

Analytic Equations of State of Simple Liquids and Liquid Mixtures

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Abstract

Based on the variational and perturbation theories of liquid state, at equilibrium conditions, an approximation technique is introduced through which it has been made possible the derivation of analytic relations for the thermodynamic properties of simple liquids in which the intermolecular potential can be represented by the Lennard-Jones ($m-n$) potential function. By the application of the hard-sphere expansion (HSE) conformal solution theory it has been possible to generalize the resulting relation of pure systems for the mixtures of simple liquids, and, consequently, analytic relations for the total and the excess thermodynamic properties of liquid mixtures are derived. For a numerical case study, the equations of state derived are applied to the systems for which the Lennard-Jones (6-12) potential function is assumed to be valid and the results are compared with the experimental values and the results of the other theories of liquids and liquid mixtures.

INTRODUCTION

There has been considerable progress during the past few years in the development of equations of state based on the fundamental theories of statistical thermodynamics, especially the distribution function theories¹⁻⁴. Because of these new developments, we are now able to predict the thermodynamic properties of, at least, simple liquids, simple liquid mixtures, and the phase equilibria properties of these systems with only a knowledge of their molecular properties. Of the theories of liquids and liquid mixtures which have been successful in this respect we can name especially the variational theory³, the perturbation theory⁴, and the conformal solution theories^{2,5}. The variational and perturbation theories are actually mathematical

approaches of expanding the thermodynamic properties of real fluids around the thermodynamic properties of the hard-sphere fluid with respect to the powers of the inverse of temperature. The basic idea behind this expansion with respect to the inverse powers of temperature is that at high enough temperatures simple fluids generally behave like assemblies of hard-spheres with only the repulsive forces effective between the molecules of the fluids. While the variational and perturbation theories have been successful in accurately predicting the thermodynamic properties of simple liquids and liquid mixtures, they are still not very applicable for engineering calculations in their existing forms. This is due to the fact that there are complicated mathematical relations involved in their formulation which require numerical calculations and excessive use of computer time.

In the present report a method is introduced through which the analytic representations of the variational and perturbation equations of state of simple liquids are made possible. Through the application of the hard-sphere expansion (HSE) theory², which is a new conformal solution approach, the results are generalized to the case of simple liquid mixtures, and the relations for excess thermodynamic properties of simple liquid mixtures are developed and are presented. Numerical comparison of the results of the present report with the original variational and perturbation calculations show that they are in excellent agreement. The formulation of the analytic equations of state of liquids and liquid mixtures introduced in the present report are simple enough to be used for process engineering applications and they are accurate enough to take the place of the original variational and perturbation equations of state.

FORMULATION OF THE PROBLEM

The equation of state for the Helmholtz free energy of a real pure system with intermolecular potential

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function $u(r) = \epsilon f(r/\sigma)$ with reference to a hard-sphere pure system is derived through the variational theory and is as follows¹:

$$\frac{A}{nRT} \leq \frac{A^{\text{hs}}(\eta)}{nRT} + \frac{48\eta}{T^*} \int_0^{\infty} U_1(s, c) G(s, \eta) ds \quad (1)$$

where $A^{\text{hs}}(\eta)$ is the Helmholtz free energy of the pure hard-sphere reference system, $\eta = N_0(\pi/6)d^3\rho$ where ρ is the molar density and $(\pi/6)d^3$ is the molecular volume of the reference hard-sphere system with diameter d , $T^* = kT/\epsilon$ dimensionless temperature, $U_1(s, c)$ is the inverse Laplace transform of $xu^*(x)$ with $x = r/\sigma$ and $u^*(x) = u(x)/4\epsilon$, $G(s, \eta)$ is the Laplace transform of $xg^{\text{hs}}(x, \eta)$ where $g^{\text{hs}}(x, \eta)$ is the radial distribution function of the hard-sphere reference system, and $c = d/\sigma$ is called the cut-off parameter.

In the case when the system of interest consists of molecules which have intermolecular potentials in the form of the Lennard-Jones (m-n) function, that is

$$u(r) = \frac{n}{(n-m)} \left(\frac{n}{m}\right)^{m/(n-m)} \epsilon \left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m \right] \quad (2)$$

The relation for $U_1(x)$ will be as follows¹:

$$U_1(s, c) = \frac{n}{4(n-m)} \left(\frac{n}{m}\right)^{m/(n-m)} \left[\frac{s^{n-2}}{(n-2)!} c^{-n} - \frac{s^{m-2}}{(m-2)!} c^{-m} \right] \quad (3)$$

and the relation for $G(s, \eta)$ is derived analytically and is given by the expression⁶

$$G(s, \eta) = L(s)/12\eta[L(s) + S(s) \exp(s)] \quad (4)$$

where

$$L(s, \eta) = 12\eta[(1 + \frac{1}{2}\eta)s + (1 + 2\eta)] \quad (4.1)$$

and

$$S(s, \eta) = (1 - \eta)^2 s^3 + 6\eta(1 - \eta)s^2 + 18\eta^2 s - 12\eta(1 + 2\eta) \quad (4.2)$$

In the case when the inequality sign in eqn. (1) is replaced with an equality sign, it will be equivalent to

the first order perturbation expansion developed originally by Zwanzig⁷. In the case when the inequality sign is retained, eqn. (1) will be the working equation for the variational theory of pure liquids¹.

While ϵ and σ , the Lennard-Jones parameters of the molecules of the real pure system, are defined values, the value of d , the diameter of the molecules of the hard-sphere reference system (and for that matter, the cut-off parameter $c = d/\sigma$), is a parameter which is at our disposal. In the case when the inequality sign in eqn. (1) is retained, the obvious choice for d (or c) is the value for which the right-hand side of eqn. (1) is a minimum, and actually d (or c) is the variational parameter used in the original variational theory. The properties of simple liquids and liquid mixtures are already calculated and are reported using eqn. (1) and similar inequalities for the case of mixtures through the variational calculations^{1,3}. The comparison of the results with the experimental results and the machine-calculated data, Monte-Carlo and molecular dynamic data, for liquids and liquid mixtures indicate good agreements at all the ranges of temperature and density from the liquid state to the gaseous state. In the original perturbation and variational calculations, in performing the integration in the second term of the right-hand side of eqn. (1), numerical methods were used. A more general and applied use of eqn. (1) is not possible if one has to solve it numerically. In the present report a method is introduced through which an analytical relation is derived for the right-hand side of eqn. (1) and the results are generalized to the case of mixtures.

