REVIEW PAPER

Supplementary graphical analysis for the multi-density expansion of associating fluids

Jaeeon Chang†

Department of Chemical Engineering, University of Seoul, Siripdae-gil 13, Dongdaemun-gu, Seoul 130-743, Korea
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Abstract−We present a detailed analysis of Wertheim's multi-density formulation for the thermodynamic properties of associating fluids with a single attraction site. Graphical expressions are explicitly illustrated for the partition function, multi-densities and direct correlation functions, and they are compared with those from the classical single-density formulation of simple fluids. The steric incompatibility among three monomers greatly simplifies cluster integrals of associating fluids, which allows dimerizing association only. Graphical expressions for the pressure and the Helmholtz energy are derived by using functional derivatives, which provide a theoretical base for TPT and SAFT equations of state.

Keywords: Associating Fluid, Graph Theory, Cluster Integral, Multi-density, TPT, SAFT

INTRODUCTION

Ever since Wertheim developed a rigorous statistical mechanical theory of associating fluids [1-4], his seminal work has established a theoretical foundation for the modern thermodynamic approaches of complex fluids, including hydrogen bonding fluids, fluids of chain molecules and polymers. In Wertheim's theory, monomer segments interact with each other by two different types of interaction potentials: nonbonded interactions represented by repulsive and weakly attractive forces, and associating interactions represented by localized strongly attractive forces. The separate treatment of the interaction potentials leads to multi-density expansions for thermodynamic and structural properties of associating fluids. The multi-density expansion of the Helmholtz energy is a starting point for thermodynamic perturbation theory (TPT) of associating fluids and chain fluids [5], also known as SAFT (statistical associating fluid theory) [6-11]. During the past decades, there have been proposed various versions of the SAFT equations of state including SAFT-VR [12], soft-SAFT [13], SAFT based on square-well chains [14-16] and PC-SAFT [17,18]. Comprehensive reviews for the SAFT equations of state are referred to recent review articles [19-21]. For the structural properties of associating fluids, the multi-density expansion for distribution functions leads to the multi-density Ornstein-Zernike (MOZ) equation [2,3] which, when solved with a closure approximation, gives the pair correlation functions of the associating fluids. The MOZ theory has been applied to associating fluids with single attraction site [22-26], polymerizable hard spheres and hard-sphere chain fluids [27-35], polyelectrolyte models [36,37], Yukawa hard-sphere chain fluids [38, 39] and colloid models [40,41]. Also, the multi-density expansion for pressure gives a virial equation of state applicable to the gas phase of associating fluids. Recent studies by explicitly evaluating cluster integrals for the associating fluids have shown that the multi-density expansion is superior to the classical single-density expansion [42,43].

The SAFT equations of state are basically the same as Wertheim's thermodynamic perturbation theory in first order (TPT1) in which the reference system is monomer fluid without associating interactions. While the SAFT approach has become popular in engineering research, the fundamental aspects of the theory might have not been fully appreciated. We believe that a better understanding of Wertheim's theory would guide future developments beyond the limit of present SAFT theories of complex fluids. For instance, developments towards this direction are TPT-D theory [28,39,44-46] and SAFT-D theory [47] that make use of structural properties of dimer fluids and the TPT of sequential polymerization [48] in which monomers are added one by one. These theories were found to be more accurate than TPT1 (or SAFT). In this paper, we discuss the fundamental aspects of Wertheim's graphical analysis which leads to multi-density expansions for the thermodynamic properties of the associating fluids. First, we review Mayer's graph theory of simple fluids by introducing definitions of terms and related theorems. Second, we discuss Wertheim's graph theory of the associating fluids in great detail, and compare it with the classical Mayer theory. In addition, we prove graphical expressions for the thermodynamic properties of associating fluids through the variation of functionals. Finally, we show how the TPT1 or SAFT approximation is formulated by relating the graph sums with the pair correlation function of the reference fluid under the condition of steric incompatibility.

