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Thermodynamic perturbation theory for association into chains and rings

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A theory for the formation of rings at equilibrium is proposed. The formalism previously derived by Wertheim [J. Stat. Phys. **35**, 19 (1984); **35**, 35 (1984); **42**, 459 (1986); **42**, 477 (1986)] is used together with a way of approximating the ring graphs which are found. The theory is developed to treat two model molecules: spheres with two attraction sites, each mediating an interaction very like a hydrogen bond, and chains of spheres with a similar site on the first and on the last sphere. Unlike previous work these molecules are allowed to form ring structures as well as chains. For both models the free energy is a simple analytical expression in terms of the fraction of attraction sites bonded, very like other work within the Wertheim formalism. The fraction of sites bonded is obtained from mass action equations. Phase diagrams are shown, and we discuss the difference in phase behavior between that predicted by the theory proposed here, and that of work which excludes rings. It is found that if the possibility of forming rings is excluded a very different phase diagram can be produced. In particular, the vapor pressure far from the critical point is severely underestimated. This corresponds to the formation of a high proportion of rings in the gas phase while the liquid phase remains dominated by chains. The case where the model molecules can only form rings is also discussed, and expressions for the free energy derived. In the limit of complete association this case reduces to an earlier result, derived and tested against simulation data by the authors. The motivation of the work on the first model is the formation of rings by both hydrogen fluoride and sulfur. The second model is motivated by the possibility of intramolecular bonding in organic compounds with two functional groups capable of forming hydrogen bonds separated by a flexible carbon backbone.

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I. INTRODUCTION

Some of the liquids which are the most interesting and difficult to understand are those that hydrogen bond. Many organic liquids, such as alcohols, and some inorganic liquids, such as hydrogen fluoride, form hydrogen bonds. The strong and highly directional nature of the hydrogen bond is very different from that of the slowly varying van der Waals interactions; the internal energy of a hydrogen-bonding system is strongly dependent on temperature. As we would expect this sensitivity of the energy means that hydrogen-bonding fluids show phase behavior not seen in fluids without hydrogen bonding, such as the so-called closed-loop behavior [1].

Recently, one of us has studied the phase behavior of aqueous mixtures of alcohols [2], using the approach developed by Wertheim [3,4]. Wertheim went back to the fugacity expansion of the grand partition function and eliminated the fugacity in favor of a set of densities, each corresponding to a different bonding state of the molecule. The resulting free energy was expressed as an infinite series of graphs with each point carrying one of the set of densities. The fugacity expansion had, much earlier, been reduced to an expansion in the total density by Morita and Hiroike [5]. The graphical expansion has been used extensively to obtain the thermodynamical functions and the structure of many liquids [6].

Although the expansion of the free energy in terms of an infinite series of graphs derived by Wertheim is exact, a tractable theory requires that only a subset of the infinite series of graphs be selected. This subset should be in some sense that of "lowest order" and all the graphs must be evaluated to obtain the free energy. A graph of m vertices represents an m-body integral, which for $m > 2$ can be difficult to evaluate. Consequently, almost all of the work to date involves the lowest order chain graph, a two-body integral. Despite involving only two vertices this graph accounts for chains of molecules of arbitrary length, a major advantage of Wertheim's formalism. There has, however, been some work beyond this level [7,8], which has gone to the next highest order in the approximation for chains and considered star-shaped molecules.

What has been excluded from previous work is the possibility of the formation of rings of molecules. There is, however, evidence that hydrogen fluoride in the vapor phase exists mainly as rings of molecules [9]. Clearly, this provides motivation for studying the equilibrium between free monomers and rings and chains of monomers. Although the previous ideas account adequately for the behavior of simple molecules, such as alkanols (see Ref. [2]), we cannot expect them to work well for hydrogen fluoride. In the following section we propose an approximate theory, within Wertheim's approach, which incorporates a ring graph. This accounts for rings of monomers of

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one length only, e.g., in the case of hydrogen fluoride we might select the most stable ring size and incorporate the corresponding ring graph. This is analogous to studies of the equilibrium between long chains and eight membered rings of sulfur atoms [10]. The theory presented in Sec. II may be considered as an extension of these studies to incorporate some but not all of the excluded volume effects. The problem of a fluid in which rings of any length are present is not treated explicitly.

A related and interesting problem in the study of fluids is that of intramolecular bonding where a bond is formed between two parts of the same molecule. This cannot be ruled out in any molecule with two functional groups which are capable of hydrogen bonding and are separated by a sufficiently long and flexible intermediate segment. An example might be ethoxybutanol, where the molecule may fold over allowing the oxygen of the ethoxy group to bond with the hydrogen of the alcohol group. A theory for intramolecular bonding is proposed in Sec. III. In Sec. IV some example phase diagrams are discussed. The phase diagrams are calculated from the theory developed in this paper as well as from the previous theory which excludes the possibility of rings.

II. ASSOCIATION INTO CHAINS AND RINGS

We start our discussion with a fluid composed of monomers, each of which has, in addition to a hard repulsive core, two interaction sites; this is the model of Wertheim [4,7]. The two sites, which are distinguishable, are labeled A and B. Each of these sites mediates a short range interaction between the monomers so that if two monomers are almost touching and they are oriented so that the A site of one is directed towards the B site of the other the two sites may overlap forming a strong bond. This bond will have an energy many times the thermal energy of a monomer. Once two sites are bonded no third site may bond to either of the two sites, i.e., the bonds are saturable like chemical bonds. The only case treated here is that of a spherical hard repulsive core although the formalism would be the same for any other shape. The two sites on the sphere subtend an angle at the center of the sphere ξ; this angle may be fixed at a definite value or it may be allowed to vary, giving the monomer an internal degree of freedom. This makes very little difference to the formalism, and only the case where ξ may vary freely will be considered here. This case is exactly the model considered by Wertheim in Ref. [7].