When eqn. (3) for U_1 is replaced in eqn. (1), we get

$$\frac{A}{nRT} \leq \frac{A^{\text{hs}}}{nRT} + \frac{\alpha\eta}{T^*} [c^{-n}f_n(\eta) - c^{-m}f_m(\eta)] \quad (5)$$

where

$$\alpha = \frac{12n}{(n-m)} \left(\frac{n}{m}\right)^{m/(n-m)} \quad (5.1)$$

and

$$f_k(\eta) = \frac{1}{(k-2)!} \int_0^{\infty} s^{k-2} G(s, \eta) ds \quad (6)$$

Numerical solution of $f_k(\eta)$ for different values of η is performed, and the result is shown by Fig. 1. This figure indicates that $f_k(\eta)$ is always a monotonic

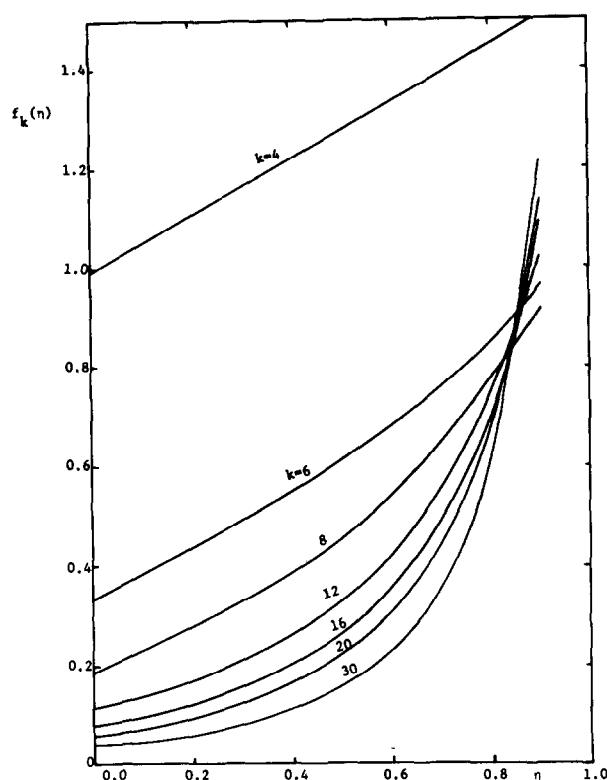


Fig. 1. Function $f_k(\eta)$ as given by eqn. (6) versus η for different values of k .

increasing function of η for $k > 2$ and for $0 \leq \eta < 1$ which is the permitted range of η for $G(x, \eta)$ given by eqn. (4). Consequently $f_n(\eta)$ and $f_m(\eta)$ be approximated by power series as follows:

$$f_n(\eta) = \sum_{i=0}^N C_{1i} \eta^i \quad (7.1)$$

$$f_m(\eta) = \sum_{i=0}^M C_{2i} \eta^i \quad (7.2)$$

The above power series can be truncated to definite numbers of terms depending on their rates of convergences, and the coefficients C_{1i} and C_{2i} can be evaluated by using the linear least square technique. For the case of the Lennard-Jones (6-12) potential function it is found that the best approximations could be obtained for $N = 4$ and $M = 3$ which give the minimum error and the smallest mean square deviations compared to the other truncations⁸. The numerical

values of the coefficients C_{1i} and C_{2i} for the Lennard-Jones (6-12) potential function are given in Table 1.

TABLE 1

Values of coefficients of functions $f_6(\eta)$ and $f_{12}(\eta)$ as shown by eqns. (7.2) and (7.1)

$f_{12}(\eta) = \sum_{i=0}^4 C_{1i} \eta^i$	$f_6(\eta) = \sum_{i=0}^3 C_{2i} \eta^i$
$C_{10} = 0.11263$	$C_{20} = 0.33359$
$C_{11} = 0.16289$	$C_{21} = 0.42548$
$C_{12} = 0.73202$	$C_{22} = 0.19218$
$C_{13} = -0.11123$	$C_{23} = 0.10650$
$C_{14} = 1.43691$	

For the hard-sphere reference pure fluid system there are several analytic relations available for A^{hs}/nRT . Carnahan and Starling⁹ gave a good and simple relation for the hard-sphere equation of state which agrees with the machine-calculated data for hard-sphere fluid better than any other relation available. Based on their work the following relation can be derived for the Helmholtz free energy of a hard-sphere fluid

$$\frac{A^{hs} - A^{id}}{nRT} = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} \quad (8)$$

Joining eqns. (7.1), (7.2) and (8) together with eqn. (5), we get

$$\frac{A - A^{id}}{nRT} \leq \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} + \frac{\alpha\eta}{T^*} \left[c^{-n} \sum_{i=0}^N C_{1i} \eta^i - c^{-m} \sum_{i=0}^M C_{2i} \eta^i \right] \quad (9)$$

THERMODYNAMIC PROPERTIES OF PURE COMPONENTS

In the right-hand side of eqn. (9) the cut-off parameter $c = d/\sigma$ is a parameter at our disposal. There are several methods available for choosing the value of c . If one replaces the inequality sign with an equality sign in relation (9), one can either treat c as a constant or take it as a function of temperature and density. In both of these cases, one can find the best values of c by fitting relation (9) to the experimental data. When

the inequality sign in relation (9) is retained, one can find the best values of c by minimizing the right-hand side of the inequality with respect to c .

(a) *The case of constant cut-off parameter*

In the case when the cut-off parameter c is taken as a constant, the most simple and obvious choice is to take $c = 1$, and, of course, replace the inequality sign by an equality sign in relation (9). If the cut-off parameter c is taken as a constant but not equal to unity, then the numerical value of c can be calculated from experimental data on thermodynamic properties similar to the method adopted by Frisch *et al.*¹⁰. In this case, relation (9) will be similar to the original perturbation equation of state proposed by Zwanzig⁷. For the Lennard-Jones (6-12) potential function for $c = 1$ the relation for the Helmholtz free energy of pure systems will be as follows:

$$\frac{A - A^{id}}{nRT} = \frac{\eta_0(4 - 3\eta_0)}{(1 - \eta_0)^2} + \frac{48\eta_0}{T^*} \sum_{i=0}^4 C_i \eta_0^i \quad (10)$$

with

$$\eta_0 = N_0 \frac{\pi}{6} \rho \sigma^3$$

and

$$C_i = C_{1i} - C_{2i} \quad \text{for } i = 1, 2, 3 \quad \text{and} \quad C_4 = C_{14}$$

and where C_{1i} and C_{2i} are given in Table 1. By the application of the thermodynamic relation between compressibility and Helmholtz free energy,

$$Z = \frac{PV}{nRT} = \rho \frac{\partial}{\partial \rho} \left(\frac{A}{nRT} \right)_T \quad (11)$$

the following relation will be derived for compressibility of pure systems:

$$Z = \frac{PV}{nRT} = \frac{1 + \eta_0 + \eta_0^2 - \eta_0^3}{(1 - \eta_0)^3} + \frac{48\eta_0}{T^*} \times \sum_{i=0}^4 (1+i) C_i \eta_0^i \quad (12)$$

Also, the internal energy is derived from the Helmholtz free energy by the application of the following thermodynamic relation.

$$\frac{U - U^{id}}{nRT} = -T \frac{\partial}{\partial T} \left(\frac{A - A^{id}}{nRT} \right)_\rho \quad (13)$$

Then the following relation will be derived for the internal energy of pure systems.

$$\frac{U - U^{id}}{nRT} = \frac{48\eta_0}{T^*} \sum_{i=0}^4 C_i \eta_0^i \quad (14)$$

In the case when the critical properties T_c, v_c , are available, instead of the intermolecular force constants ϵ, σ , we will re-define η_0 and T^* as the following:

$$\eta_0 = \eta_c(\rho v_c) \quad (15)$$

and

$$T^* = T_c^*(T/T_c) \quad (16)$$

The numerical values of η_c and T_c^* can be found by applying the characteristics of the critical point

$$\left(\frac{\partial P}{\partial \rho} \right)_{T_c} = \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{T_c} = 0$$

to eqn. (12), which are as the following

$$\eta_c = 0.154 \quad (17)$$

and

$$T_c^* = 1.33 \quad (18)$$

(b) *The case when the cut-off parameter is taken as a function of temperature and density*

In this case the cut-off parameter, c , can be calculated from the experimental data on thermodynamic properties of the substances in liquid and vapor phases, and the functional form of $c(\rho, T)$ can be found through the correlation techniques.

