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Fluids with Highly Directional Attractive Forces. IV. Equilibrium Polymerization

M. S. Wertheim[1,2]

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We investigate approximation methods for systems of molecules interacting by core repulsion and highly directional attraction due to several attraction sites. The force model chosen imitates a chemical bond by providing for bond saturation when binding occurs. The dense fluid is an equilibrium mixture of s-mers with mutual repulsion. We use a previously derived reformulation of statistical thermodynamics, in which the particle species are monomeric units with a specified set of attraction sites bonded. Thermodynamic perturbation theory (TPT) and integral equations of two types are derived. The use of TPT is illustrated by explicit calculation for a molecular model with two attraction sites, capable of forming chain and ring polymers. Successes and defects of TPT are discussed. The integral equations for pair correlations between particles of specified bonding include calculation of self-consistent densities of species. Methods of calculating thermodynamic properties from the solutions of integral equations are given.

KEY WORDS: Highly directional forces; chemical bond; polymerization; thermodynamic perturbation theory; pair correlations; integral equations.

1. INTRODUCTION

In the preceding paper,$^{(1)}$ referred to in the text as III, we developed a comprehensive reformulation of the statistical thermodynamics of associating systems consisting of molecules with several attraction sites. Here we address the problem of making suitable approximations in order to arrive at tractable methods of computation.

The initial approximations are closely tied to the types of steric incompatibility (SI) discussed in detail in Section 4 of III. The types of SI named

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[1] Mathematics Department, Rutgers University, New Brunswick, New Jersey 08903.

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SI1 and SI2W in III, when taken together, model the saturation of a chemical bond. When site $A(1)$ in molecule 1 is bonded to site $B(2)$ in molecule 2, then SI1 prohibits bonding of either site to a site of a third molecule; SI2W prohibits the bonding of either site to an additional site of the bonding partner molecule. This physical SI is incorporated into the representation in terms of graphs by the single bonding condition:

> Each attraction site of a hyperpoint is either unbonded, or bonded to a single site of another hyperpoint.

This condition is imposed in all the following approximation schemes.

For pairs of molecules, a stronger type of SI is SI2S, which forbids double bonds between molecules. It is realized for hard sphere molecules with two sites of very short-ranged attraction, separated by a reasonable bond angle, as shown in Fig. 3 of III. In this case it is certainly advantageous to build in the prohibition of double bonds from the start. On the other hand, four tetrahedrally arranged sites of attraction of moderate range may allow double-bond formation. The formalism we develop is sufficiently general to accommodate either the possibility of multiple bonding or the *a priori* restriction to single bonding.

SI3 occurs to a degree which is highly dependent on the amount of steric self-hindrance of extended s-meric structures formed by association. It is substantial for rigid structures, which exhibit little self-hindrance, but becomes much less pronounced for flexible, kinked chains with free rotation around bonds. The problem of systematic exploitation of SI3 is a difficult one; it is not addressed here.

The types of SI may be regarded as a sequence of successively stronger steric constraints. Our approach is motivated by the belief that it is highly desirable to define as clearly as possible the approximation in terms of graph neglect called for by each level of SI, before proceeding to the next level. Here this program is carried out for the first two types of SI.

For definitions and notation, reference to III may be made. Many of the results presented here are closely related to earlier papers,(2,3) referred to as I and II, concerned with dimerizing systems.

2. BONDING BETWEEN PAIRS

Any consideration of approximation schemes must begin with the possible states of bonding between pairs of molecules. The unrestricted set of possible bondings is contained in (6) of III. The primary condition to be imposed is the single-bonding restriction. The algebra of site operators, introduced in III, provides a neat way of doing just that. We define an operator $\mathring{f}(12)$, which represents a sum over site–site bonds weighted by site operators:

$$\mathring{f}(12) = \sum_{A \in \Gamma} \sum_{B \in \Gamma} f_{AB}(12)\, \varepsilon_A(1)\, \varepsilon_B(2) \tag{1}$$

Then all possible conditions of attraction bonding between 1 and 2, weighted by site operators for bonded sites, are given by

$$\exp[\mathring{f}(12)] \tag{2}$$

Here multiple bonding of sites is forbidden, but multiple bonds between hyperpoints are allowed.

If multiple bonding between hyperpoints is to be excluded, we could proceed by replacing $\exp[\mathring{f}(12)]$ by $1 + \mathring{f}(12)$. It is often more convenient to modify (1) by writing

$$\mathring{f}(12) = \sum_{A \in \Gamma} \sum_{B \in \Gamma} f_{AB}(12)\, \varepsilon_A(1)\, \varepsilon_B(2)\, \varepsilon(12) \tag{3}$$

Here $\varepsilon(12)$ is an operator which commutes with all site operators and all $\varepsilon(ij)$ if the pair i, j is not 1, 2. Furthermore it satisfies

$$\varepsilon^2(12) = 0 \tag{4}$$

The advantage is that the weighted sum of all bonding conditions is still given by (2), so that calculations using this form cover both cases. We must then add the convention that integration over 1 and/or 2 implies taking the sum of the term independent of $\varepsilon(12)$ and the coefficient of $\varepsilon(12)$ of the term linear in $\varepsilon(12)$.

