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Perturbation and variational approach for the equation of state for hard-sphere and Lennard–Jones fluids

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The present work uses the concept of a scaled particle along with the perturbation and variation approach, to develop an equation of state (EOS) for a mixture of hard sphere (HS), Lennard–Jones (LJ) fluids. A suitable flexible functional form for the radial distribution function $G(R)$ is assumed for the mixture, with R as a variable. The function $G(R)$ has an arbitrary parameter m and a different equation of state can be obtained with a suitable choice of m. For $m = 0.75$ and $m = 0.83$ results are close to molecular dynamics (MD) result for pure HS and LJ fluid respectively.

Keywords: equation of state, Lennard–Jones potential, hard-sphere potential, liquid mixture, computer simulation

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1. Introduction

The hard sphere can serve as a basic reference system for many perturbation and variation theories.[1−9] With suitable approximations, bulk and structural properties of liquids may be studied. The two parameters σ and ϵ are related to molecular diameter and the binding energy respectively of the molecule. In perturbation and variation theories it is observed that at high temperatures only the repulsive part of potential is prominent, while at lower temperatures the attractive part becomes appreciable.

For pairwise additive intermolecular potentials, all the thermodynamic functions may be expressed in terms of the radial distribution functions (RDF). The expressions are particularly simple for hard-core fluids, since in that case the internal energy reduces to that of an ideal gas, while in the pressure equation it is only the contact values rather than the full RDF that appear explicitly. Therefore, knowledge of the contact values $g(\sigma)$ of the RDF in hard-core fluids where σ is the separation at the contact between the centers of two interacting fluid particles, is sufficient to obtain the equation of state (EOS) of these systems.

In the present formulation, the EOS and the expressions for the contact values of the RDF are determined in a unique way. The use of a precise and well-defined probability distribution function[10] in a perturbation theory opens up the possibility of deriving a closed theoretical scheme for the determination of thermodynamic properties of a more realistic model. The current formulation assumes surface tension as some arbitrary function of solute cavity radius R, solvent hard sphere radii S, and ϵ, as binding energy for a solute-solvent.

The present paper is organized as follows. In Subsection 2.1 the partition function approach is used to compute the probability distribution function and related is work done. Subsection 2.2 deals with the thermodynamic work done. The EOS and expression for surface tension have been derived using computer algebra. The necessary calculation is presented in Subsection 2.3. Section 3 is devoted to the results corresponding to different values of m. The last two sections are the discussion and conclusion pertaining to the derived EOS.

2. Theory

2.1. Partition function approach

2.1.1. Work done in pure liquid

An EOS for a molecular fluid may be expressed as

$$\frac{\beta P}{\rho} = 1 + 4\eta\, g(\sigma), \quad \eta = \frac{\pi}{6}\rho\sigma^3, \quad \beta = \frac{1}{k_{\rm B}T}, \quad (1)$$

where σ denotes a minimum separation distance between a pair of molecules. The factor $(\pi/6)\sigma^3$ is the

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volume of the sphere, $V = (4\pi/3)r_\infty^3 N$ is the volume of the system, r_∞ is the maximum separation distance between molecules, N is the Avogadro number, $\rho = N/V$ is the number density, T is the temperature, P is the pressure, η is space filling ratio and $k_{\rm B}$ is the Boltzmann's constant. Thus for spheres it is only necessary to find $g(\sigma)$ the radial distribution function. Reiss *et al.*[10] have developed a simple but accurate method, called scaled particle theory (SPT) for obtaining the radial distribution function and thus compressibility factor $\beta P/\rho$.

Let $p(\sigma)$ be the probability that there is no molecule whose center lies within a sphere of radius σ, centered about some specified point and the probability is defined[11–14] by the following equation

$$p(\sigma) = \frac{\displaystyle\int_0^{r_\infty} \mathrm{e}^{-\beta u(r)} 4\pi r^2 \,\mathrm{d}r}{\displaystyle\int_0^{r_\infty} 4\pi r^2 \,\mathrm{d}r}, \tag{2}$$

where $u(r)$ is the interaction pair-potential for single solute particle averaged over N solvent particles. $u(r)$ may be written as $u(r) = u_{\rm HS} + u_1(r)$

$$\begin{aligned} u(r) &= u_{\rm HS}, \quad r < \sigma; \\ u(r) &= u_1(r), \quad r \geq \sigma, \end{aligned} \tag{3}$$

and in the following Eq. (4), the hard sphere diameter is represented by σ

$$\begin{aligned} u_{\rm HS} &= \infty, \quad r < \sigma; \\ u_{\rm HS} &= 0, \quad r \geq \sigma. \end{aligned} \tag{4}$$

So that we have the following useful Heaviside function, which is related to radial distribution function for hard sphere interaction pair-potential,

$$e_0 = \exp(-\beta \cdot u_{\rm HS}) = \text{Heaviside}(s), \quad s = r - \sigma. \tag{5}$$

Over a hard sphere interaction, a perturbation part $u_1(r)$ of the interaction potential defined over these variables is in the following set of equations

$$u_1(r) = 4\epsilon[y^{-12} - y^{-6}], \quad y = r/d, \quad d = \alpha\sigma, \tag{6}$$

where α relates HS parameter σ to the corresponding LJ parameter d. This α is found to be related to surface tension property, and magnitude of critical temperature.

