Journal of Statistical Physics, Vol. 35, Nos. 1/2, 1984

Fluids with Highly Directional Attractive Forces. II. Thermodynamic Perturbation Theory and Integral Equations

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Received August 24, 1983

The formalism of statistical thermodynamics developed in the preceding paper is used as a basis for deriving tractable approximations. The system treated is one where repulsion and highly directional attraction due to a single molecular site combine to allow the formation of dimers, but no higher s-mers. We derive thermodynamic perturbation theory, using the system interacting with only the repulsive potential as a reference system. Two distinct integral equations for the pair correlation are derived. The first one treats both parts of the interaction approximately; the other one employs the repulsive reference system used in perturbation theory. We show that each of these integral equations permits the calculation of an important thermodynamic function directly from the solution at a single state of density and temperature. In the first case this applies to a pressure consistent with the compressibility relation, in the second to the excess Helmholtz free energy over the reference system.

KEY WORDS: Highly directional forces; association; dimers; thermodynamic perturbation theory; integral equations.

1. INTRODUCTION

In the preceding paper,$^{(1)}$ referred to in the text as I, we have developed a reformulation of statistical thermodynamics suitable for systems of molecules with highly directional attractive forces which promote association into dimers, and possibly higher s-mers. The degree of difficulty in translat-

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

[2] Supported by the NSF under Grant No. CHE-82-11236 and by the U.S. Air Force under Grant No. AFOSR 82-0016A.

ing the formalism into reasonable approximation theories is highly correlated with the complexity of the class of sterically allowed s-mers.

The simplest case is that where the only nonvanishing pure s-mer graph is the dimer graph. For such systems the situation is very favorable indeed, and we are able to produce reasonable approximation schemes which contain number density ρ and monomer density ρ_0 as parameters. In ease of application these schemes are competitive with the more usual ones, which are based on ρ alone. Unlike the latter ones, they incorporate an exact treatment of the otherwise very troublesome limit of a dilute, but highly dimerized gas.

In the following we derive approximation schemes of two types: thermodynamic perturbation theory, and integral equations for the pair correlations. The type of integral equation chosen depends on whether or not a reference system is used. Each integral equation is accompanied by a method of calculating thermodynamic properties directly from the solution at a single state (ρ, β). In the final section we briefly mention the possible alternatives to be faced in dealing with the much more complicated situation where higher s-mers are allowed.

For notation and definitions, reference should be made to I.

2. EXPRESSIONS FOR ρ_0

The derivation of approximation theories is carried out in the representation where the Helmholtz free energy A and the pair correlation functions $c_{ij}(12)$ and $h_{ij}(12)$ are written as infinite sums of graphs free of articulation points. According to (14) of I, each field point i of a graph then carries a factor $\rho(i)$ if it is a monomer point, $\rho_0(i)$ if it is an s-mer point, $s \geqslant 2$. The approximations derived are formulated in terms of ρ, ρ_0, β, and the $h_{ij}(12)$ and/or $c_{ij}(12)$. For given ρ and β the monomer density ρ_0 is not a free parameter and must be determined in a self-consistent manner.

The starting point for doing this is Eq. (13) of I, which may be written

$$\rho(1)/\rho_0(1) = 1 + c_1(1) \tag{1}$$

where we recall from I that $c_1(1)$ consists of all irreducible graphs with one labeled point 1, which is an s-mer point, $s \geqslant 2$. The enormous simplification which occurs when s-mer graphs for $s > 2$ vanish occurs in the following way. The restriction to dimers implies that there is exactly one F-bond incident on the point 1. By turning the point where the F-bond originates into a point labeled 2 and deleting the factor $f_A(12)$ we obtain exactly all graphs in $g_{00}(12)$. Hence,

$$c_1(1) = \int g_{00}(12) f_A(12) \rho_0(2)\, d(2) \tag{2}$$

No such simple expression in terms of pair correlations alone is available when higher s-mers are present.