GRAPH THEORY OF SIMPLE FLUIDS

In this section, we briefly review the graph theory of simple fluids in which molecules interact with each other by spherically symmetrical potential. The grand canonical partition function Ξ is written as

$$\Xi(\mu, V, T) = 1 + \sum_{N=1}^{\infty} \frac{Z_N(N, V, T)}{N!} z^N \qquad (1)$$

where Z_N is configurational integral with the number of molecules N, V is the volume of system, T is temperature, z is the fugacity

†To whom correspondence should be addressed.
E-mail: changjaee@uos.ac.kr

defined by $z=\exp(\beta\mu)/\lambda^3$ in which β is $1/kT$, k is the Boltzmann constant, μ is chemical potential and λ is thermal wavelength. In graph theory, a multidimensional integral is represented by a graph, and mathematical operations are performed by handling graphs. We will follow the definitions of graphs and the theorems of graph theory described in ref. [49]. In terms of graphs, Eq. (1) is represented as

$$\Xi = 1 + \bullet + \bullet\!-\!\!-\!\!\bullet + \triangle + \boxtimes + \dots \tag{2}$$

where black circles are z-circles and dashed lines are e-bonds. By decomposing $e(1, 2)$ into $1+f(1, 2)$ we have

$$\Xi = 1 + \bullet + \bullet\ \bullet + \bullet\!-\!\bullet + \ ^{\bullet}_{\bullet}\,^{\bullet} + \diagup_{\bullet}^{\bullet} + \triangle + \triangle \tag{3}$$

where solid line denotes f-bond. To remove disconnected graphs in Eq. (3) we use the exponentiation theorem, the first lemma of ref. [49]. It follows that

$$\ln\Xi = \bullet + \bullet\!-\!\bullet + \triangle + \triangle + \diagup\!\!\!\diagdown + \sqcap$$
$$+ \square + \boxdiagup + \boxslash + \boxtimes + \dots \tag{4}$$

That is, $\ln\Xi$ is the sum of all connected graphs consisting of z-circles and f-bonds. The density $\rho(1)$ is obtained from the functional derivative of $\ln\Xi$ with respect to $z(1)$ as

$$\rho(1) = z(1)\frac{\delta\ln\Xi}{\delta z(1)} \tag{5}$$

For homogeneous fluids $\rho(1)$ becomes ρ/Ω and $z(1)$ becomes z/Ω where $\Omega=8\pi^2$ for asymmetric molecules or $\Omega=4\pi$ for molecules with line symmetry. In graph theory, the functional derivative with respect to $z(1)$ is given as the sum of all distinct graphs by turning black z-circle into white 1-circle, i.e., using the second lemma of ref. [49]. The density $\rho(1)$ is obtained from Eqs. (4) and (5) as

$$\rho(1) = \circ + \circ\!-\!\bullet + \triangle + \triangle + \triangle + \diagup\!\!\!\diagdown + \diagup\!\!\!\diagdown$$
$$+ \sqcap + \sqcap + \square + \boxdiagup + \boxdiagup + \boxdiagup$$
$$+ \boxslash + \boxminus + \boxtimes + \dots \tag{6}$$

where white circle carries $z(1)$. The graphs in Eq. (6) containing white and black articulation circles can be further reduced, and graphs that are free of articulation circles are called irreducible graphs. To remove white articulation circles indicated by arrows in Eq. (6), we apply the exponentiation theorem, and we then have

$$\ln\frac{\rho(1)}{z(1)} = \circ\!-\!\bullet + \triangle + \triangle + \diagup\!\!\!\diagdown + \sqcap + \square$$
$$+ \boxdiagup + \boxdiagup + \boxslash + \boxminus + \boxtimes + \dots \tag{7}$$

where white circle is 1-circle and black circles are z-circles. The circles indicated by arrows in Eq. (7) are black articulation circles. Graphs containing black articulation circles can be reduced by the virtue of "decoration theorem," the fourth lemma of ref. [49]. Graphs with black articulation circles are obtained by decorating irreducible graphs, the graphs in Eq. (7) that are free of black articulation circles, with any graphs of $\rho(1)$ in Eq. (6). This yields topological reduction that Eq. (7) is rewritten in terms of irreducible graphs while turning black z-circles into black ρ-circles. Graph sum $c(1)$ is defined as