Wertheim has reformulated the statistical thermodynamics of an associating fluid [3,4] in terms of separate number densities for each bonding state of the monomer molecule. For the two-site model there are four possible bonding states with corresponding number densities: neither of the two sites bonded with a corresponding number density of ρ_0; site A bonded but not site B with ρ_A; site B bonded but not A with ρ_B; and both sites bonded with ρ_{AB}. A site of type A may bond to a site of type B but A—A and B—B bonding is not allowed. The actual expressions for the thermodynamical functions are written in terms of combinations of these densities,

$$\begin{aligned}\sigma_0 &= \rho_0,\\ \sigma_A &= \rho_A + \rho_0,\\ \sigma_B &= \rho_B + \rho_0,\\ \sigma_\Gamma &= \rho_{AB} + \rho_A + \rho_B + \rho_0 = \rho,\end{aligned} \tag{1}$$

where $\rho = N/V$ is the total number density, i.e., the total number of monomers N divided by the volume occupied by the fluid V. The difference in Helmholtz free energy of the fluid, A, and of a fluid of molecules with identical repulsive cores but without the attraction sites, A_R, is given exactly by [7]

$$\begin{aligned}\beta(A - A_R) = \int \Bigg(&\sigma_\Gamma(1)\ln\frac{\sigma_0(\bar{1})}{\sigma_\Gamma(\bar{1})} + \sigma_\Gamma(1) - \sigma_A(1)\\ &-\sigma_B(1) + \frac{\sigma_A(1)\sigma_B(1)}{\sigma_0(1)}\Bigg)d(1)\\ &-c^{(0)} + c_R^{(0)}.\end{aligned} \tag{2}$$

The singlet densities are given as functions of the position of the center of the sphere, the orientation of the molecule, and the angle subtended by the sites, all represented by the notation (1). The densities σ_0, σ_A, and σ_B do not depend on ξ if it is allowed to vary freely; the same is true for σ_Γ in the reference system. However, ρ_{AB} and hence σ_Γ in the associating fluid will depend on ξ in a more complex manner: the molecule bonded at one site will exclude the molecule bonded at the other for some values of ξ. Thus σ_Γ differs in the associating and reference fluids. Note that the densities inside the logarithm, $\sigma_0(\bar{1})$ and $\sigma_\Gamma(\bar{1})$, have been averaged over ξ. $\beta = 1/kT$ where k is Boltzmann's constant and T is the temperature. $c^{(0)}$ is the sum of all irreducible graphs on field points [4]; each pair of points 1 and 2 may be connected by an $f_R(12)$, $F_{AB}(12)$, or $F_{BA}(12)$ bond and each point carries a factor σ_Q where Q is the complement of the set of sites bonded at that point.

The bonds $f_R(12)$ and $F_{AB}(12)$ are defined by

$$f_R(12) = e^{-\beta\phi_{\rm HS}(12)} - 1, \tag{3}$$

and

$$F_{AB}(12) = e^{-\beta\phi_{\rm HS}(12)}(e^{-\beta\phi_{AB}(12)} - 1), \tag{4}$$

and similarly for $F_{BA}(12)$. $\phi_{\rm HS}(12)$ is the hard-sphere potential and $\phi_{AB}(12)$ is the site potential, here a square well positioned off the center of the sphere [11]. $c_R^{(0)}$ is the subset of $c^{(0)}$ with only reference system bonds, f_R. $-kTc_R^{(0)}$ is the excess part of the reference system free energy which is known. The theory presented here is a perturbation theory [6], so that if the free energy and pair distribution function of the reference system are known, the free energy of the associating system can be calculated. Thus only the difference between the two graph sums concerns us,

$$\Delta c^{(0)} = c^{(0)} - c_R^{(0)}. \tag{5}$$

In order to proceed the graph sum $\Delta c^{(0)}$ must be approximated; previous approximations have included only graphs which correspond to chains [7]. Thus the theory neglects any effect due to the formation of rings of molecules by assuming that no rings are present. An attempt is made to include rings, to evaluate the number formed, and to determine their effect on the thermodynamical functions and the phase behavior. The corresponding ring graph must be included to allow a ring to form in the theory. Unfortunately, ring graphs are irreducible so for every different ring length a separate graph must be included. Here, for simplicity, the molecules are only allowed to form one species of ring comprising n molecules. Although this situation is not particularly realistic for our model, some substances such as hydrogen fluoride seem to form rings of predominantly one or a few sizes [9]. The graph for a ring of n monomers at a density low enough that interactions between the ring and other molecules may be neglected is

$$\frac{1}{n}\int \sigma_0(1)\cdots\sigma_0(n)F_{AB}(12)\cdots F_{AB}(n1)d(1)\cdots d(n). \tag{6}$$

Only nearest neighbor interactions are included and the excluded volume interactions between nonadjacent monomers are ignored. For higher densities molecules in the ring will interact with the surrounding molecules. To progress it is assumed that the indirect interaction between each successive pair of monomers around the ring, which is mediated by the surrounding fluid, can be treated independently [12]. If this pair interaction is then approximated by its value in the reference fluid the ring graph Eq. (6) may be decorated to yield

$$\begin{aligned}\frac{1}{n}\int \sigma_0(1)\cdots\sigma_0(n)F_{AB}(12)y(12)\cdots F_{AB}(n1)\\ \times y(n1)d(1)\cdots d(n),\end{aligned} \tag{7}$$

where y is the reference fluid indirect or cavity distribution function [6,13]. Using the reference fluid distribution function ignores any change in the monomer-monomer distribution upon chain formation. It is perfectly possible to just use this graph for $\Delta c^{(0)}$ in which case all the fluid is allowed to do within the theory is to form rings of length n. For greater generality the case where the monomers can also form chains of any length is treated. To do this the lowest order graph for chains is included in $\Delta c^{(0)}$; this graph corresponds to making the same approximations made earlier in decorating Eq. (6). The corresponding expression for $\Delta c^{(0)}$ becomes

$$\begin{aligned}\Delta c^{(0)} = &\int \sigma_A(1)\sigma_B(2)F_{AB}(12)y(12)d(1)d(2)\\ &+\frac{1}{n}\int \sigma_0(1)\cdots\sigma_0(n)F_{AB}(12)y(12)\cdots\\ &\times F_{AB}(n1)y(n1)d(1)\cdots d(n).\end{aligned} \tag{8}$$