Now, the probability $p(\sigma)$ is expressed as the sum of the hard sphere and perturbing Lennard–Jones parts and from Eq. (2) it is given by the following equation

$$p(\sigma) = p_0(\sigma) + [\,p_1(\sigma) + p_2(\sigma)], \tag{7}$$

where

$$\begin{aligned} p_0(\sigma) &= \left[1 - \frac{\sigma^3}{r_\infty^3}\right] = \left[1 - \frac{4\pi}{3}\sigma^3\rho\right], \\ p_1(\sigma) &= -3\beta\epsilon\left[\frac{4}{9}\alpha^{12} - \frac{4}{3}\alpha^6\right]\left(\frac{\sigma^3}{r_\infty^3}\right) = f_1\beta\epsilon\frac{4\pi}{3}\sigma^3\rho, \\ p_2(\sigma) &= \frac{3}{2}\beta^2\epsilon^2\left[\frac{16}{21}\alpha^{24} - \frac{32}{15}\alpha^{18} + \frac{16}{9}\alpha^{12}\right]\left(\frac{\sigma^3}{r_\infty^3}\right) \\ &= f_2\beta^2\epsilon^2\frac{4\pi}{3}\sigma^3\rho, \\ f_1 &= -\frac{4}{3}\alpha^6(\alpha^6 - 3), \\ f_2 &= \frac{8}{105}\alpha^{12}(15\alpha^{12} - 42\alpha^6 + 35). \end{aligned}$$

This probability is worked out by removing unwanted higher order $O(\sigma^6)$ terms. Here $p_0(\sigma)$ is the probability corresponding to hard-sphere potential part and $p_1(\sigma)$ and $p_2(\sigma)$ terms are due to the remaining non-HS potential part. Now let $p(r)$ be the probability that there is no molecule whose center lies within a sphere of radius $r \leq \sigma/2$, centered about some specified point, in N solvent particles, and the probability Eq. (7) is given now by the following equation

$$p(r) = p_0(r) + [\,p_1(r) + p_2(r)], \quad r \leq \sigma/2, \tag{8}$$

where

$$\begin{aligned} p_0(r) &= 1 - N\left(\frac{r^3}{r_\infty^3}\right) = 1 - \left(\frac{4\pi}{3}\right)r^3\rho, \\ p_1(r) &= f_1\beta\epsilon\left(\frac{4\pi}{3}\right)r^3\rho, \\ p_2(r) &= f_2\beta^2\epsilon^2\left(\frac{4\pi}{3}\right)r^3\rho. \end{aligned}$$

A general expression for probability $p(r)$ will now be given below

$$\begin{aligned} p(r) &= 1 - f(\beta\epsilon)\left(\frac{4\pi}{3}\right)r^3\rho, \\ f(\beta\epsilon) &= [1 - f_1\beta\epsilon - f_2\beta^2\epsilon^2], \qquad r \leq \sigma/2. \end{aligned}$$

Hence, if we consider a cavity of volume $v = 4\pi r^3/3$ in a liquid having volume V and containing N molecules, the probability $p(v)$ of finding a molecule in cavity may be expressed as $p(v) = f(\beta\epsilon)v\rho$ and the probability of cavity being empty is $p_c = 1 - p(v)$. It is observed from Eq. (8) that for $r \leq \sigma/2$, $-\mathrm{d}p_0(r) = 4\pi\rho r^2\,\mathrm{d}r$ is the probability of finding a hard sphere whose radius lies between r and $r + \mathrm{d}r$. Hence we have the probability of finding a hard sphere whose radius lies between r and $r + \mathrm{d}r$ by the following relation,

i.e., the probability that a spherical shell contains the molecule may be represented as

$$-\mathrm{d}p(r) = f(\beta\epsilon)4\pi\rho r^2\,\mathrm{d}r. \tag{9}$$

Using packing density $\eta = (\pi/6)\rho\sigma^3$, yields the following expression for the probability $p(r)$ of finding an empty sphere of radius r

$$p(r) = p_0(r) + [\,p_1(r) + p_2(r)], \quad r \le \sigma/2,$$

with

$$p_0(r) = 1 - 8\eta\left(\frac{r}{\sigma}\right)^3,$$
$$p_1(r) = 8\eta f_1\beta\epsilon\left(\frac{r}{\sigma}\right)^3,$$
$$p_2(r) = 8\eta f_2\beta^2\epsilon^2\left(\frac{r}{\sigma}\right)^3.$$

For $r \le \sigma/2$, not more than one molecular center can lie within a sphere of radius r, for $\sigma/2 \le r \le 3^{1/2}\sigma$, two molecule centers can lie within the sphere, at $r = \sigma$, twelve molecule centers can lie within the cavity and, therefore $p_0(r)$ is equal to unity minus the probability of there being a molecular center within the sphere, which is the part of Eq. (9) and indirectly Eq. (2).

2.1.2. Work done and radial distribution function $g(R)$ in a liquid mixture

For a liquid mixture, in the above equation we are replacing,

$$r \longmapsto (R + S_j), \quad \eta \longmapsto \left(\frac{4\pi}{3}\right)\rho\mu_0,$$
$$\left[r \le \frac{\sigma}{2}\right] \longmapsto (R \le 0). \tag{10}$$

So that we have an expression for the probability for liquid mixture containing k-component liquid molecules as given below

$$p(R) = p_0(R) + [\,p_1(R) + p_2(R)], \quad R \le 0, \tag{11}$$

where

$$p_0(R) = 1 - \frac{\eta H(0,3)}{\mu_0}, \quad p_1(R) = \frac{f_1\beta\eta H(1,3)}{\mu_0},$$
$$p_2(R) = \frac{f_2\beta^2\eta H(2,3)}{\mu_0},$$

where function $H(p,q)$ is defined as follows:

$$H(p,q) = \sum_{j=1}^{j=k}[x_j\epsilon_j^p(R + S_j)^q],$$

$$h(p,q) = \sum_{j=1}^{j=k}(x_j\epsilon_j^p S_j^q), \quad x_j = \frac{N_j}{N}.$$

Here we are indirectly obtaining an additive nature for the physical properties at a molecular level, in liquid state

$$\theta_p = \sum_{j=1}^{j=k}(x_j\epsilon_j^p S_j), \quad \zeta_p = \sum_{j=1}^{j=k}(x_j\epsilon_j^p S_j^2),$$
$$\mu_p = \sum_{j=1}^{j=k}(x_j\epsilon_j^p S_j^3).$$

