An Adaptation of the Lattice Gas to the Water Problem. II. Second-Order Approximation

Paul D. Fleming III[1] and Julian H. Gibbs[1]

The adaptation of the lattice-gas model to embody features possessed by water is further explored. On the basis of Martin's functional derivative formulation of Ising problems, a perturbation scheme is developed which allows calculation of the free energy to any desired order in the interaction potential at fixed density. The free energy correct to second order in the interaction strength is utilized here for calculation of other thermodynamic properties of the model. With reasonable choices of values of the interaction parameters these thermodynamic properties of the model can be brought into agreement with those of real water.

1. INTRODUCTION

In a previous paper,[1] hereafter referred to as III, we utilized a generalization of the lattice-gas model of Lee and Yang[2] for approximate calculations of

---

[1] Department of Chemistry, Brown University, Providence, Rhode Island.

some properties of water. In earlier papers,[3,4] hereafter called I[3] and II,[4] we presented a series of considerations, largely concerned with the phase transitions bounding the liquid phase, which clearly point to a particular physical model for the liquid phase. According to these considerations, the condensation process, which differentiates the liquid from the vapor, is a long-range "ordering" process of aggregation to form a *random* network (of hydrogen bonds in the case of water) of *macroscopic size* ("gelation"), and the melting process, which differentiates the liquid from the crystal, is a long-range disordering process of randomization of the locations and sizes of the smallest (i.e., the non-short-circuited) closed loops of hydrogen bonds (H bonds) in the network. These processes are shown in I and II to be individually highly cooperative and therefore to be capable of manifestation as two distinct first-order phase transitions. It is also indicated in I that these would be expected to coalesce into one transition (sublimation) at low pressures.

Since these cooperative processes involve changes in long-range, rather than short-range, order, the suggestion that they are indeed the basis of the two phase transitions (melting and boiling) is compatible with the modern interpretation of phase transitions and critical phenomena (see, e.g., Ref. 5), which has been gleaned in particular from studies of Ising models. A form of short-range order is, of course, imposed on liquid water (as well as the crystal and also the dense gas) by both the short-range and directional nature of the H-bond interaction, which respectively tend to fix the lengths of H bonds and fix the angles (approximately tetrahedral) between any two H bonds emanating from a common water molecule. Nevertheless, those older interpretations of the liquid phase that attribute the *essence* of its difference from gas and crystal to its possession of short-range order cannot be correct, since short-range ordering processes cannot by themselves yield first-order phase transitions (with latent entropy changes).

Thus the model for liquid water to which the considerations of I and II have led is that of a random, internally mobile network (or "gel") of H bonds. The mobility is ascribable to the fact that in this gel of H bonds, as distinct from chemically polymerized gels, the internal bonding is reshuffled in times of the order of 10^{-11} sec. Simple liquids may be analogously interpreted as internally mobile "gels" of van der Waals "bonds."

It should be noted that this picture of liquid water, which was obtained in I and II by consideration of the phase transitions bounding the liquid phase, is essentially the same as that obtained from molecular dynamics simulations of the liquid itself by Rahman and Stillinger.[6]

With the unmodified Lee–Yang lattice-gas (Ising) model, however, no distinction can be made between a randomly aggregated "gel," i.e., liquid, and a systematically interconnected array of rings the non-short-circuited members of which are of uniform size, i.e., crystal, for the lattice-gas model

itself imposes an element of crystallike order on the phases it displays, both its aggregated (i.e., condensed) phase (liquid or crystal according to one's taste) and its vapor phase. Thus the unmodified lattice-gas displays only one phase transition.

The modifications presented in III to the lattice-gas model not only introduce the possibility of accounting, approximately, for the effects of molecular rotational degrees of freedom, but also introduce the possibility of distinguishing between a phase possessing full crystalline order and one which, though aggregated to macroscopic dimensions (i.e., "gelled"), is significantly less ordered. Specifically, these modifications utilize a lattice (body-centered cubic, bcc, is convenient for water) which is composed of more than one sublattice (two tetrahedral ones in the case of the bcc lattice) and allow for a variety (albeit a discrete set) of molecular orientations on each lattice site. Half of these orientations correspond to participation in one sublattice, the remainder to participation in the other. In the less ordered condensed phase ("liquid") a network or "gel" of connected (via H bonds) molecules wanders over both sublattices. In the more ordered condensed phase ("crystal") all molecules are on sites defining one sublattice, an arrangement which permits maximum intermolecular bonding.[2]

In III the mean field approximation (MFA) was shown to give the correct critical temperature with a reasonable value of H-bond energy. Exact calculations of the second and third virial coefficients were also presented. The second virial coefficient could be placed in excellent agreement with experimental results with a reasonable choice of interaction energies. The agreement with the experimentally determined third virial coefficient was poor, however.

In this paper we further explore properties of the modified lattice gas (MLG). A formalism is developed from which properties of the model can be calculated to any desired degree of accuracy. The thermodynamic properties of a second-order approximation (SOA) to the model prove to compare favorably with those of water. This SOA, which is the simplest correction to the MFA, not only gives thermodynamic properties which agree reasonably with experiment, but gives a density maximum as well.

In Section 2 the general formalism is introduced. The SOA and random phase approximation (RPA) are derived. In Section 3 the thermodynamic properties of the SOA are calculated and compared with experiment.

---

[2] If the two-sublattice modification of the Lee–Yang model is introduced alone, that is, without the modification that allows for rotational degrees of freedom of the water molecules, as might be appropriate for a treatment of simple liquids, then one can still have a liquid–solid (as well as vapor–liquid) transition provided one still allows intra-sublattice bonding to be stronger than intersublattice bonding, perhaps as a consequence of differences in the corresponding near-neighbor distances. Such is, in fact, precisely the classical model for melting due to Lennard-Jones and Devonshire.[7]

2. FORMALISM

In this section we introduce a formalism which facilitates calculation of the properties of the MLG (or with appropriate change of indices, any Ising-like) model. This formalism involves functional derivative techniques which have proven useful in a number of branches of classical and quantum physics.[3] Our presentation is based on the treatment of the classical fluid problem and of the Ising model given by Martin[11] and somewhat on the fully renormalized formulation of statistical mechanics given by Denominicis[13] and Denominicis and Martin.[14]

In order to invoke the functional formalism, we must introduce an arbitrary external one-body potential into the MLG Hamiltonian presented in Eq. (1) of III. The modified Hamiltonian is

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

Here $\mathbf{R}$ labels a lattice site and α labels any one of the 12 molecular orientations each of which points both OH groups and both "lone pairs" toward nearest vertices of one of the tetrahedral sublattices of the bcc lattice; $n_\alpha(\mathbf{R})$, 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" $U^{\text{int}} + U_\alpha^{\text{ext}}(\mathbf{R})$ is assumed to consist of the "internal kinetic energy"[1] (of rotation, vibration, etc.) U^{int} and the external potential $U_\alpha^{\text{ext}}(\mathbf{R})$; μ is the chemical potential; and $V_{\alpha \alpha'}(\mathbf{R} - \mathbf{R}')$ is the potential energy associated with the two-body interaction between molecules in orientations α and α' separated by distance vector $\mathbf{R} - \mathbf{R}'$.

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

$$\sum_\alpha n_\alpha(\mathbf{R}) = \begin{cases} 0 & \text{(empty site)} \\ 1 & \text{(occupied site)} \end{cases} \qquad (2)$$

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

$$V_{\alpha \alpha'}(\boldsymbol{\delta}) = \begin{cases} -E & \text{if } \alpha \alpha' \text{ correspond to orientations} \\ & \text{that permit H bonding} \\ -\epsilon_1 & \text{if rotation of a single molecule} \\ & \text{permits H bonding} \\ -\epsilon_2 & \text{if rotations of both members of the pair} \\ & \text{are necessary to permit H bonding} \end{cases} \qquad (3)$$

---

[3] Functional derivative techniques in quantum field theory were first used by Schwinger.[8] These techniques were applied to nonrelativistic many-particle systems by Martin and Schwinger.[9,11] The Martin–Schwinger techniques were discussed and developed extensively by Kadanoff and Baym.[10] Also see the review by Stell.[12]

V is assumed to vanish at separations other than nearest-neighbor separations. The explicit form of the potential matrix is given in the Appendix of III.

It is convenient to use a shorthand notation for indices which will usually appear together. For example, the combination α_1, $\mathbf{R}_1$ will be denoted by just the label 1. With (1) the grand partition function takes the form

$$\exp[W(u, \phi)] = \text{Tr} \exp[\bar{u}(1)n(1) + \tfrac{1}{2}\phi(12)n(1)n(2)] \tag{4}$$

where we have introduced the dimensionless one- and two-body potential variables

$$u(1) = -\beta[U_{\alpha_1} + U_{\alpha_1}^{\text{ext}}(\mathbf{R}_1) - \mu] \tag{5a}$$

$$\phi(12) = -\beta V_{\alpha_1, \alpha_2}(\mathbf{R}_1 - \mathbf{R}_2) \tag{5b}$$

and

$$\bar{u}(1) = u(1) + \ln \bar{Z} \tag{5c}$$

$\bar{Z}$ is v_c/λ^3, where v_c is the volume of the unit cell and $\lambda = (\beta h^2/2m\pi)^{1/2}$ is the thermal wavelength (β, ln, 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 $\tfrac{3}{2}kT$ per molecule. The symbol Tr denotes a sum over all allowed states of the system, i.e., over all sets of values of the variables $n_\alpha(\mathbf{R})$ that are consistent with (2).