$$\ln\frac{\rho(1)}{z(1)} = c(1) = \circ\!-\!\bullet + \triangle + \square + \boxslash + \boxminus + \boxtimes + \dots \tag{8}$$

where graphs are irreducible graphs consisting of a white 1-circle, black ρ-circles and f-bonds. In fact, $c(1)$ is a functional derivative of $c^{(0)}$ with respect to density $\rho(1)$,

$$c(1) = \frac{\delta c^{(0)}}{\delta\rho(1)} \tag{9}$$

where

$$c^{(0)} = \bullet\!-\!\bullet + \triangle + \square + \boxslash + \boxtimes + \dots \tag{10}$$

The graphs in $c^{(0)}$ are irreducible graphs consisting of black ρ-circles and f-bonds, free of articulation circles. Thermodynamic properties are expressed in terms of $c^{(0)}$ and $c(1)$. The grand partition function and the pressure of the system is given by [50]

$$\ln\Xi = \beta pV = \int\rho(1)d1 - \int\rho(1)c(1)d1 + c^{(0)} \tag{11}$$

where integration is over positions and orientations of a molecule. For homogeneous fluids, the first integral becomes the average number of molecules, i.e., the ideal-gas term, and the last two terms represent nonideal contributions to the pressure. In fact, Eq. (11) is a graphical representation for the virial equation of state. The Helmholtz energy is given by [50]

$$\beta A = \int\rho(1)[\ln\lambda^3\rho(1)-1]d1 - c^{(0)} \tag{12}$$

Since the integral denotes the ideal gas contribution to the Helmholtz energy, $-kT\,c^{(0)}$ is nonideal contribution to the Helmholtz energy. Similar expressions in analogy to Eqs. (11) and (12) are derived for associating fluids.

GRAPH THEORY OF ASSOCIATING FLUIDS

We consider associating fluid with a single association site in which the intermolecular potential is represented as a sum of reference potential $u_R(12)$, which consists of repulsive interaction and weakly attractive interaction as in simple fluids, and associative potential $u_A(12)$ which is localized and orientation-dependent,

$$u(12)=u_R(12)+u_A(12) \tag{13}$$

Accordingly, the f-function is decomposed into the reference f_R-function and associative F-function as

$$f(12)=e_R(12)e_A(12)-1=e_R(12)[1+f_A(12)]-1$$
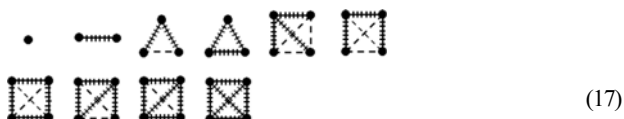
$$=e_R(12)-1+e_R(12)f_A(12)=f_R(12)+F(12) \qquad (14)$$

By Eq. (14), f-bond in graphs is replaced by f_R-bond and F-bond. When this replacement is applied to the graphs of ln Ξ in Eq. (4), we have

ln Ξ={all connected graphs consisting of z-circles,
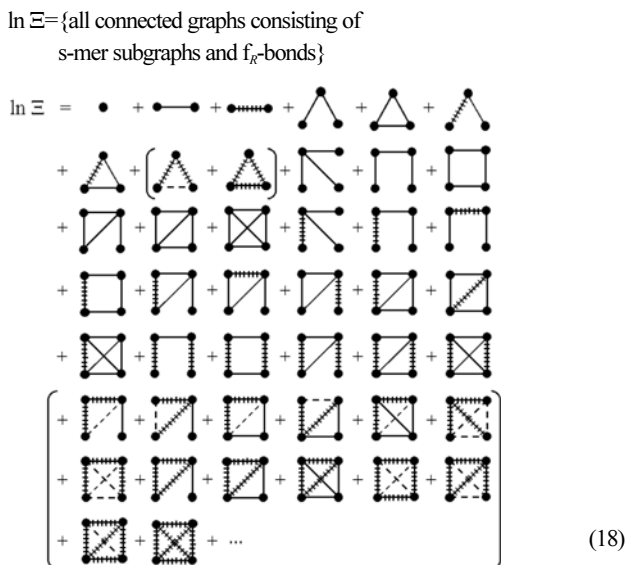f_R-bonds and F-bonds} $\qquad (15)$