The combination of (1) and (2) provides the required self-consistent relation for the monomer density:

$$\rho(1) = \rho_0(1) + \rho_0(1)\int g_{00}(12) f_A(12) \rho_0(2)\, d(2) \tag{3}$$

In the low-density limit, $g_{00}(12)$ may be replaced by the leading graph, $e_R(12)$. Equation (3) then becomes

$$\rho(1) = \rho_0(1) + \rho_0(1)\int F(12) \rho_0(2)\, d(2) \tag{4}$$

which is the mass action law of chemical equilibrium.

3. THERMODYNAMIC PERTURBATION THEORY

Numerous successful applications of thermodynamic perturbation theory (TPT) have been made to simple, multipolar and polar polarizable fluids.[3] In the usual spirit of TPT, we choose as reference system a system of molecules at the ρ and β of the real system, but interacting only with the repulsive potential $\phi_R(12)$. Part of βA is given by the graph sum $-c^{(0)}$, in which the bonds are f_R-bonds and/or F-bonds. We order by ascending number of F-bonds and truncate the series. To first order in F we obtain

$$c^{(0)} = c_R^{(0)} + \tfrac{1}{2}\int \rho_0(1) g_R(12) f_A(12) \rho_0(2)\, d(1)\, d(2) + \cdots \tag{5}$$

$$c_1(1) = \int g_R(12) f_A(12) \rho_0(2)\, d(2) + \cdots \tag{6}$$

Equation (6) implies a self-consistent $\rho_0(1)$ given by

$$\rho(1) = \rho_0(1) + \rho_0(1)\int g_R(12) f_A(12) \rho_0(2)\, d(2) \tag{7}$$

which amounts to inserting the approximation $g_{00}(12) = g_R(12)$ in (3). In the low-density limit, even if highly dimerized, we have $g_R(12) = e_R(12)$, which reduces (7) to the correct limiting form (4).

By using Eq. (21) of I for both the real system and the reference system, we obtain for the difference in free energies

$$\beta(A - A_R) = \int \left[\rho(1) \ln \frac{\rho_0(1)}{\rho(1)} - \rho_0(1) + \rho(1) \right] d(1) - c^{(0)} + c_R^{(0)} \tag{8}$$

Use of (5) and (7) reduces (8) to the form

$$\beta(A - A_R) = N(\ln x - \tfrac{1}{2}x + \tfrac{1}{2}), \qquad x = \rho_0/\rho \tag{9}$$

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[3] For references to TPT see Ref. 2.

where N is the total number of monomeric units, whether free or bound in a dimer. The ratio x is determined by Eq. (7). In this very simple result the packing effect due to size of the repulsive core enters only by the effect of $g_R(12)$ on x.

This is physically reasonable when T is not too low, so that the main effect of hard particle packing is the increase, relative to point particles at the same density, of close encounters which favor dimerization. At lower T, undoubtedly terms with more than one F-bond become important. The graphs with two F-bonds involve four-particle correlations of the reference system. Since in practice this would have to be approximated by a type of superposition, it is simpler and more promising to effect a partial summation of graphs to *all* orders in F by an integral equation. This program is carried out in Section 4.2.

4. INTEGRAL EQUATIONS

The statistical thermodynamics of associating systems in terms of ρ and ρ_0, as developed in I, shows many parallels to classical fluid theory based on ρ alone. In particular, we obtained a matrix analog of the Ornstein–Zernike equation, of the form

$$h_{ij}(12) = c_{ij}(12) + \int c_{ik}(13)\rho_{kl}(3)h_{lj}(32)\,d(3) \tag{10}$$

where $\rho_{00} = \rho$, $\rho_{01} = \rho_{10} = \rho_0$, and $\rho_{11} = 0$. In (10) and the rest of this paper we adhere to the convention that *summation over repeated indices is implied.*

In the special case of the dimerizing gas we can go much further. The restriction to at most one F-bond incident on each point makes it possible to achieve a substantial graph sum by combining (10) with relatively simple closure equations. In designing closures we are guided by past successes of the integral equation method for theories involving ρ alone.