Now $-\mathrm{d}p(R)$ is the probability of finding an empty sphere (the molecule) whose radius lies between R and $R+\mathrm{d}R$. This is equal to the product of the probability $p(R)$ of having no molecule within the radius R and conditional probability, $\mathrm{d}p_\mathrm{c}(R) = G(R)(4\pi\ R^2\,\mathrm{d}R)$ of there being a center of at least one molecule within $\mathrm{d}R$ of R when no molecule is inside the sphere of radius R. The significance of $G(R)$ arises from the fact that an empty sphere of radius $R = \sigma$ affects the remainder of the fluid precisely like another molecule, i.e.

$$G(\sigma) = g(\sigma). \tag{12}$$

And, the probability that a spherical shell contains the molecule may be represented as given by the following expression

$$-\mathrm{d}p(R) = p(R)\,\mathrm{d}p_\mathrm{c}(R) = p(R)[G(R)4\pi\rho R^2\,\mathrm{d}R],$$
$$R \le 0. \tag{13}$$

Also, the basic relation[7] gives the reversible work $W(R)$ necessary to create a cavity of radius R in the real fluid

$$\beta W(R) = -\ln[p(R)], \quad R \le 0, \tag{14}$$

i.e.,

$$\frac{\mathrm{d}p}{p} = -\beta\,\mathrm{d}W(R).$$

It is to be noted that p, W, and G depend upon (R, η, β). However, for notational simplicity we do not show this dependence explicitly. Combining the above Eqs. (13) and (14) yields the following expression

$$\frac{\mathrm{d}p}{p} = -\beta\,\mathrm{d}W = -4\pi\rho G(R)R^2\,\mathrm{d}R = -\mathrm{d}p_\mathrm{c}(R),$$
$$R \le 0, \tag{15}$$

where, for conditional probability $\mathrm{d}p_\mathrm{c}(R)$, we have the corresponding required work as $\mathrm{d}W(R)$. For physical interpretation purpose, this reversible work $W(R)$ is obtained from Eq. (14) only and reversible work is

split into W_0 term and remaining perturbing terms as given by the following equation

$$W(R) = W_0(R) + [W_1(R) + W_2(R)] + O(\eta^2), \quad R \le 0, \tag{16}$$

where

$$\beta W_0(R) = -\ln\left[1 - \frac{\eta H(0,3)}{\mu_0}\right],$$
$$\beta W_1(R) = -\frac{f_1\beta\eta H(1,3)}{\mu_0},$$
$$\beta W_2(R) = -\frac{f_2\beta^2\eta H(2,3)}{\mu_0}.$$

Here $W_0(R)$ is the reversible work corresponding to the hard sphere potential part and $[W_1(R),\ W_2(R)]$ are the reversible work done due to the remaining potential part.

Expression $\mathrm{d}W(R)$ can be easily related to work done against the external force (pressure) and internal force (surface tension). Again the above expression is built-up by removing higher order η terms, then only it leads to a unique set of critical constants for thermodynamic variables (P, V, T) in the present formulation.

The present expression for work done from partition function approach is approximated in Taylor finite polynomial for a single solute particle having cavity radius R in m-solvent. The above equation is given below

$$W(R) = \left[W(0) + \left(\frac{\mathrm{d}W}{\mathrm{d}R}\right)_{R=0} R + \left(\frac{\mathrm{d}^2W(R)}{\mathrm{d}R^2}\right)_{R=0} \frac{R^2}{2}\right], \quad R \le 0, \tag{17}$$

where,

$$W(0) = [W_0(0) + W_1(0) + W_2(0)],$$
$$\left(\frac{\mathrm{d}W}{\mathrm{d}R}\right)_{R=0} = \left[\left(\frac{\mathrm{d}W_0(R)}{\mathrm{d}R}\right)_{R=0} + \left(\frac{\mathrm{d}W_1(R)}{\mathrm{d}R}\right)_{R=0} + \left(\frac{\mathrm{d}W_0(R)}{\mathrm{d}R}\right)_{R=0}\right],$$
$$\left(\frac{\mathrm{d}^2W(R)}{\mathrm{d}R^2}\right)_{R=0} = \left[\left(\frac{\mathrm{d}^2W_0(R)}{\mathrm{d}R^2}\right)_{R=0} + \left(\frac{\mathrm{d}^2W_1(R)}{\mathrm{d}R^2}\right)_{R=0} + \left(\frac{\mathrm{d}^2W_2(R)}{\mathrm{d}R^2}\right)_{R=0}\right],$$
$$\beta W_0(0) = -\ln(1-\eta), \quad \beta W_1(0) = -\frac{f_1\beta\eta\mu_1}{\mu_0},$$
$$\beta W_2(0) = -\frac{f_2\beta^2\eta\mu_2}{\mu_0},$$
$$\left(\frac{\mathrm{d}\beta W_0(R)}{\mathrm{d}R}\right)_{R=0} = \frac{3\eta\zeta_0}{\mu_0(1-\eta)},$$
$$\left(\frac{\mathrm{d}\beta W_1(R)}{\mathrm{d}R}\right)_{R=0} = -\frac{3f_1\beta\eta\zeta_1}{\mu_0},$$
$$\left(\frac{\mathrm{d}\beta W_2(R)}{\mathrm{d}R}\right)_{R=0} = -\frac{3f_2\beta^2\eta\zeta_2}{\mu_0},$$
$$\frac{1}{2}\left(\frac{\mathrm{d}^2\beta W_0(R)}{\mathrm{d}R^2}\right)_{R=0} = \frac{3\eta\theta_0}{\mu_0(1-\eta)} + \frac{9\eta^2\zeta_0^2}{2\mu_0^2(1-\eta)^2},$$
$$\frac{1}{2}\left(\frac{\mathrm{d}^2\beta W_1(R)}{\mathrm{d}R^2}\right)_{R=0} = -\frac{3f_1\beta\eta\theta_1}{\mu_0},$$
$$\frac{1}{2}\left(\frac{\mathrm{d}^2\beta W_2(R)}{\mathrm{d}R^2}\right)_{R=0} = -\frac{3f_2\beta^2\eta\theta_2}{\mu_0}.$$