(c) *The case of variational calculations*

In the case when the inequality sign in relation (9) is retained, then the value of the cut-off parameter $c = d/\sigma$ in the right-hand side of relation (9) can be found by minimizing the right-hand side of this relation with respect to c . We can write relation (9) as the following:

$$A^*(\eta_0, T^*) \leq A_0^*(\eta_0, c) + \frac{A_1^*(\eta_0, c)}{T^*} \quad (18)$$

where $A^* = (A - A^{id})/nRT$, $A_0^* = (A^{hs} - A^{id})/nRT$, and A_1^*/T^* is equivalent to the second term in the right-hand side of relation (9). In order to bring inequality (18) closer to equality, its right-hand side must satisfy the following conditions:

$$\frac{\partial A_0^*}{\partial c} + \frac{1}{T^*} \frac{\partial A_1^*}{\partial c} = 0 \quad (19)$$

and

$$\frac{\partial^2 A_0^*}{\partial c^2} + \frac{1}{T^*} \frac{\partial^2 A_1^*}{\partial c^2} \geq 0 \quad (20)$$

If the above conditions are satisfied, there can be a relative minimum for the right-hand side of relation (18), and for that matter for the right-hand side of relation (9), with respect to c , and one can write,

$$A^*(\eta_0, T^*) \simeq A_0^*(\eta_0, c_m) + \frac{A_1^*(\eta_0, c_m)}{T^*} \quad (21)$$

where c_m is the value of c which satisfies conditions (19) and (20). In the case of inequality (18) or inequality (9), conditions (19) and (20) will be as follows:

$$\begin{aligned} \frac{2(2-\eta)}{(1-\eta)^3} + \frac{\alpha}{T^*} \left\{ c^{-n} \sum_{i=0}^N \left(1+i-\frac{n}{3}\right) C_{1i} \eta^i \right. \\ \left. - c^{-m} \sum_{i=0}^M \left(1+i-\frac{m}{3}\right) C_{2i} \eta^i \right\} = 0 \end{aligned} \quad (19.1)$$

and

$$\begin{aligned} \frac{2(5-2\eta)}{(1-\eta)^4} + \frac{\alpha}{T^*} \left\{ c^{-n} \sum_{i=0}^N \left(1+i-\frac{n}{3}\right) \left(i-\frac{n}{3}\right) C_{1i} \eta^i \right. \\ \left. - c^{-m} \sum_{i=0}^M \left(1+i-\frac{m}{3}\right) \left(i-\frac{m}{3}\right) C_{2i} \eta^i \right\} \geq 0 \end{aligned} \quad (20.1)$$

When the Lennard-Jones (6-12) potential is chosen for the real system, eqn. (19.1) can be easily solved to calculate c_m , as the following⁸:

$$c_m^3 = \{2X_1/[X_1 - (X_1^2 - T^*X_2X_3/6)^{\frac{1}{2}}]\}^{\frac{1}{2}} \quad (19.2)$$

where

$$X_1 = \sum_{i=0}^4 (1+i-4) C_{1i} \eta^i$$

$$X_2 = \sum_{i=0}^3 (1+i-3) C_{2i} \eta^i$$

$$X_3 = (2-\eta)/(1-\eta)^3; \quad \eta = N_0 \frac{\pi}{6} \rho \sigma^3 c_m^3$$

Hence, c_m can be calculated corresponding to different values of $\rho\sigma^3$ and T^* .

Using the values of c_m obtained from eqn. (19.1), the compressibility, internal energy, and the other thermodynamic properties can be derived from eqn. (21).

THERMODYNAMIC PROPERTIES OF MIXTURES

The analytic equations of state developed for the pure systems in the previous sections can be generalized to the case of mixtures. Of course, the variational and perturbation theories have been generalized to the case of the mixtures^{3,4,11} and one, in principle, should be able to use similar approximations, as it is used here, to introduce these equations of state of mixtures in analytic forms. However, the equations of state of mixtures developed through the variational and perturbation theories are more complicated than the ones for pure systems and this attempt will not be as fruitful as in the case of the pure systems. Consequently, the most practical way to generalize the equations of state of pure systems developed in the previous sections of this work, to the case of mixtures, is by the use of the principle of conformal solutions, and especially the hard-sphere expansion (HSE) theory of conformal solutions developed recently².

In the development of a conformal solution theory for mixtures, basically, two principles should be considered. One is the choice of an accurate equation of state for a reference pure system and the other is the choice of the mixing rules for the parameters of the pure reference equation of state in order to generalize them to the case of mixtures⁵. The parameters of the pure reference equation of state are usually either the intermolecular potential parameters or the critical properties. Accordingly, the pure reference equation of state for simple liquids can be shown as follows:

$$\chi_p = \chi^{id} + f(T^*, \rho^*) \quad (22)$$

where χ is the thermodynamic function such as compressibility, internal energy, free energies, enthalpy, or entropy, and T^* and ρ^* are the reduced temperature and density with respect to ϵ and σ (or with respect to T_c and v_c) as defined before.

Equation (22) is the general form of the reduced equation of state which could be the result of a fundamental theory or an empirical relation: Equation (22) is a result of some assumptions made originally by Pitzer¹² in deriving the corresponding states principle for pure systems. These assumptions include the basic requirement that the properties of a pure fluid can be derived from any pair interaction potential which has the following functional form

$$u(r) = \epsilon f(r/\sigma) \quad (23)$$

This leads to a two-parameter corresponding states theorem for pure components. Now, in order to generalize this idea to mixtures, one should find the relation between σ and ϵ (or v_c and T_c) of the pure reference fluid with the intermolecular parameters (or critical constants) of the components of the mixture⁵. This is based on the idea that a single pure fluid may hypothetically exist and possess the same properties as a mixture if each, the hypothetical pure fluid and the mixture, are at the same temperature and pressure. The intermolecular parameters (or the critical constants) of this hypothetical pure reference fluid are then the pseudo-intermolecular parameters (or the pseudo-critical constants) of the mixture. Only nonpolar, simple molecular systems have been successfully characterized in such a manner. Many different mixing rules have been published in the literature suggesting how such mixing rules may be constructed. Generally one can write

$$\left. \begin{aligned} \bar{\epsilon} &= \bar{\epsilon}(\epsilon_{ij}, \sigma_{ij}, x_i, x_j, \rho, T) \\ \bar{\sigma} &= \bar{\sigma}(\epsilon_{ij}, \sigma_{ij}, x_i, x_j, \rho, T) \end{aligned} \right\} \quad i, j = 1, 2, \dots, p \quad (24.1)$$

or

$$\left. \begin{aligned} T_{pc} &= T_{pc}(T_{cij}, v_{cij}, x_i, x_j, \rho, T) \\ v_{pc} &= v_{pc}(T_{cij}, v_{cij}, x_i, x_j, \rho, T) \end{aligned} \right\} \quad i, j = 1, 2, \dots, p \quad (24.2)$$

where $\bar{\epsilon}$, $\bar{\sigma}$ (and T_{pc} , v_{pc}) are the characteristic parameters of the hypothetical pure fluid; ϵ_{ij} , σ_{ij} (and T_{cij} , v_{cij}) are the characteristic parameters (like and unlike) of the components of the mixture; x_i , x_j are the mole fractions of the components i and j ; and p is the number of components in the mixture.