An important aspect of integral equation theories is the calculation of thermodynamic quantities. For the HNC equation[4] Morita and Hiroike$^{(3)}$ showed how to compute a free energy A from the solution of the equation at a single state (ρ, β). The A obtained this way is consistent with the virial pressure p and the internal energy U as obtained from $g(12)\phi(12)$. For the Percus–Yevick (PY) equation[4] Baxter$^{(4)}$ obtained a similar result for a pressure p consistent with the compressibility relation. For the SSC equation[4] expressions for $A - A_R$, $p - p_R$, and $U - U_R$ were derived by Wertheim.$^{(5)}$ All of these results use integration by parts to transform a coupling constant integration into a form which depends only on the solution at the end points. In the case at hand this procedure is complicated

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[4] See Refs. 1–8 in I for the PY, HNC, and SSC equations.

by the fact that ρ_0 varies as either ρ or the pair potential is varied. Nevertheless, it has proved possible to carry out this very important part of the program for the two integral equations proposed here.

4.1. Integral Equations without Reference System

Here we deal with the entire interaction by an integral equation. Since the PY equation does well for hard spheres, it is reasonable to adopt a closure which reduces to the PY equation when $f_A = 0$. The following system is similar to and suggested by our earlier work on hard diatomics.[6] The structure here is somewhat simpler, there being only two, as compared to four, terms in the decomposed f-function. We define

$$y_{ij}(12) = \delta_{0i}\delta_{0j} + (\text{graphs with no direct 12-bond}) \tag{11}$$

By splitting into reducible and irreducible parts, we obtain

$$y_{ij}(12) = \left[g_{ij}(12) - c_{ij}(12) \right] + Z_{ij}(12) \tag{12}$$

where the bracket contains the reducible graphs and $Z_{ij}(12)$ the irreducible ones. The approximation of PY type is

$$Z_{ij}(12) = 0 \tag{13}$$

The $g_{ij}(12)$ are related to the $y_{ij}(12)$ by

$$g_{ij}(12) = e_R(12)\left[y_{ij}(12) + \delta_{i1}\delta_{j1} f_A(12) y_{00}(12) \right] \tag{14}$$

Elimination of the $y_{ij}(12)$ between (11)–(13) yields the closure equations

$$e_R(12) c_{ij}(12) = f_R(12)\, g_{ij}(12) + \delta_{i1}\delta_{j1}\, g_{00}(12) f_A(12) \tag{15}$$

The graphs summed by combining (14) with (10) are simply related to the graphs summed by the PY equation for a fluid of density ρ interacting by $f(12)$. To go from $c_{\text{PY}}(12)$ or $h_{\text{PY}}(12)$ to our $c_{ij}(12)$ or $h_{ij}(12)$ carry out the following operations on the PY-graphs. Take all ways of replacing each $f(ij)$ by either $f_R(ij)$ or $F(ij)$, with the proviso that each point may have at most one F-bond incident. Relabel field points with one incident F-bond by ρ_0. Assign graph to $c_{ij}(12)$ or $h_{ij}(12)$ according to the numbers i, j of F-bonds incident at 1 and 2.

We now derive an expression for the pressure p which is consistent with the appropriate generalization of the compressibility relation

$$\beta(\partial p/\partial \bar{\rho}) = 1 - \rho \int c(12)\, d(2) \tag{16}$$

which cannot be used, because the direct correlation function $c(12)$ does not appear in our formalism. In order to obtain the required analog of (16) we use a representation of $\ln \Xi$ obtained by combining Equations (13) and

(17) of I,

$$\ln \Xi = \int \left[\rho(1) - \rho(1)c_0(1) - \rho_0(1)c_1(1) \right] d(1) + c^{(0)} \tag{17}$$