Certain graphs in Eq. (15) can be added (or resummed) by recombining f_R-bond and 1-bond into e_R-bond for any pairs of circles for which a connected path by F-bonds exists, and this resummation results in a great deal of simplification. For example, two connected graphs that appear in Eq. (15) can be added, and the sum is represented by a single graph as

$$(16)$$

where solid line is f_R-bond, hatched line is F-bond, and dashed line is e_R-bond. Building blocks of such resummed graphs are called s-mer graphs (s=1, 2, ⋯, ∞) where s is the number of circles connected by a network of F-bonds. The s-mer graphs are regarded as elementary entities, and e_R-bond in a s-mer graph is never to be broken into 1-bond and f_R-bond. All pairs of circles which are not directly connected by F-bond are filled with e_R-bonds. In the following the s-mer graphs for s≤4, including monomer circle, are listed as

$$(17)$$

The grand partition function can be rewritten in terms of s-mer graphs, and Eq. (15) is rephrased as

ln Ξ={all connected graphs consisting of
s-mer subgraphs and f_R-bonds}

$$(18)$$

The graphs enclosed in the parenthesis have s-mer subgraphs (s≥3). Note that all s-mer graphs higher than dimer graphs (s≥3) become zero because of the highly localized nature of F-bond and repulsive term of e_R-bond contained in F-bond. Physically, it reflects steric incompatibility; three and more attraction sites cannot come close
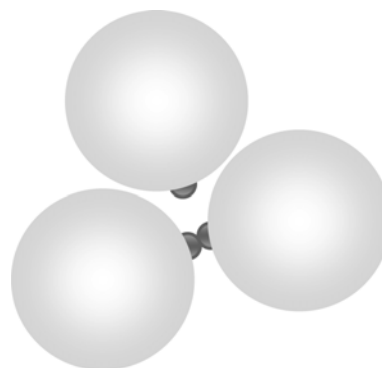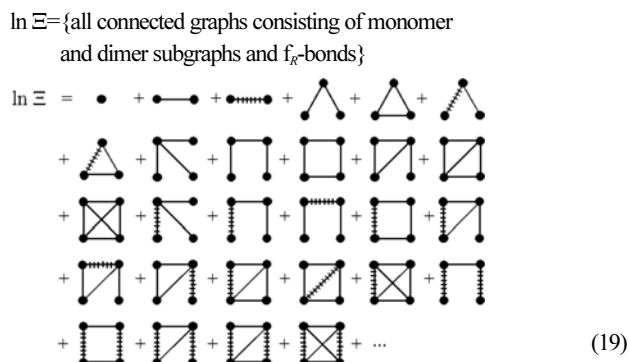
Fig. 1. Steric incompatibility among three monomers with a single attraction site. The short range of associative interaction and the repulsive cores permit the formation of dimer only, and trimer formation is prohibited.

enough to form an oligomer because of the presence of repulsive cores as is depicted in Fig. 1. At most, only dimerization is allowed with a single attraction site of short range.
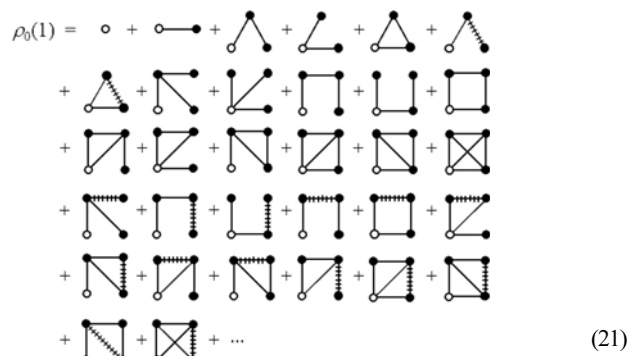
Therefore, graphs containing higher s-mer subgraphs (s≥3) except for monomer and dimer subgraphs will be omitted in further discussion, and Eq. (18) simplifies to