In Eq. (4) and in subsequent equations a summation convention is employed for repeated indices.

We use $W(u, \phi)$ as a generating function for correlation functions of the density. For example, we obtain by differentiation

$$\langle n(1) \rangle = e^{-W} \frac{\partial}{\partial u(1)} e^W \tag{6a}$$

$$\langle n(1)n(2) \rangle = e^{-W} \frac{\partial}{\partial u(1)} \frac{\partial}{\partial u(2)} e^W \tag{6b}$$

$$\vdots$$

$$\langle n(1) \cdots n(i) \rangle = e^{-W} \frac{\partial}{\partial u(1)} \cdots \frac{\partial}{\partial u(i)} e^W \tag{6c}$$

As is customary, we define the cumulants by

$$G(1 \cdots i) = \frac{\partial}{\partial u(1)} \cdots \frac{\partial}{\partial u(i)} W(u, \phi) \tag{7}$$

The correlation functions (6a)–(6c) are related to the cumulants by

$$\langle n(1) \rangle = G(1) \tag{8a}$$

$$\langle n(1)n(2) \rangle = G(1)G(2) + G(12) \tag{8b}$$

and

$$\langle n(1)n(2)n(3)\rangle = G(1)G(2)G(3) + G(1)G(23) + G(2)G(13)$$
$$+ G(3)G(12) + G(123) \tag{8c}$$

The thermodynamic potential is especially easy to evaluate when the two-body potential ϕ vanishes. The nonuniform generalization of (5) of III is

$$W(u, 0) = \sum_{\mathbf{R}_1} \ln\left(1 + \bar{Z}\sum_{\alpha_1} e^{u(1)}\right) \tag{9}$$

(9) clearly reduces to (5) of III when $U^{\text{ext}} = 0$.

The cumulants are easily obtained by differentiation. In particular the average density of water molecules at site $\mathbf{R}_1$ having orientation α_1 when $\phi = 0$ is given by

$$G_0(1) = \frac{\bar{Z}[\exp u(1)]}{\{1 + \bar{Z}\sum_{\alpha} \exp[u_{\overline{\alpha}}(\mathbf{R}_1)]\}} \tag{10}$$

We see that G_0 at a given site $\mathbf{R}_1$ and orientation α_1 does not involve the potential at sites other than $\mathbf{R}_1$ but does depend on the potential corresponding to various orientations.

For many purposes it is convenient to eliminate the one-body potential u as a variable in favor of the one-body density G. This can be accomplished by means of a Legendre transformation. To see this, we observe that

$$\left(\frac{\partial^2 W}{\partial u(1)\, \partial u(2)}\right)_\phi = G(12) = \langle[n(1) - G(1)][n(2) - G(2)]\rangle \tag{11a}$$

and

$$\left(\frac{\partial^2 W}{\partial[\frac{1}{2}\phi(12)]\, \partial[\frac{1}{2}\phi(34)]}\right)_u$$
$$= \langle[n(1)n(2) - \langle n(1)n(2)\rangle][n(3)n(4) - \langle n(3)n(4)\rangle]\rangle \tag{11b}$$

are elements of positive-definite matrices. It then follows that second derivatives of W with respect to $\{\frac{1}{2}\phi(12) + [1/\lambda(3)]u(3)\}$ for arbitrary $\lambda(3)$ are positive definite. If we choose λ such that the fluctuation is minimized, then we can show that

$$\left(\frac{\partial^2 W}{\partial[\frac{1}{2}\phi(12)]\, \partial[\frac{1}{2}\phi(34)]}\right)_u$$
$$- \frac{\partial^2 W}{\partial[\frac{1}{2}\phi(12)]\, \partial u(5)} \frac{\partial u(5)\, \partial u(6)}{\partial^2 W} \frac{\partial^2 W}{\partial[\frac{1}{2}\phi(34)]\, \partial u(6)}$$
$$= G(1234) - G(125)G^{-1}(56)G(634)$$
$$+ G(13)G(24) + G(23)G(14) \tag{12}$$

is positive definite. In (12) we have denoted the matrix inverse of the two-point cumulant by

$$G^{-1}(12) = \left(\frac{\partial u(1)}{\partial G(2)}\right)_\phi \equiv \frac{\partial u(1)\,\partial u(2)}{\partial^2 W} \equiv \left(\frac{\partial^2 W}{\partial u(1)\,\partial u(2)}\right)_\phi^{-1} \tag{13}$$

We define the (dimensionless) free energy by a Legendre transformation on the thermodynamic potential:

$$F(G_1, \phi) = -W(u, \phi) + u(1)G(1) \tag{14}$$

The natural variables for the free energy are the density and the potential, since

$$\left(\frac{\partial F(G_1, \phi)}{\partial G(1)}\right)_\phi = u(1) \tag{15a}$$

and

$$\left(\frac{\partial F(G_1, \phi)}{\partial [\frac{1}{2}\phi(12)]}\right)_{G_1} = -G(12) - G(1)G(2) \tag{15b}$$

Equation (15a) is a statement of the single-particle renormalization expressing the one-body potential as a function of the density and the potential. The second derivatives of F are indefinite, since

$$\left(\frac{\partial^2 F}{\partial G(1)\,\partial G(2)}\right)_\phi = \left(\frac{\partial u(1)}{\partial G(2)}\right)_\phi = G^{-1}(12) \tag{16a}$$

is positive definite, while

$$\frac{\partial^2 F}{\partial [\frac{1}{2}\phi(12)]\,\partial[\frac{1}{2}\phi(34)]} = -\left(\frac{\partial G(12)}{\partial [\frac{1}{2}\phi(34)]}\right)_{G_1} = -[\text{rhs of (16a)}] \tag{16b}$$

is negative definite.

The free energy can be easily obtained when the two-body potential vanishes. With use of (10) we can see that

$$u(1) = \ln\left\{G_0(1) \Big/ \left(\bar{\bar{Z}}\Big[1 - \sum_\alpha G_{0\bar{\alpha}}(\mathbf{R}_1)\Big]\right)\right\} \tag{17}$$

Thus using (9) and the definition of F, we obtain

$$F(G_0, 0) = G_0(1)\ln G_0(1)$$
$$- \sum_\mathbf{R}\Big[1 - \sum_{\alpha_1} G_0(1)\Big]\ln\Big[1 - \sum_{\alpha_1} G_0(1)\Big] - G_0(1)\ln \bar{Z} \tag{18}$$

We can now obtain a closed equation for F by integration of (15b) with respect to ϕ. It easily follows that

$$F(G, \phi) - F(G, 0) = \int_0^1 ds\, \frac{d}{ds} F(G, s\phi) = \int_0^1 ds\, \frac{\partial F(G, s\phi)}{\partial \phi(12)}\phi(12)$$
$$= -\tfrac{1}{2}G(1)\phi(12)G(2) - \tfrac{1}{2}\int_0^1 ds\, G(12, s\phi)\phi(12) \tag{19}$$

But using (16a), we can write $G(12, n, s\phi)$ in terms of a second derivative of F with respect to the density:

$$F(G, \phi) = F(G, 0) - \tfrac{1}{2}G(1)\phi(12)G(2) - \tfrac{1}{2}\int_0^1 ds \frac{\partial G(1)}{\partial^2 F(G, s\phi)} \frac{\partial G(2)}{} \phi(12) \quad (20)$$

Equation (20) is the desired equation for the free energy. It in principle uniquely determines F and can be used for calculation of F to any finite order in perturbation theory.

So far every equation in this section is exact. Obviously, exact solution of (20) is impossible. This equation is only useful if meaningful approximations can be obtained from it. As we shall see, such approximations can be readily obtained by iteration. The MFA as discussed in III is obtained, for example, by neglecting the fluctuation (integral) term in (20):

$$F_{mf}(G, \phi) = F(G, 0) - \tfrac{1}{2}G(1)\phi(12)G(2) \tag{21}$$

We can obtain the equation of state by calculating the thermodynamic potential $W = P\beta V$ as a functional of G and ϕ. From (15a)

$$u(1) \approx \frac{\partial F_{mf}(G, \phi)}{\partial G(1)} = \ln\left(\frac{G(1)}{\bar{Z}\left[1 - \sum_{\alpha} G_{\bar{\alpha}}(\mathbf{R}_1)\right]}\right) - \phi(12)G(2) \tag{22}$$

Substituting this into (21), we obtain

$$W_{mf}(G_1\phi) = -\sum_{\mathbf{R}_1} \ln\left[1 - \sum_{\alpha_1} G(1)\right] - \tfrac{1}{2}G(1)\phi(12)G(2) \tag{23}$$

In equilibrium this reduces to (12) of III for the mean-field equation of state.