By using the definition of the c-hierarchy of functions in (28) of I we obtain for the variation of $\ln \Xi$

$$\delta(\ln \Xi) = \int \delta\rho(1)\, d(1) - \int \rho_{0i}(1) c_{ij}(12) \delta\rho_{j0}(2)\, d(1)\, d(2) \tag{18}$$

This is the appropriate generalization of (16) in differential form. We can integrate over the variation ρ_{ij} from $\rho_{ij} = 0$ to the actual state. After integration by parts and insertion of the uniform system result $\ln \Xi = \beta p V$, we obtain

$$\begin{aligned} \beta p V = {}& \int \rho(1)\, d(1) - \tfrac{1}{2} \int \rho_{0i}(1) c_{ij}(12) \rho_{j0}(2)\, d(1)\, d(2) \\ & + \tfrac{1}{2} \underset{\delta}{\int} \int \rho_{0i}(1) \delta c_{ij}(12) \rho_{j0}(2)\, d(1)\, d(2) \end{aligned} \tag{19}$$

On the right hand side of (19) the integral sign with δ below it indicates the integration over the variation.

Further integration is possible provided we introduce expressions for the $\delta c_{ij}(12)$ implied by the closure approximation (14). We take a variation of the closure at constant $f_R(12)$ and $f_A(12)$, which implies constant pair potential and temperature. The closure equations are then used to eliminate $f_R(12)$ and $f_A(12)$. From the equations not containing $f_A(12)$ we obtain

$$g_\alpha(12)\delta c_\beta(12) - c_\alpha(12)\delta g_\beta(12) = 0, \qquad \text{for} \quad \alpha \neq 11, \quad \beta \neq 11 \tag{20}$$

The equation which contains $f_A(12)$ yields the result

$$\begin{aligned} & g_{00}(12)\delta c_{11}(12) - c_{00}(12)\delta g_{11}(12) + g_{11}(12)\delta c_{00}(12) \\ & \quad - c_{11}(12)\delta g_{00}(12) = 0 \end{aligned} \tag{21}$$

Multiplied by appropriate ρ-factors and summed, these equations combine into the result

$$\rho_{ij}(1)\rho_{kl}(2)\left[g_{jk}(12)\delta c_{il}(12) - \delta g_{jk}(12) c_{il}(12) \right] = 0 \tag{22}$$

which is equivalent to

$$\rho_{ij}(1)\rho_{kl}(2)\left[c_{jk}(12)\delta h_{il}(12) - \delta c_{jk}(12) h_{il}(12) \right] = \rho_{0i}(1)\delta c_{ij}(12)\rho_{j0}(2) \tag{23}$$

The right-hand side of (23) is the term to be integrated over the variation δ in Eq. (19). In order to carry this out, a further transformation of the left-hand side of (23) is needed.

We define two functions L and K, both of which consist of all rings of $n \geqslant 2$ c-bonds, with ρ-factors interposed. In L the ring of n c-bonds has the correct combinatorial weight $1/2n$, while in K the weight is 1:

$$L = \sum_{n=2}^{\infty} L_n/2n, \qquad K = \sum_{n=2}^{\infty} L_n \tag{24}$$

$$L_n = \int c_{ij}(12)\rho_{jk}(2) \ldots c_{st}(n, 1)\rho_{ti}(1)\, d(1) \ldots d(n) \tag{25}$$

In taking a variation of L_n, δ can act on any of n c's and n ρ's. In view of Eq. (9) we obtain

$$\begin{aligned} 2\delta L = &\int \rho_{ij}(1)\rho_{kl}(2)\delta c_{jk}(12)h_{il}(12)\, d(1)\, d(2) \\ &+ \int \delta\rho_{ij}(1)\left[h_{ji}(11) - c_{ji}(11)\right] d(1) \end{aligned} \tag{26}$$

The second term in (26) may be transformed using (10) for the special case of equal arguments,

$$h_{ij}(11) - c_{ij}(11) = \int c_{ik}(12)\rho_{kl}(2)h_{jl}(12)\, d(2) \tag{27}$$