ln Ξ={all connected graphs consisting of monomer
and dimer subgraphs and f_R-bonds}

$$(19)$$

The density $\rho(1)$ is obtained from the graphs of ln Ξ in Eq. (19) by turning black z-circle into white z-circle in the similar manner as in Eqs. (5) and (6). Depending on whether the white z-circle receives F-bond or not, the graphs of $\rho(1)$ are divided into the density of nonbonded monomers $\rho_0(1)$ and the density of bonded monomers $\rho_1(1)$, i.e.,

$$\rho(1)=\rho_0(1)+\rho_1(1) \qquad (20)$$

and the two densities are given by

$$(21)$$

$$\rho_1(1) = \text{(graphs)} \tag{22}$$

where white circle carries $z(1)$. While the graphs of $\rho_0(1)$ and $\rho_1(1)$ contain articulation circles, related graph sums whose graphs are free of articulation circles can be obtained in analogy to simple fluids. Graph sum $c_0(1)$ is defined as

$$c_0(1) = \ln\frac{\rho_0(1)}{z(1)} \tag{23}$$

In graph theory, this corresponds to applying the exponentiation theorem to $\rho_0(1)$ of Eq. (21). The graphs of $c_0(1)$ belong to a subset of $\rho_0(1)$ of which graphs are free of white articulation circle,

$$c_0(1) = \text{(graphs)} \tag{24}$$

where white circle is 1-circle and black circles are z-circles. When association disappears, the graph sum $c_0(1)$ reduces to $c(1)$ of the classical Mayer theory. Likewise, we define a graph sum $c_1(1)$ of which graphs belong to a subset of $\rho_1(1)$, free of white articulation circle,

$$c_1(1) = \text{(graphs)} \tag{25}$$

In fact, a graph of $\rho_1(1)$ having a white articulation circle can be obtained by multiplying a graph of $c_1(1)$ by a graph of $\rho_0(1)$. Examples for such products are shown in the following:

$$\text{(graph products)} \tag{26}$$

Trivially, the graphs of $\rho_1(1)$ without a white articulation circle are obtained by multiplying a graph of $c_1(1)$ by a white z-circle that also belongs to $\rho_0(1)$. Therefore, $\rho_1(1)$ is identified to be a product of $c_1(1)$ and $\rho_0(1)$,

$$\rho_1(1) = c_1(1)\rho_0(1) \tag{27}$$

The graphs of $c_0(1)$ and $c_1(1)$ given by Eqs. (24) and (25) are fugacity expansions, and they still contain black articulation circles. Converting the fugacity expansions into density expansions makes use of the decoration theorem, i.e., the fourth lemma of ref. [49], which eliminates the black articulation circles. All graphs of $c_0(1)$ in Eq. (24) are obtained by decorating black circles of the irreducible graphs of $c_0(1)$ with any graphs of $\rho_0(1)$ and $\rho_1(1)$ if the circle is monomer circle and by decorating the black circles with any graphs of $\rho_0(1)$ if the circle is a part of dimer subgraph with receiving F-bond. Similarly, all graphs of $c_1(1)$ are obtained by decorating the black circles of the irreducible graphs of $c_1(1)$ with any graphs of $\rho(1)$ for monomer circle and with any graphs of $\rho_0(1)$ for dimer circle. Thus, $c_0(1)$ and $c_1(1)$ can be rewritten in terms of irreducible graphs by replacing z-circles with ρ-circles and ρ_0-circles,

$$c_0(1) = \text{(graphs)} \tag{28}$$

$$c_1(1) = \text{(graphs)} \tag{29}$$

where white circle is 1-circle, black circles without receiving F-bond are ρ-circles and black circles receiving F-bond are ρ_0-circles. From the inspection of Eqn. (28) and (29), it is noted that $c_0(1)$ and $c_1(1)$ are partial functional derivatives of $c^{(0)}$ with respect to the two densities,

$$c_0(1) = \frac{\partial c^{(0)}}{\partial \rho(1)}, \quad c_1(1) = \frac{\partial c^{(0)}}{\partial \rho_0(1)} \tag{30}$$

and

$$c^{(0)} = \text{(graphs)} \tag{31}$$

where the graphs of $c^{(0)}$ are irreducible graphs consisting of black ρ-circle without receiving F-bond and black ρ_0-circle with F-bond.