The Percus-Yevick theory of fluids has been successful in producing two different equations of state for mixtures of hard-spheres¹³. While both of these equations are in good agreement with the machine-calculated data on hard-sphere mixtures, one gives an upper boundary and the other gives a lower boundary to the machine-calculated thermodynamic data on hard-sphere mixtures. By an averaging process over the above-mentioned two equations, an equation of state for hard-sphere mixtures is developed which is in excellent agreement with all the available machine-calculated data on hard-sphere mixtures¹⁴. Because of the availability of this accurate equation of state for hard-sphere mixtures it will not be necessary any more to apply the principle of corresponding states to the equations of state or the excess properties over the ideal gas system, as was given by eqn. (22), but on the excess properties over the hard-sphere system. Consequently, eqn. (22) can be replaced with the following equation for the pure systems².

$$\chi_p = \chi_p^{\text{hs}}(\rho^*) + f(T^*, \rho^*) \quad (25)$$

where χ_p^{hs} is the hard-sphere pure thermodynamic function. In order to generalize this idea to the case of mixtures one should replace χ_p^{hs} with χ_m^{hs} , and ϵ , σ with $\bar{\epsilon}$, $\bar{\sigma}$ (or T_c , v_c with T_{pc} and v_{pc}) in the pure reference equation of state (25). The relations for $\bar{\epsilon}$, $\bar{\sigma}$ (and T_{pc} , v_{pc}) as derived through the HSE conformal solution theory are as follows²:

$$\bar{\epsilon} = \left[\sum_{i,j=1}^p x_i x_j \epsilon_{ij}^2 \sigma_{ij}^3 \right] \left[\sum_{i,j=1}^p x_i x_j \epsilon_{ij} \sigma_{ij}^3 \right]^{-1} \quad (26.1)$$

$$\bar{\sigma}^3 = \left[\sum_{i,j=1}^p x_i x_j \epsilon_{ij} \sigma_{ij}^3 \right]^2 \left[\sum_{i,j=1}^p x_i x_j \epsilon_{ij}^2 \sigma_{ij}^3 \right]^{-1}$$

or

$$T_{pc} = \left[\sum_{i,j=1}^p x_i x_j T_{cij}^2 v_{cij} \right] \left[\sum_{i,j=1}^p x_i x_j T_{cij} v_{cij} \right]^{-1}$$

$$v_{pc} = \left[\sum_{i,j=1}^p x_i x_j T_{cij} v_{cij} \right]^2 \left[\sum_{i,j=1}^p x_i x_j T_{cij}^2 v_{cij} \right]^{-1} \quad (26.2)$$

In general, the pure reference equation of state available is not in the form of eqn. (25), but in the

following general form:

$$\chi_p = \chi_p(T^*, \rho^*)$$

Then, by the use of the HSE conformal solution theory, the following relation will be derived for the thermodynamic functions of the mixtures,

$$\chi_m = \chi_m^{\text{hs}}(\xi, \sigma_{ii}s) - \chi_p^{\text{hs}}(\bar{\eta}_0) + \chi_p(\bar{T}^*, \bar{\rho}^*)$$

where the bars on the top of η_0 , T^* , and ρ^* mean that these reduced properties are reduced with respect to the hypothetical parameters $\bar{\epsilon}$, $\bar{\sigma}$ (or T_{pc} , v_{pc}). Contrary to the other conformal solution theories, the HSE conformal solution theory is able to take care of the effect of the three-body forces also, which is reported elsewhere² and is out of the scope of the present report.

One of the important and effective factors in the theories of mixtures is the choice of the unlike pair interaction parameters ϵ_{ij} and σ_{ij} (or T_{cij} and v_{cij}) for $i \neq j$. In the case of the conformal solution theories the pair interaction parameters appear in the mixing rules, such as eqns. (26.1) and (26.2). The most common choice for the unlike pair interaction parameters are the following relations⁵.

$$\left. \begin{aligned} \epsilon_{ij} &= (\epsilon_{ii} \cdot \epsilon_{jj})^{\frac{1}{2}} \cdot (1 - K_{ij}) \\ \sigma_{ij} &= (\sigma_{ii} + \sigma_{jj})/2 \end{aligned} \right\} \quad (28)$$

or

$$\left. \begin{aligned} T_{cij} &= (T_{cjj} \cdot T_{cjj})^{\frac{1}{2}} \cdot (1 - K_{ij}) \\ v_{cij} &= \{(v_{cii}^{\frac{1}{3}} + v_{cjj}^{\frac{1}{3}})/2\}^3 \end{aligned} \right\} \quad (29)$$

In the above relations K_{ij} is a parameter which is generally determined experimentally.

Formulation of thermodynamic properties of mixtures

For the formulation of thermodynamic properties through the HSE conformal solution theory as presented above, we can use any of the pure equations of state developed in the previous section as the hypothetical pure reference system. In other words, we can apply the HSE theory of conformal solution to the case when the cut-off parameter is taken as a constant, to the case when the cut-off parameter is taken as a function of T and ρ , and to the case of variational calculations. In the present report the HSE theory is applied only to the case when the cut-off

parameter is taken as a constant and the numerical results are presented for $c = 1$. This is because it is our intention to produce simple analytic relations for the thermodynamic properties of mixtures.