The function K is given by

$$K = \int \rho_{ij}(1)\rho_{kl}(2)c_{jk}(12)h_{il}(12)\, d(1)\, d(2) \tag{28}$$

and its variation by

$$\begin{aligned} \delta K = {} & 2\int \delta\rho_{ij}(1)\rho_{kl}(2)c_{jk}(12)h_{il}(12)\, d(1)\, d(2) \\ & + \int \rho_{ij}(1)\rho_{kl}(2)\left[\delta c_{jk}(12)h_{il}(12) + c_{jk}(12)\delta h_{il}(12)\right] d(1)\, d(2) \end{aligned} \tag{29}$$

Equations (26) and (29) can be combined so as to eliminate $\delta\rho_{ij}$. We obtain the result

$$\delta(\tfrac{1}{2}K - 2L) = \tfrac{1}{2}\int \rho_{ij}(1)\rho_{kl}(2)\left[c_{jk}(12)\delta h_{il}(12) - \delta c_{jk}(12)h_{il}(12)\right] d(1)\, d(2) \tag{30}$$

By using successively (23) and (30) for the last term of (19), we obtain a form that can be integrated over the variation. There is no contribution from the lower limit, $\rho = 0$, where $K = L = 0$. We obtain the desired result for the pressure:

$$\beta pV = \int \rho(1)\, d(1) - \tfrac{1}{2}\int \rho_{0i}(1)c_{ij}(12)\rho_{j0}(2)\, d(1)\, d(2) + \tfrac{1}{2}K - 2L \tag{31}$$

Note that the rings of two c-bonds, which contain forbidden graphs with duplication of the direct (12)-bond, cancel from the combination $\frac{1}{2}K - 2L$.

The expression (28) for K may be replaced by the following alternative, obtained by using (27) and the fact that the infinite repulsion for two coincident particles enforces $g_{ij}(11) = 0$:

$$K = -\int \left[\rho(1) + 2\rho_0(1) + \rho_{ij}(1) c_{ji}(11) \right] d(1) \tag{32}$$

4.2. Integral Equation with Reference System

It is reasonable to expect that we can improve on the preceding treatment if we can employ exact knowledge of the reference system of molecules at the ρ and T of the real system, but interacting only by the potential $\phi_R(12)$, with Mayer function $f_R(12)$. Clearly, this is advantageous at high ρ and T, where the spatial exclusion is more important than the dimerization, since we are now calculating only the difference in spatial exclusion between the monomeric reference system and the real system. For low ρ, the reference system approach reduces to TPT, so that the exact treatment of low density, even if highly dimerized, is retained.

The reference system is assumed to be known to the extent of A and pair distribution function $g_R(12)$, from which $c_R(12)$ can also be calculated. For any graphical quantity of the real system, all graphs consisting solely of f_R-bonds constitute the reference system. For this reason, there no longer are any grounds for choosing an approximation of PY type, which has good cancellation between omitted graphs for repulsive f-bonds only. On the basis of successes of equations related to the HNC equation, it seems more promising to resort to the larger graph sum of HNC type. To this end one defines graph sums $t_{ij}(12)$ as follows:

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

With this definition, we can express the $g_{ij}(12)$ in terms of the $t_{ij}(12)$ and $g_R(12)$. In view of the restriction to at most one F-bond per point, we have[5]

$$g_{00}(12) = g_R(12)\exp\left[t_{00}(12) \right] \tag{33}$$

$$g_{10}(12) = g_{00}(12) t_{10}(12) \tag{34}$$

$$g_{11}(12) = g_{00}(12)\left[t_{10}(12) t_{01}(12) + t_{11}(12) + f_A(12) \right] \tag{35}$$

The $t_{ij}(12)$ can be split into reducible and irreducible graphs as follows:

$$t_{ij}(12) = g_{ij}(12) - c_{ij}(12) + E_{ij}(12) - \delta_{i0}\delta_{j0}\left[g_R(12) - c_R(12) + E_R(12) \right] \tag{36}$$

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[5] For a review of graph theory see Ref. 7.

