

## **MIXTURE RADIAL DISTRIBUTION FUNCTIONS: ARE THEY ALL INDEPENDENT?**

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### **ABSTRACT**

New constraints of radial distribution functions in the canonical ensemble of multicomponent mixtures are derived. These constraints indicate that mixture radial distribution functions are not all independent from each other. One of the important applications of such constraints is to test the approximation theories of mixture distribution functions. A number of examples are reported for the application of the proposed constraints.

### **INTRODUCTION**

Modern theories of statistical mechanics of liquids and liquid mixtures have benefited a great deal from the concept of radial distribution function (RDF) (McQuarrie, 1975, Boublik, et al., 1980). The RDF theories have been quite successful in describing the behavior of simple pure liquids (McQuarrie, 1975, Boublik, et al., 1980). However, the RDF theories of mixtures have lacked sufficient progress due to complexity of such theories and the increasing number of radial distribution functions in a multicomponent mixture. The present report introduces a technique through which it is now possible to introduce constraints among the mixture RDFs. Such constraints will help to

either reduce the number of independent RDFs to be considered or test the extent of validity of different RDF theories of mixtures.

In a recent study (Hamad, et al., 1988) relations among fluctuation integrals of mixtures in the grand canonical ensemble were derived. In this work a number of other constraints on mixture RDFs in the canonical ensemble are derived. The resulting expressions are used to test the validity of different approximation theories of mixture RDFs.

### CANONICAL ENSEMBLE RELATIONS

Let us consider a mixture consisting of  $c$  components. This system has a fixed values of volume,  $V$ , number of molecules of each component,  $N_i$ , and temperature,  $T$ . This kind of system is called canonical ensemble. The molecules of each component interact by a potential energy function which depends on  $q$  parameters,  $s_{ii}^{(1)}, s_{ii}^{(2)}, \dots, s_{ii}^{(q)}$ . The thermodynamic properties of this system can be obtained from the partition function,  $Q$ , which in the classical limit takes the following form (McQuarrie,1975)

$$Q(T, V, N) = Q_{\text{int}} \prod_{i=1}^c (N_i! \lambda_i^{3N_i})^{-1} \int_V \dots \int_V e^{-\Phi/kT} dr_1 \dots dr_N, \quad (1)$$

where  $N$  is the set of number of molecules,  $N_1, N_2, \dots, N_c$ ,  $Q_{\text{int}}$  is partition function due to the internal motions of the molecules,  $\Phi$  is the total potential energy of the system,  $k$  is Boltzmann constant,  $r_i$

is the position vector of molecule  $i$ ,  $\prod$  denotes the product over  $i$  and  $\lambda_i$  is the thermal wavelength of component  $i$ ,

$$\lambda_i = h/(2\pi m_i kT), \quad (2)$$

where  $h$  is Planck's constant and  $m_i$  is the mass of molecule  $i$ . All the integrals in eq. (1) are carried over the system volume. The part of the partition function which contains these integrals is called the configurational

partition function,  $Q_c$ , defined by

$$Q_c(T, V, N) = \int \dots \int e^{-\Phi/kT} dr_1 \dots dr_N. \quad (3)$$

In order to get the constraints on the distribution functions, let us start by differentiating the configurational partition function with respect to the  $n$ -th intermolecular potential parameter of component  $i$

$$[\partial Q_c / \partial s_{ii}^{(n)}]_{V, T, s'} = - (kT)^{-1} \int \dots \int [\partial \Phi / \partial s_{ii}^{(n)}]_{s'} e^{-\Phi/kT} dr_1 \dots dr_N. \quad (4)$$

where  $s'$  stands for all potential parameters except  $s_{ii}^{(n)}$ . To express the above equation in terms of the pair distribution functions, one Assumes pair-wise additivity of the total intermolecular potential energy,

$$\Phi = \sum_{1 \leq h < l}^N \sum_{h < l}^N \phi_{hl} \quad (5)$$

where  $\phi_{hl}$  is the pair potential energy between particles  $h$  and  $l$ , and  $N$  is total number of particles in the system.