We obtain corrections to MFA by treating the (functional) integral in some approximation. This can be done easily by differentiation of (22):

$$\left(\frac{\partial^2 F(G, \phi)}{\partial G(1)\, \partial G(2)}\right)_\phi = G_0^{-1}(12) - \phi(12) \equiv G_{\mathrm{RPA}}^{-1}(12) \tag{24}$$

The inverse of (24) is called the random phase approximation (RPA) to the correlation function. If one expands G_{RPA} to the order in which it can be literally believed (first order in ϕ),

$$G(12) \approx G_0(12) + G_0(13)\phi(34)G_0(42) \tag{25}$$

substitution into (19) yields

$$F_2(G, \phi) = F_{mf}(G, \phi) - \tfrac{1}{4}G_0(13)\phi(34)G_0(42)\phi(12) \tag{26}$$

where we have used $\phi(11) = 0$.

We call this the second-order approximation (SOA) to the free energy, since it is correct to second order in the potential at fixed density.

We can obtain the corresponding equation of state by differentiation of (26). The resulting expression for the thermodynamic potential is

$$W_2(G, \phi) = W_{mf}(G, \phi) - \tfrac{1}{2}G(1)[\partial G_0(53)/\partial G(1)]\phi(34)G_0(42)\phi(52) \quad (27)$$
$$+ \tfrac{1}{4}G_0(13)\phi(34)G_0(42)\phi(12)$$

In equilibrium (27) gives the second-order correction to (12) of III. Detailed discussion of this equation of state and its agreement with experiments on water will be left for Section 3.

In deriving (26) we expanded G_{RPA} only to lowest order in the potential. However, we notice that the (functional) integral in (19) can be performed analytically if we substitute G_{RPA} for G. This integration yields

$$F_{\mathrm{RPA}}(G, \phi) = F_{mf}(G, \phi) + \tfrac{1}{2} \operatorname{tr} \ln[\delta(12) - G_0(13)\phi(32)] \quad (28)$$

where the logarithm is defined by its power series expansion and the trace is taken over all the matrix indices.

Expression (28) will be referred to as the (RPA) free energy. In Appendix A we indicate how the RPA can be used in quantitative calculations. In particular, we show how to calculate G_{RPA} analytically.

A word of caution is in order here. One must be very careful in using the RPA as an approximation to be compared quantitatively with experiments. In particular, a catastrophe in its critical region is well known.[15] The cause of this catastrophe is easily seen from examination of (28) and (A.14) of Appendix A. F_{mf} is singular at the mean-field critical point. Additionally, as follows from the analysis in Appendix A, the argument of the logarithm in (28) goes through zero at the mean-field critical point. However, the condition for a critical point (i.e., $\partial^2 P/\partial n^2 = \partial P/\partial n = 0$) is satisfied at some lower temperature. Thus, there is a region between the MFA critical temperature and the RPA critical temperature where the free energy and the pressure are no longer single-valued *real* functions.

As we shall see in the following section, there are no such difficulties in the SOA. For this reason and for computational simplicity, we will use the SOA for our quantitative calculations.

3. THERMODYNAMIC PROPERTIES OF THE SECOND-ORDER APPROXIMATION

In this section we quantitatively explore the SOA. In equilibrium (26) reduces to

$$f = \frac{F_2}{N_0} = \frac{\beta A}{N_0} = n \ln \frac{n}{Z} + (1 - n) \ln(1 - n) - n^2 B_2 - \tfrac{1}{2}n^3 B_3 - \tfrac{1}{3}n^4 B_4 \quad (29)$$

where N_0 is the number of lattice sites, and

$$B_2 = B_2^{mf} + \Delta B_2$$
$$B_2^{mf} = 4(\tfrac{5}{8}\beta\epsilon_1 + \tfrac{1}{4}\beta\epsilon_2 + \tfrac{1}{8}\beta E)$$
$$\Delta B_2 = 2[\tfrac{5}{8}(\beta\epsilon_1)^2 + \tfrac{1}{4}(\beta\epsilon_2)^2 + \tfrac{1}{8}(\beta E)^2]$$
$$B_3 = -8[\tfrac{1}{8}(\beta\epsilon_1 + \beta\epsilon_2)^2 + \tfrac{1}{8}(\tfrac{3}{2}\beta\epsilon_1 + \tfrac{1}{2}\beta E)^2]$$

and

$$B_4 = 6(\tfrac{5}{8}\beta\epsilon_1 + \tfrac{1}{4}\beta\epsilon_2 + \tfrac{1}{8}\beta E)^2$$

From (27), or by direct differentiation of (29), we obtain the equation of state

$$P\beta v_c = -\ln(1 - n) - n^2 B_2 - n^3 B_3 - n^4 B_4 \qquad (30)$$

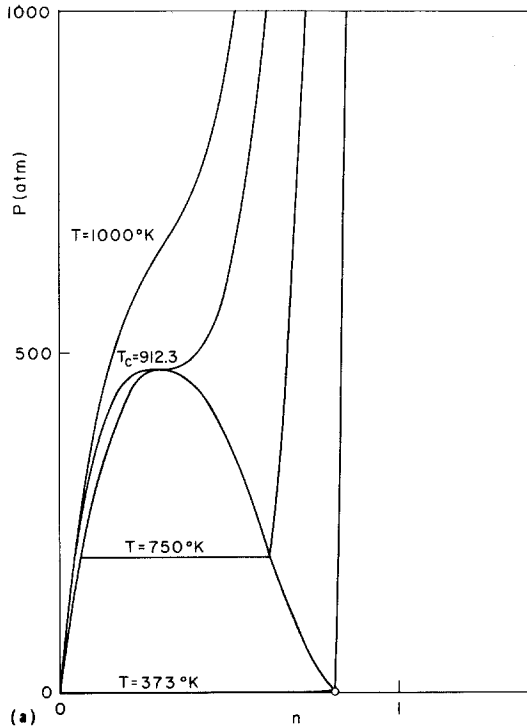The energy is obtained by differentiation of (29) at constant volume. If

Fig. 1. (a) Pressure vs. lattice density phase diagram for the SOA to the model with energy parameters $E = 4.58$ kcal/mole, $\epsilon_1 = 0.915$ kcal/mole, and $\epsilon_2 = -1.19$ kcal/mole. (b) Expanded view of the circled region of (a), showing the peculiar behavior of the liquid side of the coexistence curve in the 0–100°C range.

we allow the lattice to expand with temperature to maintain the correct nearest-neighbor distance, we must differentiate this dependence in calculating the energy. However, for simplicity we neglect this dependence in this section. The expressions, corrected for the lattice expansion, for the energy, entropy, and specific heats are given in Appendix B along with the assumed temperature dependence of v_c.

With neglect of the lattice expansion, the energy, entropy, compressibility and specific heats are as follows.[4]

[4] We also should include the effects of internal motion of single water molecules on the thermodynamics. This can be accomplished by adding a term f_{int} to the free energy (29). For our calculations we have used the rotational free energy

$$f_{int} = -n \ln[(\pi^{1/2}/2)(T^3/\theta_A\theta_B\theta_C)^{1/2}]$$

where $\theta_i = \hbar^2(2I_ik)$, the I's being the corresponding principal moments of inertial of the water molecule.
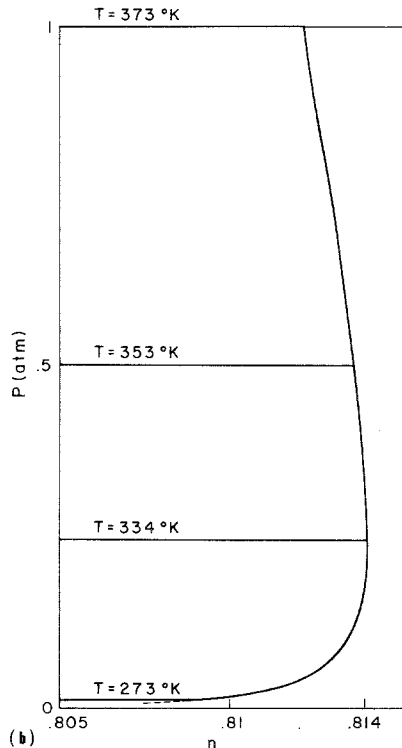

Fig. 1. Continued.

Energy:

$$\beta e = \beta \mathscr{E}/N_0 = \beta(\partial f/\partial \beta)_n$$
$$= \tfrac{3}{2}n - n^2(B_2 + \Delta B_2) - n^3 B_3 - \tfrac{2}{3}n^4 B_4 \qquad (31)$$

Entropy:

$$s = S/kN_0 = \beta e - f$$
$$= \tfrac{3}{2}n - n \ln(n/\overline{Z}) - (1 - n) \ln(1 - n) - n^2 \Delta B_2$$
$$- \tfrac{1}{2}n^3 B_3 - \tfrac{1}{3}n^4 B_4 \qquad (32)$$

Isothermal compressibility:

$$n \, \partial P \beta v_c / \partial n = [1/(1 - n)] - 2n^2 B_2 - 3n^3 B_3 - 4n^4 B_4 \qquad (33)$$

Specific heats:

$$nc_v/k = \tfrac{3}{2}n + 2n^2 \Delta B_2 + n^3 B_3 - \tfrac{2}{3}n^4 B_4 \qquad (34)$$

$$n\frac{c_p}{k} = n\frac{c_v}{k} + \frac{[n(\partial s/\partial n)_T - s]^2}{n(\partial P \beta v_c/\partial n)_T} \qquad (35)$$

where

$$n(\partial s/\partial n)_T = \tfrac{3}{2}n - n \ln(n/\overline{Z}) + n \ln(1 - n) - 2n^2 \Delta B_2 - \tfrac{3}{2}n^3 B_3 - \tfrac{4}{3}n^4 B_4 \quad (36)$$