The use of the operator form (2) to represent the attraction bonding between pairs automatically propagates the prohibition against double bonding of sites as $\mathring{f}(12)$ is composed with other functions in perturbation theory or integral equations.

3. THERMODYNAMIC PERTURBATION THEORY

Thermodynamic perturbation theory (TPT) and certain integral equation methods are based on the calculation of the excess Helmholtz free energy A over a reference system at the same temperature T and singlet density $\rho(1)$ as the real system. The reference system is assumed to be known to the extent of A_R and the pair distribution function $g_R(12)$. Here the reference system is chosen to consist of molecules which interact only with the repulsive potential $\Phi_R(12)$, with corresponding Mayer f-function

$f_R(12)$. By subtracting from (39) of III the corresponding equation for the reference system, we obtain

$$\beta(A-A_R)=\int\left[\sigma_\Gamma(1)\ln\frac{\sigma_0(1)}{\sigma_\Gamma(1)}+\sigma_\Gamma(1)+Q(1)\right]d(1)-c^{(0)}+c_R^{(0)} \tag{5}$$

Here $Q(1)$ is $\sigma_0(1)$ times a certain multilinear function of the $\hat{\sigma}_\alpha(1)=\sigma_\alpha(1)/\sigma_0(1)$. The explicit form of $Q(1)$ is given in (40) of III.

The graphs devoid of attraction bonds in $c^{(0)}$ are exactly $c_R^{(0)}$. TPT retains only graphs with attraction bonding between a single pair of points. The sum of these graphs is given in terms of $g_R(12)$ by

$$c^{(0)}-c_R^{(0)}=\tfrac{1}{2}\int g_R(12)\langle\mathring{\sigma}(1)[e^{\mathring{f}(12)}-1]\,\mathring{\sigma}(2)\rangle_{1,2}\,d(1)\,d(2) \tag{6}$$

For the $c_\alpha(1)$ with $\alpha\neq\varnothing$ the approximation (6) implies

$$\mathring{c}(1)-c_0(1)=\int g_R(12)\langle[e^{\mathring{f}(12)}-1]\,\mathring{\sigma}(2)\rangle_2\,d(2) \tag{7}$$

Since $g_R(12)>0$ and all site–site potentials satisfy $\Phi_{AB}(12)\geqslant 0$ all the $c_\alpha(1)$ are non-negative.

Some of the striking aspects of TPT are best seen by specializing to the case of greatest interest, exclusion of double bonds. The easiest way to do this is the replacement

$$\exp[\mathring{f}(12)]-1\rightarrow\mathring{f}(12) \tag{8}$$

in (6) and (7). Because of the reduction to a single attraction bond, the only σ's contained in the TPT expression for $c^{(0)}-c_R^{(0)}$ are the $\sigma_{\Gamma-A}$. As a result we have

$$c_\alpha(1)=0 \qquad \text{for} \quad n(\alpha)\geqslant 2 \tag{9}$$

where $n(\alpha)$ is the number of sites in the set α. This does *not* cause any of the $\rho_\alpha(1)$ or $\sigma_\alpha(1)$ to vanish. It does enforce the following product properties:

$$\rho_\alpha(1)=\rho_0(1)\prod_{A\in\alpha}c_A(1) \qquad \text{for} \quad \alpha\neq\varnothing \tag{10}$$

$$\frac{\rho_\alpha(1)}{\rho_0(1)}=\prod_{A\in\alpha}\frac{\rho_A(1)}{\rho_0(1)} \qquad \text{for} \quad \alpha\neq\varnothing \tag{11}$$

It is easy to show, using site operators, that this implies a similar product property for the $\hat{\sigma}_\alpha(1)$:

$$\hat{\sigma}_\alpha(1)=\prod_{A\in\alpha}\hat{\sigma}_A(1) \qquad \text{for} \quad \alpha\neq\varnothing \tag{12}$$

The presence of density parameters $\rho_\alpha(1)$ for all bonding conditions assures us that TPT is successful in reproducing the phenomenon of polymerization. To see the s-meric structures in graphical form it is necessary to consider z-graphs. As each $\sigma_\alpha(i)$, $i = 1$ or 2, is reexpressed in terms of z-graphs, the σ-graphs with a single attraction bond produce z-graphs containing all possible trees of hyperpoints connected by attraction bonds. To the extent of reproducing the formation of an infinite set of polymeric structures, the simple TPT is successful.

The set of all z-graphs produced may be characterized, in the terminology adopted in III, as consisting of trees composed of bare s-mer trees, monomer points, and f_R-bonds. The f_R-bonds represent the effect of repulsion between pairs of s-mers. Since only a rather deficient subset of graphs is included, it is difficult to guess to what extent the inter-s-mer repulsion is accounted for correctly.