In the case when c is taken as a constant, the following equation exists for the Helmholtz free energy of the pure system (replacing the inequality sign with an equality sign in relation (9)).

$$\frac{A - A^{\text{id}}}{nRT} = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} + \alpha \frac{\eta}{T^*} \times \left\{ c^{-n} \sum_{i=0}^N C_{1i} \eta^i - c^{-m} \sum_{i=0}^M C_{2i} \eta^i \right\} \quad (30)$$

Now, by the application of the HSE theory of conformal solutions, eqn. (27), we get the following equation for the Helmholtz free energy of the mixture.

$$\frac{A_m}{nRT} = \frac{A_m^{\text{hs}}(\xi, \sigma_{ii}s)}{nRT} + \frac{\delta A^{\text{hs}}}{nRT} + \alpha \frac{\bar{\eta}}{\bar{T}^*} \times \left\{ c^{-n} \sum_{i=0}^M C_{1i} \eta^i - c^{-m} \sum_{i=0}^N C_{2i} \eta^i \right\} \quad (31)$$

where A_m^{hs}/nRT is the hard-sphere mixture Helmholtz free energy as given by eqn. (A.1) of the Appendix, and

$$\frac{\delta A^{\text{hs}}}{nRT} = \frac{\bar{\eta}(4 - 3\bar{\eta})}{(1 - \bar{\eta})^2} - \frac{\bar{\eta}_0(4 - 3\bar{\eta}_0)}{(1 - \bar{\eta}_0)^2} \quad (31.1)$$

$$\bar{\eta} = N_0 \frac{\pi}{6} \rho \bar{\sigma}^3 c^3 \quad \text{or} \quad \eta_c(\rho v_{\text{pc}}) c^3 \quad (32.1)$$

$$\bar{\eta}_0 = N_0 \frac{\pi}{6} \rho \bar{\sigma}^3 \quad \text{or} \quad \eta_c(\rho v_{\text{pc}}) \quad (32.2)$$

and

$$\bar{T}^* = kT/\bar{\epsilon} \quad \text{or} \quad T_c^*(T/T_{\text{pc}}) \quad (33)$$

and where $\bar{\sigma}^3$, $\bar{\epsilon}$, v_{pc} and T_{pc} are given by eqns. (26.1) and (26.2). In the case when $c = 1$ we use the values of η_c and T_c^* as given by eqns. (17) and (18).

Similarly, for constant value of c , the following equations can be derived, from eqn. (31), for the

compressibility of the pure system,

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} + \alpha \frac{\eta}{T^*} \left\{ c^{-n} \sum_{i=0}^N (1+i) C_{1i} \eta^i - c^{-m} \sum_{i=0}^M (1+i) C_{2i} \eta^i \right\} \quad (34)$$

and by the application of the HSE conformal solution theory, the following equation can be derived for the compressibility of the mixture.

$$Z_m = Z_m^{\text{hs}} + \delta Z^{\text{hs}} + \alpha \frac{\bar{\eta}}{T^*} \left\{ c^{-n} \sum_{i=0}^N (1+i) C_{1i} \bar{\eta}^i - c^{-m} \sum_{i=0}^M (1+i) C_{2i} \bar{\eta}^i \right\} \quad (35)$$

where Z_m^{hs} is the hard-sphere mixture compressibility as given by eqn. (A.2) in the Appendix, and

$$\delta Z^{\text{hs}} = \frac{1 + \bar{\eta} + \bar{\eta}^2 - \bar{\eta}^3}{(1 - \bar{\eta})^3} - \frac{1 + \bar{\eta}_0 + \bar{\eta}_0^2 - \bar{\eta}_0^3}{(1 - \bar{\eta}_0)^3} \quad (35.1)$$

The internal energy of the mixture, in this case where c is taken as a constant, can be given by the following relation:

$$\frac{U_m - U_m^{\text{id}}}{nRT} = \alpha \frac{\bar{\eta}}{T} \left\{ c^{-n} \sum_{i=0}^N C_{1i} \bar{\eta}^i - c^{-m} \sum_{i=0}^M C_{2i} \bar{\eta}^i \right\} \quad (36)$$

Excess thermodynamic properties

Of particular importance in the thermodynamics of fluid (liquid or vapor) mixtures are the excess properties of the mixture over the properties of an ideal mixture at the same temperature and pressure. Of the excess properties the excess volume V^E , the excess Gibbs free energy G^E , and the excess enthalpy H^E , are more widely used than the other excess properties and are given here.

The excess volume at constant temperature and pressure is given by the following relation.

$$V_{T,P}^E = V_{m,T,P} - \sum_{i=1}^p x_i V_{i,T,P} \quad (37)$$

where V_m is the volume of the mixture; x_i is the mole fraction of the component i ; and V_i is the volume of the component i , all at the same temperature and pressure.

The excess Gibbs free energy of mixing at temperature T and pressure P is related to the excess Helmholtz free energy and excess volume by the following relation.

$$G_{T,P}^E = A_{T,P}^E + PV_{T,P}^E \quad (38)$$

For the excess Helmholtz free energy we have the following relation:

$$A_{T,P}^E = \Delta(A_{T,P} - A_{T,P}^{\text{id}}) - RT \ln \left(V_{m,T,P} \prod_{j=1}^p V_{j,T,P}^{x_j} \right) \quad (39)$$

where

$$\Delta(A_{T,P} - A_{T,P}^{\text{id}}) = A_{m,T,P} - A_{m,T,P}^{\text{id}} - \sum_{i=1}^p x_i (A_{i,T,P} - A_{i,T,P}^{\text{id}}) \quad (40)$$

and P^* is the ideal gas pressure, $P^* = nRT/V$.

By the application of eqns. (34) and (35) we derive the following relation for $PV_{T,P}^E$

$$PV_{T,P}^E = nRT(\Delta Z_{T,P}^{\text{hs}} + \delta Z^{\text{hs}}) + nR\alpha \left\{ c^{-n} \sum_{i=0}^N (1+i) C_{1i} \Gamma_i - c^{-m} \sum_{i=0}^M (1+i) C_{2i} \Gamma_i \right\} \quad (41)$$

where

$$\Delta Z_{T,P}^{\text{hs}} = Z_m^{\text{hs}} - \sum_{j=1}^p x_j Z_j^{\text{hs}} \quad (41.1)$$

and

$$\Gamma_i = \frac{\bar{\epsilon}}{k} \bar{\eta}^{i+1} - \sum_{j=1}^p x_j \frac{\epsilon_{jj}}{k} \eta_j^{i+1} \quad (42)$$

Similarly, from eqns. (30) and (31) we get

$$\Delta(A_{T,P} - A_{T,P}^{\text{id}}) = \Delta(A_{T,P}^{\text{hs}} - A_{T,P}^{\text{id}}) + \delta A^{\text{hs}} + nR\alpha \left\{ c^{-n} \sum_{i=0}^N C_{1i} \Gamma_i - c^{-m} \sum_{i=0}^M C_{2i} \Gamma_i \right\} \quad (43)$$

where Γ_i is given by eqn. (42), and consequently from eqns. (38), (41) and (43) we get the following equation for the excess Gibbs free energy.

$$G_{T,P}^E = \Delta(A_{T,P}^{\text{hs}} - A_{T,P}^{\text{id}}) + RT(\Delta Z_{T,P}^{\text{hs}}) + \delta A^{\text{hs}} + RT(\delta Z^{\text{hs}}) + nR\alpha \left\{ c^{-n} \sum_{i=0}^N (2+i) C_{1i} \Gamma_i - c^{-m} \sum_{i=0}^M (2+i) C_{2i} \Gamma_i \right\} - nRT \ln \left(V_{m,T,P} \prod_{j=1}^p V_{j,T,P}^{x_j} \right) \quad (44)$$

The excess enthalpy is given by the following equation

$$H_{T,P}^E = -T^2 \frac{\partial}{\partial T} (G_{T,P}^E/T)_{P,x_j} \quad (45)$$

From eqns. (44) and (45) we get

$$H_{T,P}^E = nR\alpha \left\{ c^{-n} \sum_{i=0}^N (2+i) C_{1i} \Gamma_i - c^{-m} \sum_{i=0}^M (2+i) C_{2i} \Gamma_i \right\} + nRT^2 \frac{\partial}{\partial T} \times \left\{ \ln \left(V_{m,T,P} \prod_{j=1}^p V_{j,T,P}^{x_j} \right) \right\} \quad (46)$$

RESULTS AND DISCUSSION

For the numerical calculations which are performed in the present report the Lennard-Jones (6-12) potential function is used. The first task was the calculation of coefficients C_{1i} and C_{2i} in the eqns.