The first term on the right-hand side is the first-order chain graph; it is the only graph in the first-order thermodynamic perturbation theory (TPT1) of Wertheim [4]. At equilibrium the free energy must be stationary with respect to variation in the densities σ_A, σ_B, and σ_0; the free energy must, of course, be at a minimum. Therefore, by functional differentiation of Eqs. (2) and (8) with respect to σ_0 and σ_A we find

$$\begin{aligned}\frac{\sigma_\Gamma(1)}{\sigma_0(1)} - \frac{\sigma_A(1)\sigma_B(1)}{\sigma_0(1)^2} = &\int \sigma_0(2)\cdots\sigma_0(n)F_{AB}(12)\\ &\times y(12)\cdots F_{AB}(n1)y(n1)\\ &\times d(2)\cdots d(n),\end{aligned} \tag{9}$$

and

$$-1 + \frac{\sigma_B(1)}{\sigma_0(1)} = \int \sigma_B(2)F_{AB}(12)y(12)d(2), \tag{10}$$

respectively. These two equations are those of mass action. It may be verified that if $\sigma_0(1)\times$ [Eq. (9)] is added to $\sigma_A(1)\times$ [Eq. (10)], the intuitively obvious partition of the total number density among the various bonding states is obtained. Putting Eq. (9) and Eq. (10) in Eq. (8) gives

$$\begin{aligned}\Delta c^{(0)} = &\int \left(\frac{\sigma_A(1)\sigma_B(1)}{\sigma_0(1)} - \sigma_A(1)\right) d(1)\\ &+\frac{1}{n}\int \left(\sigma_\Gamma(1) - \frac{\sigma_A(1)\sigma_B(1)}{\sigma_0(1)}\right) d(1),\end{aligned} \tag{11}$$

and then substituting this result in Eq. (2) we find

$$\begin{aligned}\beta(A - A_R) = \int \Bigg[&\sigma_\Gamma(1)\ln\frac{\sigma_0(\bar{1})}{\sigma_\Gamma(\bar{1})} + \sigma_\Gamma(1)\left(1 - \frac{1}{n}\right)\\ &-\sigma_B(1) + \frac{\sigma_A(1)\sigma_B(1)}{n\sigma_0(1)}\Bigg] d(1).\end{aligned} \tag{12}$$

In order to evaluate the free energy, the integral Eq. (7) or equivalently the one in Eq. (9) must be determined so that self-consistent solutions of the densities are obtained.

In the previous theory for chains (TPT1), the $n-1$ sphere-sphere contacts in a chain of n spheres were assumed to be independent, an assumption which greatly simplifies the problem. Here, however, if we consider any $n-1$ of the n contacts, the bond angles ξ are constrained so that the first and nth spheres are close enough to each other to form a bond. Hence, the integral of Eq. (9) is treated as n "independent" contacts subject to the constraint that $n-1$ of the bond angles are such that the first and nth spheres are near contact. If we allow the angle ξ to vary freely from 0 to π, i.e., we ignore the excluded volume interaction of the $(i-1)$th and $(i+1)$th spheres around the ith sphere, the system will behave as a freely jointed chain [10]. The distribution of the vector between the first and nth sphere of a freely jointed chain is known; it is given by the expression of Treloar in [10]. So the right-hand side of Eq. (9) becomes

$$\frac{1}{n}\sigma_0(1)\cdots\sigma_0(1^*)(KF_{AB}y_c)^n W_{n-1}, \tag{13}$$

where K is the bonding volume, i.e., the volume of overlap of the bonding sites on two spheres, $F_{AB} = \exp(-\epsilon_{SW}/kT) - 1$, where ϵ_{SW} is the square-well depth [11], and y_c is the value of the cavity distribution function between two spheres at contact. W_{n-1} is the value of the end-to-end distribution function for a freely jointed chain of $n-1$ links, when the end links are the length of one link apart. The expression of Treloar [10] for this separation of the ends is

$$W_m = \frac{m(m-1)}{8\pi} \sum_{j=0}^{l} \frac{(-1)^j}{j!(l-j)!} \left[\frac{m-1-2j}{2}\right]^{m-2}, \quad (14)$$

for l the smallest integer which satisfies

$$l \geq \frac{m-1}{2} - 1. \quad (15)$$

The link length is equal to the diameter of a sphere which we take to be our unit of length. The notation (1^*) represents a point displaced by a unit vector from (1). Also, although y is not a function of σ_0, σ_A, or σ_B, as it is a reference system function, it does depend on σ_Γ. Therefore Eq. (13) should be written in terms of a product of $y(ii^*)$'s for each pair of spheres, where (ii^*) denotes the positions of the two spheres, (i) and (i^*). Equation (13) is therefore sufficiently general to include a spatially varying σ_0, σ_A, and σ_B but not σ_Γ. Note that the original integral has been split into n pair integrals, each of which is over the small site-site overlap volume K, plus a collective part W_{n-1}. The density σ_0, the pair distribution function, and, in the case of the nth bond, W_{n-1} will vary over the overlap volume but this variation will be small. The effect of this variation has been evaluated for the original theory, without rings, and it was found to be small [11], so we assume σ_0, y, and W_{n-1} are constant and equal to their values at sphere-sphere contact. In a homogeneous fluid the dependence of the σ densities disappears so here we have from Eqs. (9), (10), and (12)

$$\frac{\sigma_\Gamma}{\sigma_0} - \frac{\sigma_A \sigma_B}{\sigma_0^2} = \sigma_0^{n-1}(KF_{AB}y_c)^n W_{n-1}, \quad (16)$$