Two serious deficiencies of TPT are also evident. First, the only s-meric structures included are trees. Thus TPT is necessarily inadequate whenever structures containing closed loops of attraction bonding are important. Secondly, the absence of internal f_R-bonds in the s-mer trees amount to total neglect of steric self-hindrance of s-mers. Such effects are critically dependent on bond angles. In contrast, TPT yields universal answers, independent of the bond angle.

We illustrate the use of TPT for a simple model. The molecules have a spherical hard core, and two attraction sites, A and B. The vectors from the center of the core to the sites form a bond angle θ. The range of attraction is short enough so that the single-bonding condition is satisfied. These molecules can form chain and ring polymers. The minimum number of links necessary to form a ring is strongly dependent on the bond angle.

We specialize to the case where A and B are distinct types of sites, with

$$\Phi_{AA} = 0, \qquad \Phi_{BB} = 0 \tag{13}$$

However, the case of two identical sites is quite similar. From (40) of III we obtain the explicit expression for $Q(1)$:

$$Q(1) = -\sigma_A(1) - \sigma_B(1) + \sigma_A(1)\,\sigma_B(1)/\sigma_0(1) \tag{14}$$

and we have

$$c^{(0)} - c_R^{(0)} = \int g_R(12)\,f_{AB}(12)\,\sigma_B(1)\,\sigma_A(2)\,d(1)\,d(2) \tag{15}$$

By differentiation we obtain for the $c_\alpha(1)$

$$c_A(1) = I\sigma_A, \qquad c_B(1) = I\sigma_B, \qquad c_{AB}(1) = 0 \tag{16}$$

$$I = \int g_R(12)\, f_{AB}(12)\, d(2) \tag{17}$$

When (16) is inserted in the subsidiary conditions, given by (11) and (12) of III, we obtain, after dropping the ubiquitous explicit argument 1,

$$\sigma_B - \sigma_0 = \sigma_0 \sigma_B I, \qquad \sigma_A - \sigma_0 = \sigma_0 \sigma_A I, \qquad \sigma_{AB}\sigma_0 = \sigma_A \sigma_B \tag{18}$$

The first two relations imply the equality $\sigma_A = \sigma_B$, which obviously must hold on physical grounds. In the following we replace both by the symbol σ_G.

Since the density parameters ρ_0, ρ_A, ρ_B, and ρ_{AB} represent densities for monomers, chain ends, and interior beads of a chain, we can calculate two measures of the degree of polymerization. Each one is the mean number of beads in a chain of molecules linked by attraction bonds. We define η to be the mean over chains of two or more links, while ν is the mean over all chains including monomers. These definitions imply

$$\eta = \frac{\rho_{AB} + 2\rho_G}{\rho_G} = \frac{\sigma_{AB} - \sigma_0}{\sigma_G - \sigma_0} \tag{19}$$

$$\nu = \frac{\rho}{\rho_G + \rho_0} = \frac{\sigma_{AB}}{\sigma_G} \tag{20}$$

The difference between them is given by

$$\eta - \nu = \frac{\sigma_0(\sigma_{AB} - \sigma_G)}{\sigma_G(\sigma_G - \sigma_0)} \tag{21}$$

so that we have, by use of the equilibrium conditions (18), the nontrivial result

$$\eta - \nu = 1 \tag{22}$$

We can now express the thermodynamics in terms of ν, which satisfies

$$\nu = \sigma_{AB}/\sigma_G = \sigma_G/\sigma_0 \tag{23}$$

The equilibrium conditions (18) imply the following for the degree of polymerization in terms of the number density $\bar{\rho}$ and the T-dependent integral I:

$$\nu = \tfrac{1}{2} + (\tfrac{1}{4} + \bar{\rho} I)^{1/2} \tag{24}$$

which goes to 1 as I goes to 0 in the high T limit. With decreasing T, v increases as $I^{1/2}$. For the excess Helmholtz free energy over the reference system one finds

$$\beta(A - A_R) = 1 - v^{-1} - 2 \ln v \tag{25}$$

A test of the range of validity of this simple expression must await computer simulation of such polymerizing systems. One would expect the approximation to be at its best for stiff chains with bond angle π, where the neglect of rings and self-hindrance is not serious.

4. SELF-CONSISTENT DENSITIES

While TPT provides quick estimates of thermodynamic properties, it conveys little structural information. To obtain the latter in the form of correlation functions between molecules of specified bonding, it is necessary to go to integral equation theories. Since integral equations contain all the densities ρ_α in the form of the σ_α, it is necessary to calculate all these densities in a self-consistent manner. Since the singlet density $\rho(1) = \sigma_\Gamma(1)$ is imposed in the calculation, this amounts to calculating all but one of the $c_\alpha(1)$ self-consistently. The condition which allows us to do this is the single bonding condition. Once it is imposed, we can find exact relations for the $c_\alpha(1)$ with $\alpha \neq \varnothing$ in terms of pair correlations.

We consider $c_\alpha(1)$ as a sum of irreducible graphs, with field hyperpoints i carrying factors of $\sigma_{\Gamma-\gamma}(i)$, where γ is the set of bonded sites at i. Between pairs of points i, j we may have no bond, a bond $f_R(ij)$, or $e_R(ij)$ in parallel with attraction bonds of type $f_{CD}(ij)$. If SI2S holds, then the limit is one attraction bond between pairs.