In Fig. 1 the pressure vs. (lattice) density phase diagram for the model is plotted for $E = 4.58$ kcal/mole, $\epsilon_1 = 0.915$ kcal/mole, and $\epsilon_2 = -1.19$ kcal/mole. These values are chosen to give a boiling point at 1 atm of 100°C with the best possible liquid density obtainable with reasonable values of the parameters. As in III, we assume that the nearest-neighbor distance is a linear function of the temperature and choose the lattice size to fit the known (from X rays) nearest-neighbor distance for water. The liquid density at 1 atm and 100°C is $n = 0.81217$, which converts to $\rho = 1.323$ g/cm³ when multiplied by the mass of a water molecule and divided by the unit cell volume. This is larger than the experimental value of $\rho = 0.958$ g/cm³. We believe that this discrepancy results because the second-order approximation is not sufficiently sensitive to the strong angular correlations. Nevertheless, this result is a significant improvement over the MFA. The phase diagram for the MFA with the same values of the parameters is shown in Fig. 2 for comparison. It is seen, for example, that the coexistence pressure at 100°C is 30 atm. To obtain a 1 atm coexistence pressure, it is necessary to multiply each energy parameter by 1.7. Clearly, this would imply too large a value for the H-bond energy (~ 8 kcal/mole). If this is done, however, the corresponding liquid density discrepancy becomes worse (calculated $\rho = 1.628$ g/cm³). The density of the vapor is reasonably good in either case (see Table I), since this density is sufficiently low that the vapor is nearly ideal.

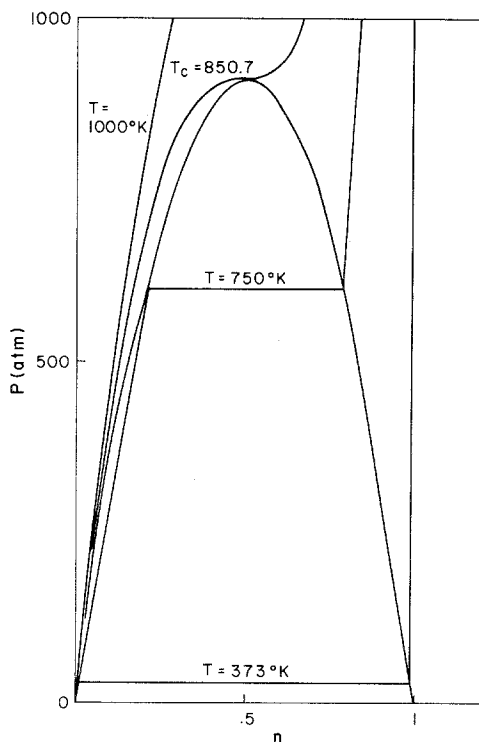The critical temperature, critical pressure, and critical density obtained

Fig. 2. Pressure vs. lattice density phase diagram for the MFA to the model for the same values of the energy parameters as in Fig. 1.

in this SOA (SO II) to the model are all too high (see Table II). If we scale the energy parameters by a factor of 0.709, we obtain the correct critical temperature, a better critical pressure, but a worse critical density. This scaling, of course, would result in a boiling point at 1 atm which would be too low. The observation that the H-bond energy which will fit the critical temperature is less than that required to fit the boiling point suggests a major

Table I. Coexisting Densities at 1 atm Pressure[a]

	Experiment	MFA	SOA
ρ_L, g/cm³	0.958	1.629	1.323
ρ_V, g/cm³	0.598×10^{-3}	0.591×10^{-3}	0.593×10^{-3}

[a] The SOA values are obtained with $E = 4.58$ kcal/mole, $\epsilon_1 = 0.915$ kcal/mole, and $\epsilon_2 = -1.19$ kcal/mole. The mean field values are obtained by multiplication each of these parameters by 1.74.

Table II. Critical Thermodynamics[a]

	Experiment	MF I	MF II	SO I	SO II
ρ_c, g/cm^3	0.325	0.688	0.612	0.412	0.353
P_c, atm	218	783	873.4	321.3	478.5
T_c, °K	647	647	850.7	647	912.3
$Z_c = (P_c\beta_c/\rho_c)m$	0.230	0.386	0.386	0.327	0.327

[a] The MF II values and SO II values are calculated with $E = 4.58$ kcal/mole, $\epsilon_1 = 0.915$ kcal/mole, and $\epsilon_2 = -1.19$ kcal/mole. These were used for comparison with thermodynamic properties in the 1 atm, 0–100°C range. The MF I and SO I values are chosen to fit T_c by scaling these values by 0.761 and 0.709, respectively.
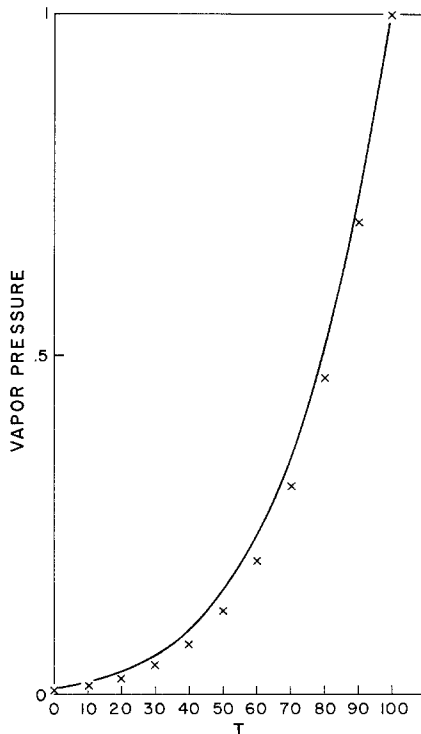

Fig. 3. Vapor pressure of the model in the SOA vs. temperature compared with experiment ($\times$), using the parameters of Fig. 1.

defect of a lattice model. One cannot hope to treat accurately the interactions between molecules in terms of temperature-independent parameters, especially when the nearest-neighbor distance is allowed to grow as a function of temperature. Clearly, the interaction energies should really be "free energies" which involve averages over intermolecular vibrations[5] and distances.

In Fig. 1(b) the 0–100°C liquid region is expanded. We see a definite maximum in the coexistence density as a function of temperature (or pressure) at 61°C and 0.25 atm. This is a necessary condition for the liquid to show a density maximum at fixed pressure. We therefore expect similar behavior of the liquid–vapor coexistence curve for real water in the neighborhood of 4°C when this curve is extended into the supercooled (with respect to crystallization) region.

In Fig. 3 the variation of vapor pressure with temperature for the model is plotted and compared with experiments.[18] The agreement with the experimental results is reasonably good.

With use of the assumed temperature dependence of the nearest-neighbor

[5] An approach to intramolecular vibrations has been given by Porosoff[16] within the context of the "gel" model introduced in I. He found that the thermodynamic properties of the liquid phase are particularly sensitive to these vibrations. A different approach to this has also been given by Fleming.[17]
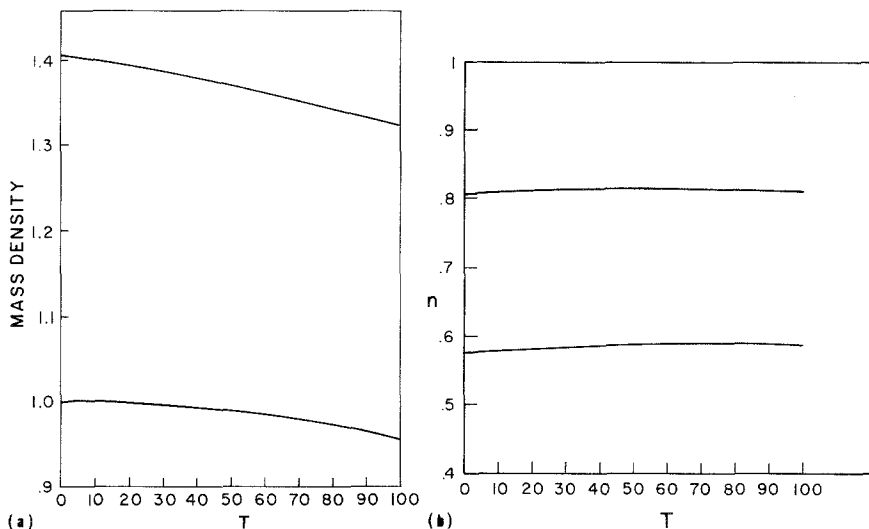

Fig. 4. (a) (Top curve) A plot of the mass density of water molecules calculated from the SOA to the model with the parameters of Fig. 1 vs. temperature at 1 atm, compared with a plot of the experimental mass density (bottom curve). (b) Lattice density vs. temperature at 1 atm. The top curve, calculated from the model, shows a maximum at 61°C, while the "experimental lattice density" (bottom curve), obtained by multiplying ρ_{exp} by v_c/m, shows a maximum at 80°C.

distance, it is easy to invert (30) numerically to obtain the density versus temperature at 1 atm. The mass density of water obtained by multiplication of the lattice density by m/v_c is plotted versus temperature and compared with experiment[19] in Fig. 4(a). We see that the calculated density is too large by a factor ~ 1.4 and should be a maximum somewhere below 0°C. However, the lattice density vs. temperature curve has a maximum at 61°C, as seen in Fig. 4(b). For comparison, the effective "lattice density" of water, obtained by multiplying the mass density by v_c/m, is also plotted and shows a maximum at 80°C. Since the maxima are so broad, we regard the agreement in the position of the maximum to be surprisingly good. It is most surprising that a density maximum is obtained at all in this simple approximation.

