

Thermodynamical Properties of Inhomogeneous Associating Fluids Using Density Functions

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Abstract

An Analytical expression for molecular association on the phase coexistence properties of fluid with one or two direction attractive centre is discussed. The basic theory of Rosenfeld for the hard sphere is extended to inhomogeneous fluids on the basis of density function. The density functional approach in the grand canonical ensemble utilized to determine thermo dynamical properties of the inhomogeneous fluids. The theoretical prediction is in good quantitative agreement with the simulation result which is available

INTRODUCTION

The theoretical methods for predicting equilibrium properties of homogeneous non-polar fluids are now well documented; much less understood are the properties of confined associating fluids. The density functional theory is routinely used to investigate the properties of simple inhomogeneous system. For anisotropic association, molecular simulations are often computationally intensive and analytical theories give faithful representation of the local fluid structure¹. The interplay between chemical association and in-homogeneity makes the phase behaviour of confined associating fluids interesting but difficult to predict.

For bulk associating fluids, Wertheim's thermodynamic perturbation theory provides a relative simple yet accurate description of thermodynamic properties

^{6,8}. Most current applications of Wertheim's theory are limited to the first order perturbation that takes into account only the structure corresponding hard sphere reference system.

A quantity of central interest is the density functional theory has proven to be a theoretical approach in the study of inhomogeneous system^{the} grand free energy Ω is written as a functional of the number density distribution $\rho(\mathbf{r})$.

2. BASIC THEORY

2 (a) Potential Model

We consider a binary mixture of neutral and

associating hard spheres confined between two parallel hard walls. The pair-wise two body potential is given by

$$u(\mathbf{r}_{12}, \omega_1, \omega_2) = u_R(\mathbf{r}_{12}) + \sum_A \sum_B u(\mathbf{r}_{AB}, \omega_1, \omega_2), \quad (1)$$

where \mathbf{r}_{12} is the center to center distance between sphere 1 and 2, ω_1 and ω_2 represents the orientations of the two spheres, and the double sum applies over all associations sites. The reference potential u_R represents hard sphere repulsion is given by

$$u_R(r_{12}) = \begin{cases} \infty, & r_{12} < (\sigma_1 + \sigma_2) / 2 \\ 0, & r_{12} > (\sigma_1 + \sigma_2) / 2, \end{cases} \quad (2)$$

where σ_1 is the hard sphere diameter for component i . The association potential u_{AB} represents the potential between a bonding site A on a spherical particle and a bonding site B from a different sphere with the condition when the attraction sites A and B on molecules 1, 2 prevents molecules 3 from coming close enough to form bond with either site A or B. The association potential is

$$u_{AB}(\mathbf{r}_{12}, \omega_1, \omega_2) = \begin{cases} -\varepsilon, & r_{12} < r_c \\ 0, & \text{otherwise} \end{cases} \quad (3)$$

2 (b) Theory

Let us consider a model in which molecules are assumed to have one bonding site that allows for the formation of dimmers in the system, short ranged, highly anisotropic attractions are obvious choices as models for chemical bonding in the frame work of density functional theory (DFT). The grand free energy can be written as a function of μ_i .

$$\Omega(\rho_i(\mathbf{r})) = F(\rho_i(\mathbf{r})) + \sum_{i=1}^3 \int d\mathbf{r} \rho_i(\mathbf{r}) [\varphi_i(\mathbf{r}) - \mu_i] \quad (4)$$

In an open system, the minimization of this grand potential at constant chemical potential μ_i , and absolute temperature T, determines the properties of the equilibrium states satisfies

$$\partial\Omega/\partial\rho_i(\mathbf{r}) = 0, \quad (5)$$

Hence Eqs.(4) leads to

$$\begin{aligned} \mu_i = & [(\partial f_{hs} \rho_i(\mathbf{r})) / (\partial \rho_i(\mathbf{r}))] + \\ & [(\partial f_{bond} \rho_i(\mathbf{r})) / (\partial \rho_i(\mathbf{r}))] \\ & + \sum_{i=1}^3 \int d\mathbf{r} \rho_i(\mathbf{r}) \varphi_{asso}(|\mathbf{r}-\mathbf{r}'|), \end{aligned} \quad (6)$$

where $f_{hs}(\rho(\mathbf{r}))$ denotes the local free energy density of a uniform hard-sphere density of a uniform hard-sphere fluid, $f_{bond}(\rho_i(\mathbf{r}))$ corresponds to the local change in the free energy, $\varphi_{asso}(|\mathbf{r}-\mathbf{r}'|)$ is the attractive part of the isotropic association potential between particles and $i=1,2,3$. The Helmholtz free energy is expressed as contribution from an ideal gas terms and an excess term due to intermolecular interactions.