For any graph in $c_\alpha(1)$, we select an arbitrary bonded site $A \in \alpha$ at 1, and trace the unique bond incident on $A(1)$ to its partner site, which we call $B(2)$. Let γ be the set of bonded sites at 2. We make 2 a labeled point and drop the factor $\sigma_{\Gamma-\gamma}(2)$. We compare the graphs obained in this way with the graphs in $c_{\alpha\gamma}(12)$. The latter graph sum is obtained from $c_\alpha(1)$ by making *any* point for which γ is the set of bonded sites a labeled point 2, and then dropping the factor $\sigma_{\Gamma-\gamma}(2)$.

We conclude that we have obtained the subset of graphs in $c_{\alpha\gamma}(12)$ such that there is a direct bond $f_{AB}(12)$ with A specified and B satisfying $B \in \gamma$.

Since $\mathring{h}(12)$ and $\mathring{c}(12)$ satisfy an equation of Ornstein–Zernike type, it follows that $c_{\alpha\gamma}(12)$ is the sum of all irreducible graphs in $h_{\alpha\gamma}(12)$. Furthermore, all graphs in $h_{\alpha\gamma}(12)$ which contain a direct bond from 1 to 2 are necessarily irreducible. It follows that our set of graphs is also equal to

> The subset of graphs in $g_{\alpha\gamma}(12) = h_{\alpha\gamma}(12)$ which contain $f_{AB}(12)$, with A specified and $B \in \gamma$.

In order to obtain a more useful characterization, it is necessary to inquire what is obtained when the bond $f_{AB}(12)$ is deleted. This requires an analysis of $\mathring{g}(12)$ analogous to $g(12)=e(12)\,y(12)$ in the one-density theory. We define the operator analog of $y(12)$ by

$$\mathring{y}(12)=1+\text{(all connected graphs with two labeled points and no direct bond from 1 to 2)} \tag{26}$$

Then $\mathring{g}(12)=\mathring{h}(12)+1$ is given by

$$\mathring{g}(12)=\mathring{y}(12)\,e_R(12)\exp[\mathring{f}(12)] \tag{27}$$

In the case at hand it is actually more convenient to use the following explicit representation:

$$\exp[\mathring{f}(12)]=\prod_{C\in\Gamma}\prod_{D\in\Gamma}[1+f_{CD}(12)\,\varepsilon_C(1)\,\varepsilon_D(2)\,\bar{\varepsilon}(12)] \tag{28}$$

$$\bar{\varepsilon}(12)=\begin{cases}\varepsilon(12) & \text{if SI2S applies}\\ 1 & \text{otherwise}\end{cases} \tag{29}$$

If the factor $f_{AB}(12)$ is present, then the site operators kill all factors with indices containing $A(1)$ or $B(2)$. If SI2S holds, then $\varepsilon(12)$ kills all other f factors. Therefore, the subset of graphs in $g_{\alpha\gamma}(12)$ containing the bond $f_{AB}(12)$ is $f_{AB}(12)$ times

$$\begin{cases}y_{\alpha-A,\gamma-B}(12)\,e_R(12) & \text{if SI2S holds}\\ g_{\alpha-A,\gamma-B}(12) & \text{otherwise}\end{cases} \tag{30}$$

Therefore, the result for $c_\alpha(1)$ is

$$c_\alpha(1)=\sum_{\substack{\gamma\subset\Gamma\\ \gamma\neq\varnothing}}\sum_{B\in\gamma}\int q_{\alpha-A,\gamma-B}(12)\,f_{AB}(12)\,\sigma_{\Gamma-\gamma}(2)\,d(2) \tag{31}$$

$$q_{\alpha-A,\gamma-B}(12)=\begin{cases}y_{\alpha-A,\gamma-B}(12)\,e_R(12) & \text{if SI2S holds}\\ g_{\alpha-A,\gamma-B}(12) & \text{otherwise}\end{cases} \tag{32}$$

We can rewrite this more compactly in a notation that will be useful later. We retain the bonding index for 1, but use sum over bondings, weighted by site operators for 2. Both cases are included in

$$c_\alpha(1)=\int\langle\mathring{g}_{\alpha-A}(12)\,\mathring{f}_A(12)\,\mathring{\sigma}(2)\rangle_2\,d(2) \tag{33}$$

because the implied operator $\varepsilon(12)$ included in $\mathring{f}_A(12)$ in the case of SI2S kills all terms in $\mathring{g}_{\alpha-A}(12)$ with direct bonds.

Expressions of this type hold for any of the sites $A\in\alpha$.