The approximation of HNC type neglects the irreducible graphs $E_{ij}(12)$:

$$E_{ij}(12) - \delta_{i0}\delta_{j0}E_R(12) = 0 \tag{37}$$

By imposing (37) and eliminating the $t_{ij}(12)$ between (33)–(35) and (36) we obtain the closure relations between the $g_{ij}(12)$ and the $c_{ij}(12)$,

$$c_{00}(12) - c_R(12) = g_{00}(12) - g_R(12) - \ln\left[g_{00}(12)/g_R(12)\right] \tag{38}$$

$$g_{00}(12)c_{10}(12) = h_{00}(12)\, g_{10}(12) \tag{39}$$

$$\begin{aligned} g_{00}(12)\left[c_{11}(12) - f_A(12)\right] &= h_{00}(12)\, g_{11}(12) \\ &\quad + g_{00}(12)\left[g_{10}(12) - c_{10}(12)\right]\left[g_{01}(12) - c_{01}(12)\right] \end{aligned} \tag{40}$$

Equations (38)–(40) together with the exact relation (10) form a closed set of integral equations to be solved.

The difference in Helmholtz free energies, $A - A_R$, can be obtained by integrating δA from the reference system to the real system as f_A is turned on from zero to the actual function. This is done at constant ρ and β, so that all reference system quantities are constants of the process. Owing to the presence of ρ_0 and the subsidiary condition (1) more than one expression for the integral of δA can be given. By applying the variation to *all* terms in (7) and then using (1) we obtain a result which greatly resembles the standard one for the formalism in ρ alone:

$$\beta(A - A_R) = -\tfrac{1}{2} \int_{\delta}\!\!\int \rho_0(1)\rho_0(2)g_{00}(12)\delta f_A(12)\, d(1)\, d(2) \tag{41}$$

It turns out to be more appropriate to employ the alternative form obtained by taking the variation only of the graphical term $c^{(0)}$. The result reflects the fact that $f_A(12)$ occurs only in the combination $\rho_0(1)f_A(12)\rho_0(2)$:

$$\begin{aligned} \beta(A - A_R) &= \int \left[\rho(1)\ln\frac{\rho_0(1)}{\rho(1)} - \rho_0(1) + \rho(1)\right] d(1) \\ &\quad - \tfrac{1}{2} \int_{\delta}\!\!\int g_{00}(12)\delta\left[\rho_0(1)f_A(12)\rho_0(2)\right] d(1)\, d(2) \end{aligned} \tag{42}$$

We now show that use of the closure approximation (38)–(40) makes it possible to express the integral over δ in terms of the solutions of the integral equation at the end points. In order to do this, we need the ring sum L and a function

$$J = \sum_{n=2}^{\infty} \tfrac{1}{2}(n-1)L_n = \tfrac{1}{2}\int \rho_{ij}(1)\rho_{kl}(2)h_{jk}(12)h_{il}(12)\, d(1)\, d(2) \tag{43}$$

We take the variation of the combination $J - 2L$, which does not contain the forbidden rings of two c-bonds. The result is

$$\delta J - 2\delta L = M_1 + M_2 \tag{44}$$

$$M_1 = \int \rho_{ij}(1)\rho_{kl}(2)\left[\delta h_{jk}(12) - \delta c_{jk}(12)\right]h_{il}(12)\,d(1)\,d(2) \tag{45}$$

$$\begin{aligned} M_2 = &\int \delta\rho_{ij}(1)\rho_{kl}(2)h_{jk}(12)h_{il}(12)\,d(1)\,d(2) \\ &- \int \delta\rho_{ij}(1)\left[h_{ji}(11) - c_{ji}(11)\right]d(1) \end{aligned} \tag{46}$$

