Thermodynamic Properties of Homogeneous Associating Fluids

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Abstarct-- The development of analytical expression for strongly homogeneous associating homogeneous fluids has proven to be difficult problems that have recently a great deal of attention. An exact statistical- mechanical treatment of homogeneous chain molecules is difficult owing to the large number of internal degree of freedom. A number of studies have been directed at the study of the relatively hard-sphere homogeneous associating chain molecules [1-5].

The equation of state for the hard –sphere homogeneous chain fluids have been obtain by Hall and co-workers [6]. One approach is to introduce the possibility of molecular association into commonly used integral equation theories. Thus Cumming and Steel [7] have solved the Percus-Yevick (PY) approximation for the chemical association by using a spherical symmetric bonding potential. The highly directional hydrogen bonding is introduced in fluids by the geometry of the interaction at an early stage of the theory. Wertheim's theory [8-11], however, is based on a resumed cluster expansion, which is made in terms of two densities, the total number of density ρ, and the monomer density ρ_0. Wertheim was able to simply the complex graphical expansions by assuming that the repulsive core of each molecule restricts the orientation ally dependent attractive site. The final expression can be written in the form of thermodynamic theory, which is relatively simple to use. In terms of theoretical developments in the field of perturbation theory and equation of state of seminal papers developing a theory for homogeneous associating fluids. It has since been shown that when the associating strength becomes strong, homogeneous chains can be formed from a fluid of associating monomers. In the simplest implementation of the theory, known as first-order thermodynamic perturbation theory.

After viewing the complexity of all these theories, one is struck by the simplicity and elegance of Wertheim's theory and it is this approach that has been extended to determine the thermodynamic properties of hard-sphere homogeneous associating chain molecules.

I. Basic Theory

1(a) Potential Model

We consider a model, short range, highly anisotropic attractions between the homogeneous associating molecules. The pair potential is given by

$$u(r_{12}, \omega_1 \omega_2) = u_R((r_{12}) + \sum_A \sum_B u(r_{AB}, \omega_1 \omega_2)$$

$$(1.1)$$

where $\quad r_{AB} = r_2 + d_B(\omega_2) - r_1 - d_A(\omega_1) \qquad (1.2)$

is a vector connecting site A on molecules 1 with site B on molecules 2. Here r_{12} is the center to center distance between molecules 1 and 2, ω_1 and ω_2 represents the orientations of the two molecules, and the double sum applies over all associations sites. The reference potential u_R represents hard sphere repulsion is given by

$$u_R(r_{12}) \quad = \infty, \quad \text{if } r < \sigma$$

$$= 0, \quad \text{if } r > \sigma, \qquad (1.3)$$

The site-site interactions u_{AB} are assumed to be purely attractive. Here σ is the hard- sphere diameter, d_B is the distance of attractive site from the sphere's center c, r_C is the cutoff distance of the attractive potential, and r_{AB} is the distance between the centers of the two sites. The square well site-site interaction is given by

$$u_{AB} = -\varepsilon_{AB} \quad \text{if } r_{AB} \leq r_C$$

$$= 0 \quad \text{if } r_{AB} \geq r_{C.} \qquad (1.4)$$

Hence, bonding occurs between two sites when they are within the cutoff distance r_C of each other.

1.2(b) Theory

The role of the integral-equation formulation is to permit calculation of the pair distribution function. The starting point for the integral equation treatment is the Ornstein-Zernike (OZ) relation, which express the total correlation function between particles 1 and 2 as the sum of a short range direct correlation and a long range indirect effect propagated through the surrounding particles. The total correlation between molecules 1 and 2 can be separated into two parts (a) a direct effect of 1 on 2, this is short range characterized by c, and (b) an indirect effect in which 1 influences other molecules 3,4, etc. which in turn effect 2.

The indirect effect is the sum of all contributions from other molecules averaged over their configurations. The total correlation function

$$h = g - 1.$$

and the direct correlation function c

$$h = c + \rho ch. \qquad (1.5)$$

For atomic fluids OZ equation

$$h(r_{12}) = c(r_{12}) + \rho \int dr_3 \, c(r_{13}) \, h(r_{32}) \qquad (1.6)$$