Upon Substitution of eq. (5) in eq. (4), all the like interaction terms drop out except for the pair  $ii$ , and one is left with  $N_i(N_i-1)/2$  similar terms of the like interactions, and  $N_i N_j$ , ( $j=1, \dots, c$ ) similar terms of the unlike interactions. Using the definition of the radial distribution function,

$$g_{ij}(r) = V^2(1-\delta_{ij}/N_j) \int \dots \int e^{-\Phi/kT} dr_3 \dots dr_N / Q_c, \quad (6)$$

in eq. (4) gives

$$[\partial \ln Q_c / \partial s_{ii}^{(n)}]_{\rho, T, s'} = -N\rho x_i / (kT) \sum_{k=1}^c x_k / (1+\delta_{ik}) \int_0^{\infty} \partial \phi_{ik} / \partial s_{ii}^{(n)} g_{ik}(r) dr \quad (7)$$

where  $g_{ij}(r)$  is the radial distribution function of molecules of species  $i$  and  $j$ , and  $\delta_{ij}$  is the Kronecker delta.

Equation (7) can be utilized to develop constraints among the mixture RDFs when  $\ln Q$  is an analytic function. Its mixed second derivatives are then equal

$$\partial^2 \ln Q / \partial s_{ii}^{(m)} \partial s_{jj}^{(n)} = \partial^2 \ln Q / \partial s_{jj}^{(n)} \partial s_{ii}^{(m)} \quad (8)$$

where  $i, j = 1, \dots, c$ ;  $m, n = 1, \dots, q$ ;  $i \neq j$  or  $m \neq n$ .

It should be pointed out that  $\ln Q$  is analytic when the derivatives  $\partial \phi_{ij} / \partial s_{kk}^{(n)}$  exist. By applying the above condition to eq. (7) one can derive the following expression

$$\begin{aligned} \sum_{k=1}^c x_j x_k / (1 + \delta_{jk}) \partial \left\{ \int \partial \phi_{jk} / \partial s_{jj}^{(n)} g_{jk}(r) dr \right\} / \partial s_{ii}^{(m)} & \quad i, j = 1, \dots, c \\ & \quad m, n = 1, \dots, q \\ & \quad i \neq j \text{ or } m \neq n \\ = \sum_{k=1}^c x_i x_k / (1 + \delta_{ik}) \partial \left\{ \int \partial \phi_{ik} / \partial s_{ii}^{(m)} g_{ik}(r) dr \right\} / \partial s_{jj}^{(n)} & \quad (9) \end{aligned}$$

These equations, which consist of  $cq(cq-1)/2$  relations, are the constraints which must be satisfied by mixture RDFs. Next These constraints will be used to test different theories of mixture RDFs.

### TEST OF THE CONFORMAL SOLUTION RDF APPROXIMATION

The conformal solution approximation relates the mixture radial distribution functions to a pure reference fluid distribution function as follows (Leland, et al., 1968)

$$g_{ij} = g_o(r/\sigma_{ij}, \rho \sigma_x^3, kT/\epsilon_x) \quad (10)$$

To find the conditions under which this approximation satisfies the present constraints one can use eq. (9). This can be performed in general for a

multicomponent mixture. However, for illustration purposes a binary mixture is considered here.

**Binary Mixtures of Conformal Molecules:** In binary mixtures there are three parameters of type  $s$ , namely  $s_{11}$ ,  $s_{12}$  and  $s_{22}$ . The parameter  $s_{12}$  is obtained from  $s_{11}$  and  $s_{22}$  and possibly other molecular parameters through combining rules. In the case where each component potential function has two parameters, like energy ( $\epsilon$ ) and size ( $\sigma$ ) parameters, such that

$$\phi_{ij} = \epsilon_{ij} f(\sigma_{ij}/r) \quad (11)$$

Under the above conditions eq. (9) gives six relations which are:

$$\begin{aligned} 3\sigma_{jj}^{-1} \partial F_{jj} / \partial \epsilon_{ii} + 6(\partial \ln \sigma_{12} / \partial \sigma_{jj}) \partial F_{12} / \partial \epsilon_{ii} + 6(\partial^2 \ln \sigma_{12} / \partial \sigma_{jj} \partial \epsilon_{ii}) F_{12} \\ = \epsilon_{ii}^{-1} \partial E_{ii} / \partial \sigma_{jj} + 2(\partial \ln \epsilon_{12} / \partial \epsilon_{ii}) \partial E_{12} / \partial \sigma_{jj} + 2(\partial^2 \ln \epsilon_{12} / \partial \sigma_{jj} \partial \epsilon_{ii}) E_{12} \end{aligned} \quad (12)$$

$i=1,2; j=1,2$

$$\begin{aligned} \epsilon_{22}^{-1} \partial E_{22} / \partial \epsilon_{11} + 2(\partial \ln \epsilon_{12} / \partial \epsilon_{22}) \partial E_{12} / \partial \epsilon_{11} \\ = \epsilon_{11}^{-1} \partial E_{11} / \partial \epsilon_{22} + 2(\partial \ln \epsilon_{12} / \partial \epsilon_{11}) \partial E_{12} / \partial \epsilon_{22} \end{aligned} \quad (13)$$

$$\begin{aligned} \sigma_{22}^{-1} \partial F_{22} / \partial \sigma_{11} + 2(\partial \ln \sigma_{12} / \partial \sigma_{22}) \partial F_{12} / \partial \sigma_{11} \\ = \sigma_{11}^{-1} \partial F_{11} / \partial \sigma_{22} + 2(\partial \ln \sigma_{12} / \partial \sigma_{11}) \partial F_{12} / \partial \sigma_{22} \end{aligned} \quad (14)$$

where

$$E_{ij} = x_i x_j N \rho / (2kT) \int_0^{\infty} \phi_{ij} g_{ij} 4\pi r^2 dr \quad (15)$$

$$F_{ij} = -x_i x_j N \rho / (6kT) \int_0^{\infty} r \phi'_{ij} g_{ij} 4\pi r^2 dr \quad (16)$$

Note that the term  $E_{ij}$  appears in the energy equation of statistical mechanics

and the term  $F_{ij}$  appears in the pressure equation of statistical mechanics (McQuarrie, 1975).

Equations (12)-(14) are not all independent. They are reduced to three independent equations by defining the following new set of variables

$$F_i = F_{ii} / \sigma_{ii} + 2(\partial \ln \sigma_{12} / \partial \sigma_{ii}) F_{12} \quad (17)$$

$$E_i = E_{ii} / \epsilon_{ii} + 2(\partial \ln \epsilon_{12} / \partial \epsilon_{ii}) E_{12} \quad (18)$$

As a result the six Equations (12)-(14) will reduce to the following equations

$$\partial F_1 / \partial \sigma_{22} = \partial F_2 / \partial \sigma_{11} \quad (19)$$

$$\partial E_1 / \partial \epsilon_{22} = \partial E_2 / \partial \epsilon_{11} \quad (20)$$

$$3 \partial F_j / \partial \epsilon_{ii} = \partial E_i / \partial \sigma_{jj} \quad \text{where } i=1,2; j=1,2 \quad (21)$$

When eq. (10) is combined with eqs. (19)-(21) and the energy and pressure equations of statistical mechanics (McQuarrie, 1975) are used, the following partial differential equation results (Hamad, 1988)

$$\alpha \partial [T \partial E / \partial T + \rho \partial E / \partial \rho] / \partial \sigma_{22} + T \partial E / \partial T + \rho \partial E / \partial \rho = 0 \quad (22)$$

where  $E = U_r / kT$ ,  $U_r$  is the residual internal energy and

$$\alpha = 2/3 \sigma_{11} [(\epsilon_{11} / \epsilon_{12}) (\sigma_{11} / \sigma_{12})^2 (x_1 / x_2) + (\sigma_{12} / \sigma_{11})] \quad (23)$$