In order to transform M_1 we must insert the expressions obtained by taking variations of the closure equations (38)–(40). Since ρ and β are held constant, $g_R(12)$ and $c_R(12)$ do not contribute, and we obtain from (38)

$$g_{00}\delta c_{00} = h_{00}\delta g_{00} \tag{47}$$

This result can be combined with the variations of (39) and (40) to yield

$$g_{00}\delta c_{10} + g_{10}\delta c_{00} = h_{00}\delta g_{10} + g_{10}\delta g_{00} \tag{48}$$

$$\begin{aligned} &g_{00}\delta c_{11} + g_{10}\delta c_{00} + g_{01}\delta c_{10} + g_{11}\delta c_{00} \\ &\quad = h_{00}\delta g_{11} + g_{10}\delta g_{01} + g_{10}\delta g_{01} + g_{11}\delta g_{00} + g_{00}\delta f_A \end{aligned} \tag{49}$$

We have omitted the arguments, which are (12) for every function in (47)–(49). These three equations can be summed with appropriate ρ-factors to yield

$$\begin{aligned} &\rho_{ij}(1)\rho_{kl}(2)\left[\delta h_{jk}(12) - \delta c_{jk}(12)\right]h_{il}(12) \\ &\quad = \rho_{0i}(1)\delta c_{ij}(12)\rho_{j0}(2) - \rho_0(1)\rho_0(2)\,g_{00}(12)\delta f_A(12) \end{aligned} \tag{50}$$

It follows that we have

$$\begin{aligned} M_1 = &\int \rho_{0i}(1)\delta c_{ij}(12)\rho_{j0}(2)\,d(1)\,d(2) \\ &- \int \rho_0(1)\rho_0(2)g_{00}(12)\delta f_A(12)\,d(1)\,d(2) \end{aligned} \tag{51}$$

In the expression (46) for M_2 we need to transform the second term using (27). Since the only nonvanishing elements of $\delta\rho_{ij}$ are the off-diagonal ones $\rho_{01} = \rho_{10} = \rho_0$, there is always one F-bond incident on the point 1. The symmetry under interchange of indices, which holds for $c_{ij}(11)$ and $h_{ij}(11)$, can be used to ensure that this F-bond always appears in a factor $c_{1i}(12)$ rather than $h_{1i}(12)$. In this way we find that

$$M_2 = 2\int \delta\rho_{10}(1)\rho_{ij}(2)\left[h_{1i}(12) - c_{1i}(12)\right]h_{0j}(12)\,d(1)\,d(2) \tag{52}$$

From the closure equations (38)–(40) summed with appropriate ρ-factors we obtain

$$\left[h_{1i}(12) - c_{1i}(12)\right]h_{0j}(12)\rho_{ij}(2) = c_{1i}(12)\rho_{i0}(2) + g_{00}(12)f_A(12)\rho_0(2) \tag{53}$$

and hence

$$\begin{aligned} M_2 = &\int \delta\left[\rho_{0i}(1)\rho_{j0}(2)\right]c_{ij}(12)\,d(1)\,d(2) \\ &+ \int \delta\left[\rho_0(1)\rho_0(2)\right]g_{00}(12)f_A(12)\,d(1)\,d(2) \end{aligned} \tag{54}$$

M_1 and M_2 combine into the following result for $\delta J - 2\delta L$:

$$\begin{aligned} \delta J - 2\delta L = &\int \delta\left[\rho_{0i}(1)c_{ij}(12)\rho_{j0}(2)\right]d(1)\,d(2) \\ &- \int g_{00}(12)\delta\left[\rho_{01}(1)f_A(12)\rho_0(2)\right]d(1)\,d(2) \end{aligned} \tag{55}$$

This enables us to integrate Eq. (42) from the reference system to the real system, with the result

$$\begin{aligned} \beta(A - A_R) = &\int\left[\rho(1)\ln\frac{\rho_0(1)}{\rho(1)} - \rho_0(1) + \rho(1)\right]d(1) \\ &- \tfrac{1}{2}\int \rho_{0i}(1)\left[c_{ij}(12) - \delta_{i0}\delta_{j0}c_R(12)\right]\rho_{j0}(2)\,d(1)\,d(2) \\ &+ \tfrac{1}{2}(J - J_R) - (L - L_R) \end{aligned} \tag{56}$$