Choosing the origin at molecules 1 the Eq. (4.1) reduces to

$$h(r) = c(r) + \rho \int dr' \, c(r') \, h(r - r') \qquad (1.7)$$

or in **K** - space

$$h(k) = c(k) + \rho \, c(k) \, h(k) \qquad (1.8)$$

or $h(k) = [c(k)/(1 - \rho c(k))]$

or $(1 + \rho h(k))(1 - \rho c(k)) = 1.$ $\qquad (1.9)$

For hard sphere $g(r) = 0$ for $r < \sigma$, where σ is the hard-sphere diameter, since there is zero probability of overlap for two hard spheres. Thus

$$h(r) = -1, \qquad r < \sigma,$$

$$C(r) = 0, \qquad r > \sigma. \qquad (1.10)$$

The simplest method of solution is based on the Wiener-Hopf factorization technique. The result for c(r) is a cubic polynomial

$c(r) = c_0 + c_1(r/\sigma) + c_3(r/\sigma)^3, \quad r < \sigma$

$\qquad = 0, \quad r < \sigma, \qquad (1.11)$

where the dimensionless constant $c_i = c_i(n)$ is given by

$$c_o = -(1 + 2\eta)^2 / (1 - \eta)^4$$

$$c_1 = 6\eta (1 + \eta/2)^2 / (1 - \eta)^4 \qquad (1.12)$$

$$c_3 = (1/2) \eta \, c_0,$$

where $\eta = (\pi/6) \rho\sigma^3$ $\qquad (1.13)$

is the packing fraction which is proportional to reduced density $\rho\sigma^3$.

The equation of state can be obtain in two ways. The first method is based on the compressibility relations

$$\rho kT\chi = 1 + \rho \int dr \, h(r) \qquad (1.14)$$

$$= [1 - \rho \int dr \, c(r)]^{-1}, \qquad (1.15)$$

Where $\chi = \rho^{-1}(\partial \rho / \partial p)$ is the isothermal compressibility and

$$\rho kT\chi = kT(\partial \rho / \partial p)$$

$$= (1 - \eta)^4 / (1 + 2\eta)^2 \qquad (1.16)$$

Integration of Eq. (4.16) with respect to density, with boundary condition $(p/\rho kT)_{\rho \to 0} \to 1$, gives the compressibility equation of state.

$$p/\rho kT = (1 + \eta + \eta^2) / (1 - \eta)^3 \qquad (\chi \text{ - route}) \qquad (1.17)$$

For the second route to the equation of state one uses the Virial relation

$$p/\rho kT = 1 - (1/6) \beta\rho \int dr \, r \, g(r) \, u'(r) \qquad (1.18)$$

which for hard-spheres reduces to

$$p/\rho kT = 1 + (2/3) \pi \rho\sigma^3 g(\sigma^+)$$

Where $g(\sigma^+)$ denotes the limit of $g(r)$ as r approaches σ from above. Using the fact that y(r) is a continuous function at $r = \sigma$, and is given in PY theory

$$Y(r) = g(r), \quad r > \sigma,$$

$$= -c(r), \quad r < \sigma. \qquad (1.19)$$

We see that $g(\sigma+) = -c(\sigma-)$. Using this result together and gives the equation of state

$$p/\rho kT = (1 + 2\eta + 3\eta^2) / (1 - \eta)^2 \qquad (\text{p -route}) \qquad (1.20)$$

If we average the PY equation of state, $P = [2/3 \, p(\chi$ - route) + $1/3 \, p$-(p- route), we obtain the phenomenological Carnahan – Starling (CS) equation of state.

$$P/\rho kT = (1 + \eta + \eta^2 - \eta^3) / (1 - \eta)^3, \quad (CS) \qquad (1..21)$$

which is seen to agree well with the simulation data for the stable fluid density range.
The excess hard- sphere free energy

$$A_{HS}^{ex} = (4\eta - 3\eta^2)/(1 - \eta)^2 \qquad (1..22)$$

The equation of state for a pure fluid of homonuclear hard-sphere chains is given by

$$Z_{HC} = Z_{HS} + Z_{chains} \qquad (1.23)$$

The pure hard-sphere compressibility factor Z_{HS} is the Eq. (4.21) and Z_{chains} made up of m hard-sphere is obtain as

$$Z_{chain} = - [(m-1)/m\{ 1 + \rho(\partial \ln g_{HS}(\sigma)/\partial \rho)\}] \qquad (1.24)$$

The hard-chain compressibility factor becomes[2]

$$Z_{HC} = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 - [(m-1)/m\{ 1 + \rho(\partial \ln g_{HS}(\sigma)/\partial \rho)\}]$$

$$= [(1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3] - [\{(m-1)/m\}((1+\eta+\eta2/2)/(1-\eta)(1-\eta/2))] \qquad (1.25)$$