$$-1 + \frac{\sigma_B}{\sigma_0} = \sigma_B K F_{AB} y_c, \quad (17)$$

and

$$\frac{\beta(A - A_R)}{N} = \ln\frac{\sigma_0}{\sigma_\Gamma} + \left(1 - \frac{1}{n}\right) - \frac{\sigma_B}{\sigma_\Gamma} + \frac{\sigma_A\sigma_B}{n\sigma_0\sigma_\Gamma}, \quad (18)$$

respectively. Equations (16) and (17) may be cast in terms of polynomials in $X_0 = \sigma_0/\sigma_\Gamma$ and $X_G = \sigma_B/\sigma_\Gamma$; note that $\sigma_A = \sigma_B$. The polynomials may then be solved to give values of X_0 and X_G, which after being inserted in Eq. (18) give the free energy. Equations (16), (17), and (18) may also be differentiated with respect to density to give the pressure p; the standard thermodynamic relation $p = -(\partial A/\partial V)_{N,T}$ is used. The resulting equation gives p in terms of derivatives of the σ densities with respect to the density. The corresponding derivatives of Eqs. (16) and (17) thus have to be determined.

It may be verified that Eq. (18) gives the correct low density but strong association limit; however, Eqs. (9) and (10) are both still approximate. It is known from studies in polymer physics [16] that a chain with excluded volume interactions is swollen at low density. Our approximation neglects these excluded volume interactions, and, consequently, will be poor at low densities; it will overestimate the probability that the two ends of a chain will be near contact, which is a particular problem for the ring graph. At high densities the approximation should be rather better for a long chain with excluded volume interactions because its behavior is similar to that of the Gaussian chain.

It has been mentioned earlier that if the chain graph was omitted from $\Delta c^{(0)}$ the fluid would form only rings. If indeed the first term in Eq. (8), the chain term, is removed and the procedure repeated for the new free energy functional, it may easily be verified that in place of Eqs. (16), (17), and (18) we obtain

$$\frac{\sigma_\Gamma}{\sigma_0} - \frac{\sigma_A \sigma_B}{\sigma_0^2} = \sigma_0^{n-1}(KF_{AB}y_c)^n W_{n-1}, \quad (19)$$

$$-1 + \frac{\sigma_B}{\sigma_0} = 0, \quad (20)$$

and

$$\frac{\beta(A - A_R)}{N} = \ln\frac{\sigma_0}{\sigma_\Gamma} + \left(1 - \frac{1}{n}\right)\left(1 - \frac{\sigma_0}{\sigma_\Gamma}\right). \quad (21)$$

Clearly Eqs. (19) and (20) may be combined to give

$$\frac{\sigma_\Gamma}{\sigma_0} - 1 = \sigma_0^{n-1}(KF_{AB}y_c)^n W_{n-1}. \quad (22)$$

These simple expressions for the free energy of the ring-forming fluid may again be differentiated to obtain the pressure.

The limit of complete association into rings is now considered. In this limit the second term on the left-hand side of Eq. (22) may be neglected and the nth root taken to yield an expression for σ_0. Putting this in Eq. (21) we find

$$\frac{\beta(A - A_R)}{N} = -\ln\left(\sigma_\Gamma^{1-\frac{1}{n}} y_c\right)\left(1 - \frac{1}{n}\right), \quad (23)$$

plus constant terms. This result was obtained previously by the present authors via a different approach [12].

Another pertinent question regards the formation of many sizes of rings. Incorporating the corresponding graphs in $\Delta c^{(0)}$ is straightforward; $\Delta c^{(0)}$ simply becomes a sum over ring graphs, plus a chain graph. As before by functional differentiation of the free energy two mass action equations are obtained which may be used to determine σ_A and σ_0. Unfortunately, the greater complexity of the free energy means that the mass action equations cannot be simply back substituted into the free energy functional, a minor problem since, if σ_A and σ_0 are known, $\Delta c^{(0)}$ may be evaluated directly. A more serious problem is that in order to treat a fluid which can form rings of arbitrary size the sum over rings must be continued up to a value of n sufficiently large so that the number of rings of this length is negligible. If the degree of association is large with very few free monomers this may require the sum to extend up to very large values of n. In the limit of complete association the decline in the number of rings of length n is only a power law, not an exponential [17].

So far the case in which ξ can vary freely has been treated extensively but the formalism is virtually identical for molecules with a fixed ξ [7]. The expressions are actually a little simpler as the terms inside the logarithm of Eq. (9) do not need to be averaged. Thus Eqs. (16), (17), and (18) can be used as they stand for molecules of fixed ξ provided the appropriate W_{n-1} is used. The problem of a chain in which successive links are constrained to be at a fixed angle has again been treated in connection with polymer physics [10].

III. ASSOCIATING CHAINS WITH INTRAMOLECULAR BONDING

The system considered now is a fluid of chains of n hard spheres where each chain has an interaction site of type A on the first sphere and a site of type B on the last sphere. Each chain may exist in one of five bonding states: neither site bonded; site A but not B bonded; site B but not A bonded; both sites bonded, each to a site on another chain; and the two sites bonded to each other closing the chain to form a ring molecule. Only site A—B bonds are allowed but no A—A and B—B bonds. Associating chains have been studied previously [14] but the chains were not allowed to form rings. The free energy is determined using a procedure similar to the one outlined in the previous section, with the same approximation for the ring graph. However, in order to form a chain we start from a mixture of n species; each species i has an identical hard-sphere core and bonds only to the $(i-1)$th species via its A type site and the $(i+1)$th species via its B type site [15,13]. There are equal numbers N of each species of monomer. Thus the degree of association of all n bonds can be controlled separately: we force $n-1$ of the bonds to complete association in order to form a chain, leaving only the two sites at the ends of the chain able to bond reversibly.