(7.1) and (7.2) for $f_{12}(\eta)$ and $f_6(\eta)$. The numerical values of these coefficients for the Lennard-Jones (6-12) potential are reported in Table 1. It is found that the maximum percentage error on $f_{12}(\eta)$, when using eqn. (7.1) as compared to eqn. (6), is 0.017, and its root mean square deviation is 0.00097. Similarly, the maximum percentage error on $f_6(\eta)$, when using eqn. (7.2) as compared to eqn. (6), is 0.066, and its root mean square deviation is 0.00061.

With the cut-off parameter c equal to one, the critical properties are calculated from eqn. (12) and the results are reported on Table 2, together with the original variational results¹, experimental results of argon⁵, and the Monte-Carlo machine calculations¹⁵. It can be seen from this table that even though $c = 1$ is not the best choice for the cut-off parameter, but the easiest, the results for the critical constants with $c = 1$ are in close agreement with the variational calculations, experimental results of argon and the machine-calculated data.

In the case when the cut-off parameter c is not taken as a constant, the variational calculation is performed and c is calculated from eqn. (19.2) and the result is reported by Fig. 2. Figure 2, which gives c^3 versus $\rho\sigma^3$ for different reduced temperatures T^* , is in very good agreement with Figure 6 of Ref. 1 which is a result of the original variational calculations. Also on Fig. 3 compressibilities as calculated by the present variational calculations are compared with the experimental and machine-calculated compressibilities. Figure 3 also is in a very good agreement with Figure 7 of Ref. 1 which is a result of the original variational calculations.

For the calculation of the thermodynamic properties of mixtures also the Lennard-Jones (6-12) potential function is used and, again, the cut-off parameter c is taken equal to unity. In this case, when $c = 1$, the relations for thermodynamic properties of mixtures greatly simplify to the following relations:

$$\frac{A_m}{nRT} = \frac{A_m^{\text{hs}}}{nRT} + \alpha \frac{\bar{\eta}}{T^*} \sum_{i=0}^4 C_i \bar{\eta}^i$$

$$Z_m = Z_m^{\text{hs}} + \alpha \frac{\bar{\eta}}{T^*} \sum_{i=0}^4 (1+i) C_i \bar{\eta}^i$$

$$\frac{U - U^{\text{id}}}{nRT} = \alpha \frac{\bar{\eta}}{T^*} \sum_{i=0}^4 C_i \bar{\eta}^i$$

TABLE 2

Critical constants for the Lennard-Jones (6-12) pure fluid as calculated by the present method with $c = 1$, the variational calculations, experimental results of argon, and the Monte-Carlo machine-calculated data

	<i>This work</i> ($c = 1$)	<i>Variational</i> ¹	<i>Experimental</i> ⁵ (Argon)*	<i>Monte-Carlo</i> ¹⁵
$T_c^* = kT_c/\epsilon$	1.33	1.36	1.26	1.32-1.36
$\rho_c^* = \rho_c \sigma^3 N_0$	0.296	0.325	0.316	0.32-0.36
$\rho_c^* = \frac{P_c \sigma^3 N_0}{\epsilon}$	0.158	0.165	0.117	0.13-0.17
$Z_c^* = \frac{P_c}{\rho_c RT_c}$	0.398	0.37	0.293	0.30-0.36

* For argon, $\sigma = 3.405 \text{ \AA}$ and $\epsilon/k = 133.5^\circ \text{K}$ are used to make the critical constants dimensionless.

$$G_{T,P}^E = \Delta(A_{T,P}^{hs} - A_{T,P}^{id}) + nRT \Delta Z_{T,P}^{hs} + nR\alpha \sum_{i=0}^4 (2+i) C_i \Gamma_i$$

$$H_{T,P}^E = nR\alpha \sum_{i=0}^4 (2+i) C_i \Gamma_i + nRT^2 \frac{\partial}{\partial T} \times \left\{ \ln \left[V_{m,T,P} \prod_{j=1}^P V_{j,T,P}^{x_j} \right]_{P,x_j} \right\}$$

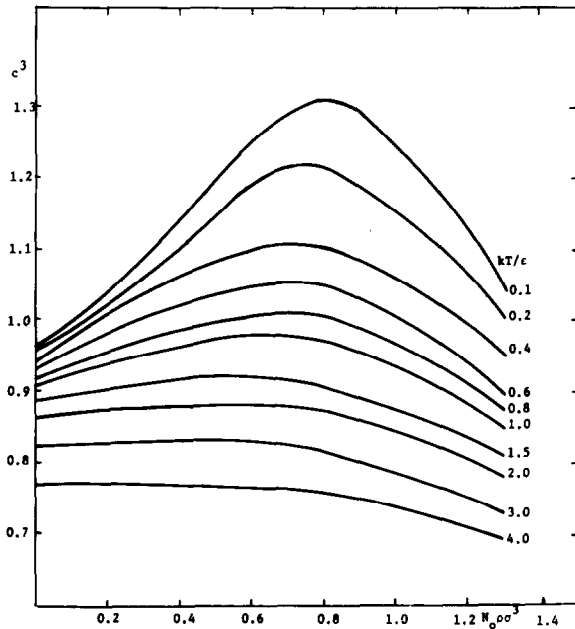


Fig. 2. Cube of the cut-off parameter vs. reduced density for different isotherms calculated by eqn. (19.2).

The excess thermodynamic properties of binary liquid mixtures are calculated by the use of the above equations⁸. In calculating the thermodynamic properties an *a priori* choice should be made for K_{ij} , the correction parameter over the geometric mean rule for ϵ_{12} as shown by eqn. (29.1). The value of K_{ij} for mixtures can be estimated by fitting certain thermodynamic properties of the mixtures, such as excess enthalpy or excess Gibbs free energy, to the experimental values of those thermodynamic properties.

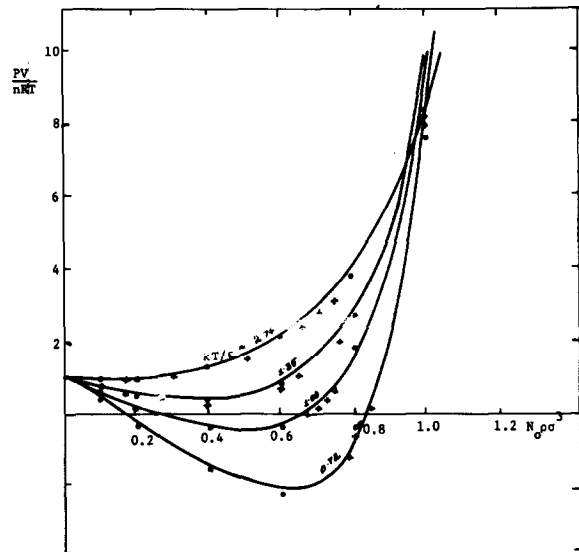


Fig. 3. Compressibility of Lennard-Jones (6-12) fluid vs. reduced density for different isotherms. The points given by (+) are experimental values¹, the points given by (•) are given by the original variational calculations¹, and solid lines are by this work.