5. INTEGRAL EQUATIONS

The derivation of integral equations is a rather straightforward generalization of the treatment of dimerizing systems given in II. The complexity of the required equations in component form is swept away by the use of site operator notation. The starting point is the generalized Ornstein–Zernike equation

$$\mathring{h}(12)=\mathring{c}(12)+\int \langle \mathring{c}(13)\,\mathring{\sigma}(3)\,\mathring{h}(32)\rangle_3\,d(3) \tag{34}$$

We anticipate the fact that the calculation of thermodynamic properties involves certain integrals over $\mathring{h}(12)$ and/or $\mathring{c}(12)$. We define L, K, J, and S by

$$L=\sum_{n=2}^{\infty} L_n/2n \tag{35}$$

$$L_n=\int \langle \mathring{\sigma}(1)\,\mathring{c}(12)\,\mathring{\sigma}(2)\cdots \mathring{c}(n1)\rangle_{1\cdots n}\,d(1)\cdots d(n) \tag{36}$$

$$K=\int \langle \mathring{\sigma}(1)\,\mathring{\sigma}(2)\,\mathring{c}(12)\,\mathring{h}(12)\rangle_{1,2}\,d(1)\,d(2) \tag{37}$$

$$J=\tfrac{1}{2}\int \langle \mathring{\sigma}(1)\,\mathring{\sigma}(2)\,\mathring{h}(12)\,\mathring{h}(12)\rangle_{1,2}\,d(1)\,d(2) \tag{38}$$

$$S=\tfrac{1}{2}\int \langle \mathring{\sigma}(1)\,\mathring{c}(12)\,\mathring{\sigma}(2)\rangle_{1,2}\,d(1)\,d(2) \tag{39}$$

We also require the variations of these four integrals. The only nontrivial case is δL, where we use (34). The explicit results are

$$\begin{aligned}\delta L=&\tfrac{1}{2}\int \langle \mathring{\sigma}(1)\,\mathring{\sigma}(2)\,\delta\mathring{c}(12)\,\mathring{h}(12)\rangle_{1,2}\,d(1)\,d(2)\\ &+\tfrac{1}{2}\int \langle \delta\mathring{\sigma}(1)\,\mathring{\sigma}(2)\,\mathring{c}(12)\,\mathring{h}(12)\rangle_{1,2}\,d(1)\,d(2)\end{aligned} \tag{40}$$

$$\begin{aligned}\delta K=&\int \langle \mathring{\sigma}(1)\,\mathring{\sigma}(2)[\mathring{c}(12)\,\delta\mathring{h}(12)+\delta\mathring{c}(12)\,\mathring{h}(12)]\rangle_{1,2}\,d(1)\,d(2)\\ &+2\int \langle \delta\mathring{\sigma}(1)\,\mathring{\sigma}(2)\,\mathring{c}(12)\,\mathring{h}(12)\rangle_{1,2}\,d(1)\,d(2)\end{aligned} \tag{41}$$

$$\delta J=\int \langle \mathring{\sigma}(1)\,\mathring{\sigma}(2)\,\mathring{h}(12)\,\delta\mathring{h}(12)\rangle_{1,2}\,d(1)\,d(2)$$

$$+\int \langle \delta\mathring{\sigma}(1)\,\mathring{\sigma}(2)\,\mathring{h}(12)\,\mathring{h}(12)\rangle_{1,2}\,d(1)\,d(2) \tag{42}$$

$$\delta S=\tfrac{1}{2}\int \langle \mathring{\sigma}(1)\,\mathring{\sigma}(2)\,\delta\mathring{c}(12)\rangle_{1,2}\,d(1)\,d(2)$$

$$+\int \langle \delta\mathring{\sigma}(1)\,\mathring{\sigma}(2)\,\mathring{c}(12)\rangle_{1,2}\,d(1)\,d(2) \tag{43}$$

Reference system values of the integrals L, K, J, and S are indicated by a subscript R. They are defined by replacing $\mathring{\sigma}(i)$, $\mathring{c}(12)$, and $\mathring{h}(12)$ by $\rho(i)$, $c_R(12)$, and $h_R(12)$. The angular brackets are then superfluous and are therefore omitted.

In order to produce a closed set of equations, (34) must be combined with a second relation between $\mathring{c}(12)$ and $\mathring{h}(12)$, the so-called closure approximation. We consider two types of closures.

5.1. Integral Equation without Reference System

When a reference system is not used, then reasonable behavior in the high-temperature limit of negligible attraction is not built in. If we choose to impose the boundary condition that reasonably good results be obtained in the hard core limit, then this dictates a closure that reduces to the Percus–Yevick (PY) equation$^{(4)}$ in this limit. The analogy to the PY equation of the following closure, provisionally named PPY (polymer PY), is totally transparent.

We split the graph sum $\mathring{y}(12)$ into reducible and irreducible graphs by

$$\mathring{y}(12)=\mathring{g}(12)-\mathring{c}(12)+\mathring{Z}(12) \tag{44}$$

where $\mathring{Z}(12)$ contains all the irreducible graphs, and $\mathring{g}(12)-\mathring{c}(12)$ all the reducible ones. The PPY approximation,

$$\mathring{Z}(12)=0 \tag{45}$$

turns

$$\mathring{y}(12)=\mathring{g}(12)-\mathring{c}(12) \tag{46}$$

combined with (27) into a closure.

The universal operator form of the PPY equation leads to different expressions in component form, depending on whether or not SI2S holds.