Where m is the number of spheres in the chain. The excess free energy due to chain is

$$A_{chain}/NkT = (m-1)/m \int_0^\eta (\beta P_{chain}/\rho - 1)d\acute{\eta} /\acute{\eta} \qquad (1.26)$$

$$= - [(m-1)/m] \ln ((1 - \eta/2)/(1 - \eta)^3)] \qquad (1.27)$$

1.2(c) Perturbation

Wertheim derived a thermodynamic perturbation theory using the hard-core repulsive potential as the reference system and M directional attractive sites as perturbation. The difference in free energy between the associating fluids and the reference fluid, A_{bond}, is given by

$$A_{bond}/NkT = \sum_A (\ln X_A - X_A/2) + M/2, \qquad .(1.28)$$

where X_A is the fraction of molecules not bonded at site A, N is the number of molecules, T is the temperature and k is the Boltzmann constant. The value of X_A are obtained from the mass-action equation.

$$X_A = 1/(1 + \sum_B \rho X_B \Delta_{AB}), \qquad (1.29)$$

where ρ is the total number density, and Δ_{AB} is defined by

$$\Delta_{AB} = \int g_R(12)f_{AB}(12)d(12). \qquad (1.30)$$

Here, $g_R(12)$ is the reference fluid pair correlation function, the Mayer f- function is

$$f_{AB}(12) = \exp(- u_{AB}(r_{AB})/kT) - 1 \qquad (1.31)$$

and d(12) denotes an unweighted average over all orientations and an integration over all separation of molecules 1 and 2.

In the case of a hard-sphere reference fluids, expression (5.30) for Δ_{AB} can also written as an integral over r_{12}, the distance between the molecular centers of 1 and 2, such that

$$\Delta_{AB} = 4 \, \pi \int g_{HS}(r_{12}) \; <f_{AB}(12)>_{\omega_1\omega_2} \; r_{12}^2 \, dr_{12} \qquad (1.32)$$

Here, $<f_{AB}(12)>_{\omega_1\omega_2}$ represents an angle average of the site-site Mayer f-function over all orientations of molecules 1 and 2.

The evaluation of Δ_{AB} for the hard-sphere reference system, we assume that $r_{12}^2 \, g_{HS}(r_{12})$ is constant and equal to the value at contact $\sigma^2 g_{HS}(\sigma)$ over the short range of the site-site potential. After introducing this approximation the expression for Δ_{AB} becomes

$$\Delta_{AB} = 4 \, \pi\sigma^2 g_{HS}(\sigma) \int \; <f_{AB}(12)>_{\omega_1\omega_2} \, dr_{12} \qquad (1.33)$$

and in terms of bonding volume K_{AB}, we have

$$\Delta_{AB} = 4 \, \pi \, g_{HS}(\sigma) \, K_{AB}F_{AB} \qquad (1.34)$$

The above analytical expression is expected to be a good representation of Δ_{AB} at moderate densities.

1. 2(d) Associating fluids

The Helmholtz free energy A for a hard-sphere homogeneous associating chain fluids and compressibility can be written as a sum of separate contribution

$$A = A_{HC} + A_{MF} + A_{bond,} \qquad (1.35)$$

$$Z = Z_{HC} + Z_{MF} + Z_{bond} \qquad (1s$$

Where A_{HC} is the free energy due to the excess hard-sphere and contribution due to chain given by

$$\beta A_{HC}/N = \beta A_{HS}/N + \beta A_{chain}/N$$
$$= [(4\eta - 3\eta^2)/(1-\eta^2)] - [(m-1)/m] \, \ln((1-\eta/2)/(1-\eta)^3)]$$

and compressibility factor

$$Z_{HC} = Z_{HS} + Z_{chain} \quad , \qquad (1.37)$$

is given by Eq.(4.25). The mean –field contribution to the free energy and compressibility factor have the form

$$A_{MF}/NkT = -\varepsilon_{MF}\eta/kT$$

$$Z_{MF} = -\varepsilon_{MF}\eta/kT \qquad (1.38)$$

The change in the free energy and compressibility factor due to only one attractive site

$$A_{bond}/NkT = (\ln X - X/2) + 1/2,$$

$$Z_{bond} = \eta(\partial X/\partial \eta)_{T,N}(1/X-1/2) \qquad (1..39)$$

The thermodynamic excess chemical potential μ^{ex}/kT contribution is a sum of free energy and equation of state, hence expression in the form of packing fraction