In the present report the value of K_{ij} for all the systems which are investigated is taken equal to unity. This is for the purpose of comparison of the results of the present report with the other theories of liquid

TABLE 3

The values of the critical temperature T_c and critical volume V_c for different substances¹⁶

Substance	$T_c(^{\circ}\text{K})$	$V_c(\text{cm}^3 \text{mol}^{-1})$
Ar	150.7	75.2
Kr	209.4	92.3
N ₂	126.2	90.1
O ₂	154.8	78
CO	133	93.1
CH ₄	190.6	98.7
CF ₄	227.6	140

TABLE 4

Comparison of the experimental and the theoretical values of the excess thermodynamic properties at $P = 0$ and $X_1 = X_2 = 0.5$ for different systems of binary liquid mixtures G^E and H^E are in J/mol and V^E is in cm^3/mol .

(The references for different methods are given in the text)

System	Variables	Guggen- Pertur- Variational HSE This work								
		Experiment	APM	$\nu dW(a)$	$\nu dW(b)$	heim	bation			
(Ar + Kr) at 116°K	G^E	84	170	37	18	50	28	42	53	41
	H^E			-50	-64	-54	-54	-33	-48	-71
	V^E	- 0.52	- 0.44	- 0.78	- 1.26	- 1.13	- 0.72	- 0.71	- 0.60	- 1.11
(Ar + N ₂) at 84°K	G^E	34	80	40	21	39	32	39	42	34
	H^E	51	105	43	19	44	27	44	42	31
	V^E	- 0.18	- 0.07	- 0.32	0.36	- 0.36	- 0.33	- 0.29	- 0.29	- 0.24
(Ar + CO) at 84°K	G^E	57		26	13	25	18	25	28	18
	H^E			32	16	34	14	33	38	2
	V^E	0.10		- 0.20	- 0.23	- 0.22	- 0.25	- 0.17	- 0.14	- 0.20
(Ar + CH ₄) at 91°K	G^E	74	170	-19	-13	- 9	-29	-11	- 8	24
	H^E	103	240	-53	-31	-43	-76	-34	-46	-24
	V^E	0.17	0.72	- 0.31	- 0.26	- 0.23	- 0.36	- 0.14	- 0.16	- 0.25
(O ₂ + Ar) at 84°K	G^E	37	1	0.5	- 0	- 0	0.5	0.55	0.60	- 0
	H^E	60	2	0.5	- 0	- 1	0.4	1.7	0.45	0.30
	V^E	0.14	0.01	- 0.00	- 0.00	- 0.00	- 0.00	- 0.00	- 0.00	- 0.00
(O ₂ + N ₂) at 78°K	G^E	42	65	51	24	46	40	50	53	41
	H^E	44	85	54	21	50	35	58	50	49
	V^E	- 0.21	- 0.11	- 0.32	- 0.30	- 0.32	- 0.34	- 0.28	- 0.25	- 0.31
(N ₂ + CO) at 84°K	G^E	23		1.0	24	1	0.9	1.2	1.7	0.74
	H^E			- 0.4	21	- 1	- 0.4	0.56	- 0.4	- 1.2
	V^E	0.13		- 0.02	- 0.30	- 0.03	- 0.02	- 0.02	- 0.03	- 0.01
(CO + CH ₄) at 91°K	G^E	115	105	75	41	87	66	77	78	80
	H^E	105	80	23	2	45	23	35	- 2.4	43
	V^E	- 0.32	- 0.50	- 0.85	- 0.86	- 0.88	- 0.63	- 0.69	- 0.95	- 0.85

mixtures for which results for $K_{ij} = 1$ are, at least, available. For different binary liquid mixtures the excess Gibbs free energy $G_{T,P}^E$, the excess volume $V_{T,P}^E$, and the excess enthalpy $H_{T,P}^E$ are calculated and are reported here. For the critical constant (T_c, v_c) of the components of the mixtures considered, the values reported on Table 3 are used¹⁶. The excess thermodynamic properties calculated for eight different equimolar mixtures, at zero pressure, and for $K_{ij} = 1$ are reported in Table 4. For the binary liquid system (CH₄ + CF₄) the excess thermodynamic properties are calculated with an estimated value of K_{ij} (other than unity) taken from the literature¹⁷ and are reported in Table 5. Also reported in Tables 4 and 5 are the experimental results, together with the results of the other theories of liquid mixtures. The sources of the experimental data are given in Refs. 2, 4, 11, 18 and 19. *APM* stands for the average potential model⁵;

TABLE 5

Comparison of the theoretical and the experimental values of the excess thermodynamic properties for the system $\text{CH}_4 + \text{CF}_4$ at $P = 0$, $T = 111^\circ\text{K}$, $x_1 = x_2 = 0.5$ with $K_{ij} = 0.907$ taken from Ref. (17).

(The references for different methods are given in the text.)

Methods	G^E (J mol ⁻¹)	H^E (J mol ⁻¹)	V^E (cm ³ mol ⁻¹)
Experimental	360	—	0.88
APM	870	—	7.1
vdW(a)	279	482	0.90
vdW(b)	171	—	1.11
Guggenheim	298	—	1.22
Perturbation	209	259	-0.97
Variational	424	770	3.13
HSE	212	403	0.52
This work	287	564	0.56

$vdW(a)$ stands for the van der Waals mixing rules joined with the empirical relations of Bellemans *et al.*¹⁸ for G , H , and V , while $vdW(b)$ stands for the van der Waals mixing rules joined with the van der Waals equation of state¹⁹; *Guggenheim* stands for van der Waals mixing rules joined with the Guggenheim equation of state¹⁹; *Perturbation* stands for the perturbation theory¹¹; *Variational* stands for the variational theory³; and *HSE* stands for the hard-sphere expansion conformal solution theory².

In order to compare the results of the different theories in Table 4. It is better to consider the mean and root-mean-square values of deviations $[X^E(\text{cal } c)/X^E(\text{obs}) - 1]$ where $X = G, H$ or V . The values for mean and root-mean-square deviations for the data of Table 4 are reported on Table 6. According to Table 6 the results of the present work are very close to the results of the HSE method.