If it does, then $\mathring{f}(12)$ contains the operator $\varepsilon(12)$, which is then introduced into $\mathring{g}(12)$ and $\mathring{c}(12)$ via (27). Our present concern, however, is not analysis of specific situations, but derivation of a general result for the pressure, consistent with the PPY closure. To this end we require the result of taking a variation of the closure, holding T and all potentials constant. After elimination of $\mathring{y}(12)$ between (27) and (46), the relation between $\mathring{c}(12)$ and $\mathring{g}(12)$ is linear. As a consequence, we obtain after weighting with $\mathring{\sigma}(1)$ and $\mathring{\sigma}(2)$

$$\langle \mathring{\sigma}(1)\,\mathring{\sigma}(2)[\mathring{g}(12)\,\delta\mathring{c}(12) - \delta\mathring{g}(12)\,\mathring{c}(12)]\rangle_{1,2} = 0 \tag{47}$$

From the variation of βpV as expressed in (33) of III we obtain

$$V\delta(\beta p) - \delta\bar{N} = \delta\left[c^{(0)} - \int \langle \mathring{c}(1)\,\mathring{\sigma}(1)\rangle\, d(1)\right] \tag{48}$$

where $\bar{N} = \int \rho(1)\, d(1)$ is the mean number of molecules in the system. We consider a variation in which the *f*-functions are held constant. Then the only variations in $c^{(0)}$ and $\mathring{c}(1)$ are due to variations in the σ's. In view of (15) and (47) of III we then have

$$\delta\left[c^{(0)} - \int \langle \mathring{c}(1)\,\mathring{\sigma}(1)\rangle\, d(1)\right] = -\int \langle \mathring{\sigma}(1)\,\mathring{c}(12)\,\delta\mathring{\sigma}(2)\rangle_{1,2}\, d(1)\, d(2) \tag{49}$$

We now verify that the following expression is consistent with the PPY closure:

$$c^{(0)} - \int \langle \mathring{c}(1)\,\mathring{\sigma}(1)\rangle\, d(1) = \tfrac{1}{2}K - 2L - S \tag{50}$$

The variation of the left-hand side of (50) is calculated in (49). The variation of the right-hand side is obtained from (40), (41), and (43):

$$\begin{aligned}
&\delta[\tfrac{1}{2}K - 2L - S] \\
&\quad = -\int \langle \mathring{\sigma}(1)\,\mathring{c}(12)\,\delta\mathring{\sigma}(2)\rangle_{1,2}\, d(1)\, d(2) \\
&\qquad + \tfrac{1}{2}\int \langle \mathring{\sigma}(1)\,\mathring{\sigma}(2)[\mathring{c}(12)\,\delta\mathring{h}(12) - \mathring{g}(12)\,\delta\mathring{c}(12)]\rangle_{1,2}\, d(1)\, d(2)
\end{aligned} \tag{51}$$

For variations at constant *f*-functions, the second term on the right-hand side vanishes by virtue of (47), the variation of the closure. The first term agrees with the right-hand side of (49). Hence, (50) is established by integration over the variation from $\rho = 0$ to the actual density, once it is verified that the two sides of (50) agree in the low-density limit. By taking the leading graphs of the expansion in $\mathring{\sigma}$ of the two sides we find

$$\begin{aligned}\lim_{\rho=0}\left[c^{(0)}-\int\langle\mathring{\sigma}(1)\,c(1)\rangle\,d(1)\right]\\ &=\lim_{\rho=0}\left(\tfrac{1}{2}K-2L-S\right)\\ &=-\tfrac{1}{2}\lim_{\rho=0}\int\langle\mathring{\sigma}(1)[f_R(12)+e_R(12)\,e^{\mathring{t}(12)}]\,\mathring{\sigma}(2)\rangle_{1,2}\,d(1)\,d(2)\end{aligned}\tag{52}$$

This establishes the result for the PPY equation,

$$\beta pV=\bar{N}+\tfrac{1}{2}K-2L-\tfrac{1}{2}S\tag{53}$$

It is noteworthy that the quantity for which a closure-consistent expression could be obtained in terms of $\mathring{c}(12)$ and $\mathring{h}(12)$ is the left-hand side of (50), rather than $c^{(0)}$ itself. As a consequence, $\mathring{c}(1)$ does not appear explicitly, and the question of what to use for $\mathring{c}(1)$ was bypassed entirely in finding an expression for the pressure. It seems reasonable that the exact expression (33) should be used. As will appear shortly, the situation is quite different for integral equations of hypernetted chain type.

5.2. Integral Equation with Reference System

The reference system that suggests itself is the same one used in TPT: the system interacting only with the repulsive forces represented by $f_R(12)$. It is assumed that the pair distribution function $g_R(12)$ of the reference system is known. From this the direct correlation function $c_R(12)$ can be calculated.

With the use of a reference system, the behavior in the purely repulsive limit is no loger an issue, and the graph sum of HNC (hypernetted chain) type is attractive for two reasons. The HNC equation$^{(5-10)}$ has rather good internal thermodynamic consistency and allows the definition of a Helmholtz free energy A in terms of its solution. Furthermore the HNC equation and equations related to it have proved successful in dealing with forces that are purely attractive or attractive in the mean.