Knowing the density as a function of temperature at 1 atm, we can calculate the temperature dependence of other thermodynamic functions at this pressure. In Fig. 5 we plot the Gibbs and Helmholtz free energies and the energy vs. temperature. In Fig. 6 we plot the entropy vs. temperature. The
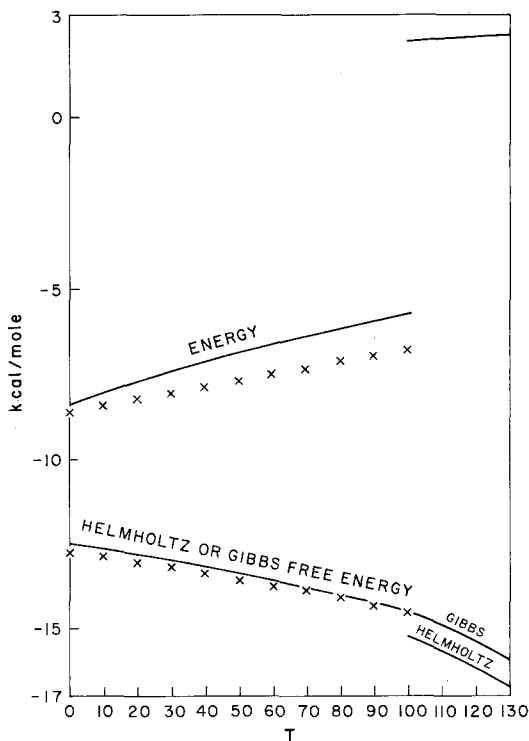

Fig. 5. Energy and free energies from the SOA and parameters of Fig. 1 vs. temperature at 1 atm compared with experiments ($\times$).

experimental values were obtained from tables compiled by Dorsey.[20] Since his zeros of energy and entropy correspond to those of a perfect ice crystal, we have shifted these quantities by constant amounts obtained from the assumption that our results are correct for the vapor phase at 373°C. This assumption is certainly very good, since the vapor density is so low that only the free-particle (ideal) contribution is important. The agreement with the numerical values of the free energies is very good. The agreement with derivatives of free energy (entropy and energy) is, of course, worse than the numerical agreement with the free energy itself. The agreement with the second derivatives of the free energy, the specific heats (Fig. 7), are fairly good, but the compressibility (Fig. 8) is in disagreement with experiments by Kell[21] by a factor two. Since the liquid density calculated for the model is too large by 40%, it is surprising that we obtain thermodynamic properties which agree as well as they do with experimental results. These calculations definitely encourage further work on the MLG in search of a better approxi-
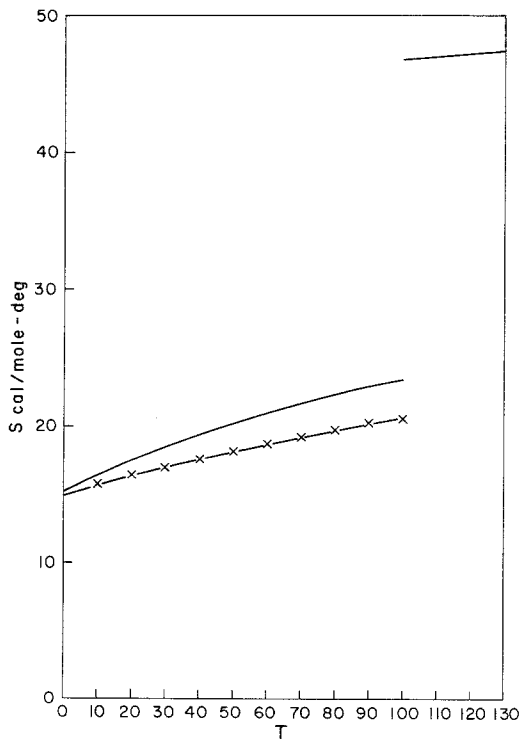

Fig. 6. Entropy from the SOA and the parameters of Fig. 1 vs. temperature at 1 atm compared with experiments (×).
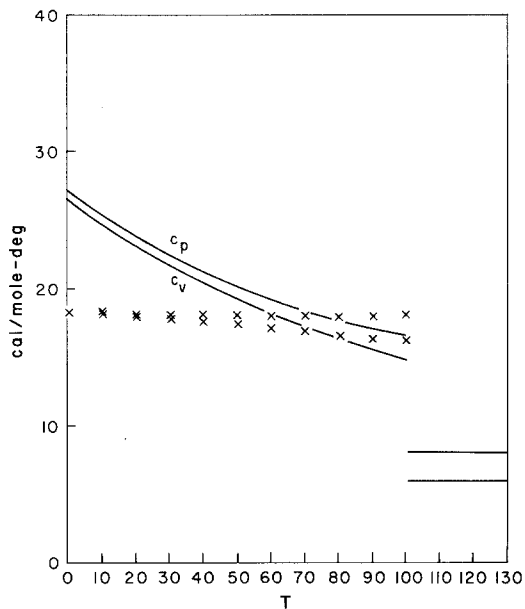
Fig. 7. Specific heats vs. temperature from the SOA and the parameters of Fig. 1 at 1 atm compared with experiments ($\times$).
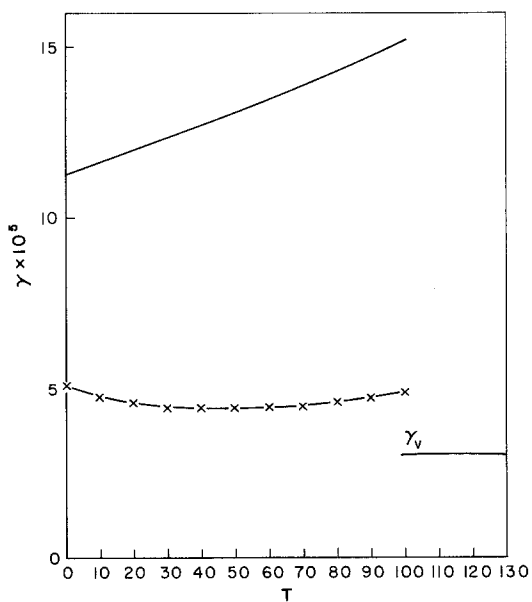

Fig. 8. Isothermal compressibility from the SOA and parameters of Fig. 1 at 1 atm vs. temperature compared with experiments ($\times$).

mation, which should include both higher-order corrections to the treatment of the configurational problem and a reasonable treatment of intermolecular vibrations.

In order to understand the correlations included in the SOA, we look at the pair correlation function consistent with it. This can be obtained directly from (25). Thus we have

$$G(1)G(2) + G(12) \equiv G(1)g(12)G(2)$$
$$= G(1)G(2) + G_0(12) + G_0(13)\phi(34)G_0(42) \quad (37)$$

We see that the pair correlation function consistent with the SOA is correct to first order in the potential.

Using the representation of the interaction given in III, we can easily obtain the value of the correlation function corresponding to the different kinds of relative orientations. For H-bonding orientations we have

$$g_{\mathrm{HB}} = g_{11-11}(\delta_1{}^1) = 1 + \beta E - n\beta(\tfrac{1}{2}E + \tfrac{3}{2}\epsilon_1) + \tfrac{1}{8}n^2(5\beta\epsilon_1 + 2\beta\epsilon_2 + \beta E) \quad (38a)$$

for ϵ_1 orientations (two kinds)

$$g_1{}^1 = g_{11-14}(\delta_1{}^1) = 1 + \beta\epsilon_1 - n(\tfrac{3}{2}\beta\epsilon_1 + \tfrac{1}{2}\beta E)$$
$$+ \tfrac{1}{8}n^2(5\beta\epsilon_1 + 2\beta\epsilon_2 + \beta E) \quad (38b)$$

$$g_1{}^2 = g_{1111}(\delta_1{}^1) = 1 + \beta\epsilon_1 - n(\tfrac{5}{4}\beta\epsilon_1 + \tfrac{1}{4}\beta E + \tfrac{1}{2}\beta E_2)$$
$$+ \tfrac{1}{8}n^2(5\beta\epsilon_1 + 2\beta\epsilon_2 + \beta E) \quad (38c)$$

$$g_1 = \tfrac{1}{5}g_1{}^1 + \tfrac{4}{5}g_1{}^2$$
$$= 1 + \beta\epsilon_1 - n(\tfrac{13}{10}\beta\epsilon_1 + \tfrac{3}{10}\beta E + \tfrac{2}{5}\beta\epsilon_2) + \tfrac{1}{8}n^2(5\beta\epsilon_1 + 2\beta\epsilon_2 + \beta E) \quad (38d)$$

and for the ϵ_2 orientations

$$g_2 = g_{11-11}(\delta_1^{-1}) = 1 + \beta\epsilon_2 - n(\beta\epsilon_2 + \beta\epsilon_2) + \tfrac{1}{8}n^2(5\beta\epsilon_1 + 2\beta\epsilon_2 + \beta E) \quad (38e)$$

Here we have employed the notation of the Appendix of III, in which the index α ($\alpha = 1$–12) is replaced by the pair of indices a, β ($a = \pm 1, \beta = 1$–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. In (38a) we have indicated components of the correlation function $g_{a\beta a'\beta'}$.