TABLE 6

Comparison of the mean and the root-mean-square deviations of the data of Table 4 from the experimental data

Methods	Mean*	Root-Mean-Square**
APM	0.93	1.16
vdW(a)	0.96	1.22
vdW(b)	1.16	1.45
Guggenheim	0.95	1.22
Perturbation	1.00	1.31
Variational	0.83	1.02
HSE	0.86	1.07
This work	0.89	1.15

* Mean = $\sum [|X^E(\text{calc})/X^E(\text{obs}) - 1|]/N$

** RMS = $\{\sum [X^E(\text{calc})/X^E(\text{obs}) - 1]^2/N\}^{1/2}$

CONCLUSIONS

Through the approximation technique which is introduced above it is shown that it is possible to produce analytic relations for the thermodynamic properties of pure liquids and liquid mixtures from the variational and perturbation theories. This is done for the generalized Lennard-Jones (n-m) potential function, while the numerical calculations are performed for the Lennard-Jones (6-12) potential function. Relation (9), which is generally an inequality, is the starting point for the calculation of thermodynamic properties of pure liquids. If the inequality sign in relation (9) is kept, the value of the cut-off parameter c can be calculated from variational calculation and it is shown that this will effectively reproduce the results of the original variational theory¹. If the inequality sign in relation (9) is replaced with an equality sign, the value of the cut-off parameter c can be calculated from the experimental data of the thermodynamic properties of the substances. It is also shown that even for $c = 1$, which is the most simple choice, we can produce simple equations for the thermodynamic properties of pure liquids (eqns. 10, 12 and 14), whose results are comparable to the results of the more complicated relations of variational and perturbation theories. Through the application of the HSE conformal solution theory it is shown that it is possible to generalize the results of the pure system to the mixture.

One significance of this work is that through the application of the fundamental theories of statistical thermodynamics we have been able to produce simple and analytic equations of state for simple substances. That is, by the treatment of the cut-off parameter c as a function of temperature and density, one should be able to find the functional form of $c(T^*, \rho^*)$ from the experimental data and then predict the thermodynamic properties of liquids and liquid mixtures from the equations introduced above. This is the conclusion of the calculations which are made above for the case of the cut-off parameter c equal to unity. It is shown that even for this simplified case the results of the analytic equations of state developed here are as good as the results of the theories upon which the present work is based. The principal significance of this work is that we could produce relations for the thermodynamic properties of simple liquids and simple liquid mixtures which are theoretically sound, and with a slight manipulation (*i.e.*, finding the functional form of the cut-off parameter c with respect to temperature and density) these relations can be used for accurate quantitative calculations.

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NOMENCLATURE

A	Helmholtz free energy
C_i	$C_{1i} - C_{2i}$
C_{1i}	defined by eqn. (7.1)
C_{2i}	defined by eqn. (7.2)
d	hard-sphere diameter
$f_k(\eta)$	defined by eqn. (6)
g	radial distribution function
G	Gibbs free energy
$G(s, \eta)$	Laplace transform of $xg^{hs}(x, \eta)$
H	enthalpy
K_{ij}	correction factor, defined by eqn. (28) or (29)
m	Lennard-Jones attractive power
n	Lennard-Jones repulsive power
n	number of moles
N_0	Avagadro Number
p	number of components in a mixture
P	pressure
r	intermolecular distance
R	universal gas constant
T	absolute temperature
T^*	kT/ϵ or $T_c^*(T/T_c)$
T_c^*	1.33
\bar{T}^*	$kT/\bar{\epsilon}$ or $T_c^*(T/T_{pc})$
$u(r)$	pair intermolecular potential function
U	internal energy
$U_1(s, c)$	inverse Laplace transform of $xu^*(x)$
v	specific volume
V	total volume
x	r/σ
x_i	mole fraction of component i
Z	compressibility

Greek symbols

α	defined by eqn. (5.1)
Γ_i	defined by eqn. (4.2)
$\delta\chi^{hs}$	$\chi^{hs}(\bar{\eta}) - \chi^{hs}(\bar{\eta}_0)$
$\Delta\chi_{T,P}$	$\chi_{m,T,P} - \sum_i x_i \chi_{i,T,P}$
ϵ	depth parameter of Lennard-Jones potential
$\bar{\epsilon}$	defined by eqn. (24.1)

η	$N_0 \left(\frac{\pi}{6} d^3 \right) \rho$
η_0	$N_0 \left(\frac{\pi}{6} \sigma^3 \right) \rho$ or $\eta_c(\rho v_c)$
$\bar{\eta}_c$	0.154
$\bar{\eta}$	$N_0 \left(\frac{\pi}{6} \bar{\sigma}^3 c^3 \right) \rho$
$\bar{\eta}_0$	$N_0 \left(\frac{\pi}{6} \bar{\sigma}^3 \right) \rho$ or $\eta_c(\rho v_{pc})$
ξ	$\sum_{i=1}^p \xi_i$
ξ_i	$N_0 \left(\frac{\pi}{6} d_i^3 \right) \rho x_i$ or $\eta_c(\rho v_{ci}) x_i$
ρ	molar density
σ	length parameter of Lennard-Jones potential
$\bar{\sigma}$	defined by eqn. (24.1)
χ	a thermodynamic function

Subscripts

c	critical
i	i th component of a mixture
i	i th term of a power series
j	j th component of a mixture
m	mixture
p	pure
pc	pseudo-critical
P	constant pressure
P^*	constant ideal gas pressure (RT/v)
T	constant temperature

Superscripts

*	dimensionless
E	excess
hs	hard-sphere
id	ideal gas

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APPENDIX

The Helmholtz free energy of the hard-sphere mixtures $A_m^{hs}(\xi, \sigma_{ii}'s)$ is given by the following relation:

$$\begin{aligned} \frac{A_m^{hs} - A_m^{id}}{nRT} = & -\frac{3}{2}(1 - y_1 + y_2 + y_3) \\ & + (3y_2 + 2y_3)(1 - \xi)^{-1} \\ & + \frac{3}{2}(1 - y_1 - y_2 - \frac{1}{3}y_3)(1 - \xi)^{-2} \\ & + (y_3 - 1) \ln(1 - \xi) \end{aligned} \quad (A.1)$$

and the compressibility of the hard-sphere mixture $Z_m^{hs}(\xi, \sigma_{ii}'s)$ is given by the following relation:

$$Z_m^{hs} = [1 + \xi(1 - 3y_1) + \xi^2(1 - 3y_2) - \xi^3y_3] \times (1 - \xi)^{-3} \quad (A.2)$$

In the above relations,

$$\xi = \sum_{i=1}^p \xi_i; \quad \sum_{i=1}^p x_i = 1$$

$$\xi_i = \frac{\pi}{6} N_0 \rho \sigma_{ii}^3 x_i$$

$$y_1 = \sum_{j>i=1}^p \Delta_{ij} (\sigma_{ii} + \sigma_{jj}) (\sigma_{ii} \sigma_{jj})^{-\frac{1}{2}}$$

$$y_2 = \sum_{j>i=1}^p \Delta_{ij} \sum_{k=1}^p \left(\frac{\xi_k}{\xi} \right) \frac{(\sigma_{ii} \sigma_{jj})^{\frac{1}{2}}}{\sigma_{kk}}$$

$$y_3 = \left[\sum_{i=1}^p \left(\frac{\xi_i}{\xi} \right)^{\frac{2}{3}} x_i^{\frac{1}{3}} \right]^{\frac{2}{3}}$$

and

$$\Delta_{ij} = [(\xi_i \xi_j)^{\frac{1}{2}} / \xi] [(\sigma_{ii} - \sigma_{jj})^2] (x_i x_j)^{\frac{1}{2}}$$