The following approximate free energy functional is used:

$$\begin{aligned}\beta(A-A_R) = {} & \sum_{\alpha=1}^{n}\int\left(\sigma_\Gamma^\alpha(1)\ln\frac{\sigma_0^\alpha(\bar{1})}{\sigma_\Gamma^\alpha(\bar{1})}+\sigma_\Gamma^\alpha(1)-\sigma_A^\alpha(1)-\sigma_B^\alpha(1)+\frac{\sigma_A^\alpha(1)\sigma_B^\alpha(1)}{\sigma_0^\alpha(1)}\right)d(1)\\ & -\sum_{\alpha=1}^{n}\int\sigma_A^\alpha(1)\sigma_B^{\alpha+1}(2)F_{AB}^{\alpha,\alpha+1}y(12)d(1)d(2)\\ & -\int\sigma_0^1(1)\cdots\sigma_0^n(n)F_{AB}^{1,2}y(12)\cdots F_{AB}^{n,1}y(n1)d(1)\cdots d(n).\end{aligned}\tag{24}$$

The superscript α is used to denote the species; note that the bonding Mayer f function F_{AB} depends on the species of the two spheres. In Eq. (24), $\alpha+1$ is taken as 1 for $\alpha=n$. If all F_{AB}'s are equivalent we recover Eq. (2). As before the functional derivatives of the free energy with respect to σ_0^α and σ_A^α are obtained as

$$\begin{aligned}\frac{\sigma_\Gamma^\alpha(\alpha)}{\sigma_0^\alpha(\alpha)}-\frac{\sigma_A^\alpha(\alpha)\sigma_B^\alpha(\alpha)}{\sigma_0^\alpha(\alpha)^2} = {} & \int\sigma_0^1(1)\cdots\sigma_0^{\alpha-1}(\alpha-1)\sigma_0^{\alpha+1}(\alpha+1)\cdots\sigma_0^n(n)F_{AB}^{1,2}(12)y(12)\cdots F_{AB}^{n,1}(n1)\\ & \times y(n1)d(1)\cdots d(\alpha-1)d(\alpha+1)\cdots d(n),\end{aligned}\tag{25}$$

and

$$-1+\frac{\sigma_B^\alpha(1)}{\sigma_0^\alpha(1)}=\int\sigma_B^{\alpha+1}(2)F_{AB}^{\alpha,\alpha+1}(12)y(12)d(2).\tag{26}$$

These are the mass action equations which determine the self-consistent densities. Substituting Eqs. (25) and (26) into (24) we find

$$\begin{aligned}\beta(A-A_R) = {} & \sum_{\alpha=1}^{n}\int\left(\sigma_\Gamma^\alpha(1)\ln\frac{\sigma_0^\alpha(\bar{1})}{\sigma_\Gamma^\alpha(\bar{1})}\right.\\ & \left.+\sigma_\Gamma^\alpha(1)-\sigma_B^\alpha(1)\right)d(1)\\ & -\int\left(\sigma_\Gamma^1(1)-\frac{\sigma_A^1(1)\sigma_B^1(1)}{\sigma_0^1(1)}\right)d(1).\end{aligned}\tag{27}$$

The species superscript on the σ's in the second term is arbitrary, and the difference inside the parentheses is the same for all species; it is actually the number density of rings within our approximation. The chain is now formed as in Ref. [13], and Eq. (26) becomes

$$\frac{\sigma_B^\alpha(1)}{\sigma_0^\alpha(1)}=1+\lambda y_c\sigma_B^{\alpha+1}(1^*),\quad \alpha\neq n.\tag{28}$$

This is for association at contact, and the parameter λ controls the extent of bonding. For very large values of λ we may neglect the 1 and invert the expression to obtain

$$\sigma_0^\alpha(1)=\frac{\sigma_B^\alpha(1)}{\lambda y_c\sigma_B^{\alpha+1}(1^*)},\quad \alpha\neq n.\tag{29}$$

Now for $\alpha = n$ from Eq. (26) we obtain

$$\frac{\sigma_B^n(1)}{\sigma_0^n(1)} = 1 + \sigma_B^1(1^*)\Delta, \tag{30}$$

where

$$\Delta = KF_{AB}^{n,1}y_c. \tag{31}$$

The distribution function in the bonding volume has been approximated by its value at contact, and the sites are square wells so $F_{AB}^{n,1}$ is constant throughout K. In the case of bonding at contact, Eq. (25) for $\alpha = 1$ becomes

$$\sigma_\Gamma^1(1) = \frac{\sigma_A^1(1)\sigma_B^1(1)}{\sigma_0^1(1)} + \sigma_0^1(1)\cdots\sigma_0^n(1^*) \times (\lambda y_c)^{n-1}W_{n-1}\Delta. \tag{32}$$

If Eq. (29) is substituted in Eq. (32) we find

$$\sigma_\Gamma^1(1) = \frac{\sigma_A^1(1)\sigma_B^1(1)}{\sigma_0^1(1)} + \frac{\sigma_B^1(1)}{1+\sigma_B^1(1)\Delta}W_{n-1}\Delta. \tag{33}$$

But

$$\frac{\sigma_A^1(1)}{\sigma_0^1(1)} = 1 + \sigma_A^n(1^*)\Delta, \tag{34}$$

as may be verified by functional differentiation of the free energy with respect to σ_B^1. Using this result and the fact that $\sigma_A^n(1) = \sigma_B^1(1)$ we obtain

$$\sigma_\Gamma^1(1) = \sigma_B^1(1) + \sigma_B^1(1)\sigma_B^1(1^*)\Delta + \frac{\sigma_B^1(1)}{1+\sigma_B^1(1)\Delta}W_{n-1}\Delta. \tag{35}$$

For a homogeneous fluid σ_B and σ_Γ are no longer functions of the coordinates (1), and Eq. (35) may therefore be written in terms of the parameter $X = \sigma_B^1/\sigma_\Gamma^1$. A third-order polynomial in X results which may be solved to give X.