The pressure and the Helmholtz energy of associating fluids are given in terms of $c^{(0)}$ and the multi-densities [1]. Here, we derive the expressions by using functional derivatives [50]. To do this, Eq. (5) is written in variational form as

$$\delta\ln\Xi = \int\rho(1)\frac{\delta z(1)}{z(1)}d1 \tag{32}$$

Also, the variational form of Eq. (23) is written as

$$\delta c_0(1) = \frac{\delta \rho_0(1)}{\rho_0(1)} - \frac{\delta z(1)}{z(1)} \tag{33}$$

Substituting Eq. (33) into Eq. (32) to eliminate $z(1)$, we have

$$\delta \ln \Xi = \delta \int \rho_0(1) d1 - \int \rho(1) \delta c_0(1) d1 + \int c_1(1) \delta \rho_0(1) d1 \tag{34}$$

where we used the fact that $c_1(1) = \rho_1(1)/\rho_0(1)$. Integration by part for the second integral of Eq. (34) gives

$$\delta \ln \Xi = \delta \int \rho_0(1) d1 - \delta \int \rho(1) c_0(1) d1 \\ + \int c_0(1) \delta \rho(1) d1 + \int c_1(1) \delta \rho_0(1) d1 \tag{35}$$

The last two integrals in Eq. (35) are identified as a variation of $c^{(0)}$

$$\int c_0(1) \delta \rho(1) d1 + \int c_1(1) \delta \rho_0(1) d1 = \int \frac{\partial c^{(0)}}{\partial \rho(1)} \delta \rho(1) d1 \\ + \int \frac{\partial c^{(0)}}{\partial \rho_0(1)} \delta \rho_0(1) d1 = \delta c^{(0)} \tag{36}$$

Substitution of Eq. (36) into Eq. (35) gives

$$\delta \ln \Xi = \delta [\int \rho_0(1) d1 - \int \rho(1) c_0(1) d1 + c^{(0)}] \tag{37}$$

Integrating over variations, we have

$$\ln \Xi = \beta p V = \int \rho_0(1) d1 - \int \rho(1) c_0(1) d1 + c^{(0)} \tag{38}$$

with an additive function independent of density. This additive function must be zero so as to satisfy the ideal-gas law in the limit of zero density. To derive an expression for the Helmholtz energy, consider homogeneous fluids for which the Helmholtz energy is written as

$$\beta A = N \beta \mu - \beta p V = N \ln(\lambda^3 z) - \ln \Xi \tag{39}$$

General expression for inhomogeneous fluids should be in the form,

$$\beta A = \int \rho(1) \ln[\lambda^3 z(1)] d1 - \ln \Xi \tag{40}$$

Substituting Eqs. (38) and (23) into (40) gives an expression for the Helmholtz energy of associating fluids as

$$\beta A = \int \rho(1) \ln[\lambda^3 \rho_0(1)] d1 - \int \rho_0(1) d1 - c^{(0)} \tag{41}$$

For a given monomer density $\rho(1)$, the nonbonded monomer density $\rho_0(1)$ can be determined from Eq. (27), and this requires evaluating the graphs of $c_1(1)$ in Eq. (29). Provided that only dimerization is allowed, Wertheim [2] found an exact self-consistent expression which relates $c_1(1)$ to the partial pair correlation function $g_{00}(12)$,

$$c_1(1) = \int g_{00}(12) f_A(12) \rho_0(2) d2 \tag{42}$$

where

$$\tag{43}$$

The graphs of $g_{00}(12)$ consist of irreducible graphs, free of connect-

ing circles, with two white 1-circles directly connected by e_R-bond and not receiving F-bonds. Interestingly, $g_{00}(12)$ is rather a mathematical quantity which is not measurable from computer simulations or experiments.