From Eq. (1) the compressibility factor Z and radial distribution function $g(R)$, from the partition function approach for any fluid is given below

$$Z = \frac{\beta P}{\rho} = 1 + 4\eta g(\sigma). \tag{18}$$

Here function $g(R)$ denotes radial distribution function from partition function approach, and $g(\sigma)$ can be easily obtained from the following equation

$$g(R) = [g_0(R) + g_1(R) + g_2(R)] = \frac{1}{\rho}\frac{[\partial\beta W(R)/\partial R]}{[\partial V/\partial R]}, \quad R \le 0, \tag{19}$$

where ρ denotes the number density in a liquid mixture

$$\rho = \frac{3\eta}{(4\pi\mu_0)} = \frac{\eta}{V(0)},$$
$$A(R) = 4\pi H(0,2) = \text{area},$$
$$V(R) = \left(\frac{4\pi}{3}\right) H(0,3) = \text{volume}.$$

Hence a simple form of radial distribution function $g(R)$ is given below,

$$g(R) = \frac{1}{\rho}\frac{\partial\beta W(R)}{\partial V} = \frac{(wr + 2wsR)\mu_0}{3\eta H(0,2)}, \tag{20}$$

where

$$wr = \left(\frac{\mathrm{d}\beta W(R)}{\mathrm{d}R}\right)_{R=0}, \quad ws = \frac{1}{2}\left(\frac{\mathrm{d}^2\beta W(R)}{\mathrm{d}R^2}\right)_{R=0}.$$

For continuity, i.e., writing an expression for tangent at $R = 0$ for $g(R)$, we have the following equations

$$g(R)_{\text{tangent}} = \left(\left[g(R)\right]_{R=0} + \left[\frac{\mathrm{d}g(R)}{\mathrm{d}R}\right]_{R=0} R\right), \quad R \le 0, \tag{21}$$
$$[g(R)]_{R=0} = [g_0(R)]_{R=0} + [g_1(R)]_{R=0} + [g_2(R)]_{R=0},$$
$$\left[\frac{\mathrm{d}g(R)}{\mathrm{d}R}\right]_{R=0} = \left[\frac{\mathrm{d}g_0(R)}{\mathrm{d}R}\right]_{R=0} + \left[\frac{\mathrm{d}g_1(R)}{\mathrm{d}R}\right]_{R=0} + \left[\frac{\mathrm{d}g_2(R)}{\mathrm{d}R}\right]_{R=0},$$

where

$$[\,g_k(R)]_{R=0} = \frac{\mu_0}{3\eta\zeta_0}\left[\frac{\mathrm{d}\beta W_k(R)}{\mathrm{d}R}\right]_{R=0}, \quad k=(0,1,2),$$
$$\left[\frac{\mathrm{d}g_k(R)}{\mathrm{d}R}\right]_{R=0} = -\frac{2}{3}\frac{\mu_0}{\eta\zeta_0^2}\Bigg(-\zeta_0\left[\frac{1}{2}\frac{\mathrm{d}^2\beta W_k(R)}{\mathrm{d}R^2}\right]_{R=0} + \theta_0\left[\frac{\mathrm{d}\beta W_k(R)}{\mathrm{d}R}\right]_{R=0}\Bigg), \; k=(0,1,2).$$

2.2. Thermodynamic function approach for work done and radial distribution function $G(R)$

Now for liquid mixtures a general expression for work done for positive $\mathrm{d}V$ and $\mathrm{d}A$ against external force (pressure) and internal force (surface tension) is given as follows:

$$\mathrm{d}W(R) = P\mathrm{d}V - S\mathrm{d}A = k_BT\rho G(R)\mathrm{d}V, \quad R \geq 0, \tag{22}$$

where we introduce the minus sign because $P\mathrm{d}V$, is work done due to external/internal forces while $S\mathrm{d}A$, is the work done due to internal/external forces ($S=$ surface tension, $A=$ surface area, and $V=$ volume of the system) so that reference potential (hard sphere) along with perturbing potential LJ contributes an effective positive value for surface tension S, for real fluid. Hard sphere potential contributes much more as compared to the perturbing potential part. The above sign convention always leads to correct sign prediction for surface tension and it does not require following logic, i.e., ***the hard sphere fluid has no attractive forces and so can be maintained at finite volume only by means of an external pressure***. Therefore, we have radial distribution function $G(R)$ as given below

$$G(R) = \frac{1}{\rho}\frac{\partial\beta W}{\partial V} = \frac{\beta}{\rho}\left[P + S(R)\frac{\partial A(R)}{\partial V}\right], \quad A=A(R), \;\; V=V(R), \;\; R\geq 0, \tag{23}$$

where

$$S(R)\frac{\partial A}{\partial V} = 2\left[\frac{AH(0,1)}{\theta_0 H(0,2)} - \frac{mB}{H(0,2)} + \frac{(1-m)B}{\zeta_0}\right]\frac{\rho\zeta_0}{\beta}.$$

The thermodynamic property surface tension $S(R)$ defined in terms of dimensionless A and B is shown that the function $G(R)$ is universal in the sense that it is a common function for all the pairs, regardless of the composition and number of components of the mixture. Of course, the function $G(R)$ is different for an assumed value of m.