Integrating Eq. (22) once with respect to  $\sigma_{22}$  to get

$$T \partial E / \partial T + \rho \partial E / \partial \rho = \sigma_{11}^3 x_2 K / (\sigma_{11}^3 x_1 (\epsilon_{11} / \epsilon_{12}) + \sigma_{12}^3 x_2) \quad (24)$$

where  $K = K(\rho, T, x_1, \epsilon_{11}, \epsilon_{12}, \sigma_{11})$  is an arbitrary function and  $\sigma_{12} = (\sigma_{11} + \sigma_{22}) / 2$ .

For  $x_1=0$  eq. (24) reduces to

$$T\partial E_2/\partial T + \rho\partial E_2/\partial\rho = \sigma_{11}^3/\sigma_{12}^3 K(\rho, T, x_1, \epsilon_{11}, \epsilon_{12}, \sigma_{11}) \quad (25)$$

where  $E_2$  is pure component 2 property. Since the pure component energy can not depend on  $\sigma_{11}$ ,  $K(\rho, T, x_1, \epsilon_{11}, \epsilon_{12}, \sigma_{11})$  has to be zero. Equation (25) then becomes

$$T\partial E_2/\partial T + \rho\partial E_2/\partial\rho = 0 \quad (26)$$

which has the solution  $E_2 = U_{2r}/kT = H(\rho/T)$ , where  $H$  is an arbitrary function.

From this one concludes that for the canonical ensemble relations to be satisfied under the conformal solution approximation, the pure fluid internal energy has to be of the form  $U_r/kT = H(\rho/T)$ . This requirement is too restrictive and can only be satisfied if the potential function of the pure fluid is proportional to  $1/r^3$  ( $r$  is the distance between the centers of two molecules) for the entire range of  $r$ ,  $r \geq 0$ . Real molecules have a repulsive part which is approximately proportional to  $1/r^n$ , where  $n \geq 12$ ; in addition to an attractive part which is approximately proportional to  $1/r^6$ . For the empirical van der Waals equation of state  $U_r/kT = -ap/kT$  which satisfies the above requirement.

The test then shows that the potential function of pure fluids has to be inversely proportional to the third power of distance in order for this approximation to be obeyed.

### TEST OF THE MEAN DENSITY RDF APPROXIMATION

The mean density approximation is another theory which relates the mixture RDFs to a pure reference fluid distribution function. This approximation can be written as (Mansoori and Leland, 1972)

$$g_{ij} = g_o(r/\sigma_{ij}, \rho\sigma_x^3/kT/\epsilon_{ij}) \quad (27)$$

The only difference between this approximation and the conformal solution theory is the use of  $\epsilon_{ij}$  to scale temperature rather than  $\epsilon_x$  as in eq. (10).

Combining eq. (27) with eqs. (12)-(14) one can derive the following differential equation for  $E_{ij}$

$$3\rho \partial E_{ij} / \partial \rho - \sigma_{ij} \partial E_{ij} / \partial \sigma_{ij} = 0 \quad (28)$$

where it was assumed that  $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$  and  $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$ . The solution of this equation is  $E_{ij} = H(\rho\sigma_{ij}^3, T, x_i)$ , where  $H$  is an arbitrary function. This implies that the mean density approximation does not satisfy the present constraints. To satisfy those constraints the density has to be scaled by  $\sigma_{ij}^3$  (when  $kT$  is scaled by  $\epsilon_{ij}$ ) rather than  $\sigma_x^3$ . When all the intermolecular energy parameters  $\epsilon_{ij}$  are equal the mean density approximation becomes identical to the conformal solution approximation and the conclusions of Section 3 apply.

## CONCLUSIONS

New relations among integrals of the radial distribution functions of a mixture are derived. These canonical ensemble constraints are given in terms of the intermolecular potential energy parameters. Such relations minimize the number of approximations needed for mixture property calculations. These constraints can also be used to test theories of mixture radial distribution functions.

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