THE FIRST-ORDER APPROXIMATION

As given by Eqs. (41) and (42), the Helmholtz energy and the self-consistent relation to determine the nonbonded monomer density, are used as a theoretical base for developing approximate theories such as TPT (SAFT) theories. The difference in the Helmholtz energy between an associating fluid of interest and the corresponding reference fluid without association is given by subtracting Eqs. (41) and (12),

$$\beta(A - A_R) = \int \left[\rho(1) \ln \frac{\rho_0(1)}{\rho(1)} - \rho_0(1) + \rho(1) \right] d1 - c^{(0)} + c_R^{(0)} \tag{44}$$

where the subscript R denotes the reference fluid. In TPT1 (SAFT) theories, the difference in $c^{(0)}$ is approximated in first order by integrating the pair distribution function of the reference fluid $g_R(12)$ [2],

$$c^{(0)} - c_R^{(0)} = \frac{1}{2} \int \rho_0(1) g_R(12) f_A(12) \rho_0(2) d1 d2 + \cdots \tag{45}$$

where

$$\tag{46}$$

In graphical representation, the approximation of Eq. (45) corresponds to retaining graphs with a single F-bond, given as

$$\tag{47}$$

The factor 1/2 in Eq. (45) accounts for the symmetry of graphs in Eq. (47). Also, by the first-order approximation it is assumed that the effect of association on the liquid structure is neglected. In a similar way, $c_1(1)$ is approximated from the integration of $g_R(12)$ by retaining graphs with a single F-bond as

$$c_1(1) = \int g_R(12) f_A(12) \rho_0(2) d2 + \cdots$$

$$\tag{48}$$

By comparing Eq. (48) of TPT1 with the exact relation of Eq. (42), $g_{00}(12)$ of associating fluid is approximated by $g_R(12)$ of non-associating reference fluid. The superior accuracy of TPT1 approximation has been confirmed for hard diatomic fluids [22].

Since $c_1(1) = \rho_1(1)/\rho_0(1)$, Eq. (48) determines the multi-densities in a self-consistent manner that

$$\rho(1) = \rho_0(1) + \rho_0(1) \int g_R(12) f_A(12) \rho_0(2) d2 \tag{49}$$

By comparing Eqs. (45) and (48) or inspecting graphs in Eqs. (47) and (48), we have

$$c^{(0)} - c_R^{(0)} = \frac{1}{2} \int \rho_0(1) c_1(1) d1 = \frac{1}{2} \int [\rho(1) - \rho_0(1)] d1 \tag{50}$$

The last equality comes from the definition of $c_i(1)$. Substitution of Eq. (50) into Eq. (44) gives

$$\beta(A - A_R) = \int \rho(1) \left[\ln \frac{\rho_0(1)}{\rho(1)} - \frac{1}{2} \frac{\rho_0(1)}{\rho(1)} + \frac{1}{2} \right] d1 \tag{51}$$

For homogeneous fluids, all densities become constant, and integration over the positions and orientations of a molecule gives

$$\frac{\beta(A - A_R)}{N} = \ln X - \frac{X}{2} + \frac{1}{2} \tag{52}$$

where $X = \rho_0 / \rho$, the fraction of nonbonded monomers. The value of X is determined from Eq. (49), which is called the law of mass action. Eq. (49) is rewritten for homogeneous fluids as

$$X + \rho \Delta X^2 = 1 \tag{53}$$

$$\Delta = \Omega^{-2} \int\int g_R(12) f_A(12) d\omega_1 d2 \tag{54}$$

The integration in Eq. (54) is over all orientations of the first molecule and over all positions and orientations of the second molecule. For reference fluids with spherical symmetry, Eq. (54) becomes

$$\Delta = 4\pi \int_0^\infty g_R(r_{12}) \overline{f_A}(r_{12}) r_{12}^2 dr_{12} \tag{55}$$

where the integration is over all relative separations between two molecules r_{12}, and $\overline{f_A}$ represents orientation-averaged association interactions given by

$$\overline{f_A}(r_{12}) = \Omega^{-2} \int\int f_A(12) d\omega_1 d\omega_2 \tag{56}$$

where the integration denotes unweighted orientation average over all orientations of the two monomer molecules.