Once operator notation is introduced, it becomes easy to generalize the procedure used in II for a single attraction site to the closure suggested here, the PXHNC (polymer excess HNC) closure. It is formulated in terms of the graphs $\mathring{t}(12)$, characterized by

$\mathring{t}(12)$ = all connected graphs without direct (12)-bond which remain connected when all connections at 1 and 2 are broken. There is at least one attraction bond.

The relation between $\mathring{t}(12)$ and $\mathring{y}(12)$ is

$$\mathring{t}(12) = \ln \frac{\mathring{y}(12)}{y_R(12)} \tag{54}$$

An exact expression for the component functions $g_{\alpha\gamma}(12)$ in operator form is

$$\mathring{g}(12) = g_R(12) \exp[\mathring{t}(12) + \mathring{f}(12)] \tag{55}$$

This holds, whether or not SI2S prevails. If it does, then $\mathring{f}(12)$ contains the operator $\varepsilon(12)$.

The graphs in $\mathring{t}(12)$ can be split into reducible and irreducible graphs by

$$\mathring{t}(12) = \mathring{h}(12) - \mathring{c}(12) + \mathring{E}(12) - [h_R(12) - c_R(12) + E_R(12)] \tag{56}$$

where $\mathring{E}(12) - E_R(12)$ is the sum of all the irreducible graphs. The approximation of HNC type is

$$\mathring{E}(12) - E_R(12) = 0 \tag{57}$$

After inserting (57) in (56), and using the logarithm of (55) to eliminate $\mathring{t}(12)$, we have the PXHNC closure,

$$\ln \frac{\mathring{g}(12)}{g_R(12)} = \mathring{h}(12) - \mathring{c}(12) + \mathring{f}(12) - h_R(12) + c_R(12) \tag{58}$$

If SI2S prevails, then the presence of $\mathring{f}(12)$ introduces the operator $\varepsilon(12)$ into direct attraction bonds in $\mathring{c}(12)$ and $\mathring{g}(12)$. As in the case of PPY, the component form of the closure will look quite different from the case where SI2S is not imposed.

The calculation of $A - A_R$ compels us to consider variations in which the reference system is held constant. Applying this to (58) yields

$$\mathring{h}(12)\, \delta\mathring{h}(12) - \mathring{g}(12)[\delta\mathring{c}(12) - \delta\mathring{f}(12)] = 0 \tag{59}$$

The calculation of an expression for $\beta(A - A_R)$ starts with (5). The only terms for which expressions have to be found are the nonexplicit graphical terms $-c^{(0)} + c_R^{(0)}$. In the variation due to turning on $\mathring{f}(12)$ from $\mathring{f}(12) = 0$ to the actual values, all the σ_α with the exception of $\sigma_\Gamma = \rho$ change. The constancy of the reference system implies that ρ and β are held constant. For the variation of $c^{(0)}$ we obtain the exact result

$$\delta c^{(0)} = \tfrac{1}{2} \int \langle \mathring{\sigma}(1)\, \mathring{g}(12)\, \delta\mathring{f}(12)\, \mathring{\sigma}(2) \rangle_{1,2}\, d(1)\, d(2)$$

$$+ \int \langle \mathring{c}(1)\, \delta\mathring{\sigma}(1) \rangle\, d(1) \tag{60}$$

The expression which fulfills (60) within the PXHNC approximation is

$$c^{(0)} - c_R^{(0)} = -\tfrac{1}{2}(J - J_R) + (L - L_R) + (S - S_R) \tag{61}$$

It is clear that both sides become zero when the attractive interactions are turned off. Therefore it is necessary only to compare the variation of the right-hand side of (61) with (60). From (40), (42), and (43) we obtain

$$\delta(-\tfrac{1}{2}J + L + S) = M_1 + M_2 \tag{62}$$

$$M_1 = \tfrac{1}{2}\int \langle \mathring{\sigma}(1)[\mathring{g}(12)\,\delta\mathring{c}(12) - \mathring{h}(12)\,\delta\mathring{h}(12)]\,\mathring{\sigma}(2)\rangle_{1,2}\,d(1)\,d(2) \tag{63}$$

$$M_2 = \int \langle \delta\mathring{\sigma}(1)\{\mathring{c}(12) - \tfrac{1}{2}[\mathring{h}(12) - \mathring{c}(12)]\,\mathring{h}(12)\}\,\mathring{\sigma}(2)\rangle_{1,2}\,d(1)\,d(2) \tag{64}$$