The average value of the correlation function is obtained by appropriate summation over orientations. This averaging yields

$$\bar{g} = \tfrac{5}{8}g_1 + \tfrac{1}{4}g_2 + \tfrac{1}{8}g_{\mathrm{HB}}$$
$$= 1 + \tfrac{1}{8}(1 - n)^2(5\beta\epsilon_1 + 2\beta\epsilon_2 + \beta E) \quad (39)$$

The average number of nearest neighbors of a given type is obtained by multiplication of the correlation function for that type by the density and by the average number of nearest neighbors which can have the required

orientation. By this method we obtain

$$N_{HB} = ng_{HB} \tag{40a}$$

$$N_1 = 5ng_1 \tag{40b}$$

$$N_1 = 2ng_2 \tag{40c}$$

$$N_{tot} = 8n\bar{g} \tag{40d}$$

In Fig. 9 we plot these quantities vs. temperature for the values of the density corresponding to 1 atm. The total number of nearest neighbors is essentially constant over this temperature range, as observed experimentally.[22] However, the number of neighbors we obtain, 6.8, is larger than the observed value, 4.5[22], by about the same factor (~ 1.4) as was found for the density. Thus, if the "correct lattice density" is substituted into (40d), we obtain essentially the observed number of nearest neighbors. More interesting, however, is the temperature dependence of the other types of neighbors. The rise with temperature in the average number of non-H-bonded neighbors of a
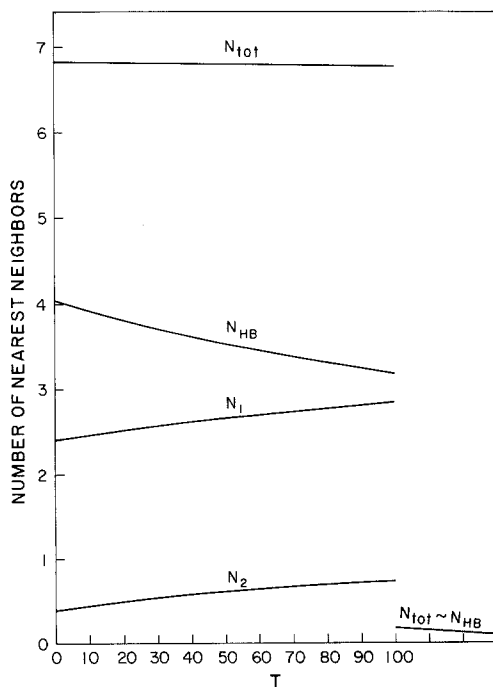
Fig. 9. Number of nearest neighbors calculated from the approximate correlation function of the model as a function of temperature for 1 atm. N_{tot} is the total number of neighbors, N_{HB} is the number of hydrogen-bonded neighbors, N_1 is the number of neighbors that interact by ϵ_1, and N_2 is the number that interact by ϵ_2.

typical molecule is combined with a corresponding decrease in its number of H-bonded neighbors, while the total number of neighbors at the given (typical) molecule remains (approximately) fixed and the density traverses a maximum.

4. CONCLUSION

Although the SOA is the simplest correction to the MFA, it appears to display some of the sensitivity to angular correlations expected in the model. We have seen that this approximation is sufficient to show a maximum in the density as a function of temperature both along the coexistence curve and at 1 atm. Although the liquid density is too large, surprisingly good agreement with experimentally obtained values for other thermodynamic functions has been found. A better approximation to the MLG might achieve even better agreement.

An important point to note is that we started with a model which makes no assumption of the existence of the liquid. We have shown that the model possesses a phase transition which can be identified with the vapor–liquid transition of water. This is to be contrasted with other "model" theories[6] which also give good agreement with experiments in the very small (with respect to the whole phase diagram—see Fig. 1a) *PnT* region corresponding to 1 atm and 0–100°C, but are incapable of discussing phase transitions, virial coefficients, etc.

The disadvantage of this model is its use of the lattice. One hopes that ultimately a quantitative theory of water can be developed with full translational invariance and a continuous potential. With recognition of recent progress in perturbation theory of liquids[24] this goal seems realizable in the near future. In fact, progress is being made[25] toward a reasonable continuum theory of water. The "gel" model yielded by the considerations of I and II can potentially yield an approximate theory of liquid water which makes no reference to a lattice (even for treatment of repulsions as in I and II). Nevertheless, at this time the calculation simplifications afforded by a lattice model warrant further study of the MLG, especially in light of the results obtained here.

APPENDIX A. EIGENVALUES AND EIGENVECTORS OF G_{RPA}

In this appendix we invert Eq. (24) by finding the eigenvectors of G_{RPA}^{-1}. In terms of the basis defined in the Appendix of III, (24) becomes

$$G_{a\beta a^1 \beta^1}^{-1}(\mathbf{k}) = \frac{12}{n}\,\delta_{aa^1}\delta_{\beta\beta^1} + \frac{1}{1-n} - \phi^0(\mathbf{k}) - [\phi_{\beta\beta^1}^a(\mathbf{k}) + \phi_a{}^2(\mathbf{k})]\,\delta_{a-a^1} \quad (A.1)$$

[6] See Ref. 23 for a review of model theories of water.

where

$$\phi^0(\mathbf{k}) = \beta\epsilon_1 \sum_{\gamma, a} \exp(-i\mathbf{k}\cdot\boldsymbol{\delta}_\gamma{}^a), \qquad \phi_a{}^2(\mathbf{k}) = \beta(\epsilon_2 - \epsilon_1) \sum_\gamma \exp(i\mathbf{k}\cdot\boldsymbol{\delta}_\gamma{}^a)$$

and

$$G_{a\beta a^1\beta^1}(\mathbf{k}) = \sum_{\mathbf{R}-\mathbf{R}^1} \{\exp[-i\mathbf{k}\cdot(\mathbf{R} - \mathbf{R}^1)]\}G_{a\beta a^1\beta^1}(\mathbf{R} - \mathbf{R}^1)$$

Two eigenvalues can be found by inspection, since

$$G_{a\beta a^1\beta^1}^{-1}(\mathbf{k})\psi_{a^1\beta^1}^{0\mu}(\mathbf{k}) = \left\{\frac{12}{n} + 6\left[\frac{1}{1-n} - \phi^0(\mathbf{k})\right]\right.$$

$$\left. - \mu\middle|\phi_0(\mathbf{k}) - 6\left[\frac{1}{1-n} - \phi^0(\mathbf{k}) - \phi_1{}^2(\mathbf{k})\right]\middle|\right\}\psi_{a\beta}^{0\mu}(\mathbf{k}) \quad \text{(A.2)}$$

where

$$\psi_{a\beta}^{0\mu}(\mathbf{k}) = (1/\sqrt{12})(\delta_{a1} + \mu e^{-i\eta(\mathbf{k})}\delta_{a-1}), \qquad \mu = \pm 1$$

$$\phi_0(\mathbf{k}) = 3\beta(E - \epsilon) \sum \exp(-i\mathbf{k}\cdot\boldsymbol{\delta}_\gamma{}^1)$$

and

$$\eta(\mathbf{k}) = \arg\left\{\phi_0(\mathbf{k}) + 6\left[\phi_1{}^2(\mathbf{k}) + \phi^0(\mathbf{k}) - \frac{1}{1-n}\right]\right\}$$

The remaining eigenvalues in the subspace orthogonal to $\psi^{0\mu}$ $\mu = \pm 1$ can be obtained from the eigenvalues of ϕ in that subspace. This eigenvalue problem can be stated as

$$\phi_{a\beta a^1\beta^1}^1(\mathbf{k})\psi_{a^1\beta^1}^{\lambda\mu}(\mathbf{k}) = \phi_{\beta\beta^1}^a(\mathbf{k})\psi_{-a\beta^1}^{\lambda\mu}(\mathbf{k}) = \mu\phi_\lambda(\mathbf{k})\psi_{a\beta}^{\lambda\mu}(\mathbf{k})$$
$$\lambda = 1\text{--}5, \quad \mu = \pm 1 \tag{A.3}$$

The eigenvalues ϕ_λ are real since ϕ^1 is Hermitian and can be chosen positive.