Wertheim's associating fluid theory can also be used to estimate the Helmholtz energy for the formation of permanent bond of fixed bond length. It is the so-called sticky limit in which the association interaction becomes infinitesimally localized at the bond length while its association strength becomes infinite. In the sticky limit, the orientation-averaged interaction is represented by the Dirac δ-function,

$$\overline{f_A}(r_{12}) = f l \delta(r_{12} - l) \tag{57}$$

where f is parameter for the strength of association and l is the bond length. Substituting Eq. (57) into Eq. (55) gives

$$\Delta = 4\pi l^3 f g_R(l) \tag{58}$$

As the association strength f tends to infinity, Δ becomes infinite and the fraction of nonbonded monomers X becomes zero. In this complete association limit, the mass action law, Eq. (53), reduces to

$$\rho \Delta X^2 = 1 \tag{60}$$

Equivalently,

$$\ln X = -\frac{1}{2} \ln \rho \Delta = -\frac{1}{2} \ln [4\pi \rho l^3 f g_R(l)] \tag{61}$$

The difference in the Helmholtz energy, given by Eq. (52), between the dimer fluid obtained in the complete association limit and the reference fluid becomes

$$\frac{\beta(A - A_R)}{N} = \ln X = -\frac{1}{2} \ln [4\pi \rho l^3 f g_R(l)] \tag{62}$$

The corresponding expression for ideal gases at the same density and temperature, for which $g_R(r_{12})$ becomes unity, is given by

$$\frac{\beta(A^{ig} - A_R^{ig})}{N} = -\frac{1}{2} \ln (4\pi \rho l^3 f) \tag{63}$$

Subtracting Eq. (63) from Eq. (62), we have an expression for the residual Helmholtz energies

$$\frac{\beta(A^r - A_R^r)}{N} = -\frac{1}{2} \ln g_R(l) \tag{64}$$

where the superscript 'r' stands for the residual properties. The amount of the Helmholtz energy that is necessary for the formation of a bond can be written as

$$\frac{A^r - A_R^r}{N_d} = -kT \ln g_R(l) \tag{65}$$

Here, $N_d = N/2$, is the number of dimer molecules formed in the complete association limit, equal to the number of bonds in the dimer fluid. The same expression was obtained by regarding the difference in the Helmholtz energy as a reversible work required to bring two arbitrarily separated monomers to the bond length. The reversible work turns out to be equal to the potential of mean force at the bond length [44].

CONCLUSIONS

We explained in great detail the graphical analysis of Wertheim's multi-density formulation of associating fluids with a single attraction site. The physical notions of multi-densities based on the bonding state of labeled circles of graphs are crucial in determining the fraction of nonbonded monomers. The steric incompatibility resulting from the localized nature of association significantly simplifies topological reductions. It is shown that the expressions for the pressure and the Helmholtz energy are easily derived by using functional derivatives. Also, the steric incompatibility, which allows dimerizing association only, gives the exact relation by which the multi-densities are determined self-consistently. The origin and approximations invoked in the first-order TPT and SAFT are clearly illustrated in terms of the graphs and the correlation functions.

ACKNOWLEDGEMENT

NOMENCLATURE

A : Helmholtz energy
c : irreducible graph sum
e : Boltzmann factor
F : associating bond
f : Mayer f-function
g : pair correlation function
k : Boltzmann constant
l : bond length

N : number of molecules
p : pressure
U : potential energy
u : interatomic potential energy
V : volume
s : order of association
T : temperature
X : the fraction of nonbonded monomers
Z : configurational integral
z : fugacity

Greek Letters

β : the inverse of kT
Δ : association integral
λ : thermal wavelength
μ : chemical potential
ρ : number density
Ξ : grand partition function
Ω : solid angle
ω : orientation

Superscripts

(0) : zero-th hierarchy
r : residual property

Subscripts

0 : nonbonded
1 : bonded
A : association
d : dimer
N : the number of molecules
R : reference

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