)$ $E = 2.89$, $\epsilon_1 = 0.269$, $\epsilon_2 = -0.942$; $(\bigcirc)$ $E = 2.87$, $\epsilon_1 = 0.350$, $\epsilon_2 = -0.961$; and $(\times)$ $E = 2.89$, $\epsilon_1 = 0.060$, $\epsilon_2 = -0.098$.

In a similar manner we calculate the third virial coefficient. This coefficient is given by

$$B_3 = (1/3N_0)(1/12^3) \sum_{\substack{R_1R_2R_3 \\ \alpha_1,\alpha_2,\alpha_3}} \{\exp [-\beta V_{\alpha_1\alpha_2}(R_1 - R_2)] - 1\}$$
$$\times \{\exp [-\beta V_{\alpha_2\alpha_3}(R_2 - R_3)] - 1\}\{\exp [-\beta V_{\alpha_1\alpha_3}(R_1 - R_3)] - 1\} \quad (17)$$

where N_0 is the number of lattice sites.

$$B_3 = \tfrac{1}{3} + 12^{-3} \sum_{\delta} \{\exp [-\beta V_{\alpha_2\alpha_3}(\delta)] - 1\}\{\exp [-\beta V_{\alpha_1\alpha_2}(\delta)] - 1\}$$
$$- (3 \cdot 12)^{-3} \sum_{\substack{\delta_1\delta_2\delta_3 \\ \alpha_1\alpha_2\alpha_3}} \delta_{\delta_1 + \delta_2 + \delta_3, 0}\{\exp [-\beta V_{\alpha_1\alpha_2}(\delta_1)] - 1\}$$
$$\times \{\exp [-\beta V_{\alpha_2\alpha_3}(\delta_2)] - 1\}\{\exp [-\beta V_{\alpha_1\alpha_3}(\delta_3)] - 1\} \quad (18)$$

The third term vanishes for a bcc lattice, it being impossible to form a triangle with three-nearest neighbor vectors. Thus, using the explicit form for the potential, we obtain

$$B_3 = \tfrac{1}{3} + (\tfrac{3}{2}e^{\beta\epsilon_1} + \tfrac{1}{2}e^{\beta E} - 2)^2 + (e^{\beta\epsilon_1} + e^{\beta\epsilon_2} - 2)^2 \quad (19)$$
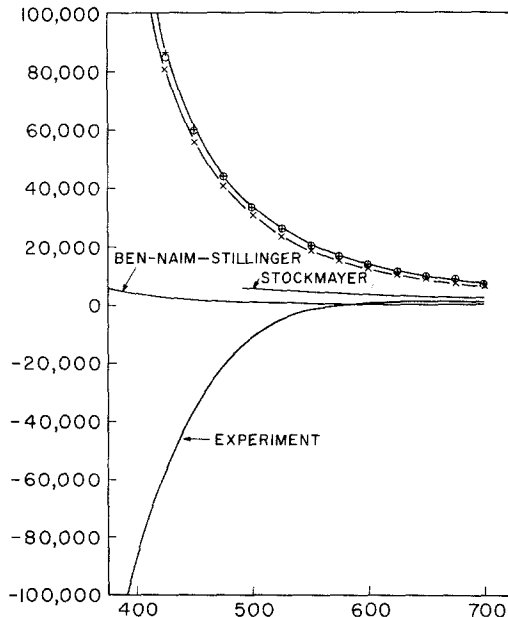

Fig. 4. Third virial coefficient $C(T)$ for water. The solid line represents an empirical formula which fits the data of Kell et al.[19] The values of the coefficient calculated from the model are shown for the same values of the energy parameters as in Fig. 3. Values of the coefficient obtained by numerical integration of the Stockmayer[20] and Ben-Naim–Stillinger[11] potentials are also shown.

For comparison with experimental results (19) must be multiplied by $(Nv_c)^2$. The calculated coefficient is plotted versus temperature in Fig. 4 for the same values of the parameters as in Fig. 3. This calculation is compared with an empirical formula which fits the third virial coefficient measurements of Kell et al.[19] It is also compared with the third virial coefficient obtained by direct numerical integration of the Ben-Naim–Stillinger potential[11] and the Stockmayer[20] potential.

If we had employed Bell's three-body repulsive energy as a third parameter instead of our ϵ_2, we would have obtained even worse agreement with the third virial coefficient.[21] Bell's model would give its best agreement when its three-body energy (not an energy associated with a triplet held together by two H bonds) is taken as attractive. It is more likely, however, that the dominant contribution to the actual third virial coefficient in water is a "cooperative H-bond" three-body energy.[12]

5. SUMMARY AND CONCLUSIONS

We have introduced a model for water which is a generalization of the lattice-gas model in that it includes the degrees of freedom associated with molecular orientation. We have suggested that this model should exhibit at least two phase transitions, these two corresponding to melting and boiling. The first nontrivial self-consistent approximation (MFA) has been examined and shown to be in agreement with the correct critical temperature for water (with a reasonable choice for the interaction parameters) but in disagreement with the critical density and pressure.

In order to test more severely the model itself (rather than an approximation to it), we have exactly calculated its second and third virial coefficients. Since it is well known that the third coefficient is very sensitive to a possible three-body correction to the otherwise pairwise additive potential,[11,12] the disagreement with it obtained with no three-body correction should not be taken too seriously. If Bell's[10] three-body interaction is employed instead of our distinct ϵ_2, the agreement with the third virial coefficient is worsened unless this interaction is made attractive.[21] Bell[10] has shown, however, that in his model this interaction must be repulsive if a density maximum and compressibility minimum are to be obtained. With Bell's model and ours (as well as those of Stockmayer and of Ben-Naim and Stillinger) the disagreement with the third virial coefficient is almost certainly related to neglect of the "cooperative H-bond interaction"[12] of three water molecules.