For $m=0.75$ and $m=0.83$ we obtain good EOS which is close to the MD result. Now the authors shortly elaborate on the basis of the present different choice of parameter m. It has been observed[15] that the different EOSs that can be obtained for HS fluid are $m=1$ for SPT, and $m=0$ for PY(P), $m=4/5$ for numerically close CS, and lastly $m=3/4$ for the MD result. The limiting behavior of the thermodynamic radial distribution function yields the following important result

$$G(\infty) \approx \frac{\beta P}{\rho}, \;\; m\neq 1, \;\; G(\infty) = \frac{\beta P}{\rho}, \;\; m=1. \tag{24}$$

Now this thermodynamic radial distribution function $G(R)$ for a solute cavity radius is equal to solvent radius $S_j=(\sigma/2)$

$$\big[R=S_j\big] \longmapsto \big[R=S_j\cdot ge\big]. \tag{25}$$

Replacing R by $S_j\cdot ge$ in Eq. (23) we obtain

$$G = \frac{\beta P}{\rho} + \frac{2A}{(ge+1)} - \frac{2mB}{(ge+1)^2} + 2B - 2Bm, \tag{26}$$

where $ge(R)$ is seen to be a self-consistent function from Table 1

$$\ln\big[\,e(R)\big] = -k[\,\beta W_1(R) + \beta W_2(R)], \quad k=(\eta\beta\epsilon)_{\mathrm{c}}. \tag{27}$$

And for $R=0$, ge is given below

$$\ln(ge) = [k\eta(\beta\epsilon f_1 + (\beta\epsilon)^2 f_2)], \quad k=(\eta\beta\epsilon)_{\mathrm{c}}.$$

Note that if $k=0$ then ge is density- and temperature-independent and the original condition Eq. (25) is restored. This substitution modifies the final result for $\beta P/\rho$ which improves upon the second order Barker–Henderson perturbation theory result.

The significance of the thermodynamic radial distribution function $G(R)$ arises from the fact that an empty sphere of radius R affects the remainder of the fluid precisely like another molecule. Now the RDF from the partition function approach is congruent to that from the thermodynamic approach, first imposing condition $g(\sigma)=G(\sigma)$ on basic Eq. (1), we have the following equation

$$Z = \frac{\beta P}{\rho} = 1 + 4\eta G(\sigma). \tag{28}$$

Solving for Z and G and on rearranging we obtain

$$Z = z_0 + Az_a + Bz_b, \tag{29}$$

$$z_0 = \frac{-1}{(-1+4\eta)}, \quad z_a = \frac{-8\eta}{(-1+4\eta)(ge+1)},$$
$$z_b = \frac{-8\eta}{(-1+4\eta)} + \frac{8\eta(ge^2+2ge+2)m}{(ge+1)^2(-1+4\eta)}.$$

And the physical contact RDF is given by the following equation

$$G(R) = \left[\frac{-8\eta}{(-1+4\eta)(ge+1)} + \frac{2H(0,1)\zeta_0}{\theta_0 H(0,2)}\right]A + \left[\frac{-8\eta}{(-1+4\eta)} + \frac{8\eta(ge^2+2ge+2)m}{(ge+1)^2(-1+4\eta)} + 2\left(-\frac{m}{H(0,2)} + \frac{(1-m)}{\zeta_0}\right)\zeta_0\right]B - \frac{1}{(-1+4\eta)}, \quad R \geq 0.$$

For continuity of RDF, writing an expression for tangent at $R \geq 0$ for $G(R)$ we have

$$G(R)_{\text{tangent}} = \left([G(R)]_{R=0} + \left[\frac{\mathrm{d}G(R)}{\mathrm{d}R}\right]_{R=0} R\right), \quad R \geq 0, \tag{30}$$
$$[G(R)]_{R=0} = [\,g_0(R)]_{R=0} + [\,g_1(R)]_{R=0} A + [\,g_2(R)]_{R=0} B,$$

where

$$[\,g_0(R)]_{R=0} = -\frac{1}{(-1+4\eta)}, \quad [\,g_1(R)]_{R=0} = \frac{2(-ge-1+4\eta ge)}{(-1+4\eta)(ge+1)},$$
$$[\,g_2(R)]_{R=0} = -\frac{2(4\eta mge^2+8\eta mge+ge^2+2ge+1-2mge^2-4mge-2m)}{(-1+4\eta)(ge+1)^2},$$
$$\left[\frac{\mathrm{d}G(R)}{\mathrm{d}R}\right]_{R=0} = \left[\frac{\mathrm{d}g_0(R)}{\mathrm{d}R}\right]_{R=0} + \left[\frac{\mathrm{d}g_1(R)}{\mathrm{d}R}\right]_{R=0} A + \left[\frac{\mathrm{d}g_2(R)}{\mathrm{d}R}\right]_{R=0} B,$$

and

$$\left[\frac{\mathrm{d}g_0(R)}{\mathrm{d}R}\right]_{R=0} = 0, \quad \left[\frac{\mathrm{d}g_1(R)}{\mathrm{d}R}\right]_{R=0} = -\frac{2(-\zeta_0+2\theta_0^2)}{\zeta_0\theta_0}, \quad \left[\frac{\mathrm{d}g_2(R)}{\mathrm{d}R}\right]_{R=0} = \frac{4m\theta_0}{\zeta_0}.$$

2.3. EOS and thermodynamic properties in terms of dimensionless *A* and *B* terms

Here we use the following hard sphere approximation of the SPT, (partition function approach) that for $R \leq 0$

$$g(R)_{\text{tangent}} = \left([g(R)]_{R=0} + \left[\frac{\mathrm{d}g(R)}{\mathrm{d}R}\right]_{R=0} R\right), \quad R \leq 0. \tag{31}$$

From the thermodynamic approach, for $R \geq 0$ we have the following expression

$$G(R)_{\text{tangent}} = \left([G(R)]_{R=0} + \left[\frac{\mathrm{d}G(R)}{\mathrm{d}R}\right]_{R=0} R\right), \quad R \geq 0. \tag{32}$$