Substituting Eqs. (29) and (33) into (27) for the free energy we have

$$\beta(A - A_R) = \int\left[\sigma_\Gamma(1)\ln\left(\frac{\sigma_B^1(1)}{[\sigma_\Gamma(1)]^n(\lambda y_c)^{n-1}[1+\sigma_B^1(1^*)\Delta]}\right) + n\sigma_\Gamma(1)\right]d(1) - \int\sigma_B^1(1)d(1) - \int\left(\frac{\sigma_B^1(1)}{1+\sigma_B^1(1)\Delta}W_{n-1}\Delta\right)d(1). \tag{36}$$

Note that $\sigma_B^\alpha = 0$ for $\alpha \neq 1$, and that the species superscript on σ_Γ is dropped as all σ_Γ's are the same. In the present approximation ξ is allowed to vary freely for all densities, even σ_Γ. Therefore all densities are independent of ξ, and the distinction between $\sigma(1)$ and $\sigma(\bar{1})$ thus disappears. For a homogeneous fluid

$$\frac{\beta(A - A_R)}{N} = -(n-1)\ln(\sigma_\Gamma\lambda y_c) + \ln\left(\frac{X}{1+X\sigma_\Gamma\Delta}\right) + n - X - \frac{X}{1+X\sigma_\Gamma\Delta}W_{n-1}\Delta. \tag{37}$$

The parameter λ, which is in effect an integrated energy of association, is a constant; it therefore has no effect on observable properties and may be discarded. Again Eqs. (35) and (36) can be differentiated with respect to density to give the pressure.

In the limit of low density but strong association Eq. (37) gives the correct result for intramolecular bonding but Eq. (35) is still approximate. The free energy of a gas of chains at a density low enough that the excluded volume interactions between chains are negligible is given exactly in terms of X by Eq. (37). However, the excluded volume interactions within a chain will remain, so that Eq. (35) will still be approximate.

A fluid of chains which can only self-associate, i.e., the chains can only close to form rings, is now considered. This is treated by the free energy functional of Eq. (24) but without the $\alpha = n$ term in the second sum. This prevents the first and nth spheres from bonding except to form a ring. If the previous procedure is repeated for a new functional we obtain the new mass action equation as

$$1 = X + XW_{n-1}\Delta, \tag{38}$$

and the free energy as

$$\frac{\beta(A - A_R)}{N} = -(n-1)\ln(\sigma_\Gamma\lambda y_c) + (n-1) + \ln X. \tag{39}$$

The first two terms of the free energy account for the formation of the chain, and only the last term arises from the ring-closure equilibrium. If the limit of complete association is taken our earlier result is again obtained. It is a notable feature of Wertheim's formalism that theories based on it give accurately the limit of complete association. Computer simulations have been performed on rings in this limit. The present theory was found to be in excellent agreement with simulation data for the equation of state of small rigid rings. It is also argued in Ref. [12] that the theory will work well for flexible rings even if they are large.

IV. NUMERICAL CALCULATIONS

For the associating monomers Eqs. (16) and (17) are solved numerically using an iterative scheme. The resulting self-consistent densities are substituted in Eq. (18) to yield the free energy. The appropriate derivatives with respect to density are then solved to yield the pressure. The reference fluid of hard spheres is well known; the free energy and pressure are required as well as the distribution function at contact [18,11]. In order to study the effect of the association on the phase diagram, a mean-field term is added to the free energy, of the form [11]

$$\frac{\beta A^{\mathrm{MF}}}{N} = -\beta \epsilon_{\mathrm{MF}} \eta, \tag{40}$$

where $\eta = \pi/6\rho$ and the diameter of the spheres is set to unity. Thus the parameters of the model are the bonding volume K, the ratio of the square-well energy ϵ_{SW} to the mean-field energy ϵ_{MF}, and the size n of the permitted ring. Once these parameters are set, a temperature and density may be selected, and, as discussed earlier, Eqs. (16) and (17) may be solved iteratively for X_0 and X_G in order to give the free energy and pressure. Once X_0 and X_G are known the fraction of rings can be calculated from Eq. (9), which is just the number density of rings divided by σ_0. So from Eq. (9) the fraction of rings is $1 - X_G^2/X_0$.

The numerical solutions are simpler for the fluid of associating chain molecules; the mass action Eq. (35) is rewritten for a homogeneous fluid

$$1 = X + X^2\Delta + \frac{X}{1 + X\sigma_\Gamma \Delta} W_{n-1}\Delta. \tag{41}$$

On the right-hand side the first term is the fraction of molecules with a site of type A free, the second term is the fraction of sites of type A which are part of an intermolecular bond, and the third term is the fraction of sites of type A that are part of an intramolecular bond. In this case the symmetry between the A and B sites means Eq. (41) applies equally to the sites of type B. Equation (41) can be solved for X; this value for X will give the free energy when inserted in Eq. (37) and the number of rings when substituted in the last term of Eq. (41). For the solution of nonlinear equations such as Eq. (41), see [19]. Note that an analytical solution is available for the cubic equation, but that the numerical approach is a little better behaved. The parameters are the same as before, but here n is the length of the chain, and the mean-field interaction Eq. (40) is added per sphere of the chain.

The chemical potential μ is required to obtain the phase diagram of these systems; the standard thermodynamical relation $\mu = (A + pV)/N$ for the pure fluid is used. At coexistence the pressure and chemical potential of the vapor and liquid phases are equal. Two simultaneous nonlinear equations result from these conditions which are then solved iteratively for a given temperature to obtain the coexisting densities and the vapor pressure. The temperature scale is defined by the mean-field parameter ϵ_{MF}; the reduced temperature $T^* = kT/\epsilon_{\mathrm{MF}}$ is used. The model can then be described by the ratio $\epsilon_{\mathrm{SW}}/\epsilon_{\mathrm{MF}}$ and by K. For completeness the reduced pressure used is also stated; it is $p^* = \beta p\pi/6$.