$$\mu^{ex}/kT = [\, \ln(\eta) + \{(8\eta - 9\eta^2 + 3\eta^3)/(1-\eta)^3\} - \{2\varepsilon_{MF}\eta/kT\} + \{((\ln X - X/2) + 1/2)$$

$$+ \eta(\partial X/\partial \eta)_{T,N}(1/X-1/2)\}] \qquad (1..40)$$

II. RESULTS AND DISCUSSION

It is important to determine the adequacy of Eq. (1.25) and Eq.(1.26) in predicting the thermodynamic properties of homonuclear chains of hard sphere for a chain of different fixed lengths. A comparison of compressibility factor for different spheres of chain lengths with the reduced density $\rho^*(=\rho\sigma^3)$ and compared with computer simulation results of Dickman and Hall [6], excellent agreement is found for low number of spheres of chains as shown in Fig.-1.1.

The value of compressibility factor increases with increase of reduced density and for large number of spheres in chain solidification started and for low number of spheres the calculated value of compressibility factor agree with computer simulation results.

The excess free energy is the sum of the two terms: contribution of hard spheres and that of chains. Contribution of hard sphere is positive while that of chain is negative. These are shown in fig.1.2 as a function of η for different values of m..
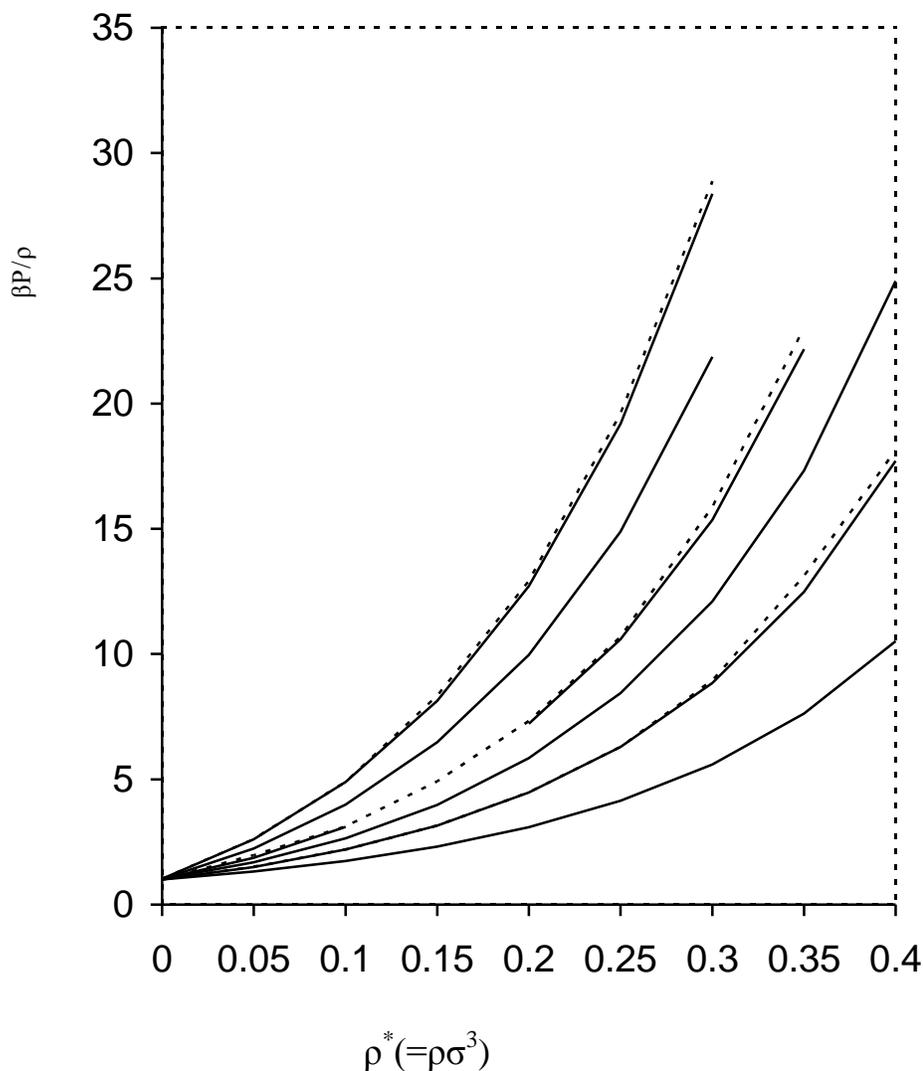