On the condition that the RDF is to be continuous at a contact point $g(R)_{\text{tangent}} = G(R)_{\text{tangent}}$ on solute molecular surface, then the difference of RDF is given by equation

$$[\,g(R) - G(R)] = 0, \quad R = 0, \tag{33}$$

where

$$[\,g(R) - G(R)]$$
$$= \left(-[\,g_1(R)]_{R=0} - \left[\frac{\mathrm{d}g_1(R)}{\mathrm{d}R}\right]_{R=0} R\right) A + \left(-[\,g_2(R)]_{R=0} - \left[\frac{\mathrm{d}g_2(R)}{\mathrm{d}R}\right]_{R=0} R\right) B - [\,g_0(R)]_{R=0} - \left[\frac{\mathrm{d}g_0(R)}{\mathrm{d}R}\right]_{R=0} R + \frac{\mu_0}{3\eta\zeta_0}\left[\frac{\mathrm{d}\beta W_0(R)}{\mathrm{d}R}\right]_{R=0} - \frac{2\mu_0}{3\eta\zeta_0^2}\left[\theta_0\left(\frac{\mathrm{d}\beta W_0(R)}{\mathrm{d}R}\right)_{R=0} - \frac{\zeta_0}{2}\left(\frac{\mathrm{d}^2\beta W_0(R)}{\mathrm{d}R^2}\right)_{R=0}\right]R + \frac{\mu_0}{3\eta\zeta_0}\left[\frac{\mathrm{d}\beta W_1(R)}{\mathrm{d}R}\right]_{R=0} - \frac{2\mu_0}{3\eta\zeta_0^2}\left[\theta_0\left(\frac{\mathrm{d}\beta W_1(R)}{\mathrm{d}R}\right)_{R=0} - \frac{\zeta_0}{2}\left(\frac{\mathrm{d}^2\beta W_1(R)}{\mathrm{d}R^2}\right)_{R=0}\right]R + \frac{\mu_0}{3\eta\zeta_0}\left[\frac{\mathrm{d}\beta W_2(R)}{\mathrm{d}R}\right]_{R=0} - \frac{2\mu_0}{3\eta\zeta_0^2}\left[\theta_0\left(\frac{\mathrm{d}\beta W_2(R)}{\mathrm{d}R}\right)_{R=0} - \frac{\zeta_0}{2}\left(\frac{\mathrm{d}^2\beta W_2(R)}{\mathrm{d}R^2}\right)_{R=0}\right]R,$$

and the gradient of the difference of RDF is given by the following equation

$$\frac{\partial[\,g(R)-G(R)]}{\partial R}=0,\qquad R=0, \tag{34}$$

where

$$\begin{aligned}
&\frac{\partial[\,g(R)-G(R)]}{\partial R}\\
&=-\left[\frac{\mathrm{d}g_1(R)}{\mathrm{d}R}\right]_{R=0}A-\left[\frac{\mathrm{d}g_2(R)}{\mathrm{d}R}\right]_{R=0}B\\
&\quad-\left[\frac{\mathrm{d}g_0(R)}{\mathrm{d}R}\right]_{R=0}-\frac{2\mu_0}{3\eta\zeta_0^2}\left[\theta_0\left(\frac{\mathrm{d}\beta W_0(R)}{\mathrm{d}R}\right)_{R=0}\right.\\
&\quad\left.-\frac{\zeta_0}{2}\left(\frac{\mathrm{d}^2\beta W_0(R)}{\mathrm{d}R^2}\right)_{R=0}\right]\\
&\quad-\frac{2\mu_0}{3\eta\zeta_0^2}\left[\theta_0\left(\frac{\mathrm{d}\beta W_1(R)}{\mathrm{d}R}\right)_{R=0}\right.\\
&\quad\left.-\frac{\zeta_0}{2}\left(\frac{\mathrm{d}^2\beta W_1(R)}{\mathrm{d}R^2}\right)_{R=0}\right]\\
&\quad-\frac{2\mu_0}{3\eta\zeta_0^2}\left[\theta_0\left(\frac{\mathrm{d}\beta W_2(R)}{\mathrm{d}R}\right)_{R=0}\right.\\
&\quad\left.-\frac{\zeta_0}{2}\left(\frac{\mathrm{d}^2\beta W_2(R)}{\mathrm{d}R^2}\right)_{R=0}\right].
\end{aligned}$$

Expressions for $[\,g(R)-G(R)]$ and $\partial[\,g(R)-G(R)]/\partial R)$ were obtained by computer algebra. The functional form of $[\,g(R)-G(R)]=0$ and $\partial[\,g(R)-G(R)]/\partial R=0$ at $R=0$ using substitution in terms of θ_p and ζ_p leads to simplification $[\,g(R)-G(R)]$ and $\partial[\,g(R)-G(R)]/\partial R$ in terms of the equation

$$\begin{aligned}
&[\,g(R)-G(R)]_{R=0}=0,\\
&\left[\frac{\partial[\,g(R)-G(R)]}{\partial R}\right]_{R=0}=0,
\end{aligned} \tag{35}$$

where

$$\begin{aligned}
&[\,g(R)-G(R)]_{R=0}\\
&=-[\,g_0(R)]_{R=0}-[\,g_1(R)]_{R=0}A-[\,g_2(R)]_{R=0}B\\
&\quad+\frac{\mu_0}{3\eta\zeta_0}\left[\frac{\mathrm{d}\beta W_0(R)}{\mathrm{d}R}\right]_{R=0}+\frac{\mu_0}{3\eta\zeta_0}\left[\frac{\mathrm{d}\beta W_1(R)}{\mathrm{d}R}\right]_{R=0}\\
&\quad+\frac{\mu_0}{3\eta\zeta_0}\left[\frac{\mathrm{d}\beta W_2(R)}{\mathrm{d}R}\right]_{R=0},
\end{aligned}$$