If we consider the set of eigenvectors $\{\lambda = 0\text{--}5, \mu = \pm 1\}$, then it follows that

$$\psi_{a\beta}^{*\lambda\mu}(\mathbf{k})G_{a\beta a^1\beta^1}^{-1}(\mathbf{k})\psi_{a^1\beta^1}^{\lambda^1\mu^1}(\mathbf{k}) = G_{\lambda\mu}^{1-}(\mathbf{k})\delta_{\mu\mu^1}\delta_{\lambda\lambda^1} \tag{A.4}$$

where

$$G_{\mu\lambda}^{-1}(\mathbf{k}) = \frac{12}{n} + 6\delta_{\lambda 0}\left[\frac{1}{1-n} - \phi^0(\mathbf{k})\right]$$

$$- \mu\middle|\phi_\lambda(\mathbf{k}) - 6\delta_{\lambda 0}\left[\frac{1}{1-n} - \phi^0(\mathbf{k}) - \phi_1{}^2(\mathbf{k})\right]\middle|$$

Thus we see that the RPA correlation function can be determined in terms of the eigenvalues of ϕ. The eigenvalue problem is greatly simplified

if we notice that four of the eigenvalues are zero. It is easy to verify that

$$\phi^{a}_{\beta\beta^1}(\mathbf{k})\psi^{\lambda\mu}_{a\beta} = 0 \qquad \text{for} \qquad \lambda = 4, 5, \quad \mu = \pm 1$$

where

$$\psi^{4\mu}_{a\beta} = (1/\sqrt{12})\begin{pmatrix} 2 \\ -1 \\ -1 \\ 2 \\ -1 \\ -1 \end{pmatrix}\delta_{\mu a} \qquad \text{and} \qquad \psi^{5\mu}_{a\beta} = \tfrac{1}{2}\begin{pmatrix} 0 \\ +1 \\ -1 \\ 0 \\ 1 \\ -1 \end{pmatrix}\delta_{\mu a} \qquad (A.5)$$

We project out the remaining subspace of eigenvectors in terms of the ortho-normal vectors

$$\psi^{1\bar{a}}_{a\beta} = (\delta_{\bar{a}a}/\sqrt{2})\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ -1 \\ 0 \end{pmatrix}, \quad \psi^{2\bar{a}}_{a\beta} = (\delta_{\bar{a}a}/\sqrt{2})\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ -1 \end{pmatrix},$$

$$\psi^{3\bar{a}}_{a\beta} = (\delta_{\bar{a}a}/\sqrt{2})\begin{pmatrix} -1 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \qquad (A.6)$$

It is easily verified that the vectors are orthogonal to the $\psi^{\lambda\mu}$ for $\lambda = 0, 4, 5$. In this subspace we obtain the projected matrix

$$\psi^{\nu\bar{a}}_{a\beta}\phi_{a\beta a^1\beta^1}(\mathbf{k})\psi^{\nu^1\bar{a}^1}_{a^1\beta^1} = \psi^{\nu\bar{a}}_{a\beta}\phi^{v}_{\beta\beta^1}(\mathbf{k})\psi^{\nu^1\bar{a}^1}_{-a\beta^1}$$

$$= \phi^{\bar{a}}_{\nu\nu^1}(\mathbf{k})\delta_{\bar{a}-\bar{a}^1} \qquad (A.7)$$

where

$$\phi^{1}_{\nu\nu^1}(\mathbf{k}) = (\phi^{-1}_{\nu\nu^1}(\mathbf{k}))^* = \begin{pmatrix} \tfrac{1}{3}\phi_0(\mathbf{k}) & A_1(\mathbf{k}) & -A_2(\mathbf{k}) \\ A_1(\mathbf{k}) & \tfrac{1}{3}\phi_0(\mathbf{k}) & -A_3(\mathbf{k}) \\ -A_2(\mathbf{k}) & -A_3(\mathbf{k}) & \tfrac{1}{3}\phi_0(\mathbf{k}) \end{pmatrix}$$

with

$$A_1(\mathbf{k}) = \beta(E - \epsilon_1)[\exp(-i\mathbf{k}\cdot\mathbf{\delta}_1{}^1) + \exp(-i\mathbf{k}\cdot\mathbf{\delta}_2{}^1) - \exp(-i\mathbf{k}\cdot\mathbf{\delta}_3{}^1) - \exp(-i\mathbf{k}\cdot\mathbf{\delta}_4{}^1)]$$

$$A_2(\mathbf{k}) = \beta(E - \epsilon_1)[\exp(-i\mathbf{k}\cdot\mathbf{\delta}_1{}^1) + \exp(-i\mathbf{k}\cdot\mathbf{\delta}_3{}^1) - \exp(-i\mathbf{k}\cdot\mathbf{\delta}_2{}^1) - \exp(-i\mathbf{k}\cdot\mathbf{\delta}_4{}^1)]$$

and

$$A_3(\mathbf{k}) = \beta(E - \epsilon_1)[\exp(-i\mathbf{k}\cdot\boldsymbol{\delta}_1{}^1) + \exp(-i\mathbf{k}\cdot\boldsymbol{\delta}_4{}^1)$$
$$- \exp(-i\mathbf{k}\cdot\boldsymbol{\delta}_3{}^1) - \exp(i\mathbf{k}\cdot\boldsymbol{\delta}_4{}^1)]$$

The eigenvalue problem (A.3) is transformed to

$$\phi_{\nu\nu1}^a(\mathbf{k})\psi_{-a\nu1}^{\lambda\nu}(\mathbf{k}) = \mu\phi_\lambda(\mathbf{k})\psi_{a\nu}^{\lambda\mu}(\mathbf{k}) \qquad (A.8)$$

where

$$\psi_{a\beta}^{\lambda\mu}(\mathbf{k}) = \psi_{\bar{a}\nu}^{\lambda\mu}(\mathbf{k})\psi_{a\beta}^{\nu\bar{a}}$$

Finally, (A.8) can be reduced to a 3 × 3 matrix equation, since it is equivalent to

$$\phi_{\nu\nu}^a(\mathbf{k})_{\bar{\nu}\nu1}^{-a}(\mathbf{k})\psi_{a\nu1}^{\lambda\mu}(\mathbf{k}) = [\phi_\lambda(\mathbf{k})]^2\psi_{a\nu}^{\lambda\mu}(\mathbf{k}) \qquad (A.9)$$

Equation (A.9) can be solved analytically for the eigenvalues ϕ^2 and the corresponding eigenvectors, since the eigenvalue equation is cubic. If we solve for the eigenvalues of $\phi^1\phi^{-1}$, we obtain

$$[\phi_\lambda(\mathbf{k})]^2 = \tfrac{1}{9}|\phi_0(\mathbf{k})|^2 + \tfrac{2}{3}|A_1(\mathbf{k})|^2 + \tfrac{2}{3}|A_2(\mathbf{k})|^2 + \tfrac{2}{3}|A_3(\mathbf{k})|^2$$
$$+ (1)_\lambda^{1/3}s_1(\mathbf{k}) + ((1)_\lambda^{1/3})^*s_2(\mathbf{k}) \qquad (A.10)$$

where $\lambda = 1, 2, 3$ label the three cube roots of one,

$$s_2^1(\mathbf{k}) = \left\{\frac{a_0(\mathbf{k})}{2} \pm i\left[\frac{[a_1(\mathbf{k})]^3}{27} - \frac{a_0(\mathbf{k})}{4}\right]^{1/2}\right\}^{1/3}$$

with

$$a_0(\mathbf{k}) = 2\,\mathrm{Re}[B_4(\mathbf{k})B_5{}^*(\mathbf{k})B_6(\mathbf{k})] + B_1(\mathbf{k})B_2(\mathbf{k})B_3(\mathbf{k})$$
$$+ B_1(\mathbf{k})|B_6(\mathbf{k})|^2 + B_2(\mathbf{k})|B_5(\mathbf{k})|^2 + B_3(\mathbf{k})|B_4(\mathbf{k})|^2$$

and

$$a_1(\mathbf{k}) = |B_4(\mathbf{k})|^2 + |B_5(\mathbf{k})|^2 + |B_6(\mathbf{k})|^2 - B_2(\mathbf{k})B_3(\mathbf{k})$$
$$- B_3(\mathbf{k})B_1(\mathbf{k}) - B_1(\mathbf{k})B_2(\mathbf{k})$$

where

$$B_1(\mathbf{k}) = \tfrac{1}{3}[|A_1(\mathbf{k})|^2 + |A_2(\mathbf{k})|^2 - 2|A_3(\mathbf{k})|^2]$$
$$B_2(\mathbf{k}) = \tfrac{1}{3}[|A_1(\mathbf{k})|^2 + |A_3(\mathbf{k})|^2 - 2|A_2(\mathbf{k})|^2]$$
$$B_3(\mathbf{k}) = \tfrac{1}{2}[|A_2(\mathbf{k})|^2 + |A_3(\mathbf{k})|^2 - 2|A_1(\mathbf{k})|^2]$$
$$B_4(\mathbf{k}) = \tfrac{2}{3}\,\mathrm{Re}[\phi_0(\mathbf{k})A_1{}^*(\mathbf{k})] + A_2(\mathbf{k})A_3{}^*(\mathbf{k})$$
$$B_5(\mathbf{k}) = -\tfrac{2}{3}\,\mathrm{Re}[\phi_0(\mathbf{k})A_2{}^*(\mathbf{k})] - A_3{}^*(\mathbf{k})A_1(\mathbf{k})$$
$$B_6(\mathbf{k}) = -\tfrac{2}{3}\,\mathrm{Re}[\phi_0(\mathbf{k})A_3{}^*(\mathbf{k})] - A_1(\mathbf{k})A_2{}^*(\mathbf{k})$$