Although the three-body interaction may dominate the third virial coefficient, explicit incorporation of it into treatment of thermodynamic properties in the liquid phase may well not be necessary. Most interpretations of liquid water, including the "gel" model proposed in Refs. 2 and 4, suggest

a high degree of H bonding in the liquid. In such a case virtually every H-bond energy is subject to the "cooperative" three-body enhancement. Therefore the principal effect of this cooperativity may be accounted for by choice of an average energy per H-bonded pair which is larger than that determined for isolated pairs in the vapor by fitting to the second virial coefficient.

In a subsequent paper[13] we will establish a formalism from which a series of self-consistent approximations (MFA being the first and simplest) can be generated. The first improvement of MFA will be seen to be sufficient to give a density maximum for the liquid in the correct temperature range. Other thermodynamic properties of the liquid are brought into significantly better agreement with experimental results by this less drastic approximation.

APPENDIX. INTERACTION POTENTIAL MATRIX

In this appendix we exhibit the explicit form of the interaction matrix. The index α $(= 1\text{--}12)$ can be replaced by the pair of indices a, β $(a = \pm 1, \beta = 1\text{--}6)$. The index a labels the two sets of tetrahedrally disposed nearest-neighbors and β labels the six elements of the point group of a water molecule with respect to the ath sublattice. Clearly this assignment is not unique; we use the assignment defined in Fig. 1. The potential breaks into three parts,

$$V_{a\beta a'\beta'}(\mathbf{R}) = V^0(\mathbf{R}) + V^2_{a\beta a'\beta'}(\mathbf{R}) + V^2_{a\beta a'\beta'}(\mathbf{R}) \tag{A.1}$$

$V^0(\mathbf{R})$ is the isotropic "van der Waals" interaction. If $\boldsymbol{\delta}_\gamma{}^a$ is the γth $(\gamma = 1\text{--}4)$ nearest neighbor of the ath type, then

$$V^0(\boldsymbol{\delta}_\gamma{}^a) = -\epsilon_1 \tag{A.2}$$

and vanishes for any other separation.

V^1 is the hydrogen bonding potential. If we use the same coordinate system to label the nearest neighbors at each site, then it is clear that two hydrogen-bonded neighbors must have values of a of opposite sign. There V^1 must be of the form

$$V^1_{a\beta a'\beta'}(\boldsymbol{\delta}_\gamma{}^{a''}) = V^1_{\beta\beta'}(\boldsymbol{\delta}_\gamma{}^a)\,\delta_{\alpha\alpha''}\,\delta_{a-a'} = V^1_{a'\beta'a\beta}(-\boldsymbol{\delta}_\gamma{}^{a''}) \tag{A.3}$$

By consulting Fig. 1, we can explicitly enumerate this matrix

$$V^1_{\beta\beta'}(\boldsymbol{\delta}_1{}^1) = V_{\beta\beta'}(\boldsymbol{\delta}_1{}^{-1}) = \begin{bmatrix} 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 & 1 \end{bmatrix} (E - \epsilon_1) \tag{A.4a}$$

$$V^1_{\beta\beta'}(\delta_2{}^1) = V^1_{\beta\beta'}(\delta_2^{-1}) = \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 1 \\ 0 & 1 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 0 & 0 & 0 & 1 & 1 \end{bmatrix}(E - \epsilon_1) \qquad \text{(A.4b)}$$

$$V^1_{\beta\beta'}(\delta_3{}^1) = V^1_{\beta\beta'}(\delta_3^{-1}) = \begin{bmatrix} 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 & 0 & 1 \end{bmatrix}(E - \epsilon_1) \qquad \text{(A.4c)}$$

$$V^1_{\beta\beta'}(\delta_4{}^1) = V^1_{\beta\beta'}(\delta_4^{-1}) = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 & 1 & 0 \\ 1 & 1 & 0 & 0 & 0 & 1 \end{bmatrix}(E - \epsilon_1) \qquad \text{(A.4d)}$$

The Fourier transform of V^1 is

$$V_{\alpha\beta\alpha'\beta'}(k) = \sum_{\alpha''} [\exp(-i\mathbf{k}\cdot\delta_\gamma{}^\alpha)]V^1_{\alpha\beta\alpha'\beta'}(\delta_\gamma{}^\alpha) = V^\alpha_{\beta\beta'}(\mathbf{k})\,\delta_{\alpha-\alpha'} \qquad \text{(A.5)}$$

where

$$V^\alpha_{\beta\beta'}(\mathbf{k}) = \sum_\gamma [\exp(-i\mathbf{k}\cdot\delta^\alpha)]V^1_{\beta\beta'}(\delta_\gamma{}^\alpha)$$

Since $\delta_\gamma{}^\alpha = -\delta_\gamma^{-\alpha}$, we see that

$$V^\alpha_{\beta\beta'}(\mathbf{k}) = (V^{-\alpha}_{\beta\beta'}(\mathbf{k}))^* = V^{-\alpha}_{\beta\beta'}(-\mathbf{k}) \qquad \text{(A.6)}$$

Finally V^2 takes into account the repulsion[14] between sublattices. This part also only involves neighbors with different values of a. However, since they must be in totally unfavorable positions for hydrogen bonding, we must have

$$V^2_{\alpha\beta\alpha'\beta'}(\delta_r{}^{\alpha''}) = (\epsilon_2 - \epsilon_1)\,\delta_{\alpha'\alpha''}\,\delta_{\alpha-\alpha'} \qquad \text{(A.7)}$$

If V^2 is to correspond to an effective repulsion, we must have $\epsilon_2 - \epsilon_1 < 0$.

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