and

$$\begin{aligned}
&\left[\frac{\partial[\,g(R)-G(R)]}{\partial R}\right]_{R=0}\\
&=-\left[\frac{\mathrm{d}g_0(R)}{\mathrm{d}R}\right]_{R=0}-\left[\frac{\mathrm{d}g_1(R)}{\mathrm{d}R}\right]_{R=0}A\\
&\quad-\left[\frac{\mathrm{d}g_2(R)}{\mathrm{d}R}\right]_{R=0}B-\frac{2}{3}\frac{\mu_0}{\eta\zeta_0^2}\left(\theta_0\left[\frac{\mathrm{d}\beta W_0(R)}{\mathrm{d}R}\right]_{R=0}\right.\\
&\quad\left.-\zeta_0\left[\frac{1}{2}\frac{\mathrm{d}^2\beta W_0(R)}{\mathrm{d}R^2}\right]_{R=0}\right)\\
&\quad-\frac{2}{3}\frac{\mu_0}{\eta\zeta_0^2}\left(\theta_0\left[\frac{\mathrm{d}\beta W_1(R)}{\mathrm{d}R}\right]_{R=0}\right.\\
&\quad\left.-\zeta_0\left[\frac{1}{2}\frac{\mathrm{d}^2\beta W_1(R)}{\mathrm{d}R^2}\right]_{R=0}\right)\\
&\quad-\frac{2}{3}\frac{\mu_0}{\eta\zeta_0^2}\left(\theta_0\left[\frac{\mathrm{d}\beta W_2(R)}{\mathrm{d}R}\right]_{R=0}\right.\\
&\quad\left.-\zeta_0\left[\frac{1}{2}\frac{\mathrm{d}^2\beta W_2(R)}{\mathrm{d}R^2}\right]_{R=0}\right).
\end{aligned}$$

2.4. Thermodynamic properties of simple liquid mixture with different value of (m,α)

The expression for A and B and thus the thermodynamic properties can be obtained by requiring that the RDF is to be continuous at a contact point, i.e.,

$$g(R)_{\text{tangent}}=G(R)_{\text{tangent}}. \tag{36}$$

Thus the resulting values for A and B are obtained by solving $[\,g(R)-G(R)]_{R=0}=0$ and $[\partial[\,g(R)-G(R)]/\partial R]_{R=0}=0$. The resulting values for liquid mixture are given below

$$A=-(A_0+A_1),\qquad B=-(B_0+B_1). \tag{37}$$

The general thermodynamic EOS for model fluid mixture becomes

$$\frac{\beta P}{\rho}=Z=Z_0+Z_1. \tag{38}$$

Note that reference terms A_0, B_0, Z_0 do not contain parameter (an appendix for mixture) α but depend upon choice of m. But higher order terms A_1, B_1, Z_1 depend upon m as well as α.

3. Results

Here we consider algebraically important cases for different values of m and the corresponding EOSs are given below. We first discuss the special case for pure liquid.

For a pure liquid, i.e., the single component liquid, the resulting simplification can be obtained by substituting

$$\begin{aligned}
\theta_p&=\sum_{j=1}^{j=k}(x_j\epsilon_j^pS_j)=\epsilon^pS,\\
\zeta_p&=\sum_{j=1}^{j=k}(x_j\epsilon_j^pS_j^2)=\epsilon^pS^2,\\
\mu_p&=\sum_{j=1}^{j=k}(x_j\epsilon_j^pS_j^3)=\epsilon^pS^3,
\end{aligned} \tag{39}$$

which yields the following new result for the EOS $(\beta P/\rho) = Z$, and the thermodynamic property surface tension, etc. by the following equations

$$Z = (z_0 + z_1), \quad A = (a_0 + a_1), \quad B = (b_0 + b_1). \quad (40)$$

It is observed from the above z_0 term that it is totally generated through ge (an appendix for pure).

In the present study, we tabulate the variational approach result and the root-mean-square (rms) deviation for $Z = Z(ge)$ in Table 1 for different initial choices of ge, i.e., $[\eta_c, (\beta\epsilon)_c]$. It is observed that starting with initial guess 0.15 for η_c and 0.70 for $(\beta\epsilon)_c$ yields, for $m = 0.75$ the best EOS for HS fluid, while for $m = 0.83$ yields the best EOS for LJ fluid, at the end of the fourth choice. From Table 1, we conclude that the present predictor–corrector approach is auto-convergent in nature. After the third choice, corrections in η_c and $(\beta\epsilon)_c$ come out to be negligible showing self-consistency of the choice.

Table 1. Comparison of rms deviation in Z for LJ fluid, $\alpha = (3/2)^{1/6}$.

Series number	Choice	η_c	$(\beta\epsilon)_c$	rms deviation in Z
1	arbitrary	0.1500000000	0.7000000000	arbitrary value
2	first	0.1587167071	0.7489885407	0.04817327714
3	second	0.1584732838	0.7500937201	0.04115862631
4	third	0.1584734101	0.7500931460	0.04115240603
5	fourth	0.1584734100	0.7500931463	0.04115240879
6	fifth	0.1584734100	0.7500931463	0.04115240879

The algorithm used in deriving the present EOS gives the highest accuracy for the hard sphere part of fluid. The results computed are better than those found using Barker and Henderson's second-order perturbation approach. For better numerical closeness to the molecular dynamics Z (MD) result, the algorithm needs to be confined with a termination of the higher terms in the probability expression.

We have an EOS which is closer to Z (MD). $Z2$ (present) with critical constant corresponding to $m = 0.83$

$$\eta_c = 0.1584734100, \quad (\beta\epsilon)_c = 0.7500931463.$$

And $Z4$ (present) with critical constant corresponding to $m = 0.75$, which is selected from Table 4 as

$$\eta_c = 0.1552861210, \quad (\beta\epsilon)_c = 0.7458852046.$$

In the following Table 2, we have shown a different EOS for LJ fluid at critical temperature, where $Z1 = Z1$ (MD), $Z2 = Z2$ (present) with $m = 0.83$, $Z3 = Z3$ (BH2), $Z4 = Z4$ (present) with $m = 0.75$. In the present formulation, it is observed from Table 2 that $Z2$ (present), $Z3$ (BH2), and $Z4$ (present) have rms deviation = 0.041152, rms deviation = 0.041593, rms deviation = 0.054545 respectively, showing better closeness with computer simulation result $Z1$ (MD) than $Z3$ (BH2), a second-order Barker–Henderson perturbation theory.