$$F(\rho(\mathbf{r})) = F_{id}\rho_i(\mathbf{r}) + F_{ex}\rho_i(\mathbf{r}). \quad (7)$$

The ideal gas contribution is given by the exact expression

$$F_{id} \rho_i(\mathbf{r}) = kT \sum_{i=1}^3 \int d\rho_i(\mathbf{r}) \{ \ln(\rho_i(\mathbf{r}) \lambda_i^3) - 1 \}, \quad (8)$$

where $\lambda_i = (h/(2\pi mkT))^{1/2}$ represents the thermal wavelength. Here in a typical perturbation approach, the Helmholtz free energy for a system of inhomogeneous associating hard-sphere consists of hard sphere reference system and perturbation.

$$F_{ex}(\rho_i(\mathbf{r})) = kT \int d\mathbf{r} [\varphi_{hs}(\bar{\rho}_i(\mathbf{r})) + \varphi_{asso}\{\rho_i(\mathbf{r})\}]. \quad (9)$$

Once we have an expression for the intrinsic Helmholtz free energy, solution to Eq.(5) gives the equilibrium density profiles and subsequently, thermodynamics properties. Equating the chemical potential of each component to that of the bulk fluid mixture of density (ρ_i^0) with which it is in equilibrium, the density distribution for the i^{th} component can be expressed as

$$\rho_i(\mathbf{r}) = \rho_i^0 \exp[-\beta\varphi_i(\mathbf{r}) + c_i^{(1)}(\mathbf{r}; [\rho_i(\mathbf{r}) - c_i^{(1)}(\{\rho_i^0\})]) \quad (10)$$

where $c_i^{(1)}(\mathbf{r}; \{\rho_i(\mathbf{r})\})$ is the one particle DCF of the i^{th} component, is defined as the functional derivative of the excess free energy functional F_{ex} . i.e

$$c_i^{(1)}(\mathbf{r}; \{\rho_i(\mathbf{r})\}) = -\beta [\partial F_{ex}(\rho_i(\mathbf{r})) / (\partial \rho_i(\mathbf{r}))]. \quad (11)$$

The density Eq.(10) for the non-uniform fluid, on using the least particle method due to Percus, provides a route for the calculation of the RDF of the uniform fluid given by

$$g_{ij}(\mathbf{r}) = \exp[-\beta u_{ij}(\mathbf{r}) + c_i^{(1)}(\mathbf{r}; [\rho_i^0 g_{ij}(\mathbf{r})]) - c_i^{(1)}(\{\rho_i^0\})] \quad (12)$$

Although Eqs.(10) and Eqs.(12) are formally exact for their practical implementation. The fundamental-measure theory of Resenfeld provides an expression for the excess intrinsic Helmholtz free energy density is represented as a function of weighted densities $\bar{\rho}_i(\mathbf{r})$

$$\bar{\rho}_i(\mathbf{r}) = \sum_i \bar{\rho}_{\alpha,i}(\mathbf{r}) = \sum_j \int \rho_j(\mathbf{r}') \omega_{ij}(\mathbf{r}-\mathbf{r}') d\mathbf{r}', \quad (13)$$

weights functions $\omega_{ij}(\mathbf{r})$, characterize the geometry of a spherical particle.