The corresponding eigenvectors of $\phi^1\phi^{-1}$ are

$$\psi_\nu{}^\lambda(\mathbf{k}) = b_\nu{}^\lambda(\mathbf{k})/N_\nu(\mathbf{k})$$

where

$$b_1{}^\lambda(\mathbf{k}) = B_4(\mathbf{k})B_6(\mathbf{k}) - \{B_2(\mathbf{k}) - \delta[\phi_\lambda(\mathbf{k})]^2\}B_5(\mathbf{k})$$
$$b_2{}^\lambda(\mathbf{k}) = B_4(\mathbf{k})B_5(\mathbf{k}) - \{B_1(\mathbf{k}) - \delta[\phi_\lambda(\mathbf{k})]^2\}B_6(\mathbf{k})$$
$$b_3{}^\lambda(\mathbf{k}) = \{B_1(\mathbf{k}) - \delta[\phi_\lambda(\mathbf{k})]^2\}\{B_2(\mathbf{k}) - \delta[\phi_\lambda(\mathbf{k})]^2\} - |B_4(\mathbf{k})|^2$$

with

$$\delta[\phi_\lambda(\mathbf{k})]^2 = (1)^{1/3}s_1(\mathbf{k}) + ((1)^{1/3})^*s_2(\mathbf{k})$$

and

$$N_\lambda(\mathbf{k}) = \sum_\nu |b_\nu{}^\lambda(\mathbf{k})|^2$$

In terms of these vectors we identify

$$\psi_{a\nu}^{\lambda\mu}(\mathbf{k}) = \tfrac{1}{2}[\psi_\nu{}^\lambda(\mathbf{k})\delta_{a1} + \mu\psi_\nu^{*\lambda}(\mathbf{k})\delta_{a-1}] \tag{A.11}$$

The RPA free energy can be evaluated by noting that the logarithmic term in (25) can be written as

$$\text{tr}\ln[\delta(12) - G_0(13)\phi(32)] = \text{tr}\ln[G_0(13)G^{-1}(32)]$$
$$= \text{tr}\ln G_0(13) - \text{tr}\ln G^{-1}(32) \tag{A.12}$$

Now in equilibrium

$$G_{0\alpha\beta\,{}^1\beta}(k) = (12/n)\delta_{\alpha\alpha{}^1}\delta_{\beta\beta{}^1} + [1/(1-n)] \tag{A.13}$$

It is easily seen that the eigenvalues of G_0 are $1/n(1-n)$ and $1/n$ (11 times). Therefore

$$\text{tr}\ln G_0(13) = -N_0 \ln n^{12}(1-n) \tag{A.14}$$

The second term in (A.12) can be obtained in terms of the $G_{\mu\lambda}(\mathbf{k})$ as

$$\text{tr}\ln G^{-1}(32) = N_0 \frac{1}{v_c} \int \frac{d^3k}{(2\pi)^3} \sum_{\substack{\lambda=1\\\mu=\pm1}}^6 \ln G_{\mu\lambda}^{-1}(\mathbf{k}) \tag{A.15}$$

Then F_{RPA} can be calculated from $G_{\mu\lambda}(\mathbf{k})$ using (A.14) and (A.15).

APPENDIX B. EFFECT OF LATTICE EXPANSION ON THERMODYNAMIC FUNCTIONS

In this appendix we indicate how the lattice expansion can be incorporated into the calculation of thermodynamic functions. The free energy F in Eq. (29) is related to the (extensive) Helmholtz free energy A by

$$\beta A/N_0 = f_{\text{int}} + f \tag{B.1}$$

where f_{int} is the internal free energy discussed in footnote 4.

The equation of state is unchanged, since its evaluation involves only constant-temperature derivatives of the free energy with respect to the density. f_{int} does not contribute, since

$$f_{int} = n(\partial f_{int}/\partial n)_T \tag{B.2}$$

However, we must include the lattice expansion in calculating the energy, since it is related to the free energy by a temperature derivative. We can easily show that

$$\beta e = \frac{\beta}{N_0} \frac{d(\beta A)}{d\beta} = \beta \left[\frac{\partial (f + f_{int})}{\partial \beta} \right]_n + \left(n \left(\frac{\partial f}{\partial n} \right)_T - f \right) \frac{\partial \ln v_c}{\partial \beta} \tag{B.3}$$

But $n(\partial f/\partial n) - f$ is just $P\beta v_c$, so the energy becomes

$$\beta e = 3n - n^2(B_2 + \Delta B_2) - n^3 B_3 - \frac{n^4 B_4}{3} + (P\beta v_c - n) \frac{\partial \ln v_c}{\partial \ln \beta} \tag{B.4}$$

The factor $-n \, \partial(\ln v_c)/\partial \ln \beta$ arises from differentiation of the explicit v_c dependence of $\bar{Z}$ in f.

The entropy is obtained in the usual manner from

$$s = \beta e - f - f_{int} \tag{B.5}$$

The isothermal compressibility is unchanged, and c_v is given (including an internal contribution of $\frac{3}{2}k$) by

$$n \frac{c_v}{k} = 3n + 2n^2 \Delta B_2 + n^3 B_3 + \frac{n^4 B_4}{3} - (P\beta v_c - n) \frac{\partial^2 \ln v_c}{\partial \ln \beta^2}$$
$$+ \left[s - n \left(\frac{\partial s}{\partial n} \right)_T - n - \beta \left(\frac{\partial p \beta v_c}{\partial \beta} \right)_n \right] \frac{\partial \ln v_c}{\partial \ln \beta} \tag{B.6}$$

where

$$n \left(\frac{\partial s}{\partial n} \right)_T = 3n - n \ln \frac{n}{Z} + n \ln(1 - n) - 2n^2 \Delta B_2 - \frac{n^3 B_3}{2} - \frac{n^4 B_4}{3}$$
$$+ \left[n \left(\frac{\partial p \beta v_c}{\partial n} \right)_T - n \right] \frac{\partial \ln v_c}{\partial \ln \beta}$$

and

$$\beta(\partial P \beta v_c/\partial \beta)_n = -n^2(B_2 + \Delta B_2) - n^3 B_3 - \frac{2}{3}n^4 B_4$$

c_p is related to c_v by (35), provided the corrected expressions for s and $n(\partial s/\partial n)_T$ are used.

In all our calculations we have assumed that the nearest-neighbor distance as a function of temperature is (in angstroms)

$$R_{NN} = 2.82 + 0.00061(T - 277) \tag{B.7}$$

This equation fits the experimental[22] R_{NN} between 0 and 200°C. From this dependence it is easy to calculate the derivatives of the unit cell volume with respect to temperature:

$$\frac{\partial \ln v_c}{\partial \ln \beta} = -3\frac{\partial \ln R_{NN}}{\partial \ln T} = -\frac{0.00183T}{R_{NN}} \qquad \text{(B.8a)}$$

and

$$\frac{\partial^2 \ln v_c}{\partial \ln \beta^2} = -\frac{\partial \ln v_c}{\partial \ln \beta} - \left(\frac{\partial \ln v_c}{\partial \ln \beta}\right)^2 \qquad \text{(B.8b)}$$

ACKNOWLEDGMENTS

REFERENCES

1. P. D. Fleming and J. H. Gibbs, *J. Stat. Phys.* **10**:47 (1974).
2. T. D. Lee and C. N. Yang, *Phys. Rev.* **87**:410 (1952).
3. J. H. Gibbs, C. Cohen, P. D. Fleming, and H. Porosoff, *J. Sol. Chem.* **2**:277 (1973) (Henry Frank Symposium Volume).
4. C. Cohen, J. H. Gibbs, and P. D. Fleming, *J. Chem. Phys.* **59**:5511 (1973).
5. H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford University Press, New York (1971).
6. A. Rahman and F. H. Stillinger, *J. Chem. Phys.* **55**:3336 (1971); **57**:1281 (1972); and to be published.
7. J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)* **A163**:63 (1937); **A169**:317 (1939); **A170**:463 (1939); J. E. Lennard-Jones, *Proc. Phys. Soc. (London)* **52**:38 (1940).
8. J. Schwinger, *Proc. Nat. Acad. Sci. U.S.* **37**:952 (1951).
9. P. C. Martin and J. Schwinger, *Phys. Rev.* **115**:1342 (1959).
10. L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics*, Benjamin, New York (1962).
11. P. C. Martin, lecture notes (unpublished).
12. G. Stell, in *The Equilibrium Theory of Classical Fluids*, J. Lebowitz and H. Frisch (eds.), Benjamin, New York (1964).
13. C. DeDominicis, *J. Math. Phys.* **3**:983 (1962).
14. C. DeDominicis and P. C. Martin, *J. Math. Phys.* **5**:14, 31 (1964).
15. J. C. Wheeler and D. Chandler, *J. Chem. Phys.* **55**:1645 (1971).
16. H. Porosoff, Ph.D. Thesis, Brown University, 1970 (unpublished).
17. P. D. Fleming, unpublished.
18. E. W. Washburn, *Monthly Weather Review* **52**:488 (1924).
19. *Smithsonian Tables*, compiled from various authors.
20. N. E. Dorsey, *Properties of Ordinary Water-Substance*, ACS Monograph No. 81, Reinhold Publishing Co., New York (1940).
21. G. S. Kell, *J. Chem. Eng. Data* **12**:66 (1967).

22. A. H. Narten, M. D. Danford, and H. A. Levy, *Disc. Faraday Soc.* **43**:97 (1967).
23. D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, New York (1969), Chapter 4.
24. H. C. Anderson, D. Chandler, and J. D. Weeks, *J. Chem. Phys.* **56**:3812 (1972); **57**:2626 (1972); H. C. Anderson and D. Chandler, **57**:1918, 1930 (1972).
25. H. C. Anderson, preprint and private communication.