4.3. Spherically Symmetric $\phi_R(12)$

The integral equation schemes derived are sensible whether or not the repulsive potential $\phi_R(12)$ is spherically symmetric. If it is so, $\phi_R(12) = \phi_R(r_{12})$, then tremendous computational simplification occurs due to the restriction of at most one F-bond per point. As a result, the products of functions containing the labeled point i in either Eq. (9) or the closure equations (38)–(40) can have at most one factor which depends on Ω_i. Therefore, these equations may be integrated over the orientations. Their form remains unchanged, except for the following replacements in the arguments, with p standing for either c or h:

$$p_{ij}(12) \to \bar{p}_{ij}(r_{12}) = \Omega^{-2}\int p_{ij}(12)\,d\Omega_1\,d\Omega_2 \tag{57}$$

$$\rho_{ij}(\alpha) \to \bar{\rho}_{ij} = \rho_{ij}\Omega, \qquad d(\alpha) \to d\mathbf{r}_\alpha \tag{58}$$

The integral equations now involve only spherically symmetric functions.

The calculation of the ring sum L also becomes materially simplified.

We define

$$c_{ij}(q) = \frac{2\pi}{q}\int_0^\infty \bar{c}_{ij}(r)\sin(qr)r\,dr \tag{59}$$

$$B_{ij}(q) = c_{ik}(q)\bar{\rho}_{kj} \tag{60}$$

and denote the two eigenvalues of the matrix $B_{ij}(q)$ by $B_+(q)$ and $B_-(q)$. Then the ring sum can be taken in the usual way, with the result

$$L = \frac{V}{4\pi^2}\sum_{k=+,-}\int_0^\infty \{-B_k(q) - \ln[1 - B_k(q)]\}q^2\,dq \tag{61}$$

In order to secure the fastest fall-off at large q, it is advisable to use similar forms for J and K, so that the lowest power of $B_k(q)$ in series expansion is $B_k^3(q)$. The explicit forms are

$$\tfrac{1}{2}K - 2L = \frac{V}{2\pi^2}\sum_{+,-}\int_0^\infty \left\{ \frac{\frac{1}{2}B_k^2(q)}{1 - B_k(q)} + B_k(q) + \ln[1 - B_k(q)] \right\} q^2\,dq \tag{62}$$

$$\tfrac{1}{2}J - L = \frac{V}{4\pi^2}\sum_{+,-}\int_0^\infty \left\{ \frac{B_k^2(q)}{2[1 - B_k(q)]^2} + B_k(q) + \ln[1 - B_k(q)] \right\} q^2\,dq \tag{63}$$

5. COMPLEX SYSTEMS

Two ways of increasing the complexity of the model are (1) a single attractive site with longer-ranged attraction, so that several oligomers are allowed and non-negligible, and (2) presence of more than one molecular attraction site.

The complication due to (1) can quickly become formidable. If we insist on including all the allowed oligomer graphs exactly, then it appears necessary to go to theories with higher distribution functions in order to get a graph sum capable of representing the mutual repulsion of oligomers at high densities. A more attractive alternative seems to be a scheme restricted to pair functions, with the closure of an integral equation generating the oligomer graphs. This involves approximations and partly destroys the optimal steric incompatibility which arises from the fact that the s-mer graphs are "filled with e_R bonds," (see I, Sections 4 and 8). A closely related difficulty is the fact that Eq. (2) for ρ_0 must be replaced by a much more complicated expression.

The case of additional molecular attraction sites is highly dependent on the geometry. We will return to some sterically favorable cases in a future paper.

6. CONCLUSION

We have developed promising approximation schemes of two types for dimerizing systems of particles interacting by short-ranged repulsion and highly directional short-ranged attraction. For spherically symmetric repulsion the ease of execution of these schemes is competitive with standard methods for multipolar fluids or mixtures of simple fluids.

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