2 (c) Thermodynamic perturbation theory

Thermodynamic perturbation theory for mixture using the hard-core repulsive potential as the reference system and the second from perturbation as described in Eq.(9), therefore, the Helmholtz free energy density due to associations is given by

$$\varphi_{asso} = \sum_i M_{ij} \rho_j (\ln X_A - (X_B/2) + (1/2)), \quad (14)$$

where M_i is the number of association sites per molecule of species i , and X_A is the fraction of molecules of component i not bonded at site A. In Eq. (6.14) X_A is calculated from

$$X_A = 1 / (1 + \sum_i \rho_i X_A \Delta_{ij}), \quad (15)$$

where

$$\Delta_{ij} = 4\pi g_{ij}^{hs}(\sigma_{ij}) \cdot f_{AB} K_{AB}. \quad (16)$$

Here K_{AB} is a constant reflecting the volume available for bonding of the two sites on molecules 1 and 2, $f_{AB} = [\exp(\epsilon/kT) - 1]$ represents the Mayer

function and $g_{ij}^{hs}(\sigma_{ij})$ is contact value of the hard-sphere pair correlation function for mixture.

$$g_{ij}^{hs}(\sigma_{ij}) = (1/(1-\xi_3) + (3\sigma_i\sigma_j/(\sigma_i+\sigma_j)\xi_2/(1-\xi_3)^2) + 2(\sigma_i\sigma_j/(\sigma_i+\sigma_j)^2)\xi_2^2/(1-\xi_3)), \quad (17)$$

$$\xi_m = (\pi/6) \sum_{i=1}^2 \rho_i \sigma_i^m, \quad (18)$$

where

$$m = 1, 2, 3 \text{ and } \sigma_{ij} = (\sigma_1 + \sigma_2). \quad (19)$$

If $i = j$, for contact value of the pair distribution function of the hard core reference fluid is given by

$$g_{HS}(\sigma) = (1 - \eta/2)/(1 - \eta)^3. \quad (20)$$

Once we have an expression for the intrinsic Helmholtz free energy, minimization of the grand potential with respect to the density distributions Eq.(10) leads to the Euler Lagrange equation

$$\rho_i(r) = \Lambda_i^{-3} \exp[c_i^1[\mathbf{r}; \rho_i(r)] + [\mu_i - \Phi_i(r)]/(kT)], \quad (21)$$

where $c_i^{(1)}[\mathbf{r}; \rho_i(\mathbf{r})]$ is the one particle direct correlation function, obtained from

$$c_i^{(1)}[\mathbf{r}; \rho_i(\mathbf{r})] = -(1/kT) \left\{ \partial F_{ex}(\rho_i(r))/\partial \rho_i(r) \right\} \\ = - \int d\mathbf{r}' \sum_A \partial [(\Phi_{hs} + \Phi_{asso})/\partial \rho_i(\mathbf{r})] \omega_{ij}(\mathbf{r} - \mathbf{r}'). \quad (22)$$

At equilibrium, the chemical potentials of all species remain constant. When the confined fluid is in equilibrium with a bulk phase. The chemical potential can be calculated from

$$\mu_i = kT \ln(\rho_i + \Lambda_i^{-3}) + \mu_i^{ex,HS} + \mu_i^{ex,assoc}. \quad (23)$$

The first term of the Eq.(23) comes from the ideal gas, second term is the hard sphere and last term due to association chemical potential is calculated from Wertheim's thermodynamic perturbation theory. The bulk hard-sphere mixture characterized by the diameter ratio $\alpha = \sigma_1/\sigma_2$ with $\sigma_2 > \sigma_1$ the concentration $x = \rho_2^0/\rho_0$ with $\rho_0 = \rho_1^0 + \rho_2^0$ and the bulk packing fraction η is expressed as

$$\eta = \frac{\pi}{6} [\rho_1^0 \sigma_1^3 + \rho_2^0 \sigma_2^3] \\ = \frac{\pi}{6} [x + (1-x)\alpha^3] \rho_0 \sigma_2^3. \quad (24)$$

The compressibility equation is given by

$$\beta P/\rho_0 = [(1 + \xi_3 + \xi_3^2)/(1 - \xi_3)^3] \\ - 3\eta_1 x \left(\frac{1}{\alpha} - 1 \right)^2 \left[\left\{ \left(1 + \frac{1}{\alpha} \right) + \sigma_2 \xi_2 \right\} / (1 - \xi_3)^3 \right], \quad (25)$$

where

$$\eta_1 = \frac{\pi}{6} \rho_1^0 \sigma_1^3 = [(\pi/6) \{x + (1-x)\alpha^3\}] \rho_0 \sigma_2^3. \quad (26)$$