M_1 can be transformed using the closure given in (59). The result is

$$M_1 = \tfrac{1}{2}\int \langle \mathring{\sigma}(1)\,\mathring{g}(12)\,\delta\mathring{f}(12)\,\mathring{\sigma}(2)\rangle_{1,2}\,d(1)\,d(2) \tag{65}$$

which agrees with the first term on the right-hand side of (60). Somewhat more complicated manipulations are required for M_2. First, it is necessary to exhibit a symmetry in part of the integrand in (64). We use the notation introduced in (33), retaining the bonding index for 1, but using operator sums for the labeled point 2. Then we have by use of (34),

$$\begin{aligned} &\int \langle [\mathring{h}_\alpha(12) - \mathring{c}_\alpha(12)]\,\mathring{\sigma}(2)\,\mathring{h}_\gamma(21)\rangle_2\,d(2) \\ &\quad = \int \langle \mathring{h}_\alpha(13)\,\mathring{\sigma}(3)\,\mathring{c}(32)\,\mathring{\sigma}(2)\,\mathring{h}_\gamma(21)\rangle_{2,3}\,d(2)\,d(3) \\ &\quad = \int \langle \mathring{h}_\alpha(12)\,\mathring{\sigma}(2)[\mathring{h}_\gamma(21) - \mathring{c}_\gamma(21)]\rangle_2\,d(2) \end{aligned} \tag{66}$$

which indicates that we may interchange the bonding indices of the two factors at 1.

We use the symmetry in the following way. Let $p_{\alpha\gamma}(12)$ denote the coefficient of $\delta\sigma_{\Gamma-\alpha}(1)\,\sigma_{\Gamma-\gamma}(2)$ in the integral (64) for M_2. The product terms involve partitions of α and γ into two subsets. No rearrangement is required for partitions of γ. At the labeled point 1, we select an arbitrary bonded site $A \in \alpha$. For every partition of α into two subsets, we assign the subset containing A as the bonding index of the t-factor, the complement as the bonding index of the h-factor. Since half the original terms had their indices switched, we gain a factor of 2 for the surviving terms. With this rearrangement we have

$$p_{\alpha\gamma}(12)=c_{\alpha\gamma}(12)-\sum_{\substack{\omega\subset\alpha\\ A\in\omega}}\sum_{\tau\subset\gamma} t_{\omega\tau}(12)\,h_{\alpha-\omega,\gamma-\tau}(12) \tag{67}$$

This may be rewritten in terms of the *g*'s by using

$$g_{\alpha\gamma}(12)=h_{\alpha\gamma}(12)+\delta_{\alpha,\phi}\delta_{\gamma,\phi} \tag{68}$$

and eliminating $c_{\alpha\gamma}(12)$. This replaces (67) by

$$p_{\alpha\gamma}(12)=g_{\alpha\gamma}(12)-\sum_{\substack{\omega\subset\alpha\\ A\in\omega}}\sum_{\tau\subset\gamma} t_{\omega\tau}(12)\,g_{\alpha-\omega,\gamma-\tau}(12) \tag{69}$$

This is to be compared with $g_{\alpha\gamma}(12)$ as obtained from (27) in component form. The subtraction of the double sum in (69) removes from $g_{\alpha\gamma}(12)$ all those terms for which $A(1)$ is bonded to a field point. Therefore, the balance $p_{\alpha\gamma}(12)$ consists of all graphs in $g_{\alpha\gamma}(12)$ such that $A(1)$ is bonded to a site in 2. Using the results of Section 3, we can conclude immediately that we have

$$\sum_{\gamma\subset\Gamma}\int p_{\alpha\gamma}(12)\,\sigma_{\Gamma-\gamma}(2)\,d(2)=c_\alpha(1) \tag{70}$$

Of course, we could have proceeded algebraically, using (55). Since this is an exact relation, we then obtain $c_\alpha(1)$ in the form (33). From (70) it finally follows that we have

$$M_2=\int\langle\mathring{c}(1)\,\delta\mathring{\sigma}(1)\rangle\,d(1) \tag{71}$$

which completes the proof of (61).

Thus our final result for the Helmholtz free energy for the PXHNC equation is

$$\begin{aligned}\beta(A-A_R)=\int\left[\sigma_\Gamma(1)\ln\frac{\sigma_0(1)}{\sigma_\Gamma(1)}+\sigma_\Gamma(1)+Q(1)\right]d(1)\\ +\tfrac{1}{2}(J-J_R)-(L-L_R)-(S-S_R)\end{aligned} \tag{72}$$

It is noteworthy that the closure-consistent expression for *A* actually demanded incorporation of the exact relations (33) for the $c_\alpha(1)$. This implies that the minimum property of *A* is preserved in the PXHNC approximation. For constant $\rho=\sigma_\Gamma$ and all *f*-functions held fixed, *A* is stationary with respect to variations of the σ_α with $\alpha\neq\Gamma$.

6. CONCLUSION

Our aim has not been the production of a catalog of all conceivable integral equations or versions of TPT. The types singled out appear promising on intuitive grounds, but need to be tested by actual calculation for a system that is also simulated by Monte Carlo or molecular dynamics in order to have exact results for comparison.

The examples chosen illustrate the great scope for deriving new calculational methods inherent in the multidensity formalism. Much more needs to be done; first and foremost, the problem of successful incorporation of SI3 needs to be addressed. Undoubtedly, this will entail even more detailed consideration of the geometry of interactions for the physical system considered.

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