Fig1..1. The compressibility factor (P/ρ kT) for chains of different fixed length as a function of reduced density $\rho^*(=\rho\sigma^3)$.The dot points represent the values for Dickman and Hall and solid curves represent present result.
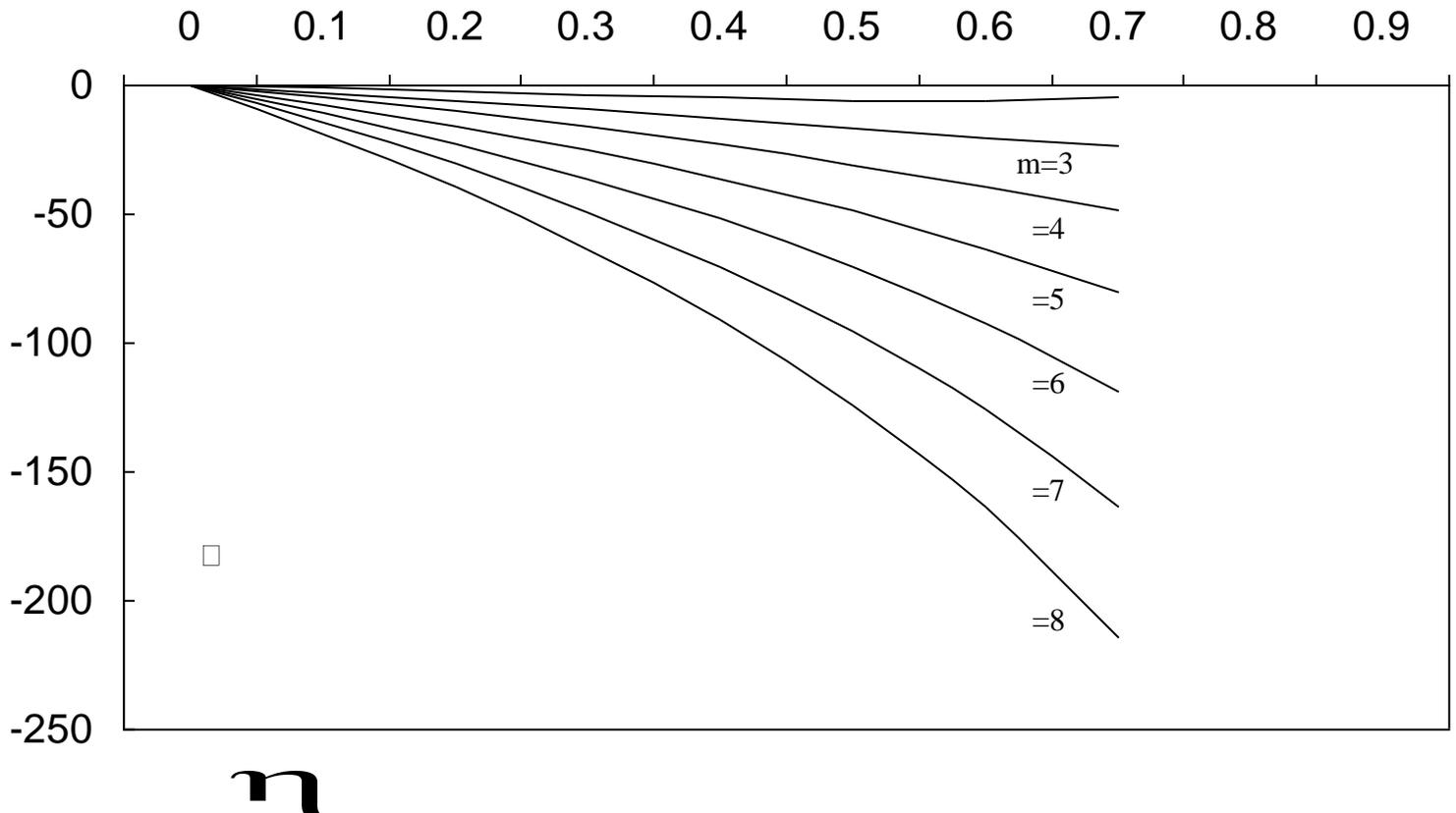
Fig.1.2 The Free energy contribution $\beta A_{chaind}/N$ with packing fraction η for chain of m hard-sphere.

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