Since $\alpha = (\sigma_1/\sigma_2)$, and $\sigma_2 > \sigma_1$, therefore $\sigma < 1$. The value of

$$x = (\rho_2^0/\rho_0) \text{ and } \eta_1 = [(\pi/6) \rho_1^0 \sigma_1^3], \quad (27)$$

RESULTS AND DISCUSSION :

In Fig.1 the calculated value of $\alpha (= \sigma_1/\sigma_2)$ plotted against $\Gamma (= \rho \sigma_2^3)$ at constant $\eta (= 0.1)$ and $x (= \rho_2^0/\rho)$ at 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6. The fig. shows the value of $x (= \rho_2^0/\rho)$ increases the corresponding value $\Gamma (= \rho \sigma_2^3)$ decreases and justify that the values approaches to where the ratio $x (= \rho_2^0/\rho)$ becomes 1.0.

In Fig.2 we have calculated the value of compressibility factor $\beta p/\rho_0$ with hard-sphere diameter ratio $\alpha = 0.5$ at constant mole fraction 0.25, 0.5, 0.75. The mole fraction ratio x increase the compressibility increases. The calculated results compared with available data of C. Barrio and J.R. Solana. The agreement is found good.

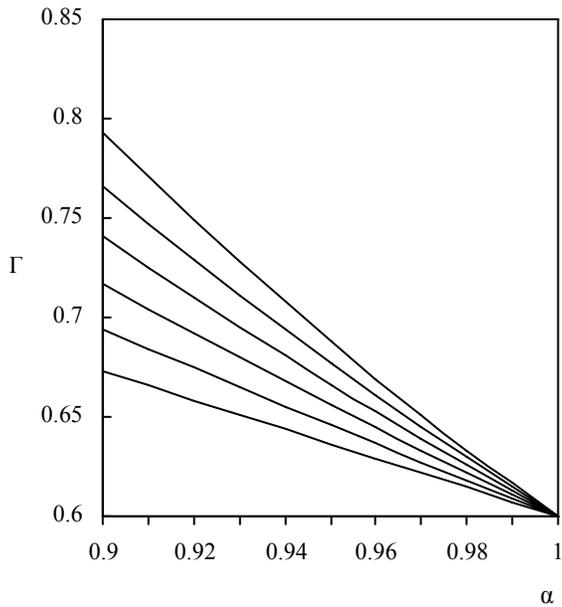


Fig.1 The value of Γ with respect to α at constant packing fraction and constant X

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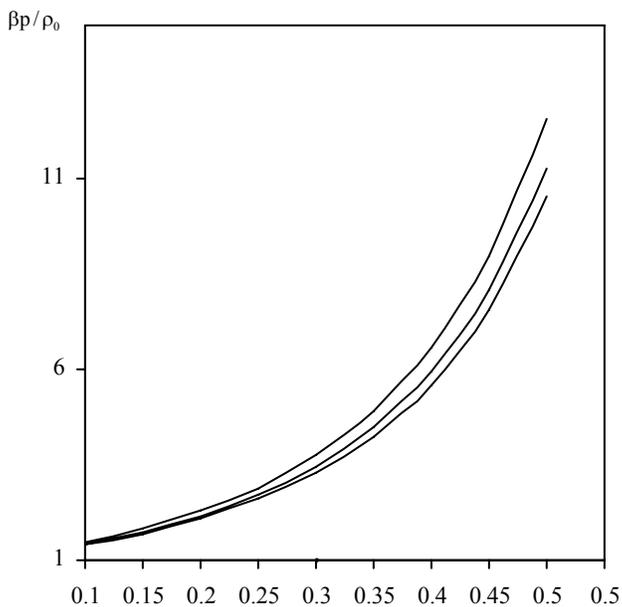


Fig.2 The compressibility factors for hard sphere mixture with diameter ratio constant value 0.5 with mole fraction 0.25, 0.5, 0.75.