V. RESULTS AND DISCUSSION

Example calculations have been performed, and the resulting phase diagrams are shown in Figs. 1–4 below. Before these diagrams are discussed the general qualitative features of the equilibrium between single monomers and chains and rings of monomers are examined. Using the notation of the previous sections, if the number density of monomers is σ_0, then the number of chains of length n will be of the order of $\sigma_0^n K^{n-1} F_{AB}^{n-1}$, and the number of rings of size n will be of the order of $\sigma_0^n K^n F_{AB}^n W_{n-1}$. The difference between a chain and ring of the same length is, of course, that the latter has an extra bond but is constrained so that the ends meet. For the equilibrium of a chain and ring of the same length, the longer the length, the more the equilibrium is shifted toward the chain. Conversely, the larger the energy of association the more the equilibrium is shifted toward the ring. Another consideration, which is particularly relevant to phase behavior is the competition between inter- and intramolecular bonding. Intermolecular bonding sticks two groups together to form a larger group of monomers; intramolecular bonding does not. For example, consider the fluid of associating chain molecules, or, to be more specific, a chain of these molecules bonded together. An end molecule can break off this chain and close up to form a ring. Here, the net energy penalty is zero but the number density of free species increases adding to the translational entropy, at a cost in conformational entropy of the molecule which has formed a ring. Thus although a decrease in temperature favors chains as well as rings, a decrease in density favors rings over chains.

In Fig. 1 the phase diagrams obtained for the associating monomers are shown. It is clear that only allowing the fluid to form chains produces marked changes in the phase diagram. Although the scale of the graphs is too coarse to show it, even in the more weakly hydrogen-bonded system with $n = 6$ the vapor pressure far from the critical point is much higher than for the case with only chains. The vapor pressure is consistently increased by allowing ring formation. It is also worth noting that, apart from increasing the vapor pressure at low temperatures, allowing the fluid to form rings makes little difference unless the hydrogen bonding is strong. Although it is not shown, the curves for the systems with $\epsilon_{\mathrm{SW}}/\epsilon_{\mathrm{MF}} = 2$ are almost superimposed. This does not mean that rings are not formed for $\epsilon_{\mathrm{SW}}/\epsilon_{\mathrm{MF}} = 2$, as is shown in Fig. 2. The number of rings is small but the behavior as the temperature changes is interesting.

This behavior results from the extreme sensitivity of the ring-closing equilibria to temperature and density. At low temperatures the vapor phase has a larger number of rings, but as the temperature is increased and the density of the coexisting vapor increases, the number of rings in the liquid becomes greater than in the vapor. This crossover occurs close to the critical point.

The phase diagram for the associating chains is shown in Fig. 3 and the fraction of rings along the coexistence curve is shown in Fig. 4. The dramatic change in the phase behavior for the larger $\epsilon_{SW}/\epsilon_{MF}$ ratio is evident. If Figs. 3 and 4 are compared it is seen that in the case of the smaller $\epsilon_{SW}/\epsilon_{MF}$ ratio the number of rings in the two phases is very similar near the critical point, and that the critical point is close to that of the system which only forms chains. In contrast, for the larger $\epsilon_{SW}/\epsilon_{MF}$ ratio the fraction of rings in the two phases quickly diverges below the critical point and the critical point is far from that of the system in which only chains are allowed. As for the associating monomers, the fluids which are allowed to form rings are much more volatile far from the critical point. However, for the case of $\epsilon_{SW}/\epsilon_{MF} = 2$

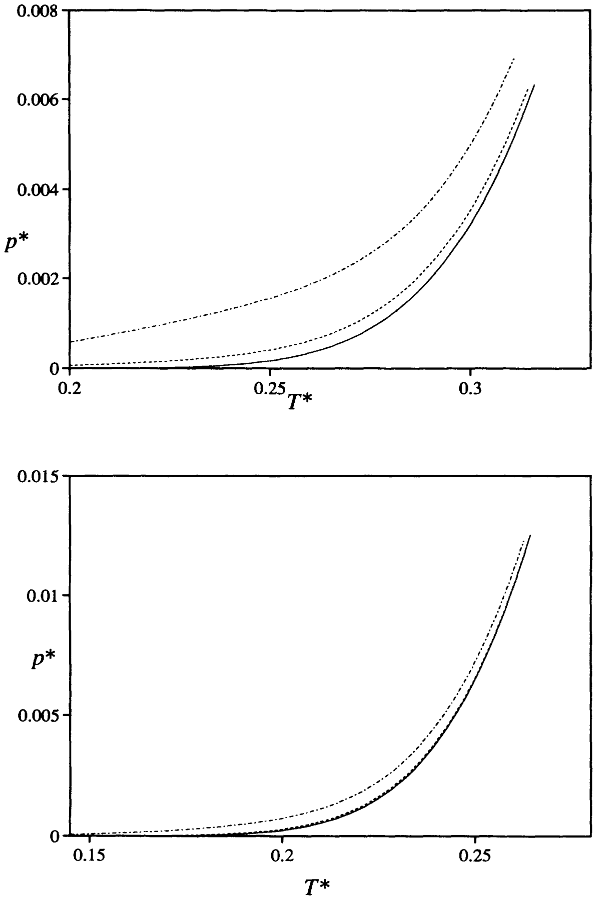

FIG. 1. The figure shows the phase diagram for a fluid of associating monomers with free energy Eq. (18). The curves, of course, all end at the critical point. In both graphs $K = 8.7791 \times 10^{-4}$; this corresponds to a square well displaced 0.4 from the center of the sphere with a range of 0.3 [11], but note that a different convention is used for K in this reference. The solid curves are for the previous theory with chains only, the dashed curves for $n = 6$, and the dot-dashed curves for $n = 4$. The top graph corresponds to $\epsilon_{SW}/\epsilon_{MF} = 4$ and the lower graph to $\epsilon_{SW}/\epsilon_{MF} = 3$.

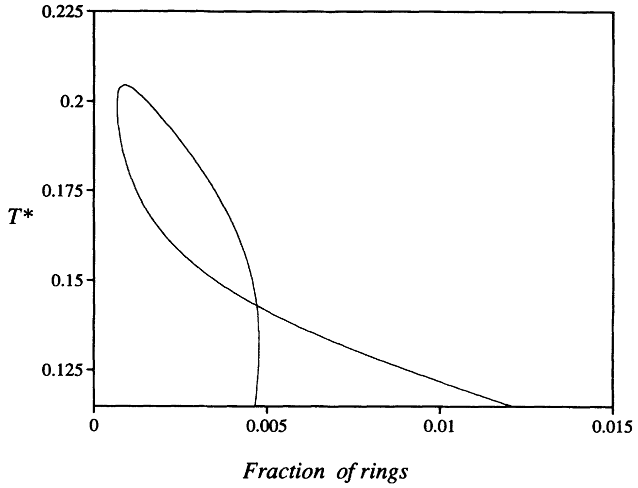

FIG. 2. The fraction of rings X along the coexistence curve is plotted against T^*. This is for the associating monomers with free energy Eq. (18). The gas phase has the larger number of rings at low temperature. $\epsilon_{SW}/\epsilon_{MF} = 2$, $K = 8.7791 \times 10^{-4}$, and $n = 6$.

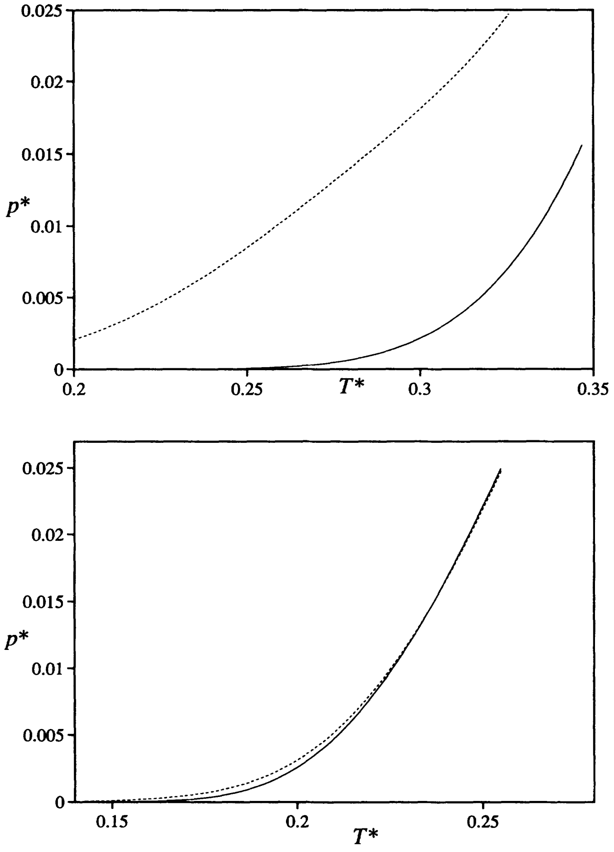

FIG. 3. The figure shows the phase diagram for a fluid of associating chains. $K = 8.7791 \times 10^{-4}$ and both lines correspond to chains of six spheres. The dashed line is for chains with the free energy of Eq. (37) while the solid line is for association only into chains, i.e., the earlier theory without the ring graph. The top graph corresponds to $\epsilon_{SW}/\epsilon_{MF} = 4$ and the lower graph to $\epsilon_{SW}/\epsilon_{MF} = 2$.

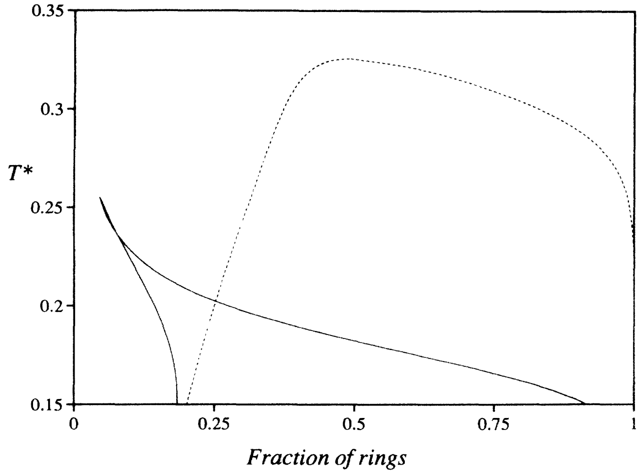

FIG. 4. The fraction of the chain molecules with free energy Eq. (37) which have formed rings, in the coexisting vapor and liquid phases, is plotted against T^*. The dashed curve is for $\epsilon_{\rm SW}/\epsilon_{\rm MF} = 4$ and the solid curve for $\epsilon_{\rm SW}/\epsilon_{\rm MF} = 2$. Hence, the dashed curve corresponds to the dashed curve in the top graph in Fig. 3 while the solid curve corresponds to the dashed curve in the bottom graph of Fig. 3. Note that the gas phase is to the right of the critical point, i.e., there are more rings in the gas phase.

the p^*T projection crosses that of the system which only forms chains.

VI. CONCLUSION

The original approximation of Wertheim has been extensively tested against computer simulation data [11,20] and found to be highly accurate despite its simple form. The obvious question is: What is the accuracy of the present approximation? In approximating the ring graphs the end-to-end distribution of a chain of hard spheres has been replaced by that of a freely jointed chain. Although this may be reasonably accurate for long chains at high density, it will overestimate the probability W_{n-1} for our shorter chains. The effect of excluded volume on the properties of chains has been studied extensively, and these results could be employed to improve W_{n-1}. Of more relevance to real fluids is a model with fixed ξ, or with ξ allowed to vary over a narrow range; for hydrogen fluoride at least the conformation of the ring clusters seems to be determined by the need to keep the optimum FHF angle [9]. For the chain models the corresponding real molecules would commonly have a carbon backbone, which has been modeled as a chain with fixed angles between the successive links [10]. A source of error at high density is the approximation in going from Eq. (6) to Eq. (7). The low density graph should be decorated with an n-body cavity distribution function of the actual, not the reference, fluid. Assuming the contacts are independent works well for chains, and has been tested in the limit of complete association [12].

Finally, there is a recent study [21] in which the closing of quite large chains to rings was examined. It should be noted, however, that this was for a two-dimensional lattice system.

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