Table 2. Comparison of EOS for LJ fluid at critical temperature.

Series number	η	$Z1$ (MD)	$Z2$ ($m = 0.83$)	$Z3$ (BH2)	$Z4$ ($m = 0.75$)
1	0.052	0.72	0.76	0.74	0.75
2	0.105	0.50	0.54	0.52	0.53
3	0.157	0.35	0.38	0.36	0.37
4	0.209	0.27	0.30	0.26	0.30
5	0.262	0.30	0.36	0.27	0.36
6	0.288	0.41	0.46	0.35	0.47
7	0.340	0.80	0.88	0.74	0.91
8	0.393	1.73	1.75	1.64	1.79
9	0.445	3.37	3.38	3.36	3.40
10	0.497	6.32	6.35	6.32	6.27

For HS fluid, let $Z1 = Z1$ (MD) for computer simulation, $Z2 = Z2$ (present) with $m = 0.83$, $Z3 = Z3$ (CS) = Carnahan–Starling, $Z4 = Z4$ (present) with $m = 0.75$, be denoting different EOS in Table 3. Again in the present formulation, it is observed from Table 3 that $Z4$ (present) has a better closeness with computer simulation result $Z1$ (MD). Hence we have to show the closeness of different Z as given below

$$Z2 \text{ (present)} < Z3 \text{ (CS)} < Z4 \text{ (present)} < Z1 \text{ (MD)}.$$

Table 3. Comparison of the EOS for HS fluid.

Series number	η	$Z1$ (MD)	$Z2$ ($m = 0.83$)	$Z3$ (CS)	$Z4$ ($m = 0.75$)
1	0.052	1.24	1.24	1.24	1.24
2	0.105	1.55	1.55	1.55	1.55
3	0.157	1.97	1.97	1.97	1.97
4	0.209	2.52	2.53	2.52	2.52
5	0.262	3.27	3.28	3.26	3.27
6	0.314	4.29	4.31	4.28	4.29
7	0.367	5.71	5.76	5.71	5.70
8	0.419	7.73	7.83	7.75	7.71
9	0.471	10.70	10.86	10.75	10.63
10	0.524	15.00	15.43	15.30	14.99

4. Discussion

In the present study, we tabulate in Table 4 the rms deviation for different choices of m. It is observed that for $m = 0.75$ it yields the best EOS for HS fluid while for $m = 0.83$ it yields the best EOS for LJ fluid

$$ge = \exp\left[k\eta\left(3\beta\epsilon + \frac{69}{70}(\beta\epsilon)^2\right)\right],$$
$$k = (\eta\beta\epsilon)_{\rm c} = \eta_{\rm c}\beta\epsilon_{\rm c} = 0.1188698187.$$

Table 4. Comparison of rms deviation for different EOSs for LJ fluid, $\alpha = (3/2)^{1/6}$.

Series number	m	$\eta_{\rm c}$	$(\beta\epsilon)_{\rm c}$	rms deviation in Z
1	0.75	0.1552861210	0.7458852046	0.05454500924
2	0.80	0.1572508244	0.7485042473	0.04378557233
3	0.82	0.1580620801	0.7495620551	0.04156998778
4	0.83	0.1584734100	0.7500931463	0.04115240879
5	0.84	0.1588886354	0.7506256963	0.04126606680
6	0.85	0.1593078292	0.7511597052	0.04194518893

Now we tabulate in Table 5 the rms deviation for different choices of m. It is observed that for $m = 0.80$ it yields relative good EOS for LJ fluid, but inferior to the above choice of α.

Table 5. Comparison of the rms deviation for different EOSs for LJ fluid, $\alpha = (3)^{1/6}$.

Series number	m	$\eta_{\rm c}$	$(\beta\epsilon)_{\rm c}$	rms deviation in Z
1	0.75	0.1564568791	0.3026944338	0.1815110862
2	0.80	0.1584527015	0.3032335093	0.1812756290
3	0.82	0.1592758586	0.3034492333	0.1813953479
4	0.83	0.1596929937	0.3035570915	0.1815034442
5	0.84	0.1601139165	0.3036649387	0.1816445138
6	0.85	0.1605386913	0.3037727682	0.1818191911

Again we tabulate the rms deviation in Table 6 for different choices of m. Here also it is observed that for $m = 0.75$ it yields a relative good EOS for LJ fluid, but inferior to the above choice of α, but it yields the relatively best EOS for HS fluid.

Table 6. Comparison of the rms deviation for different EOSs for LJ fluid, $\alpha = (1)^{1/6}$.

Series number	m	η_c	$(\beta\epsilon)_c$	rms deviation in Z
1	0.73	0.1541921766	0.8716459807	0.07219640197
2	0.74	0.1545692676	0.8722948020	0.07165544852
3	0.75	0.1549496819	0.8729458482	0.07141192348
4	0.76	0.1553334776	0.8735991318	0.07148996395
5	0.77	0.1557207144	0.8742546654	0.07191116119

The present mixing rules (additive rules for mixture) are not coupled with any axiomatic relations but are the part of the EOS through the probability for cavity creation approximation which is introduced by Eq. (2) and its logical generalization in terms of $H(p, q)$. It is shown that it is possible to produce different analytic EOSs and the related thermodynamic property through A and B of pure liquids and liquid mixture from the central approximation through $G(R)$, which seems to be a generalized function as it gives different EOSs for different m. It is observed that binding energy $(\beta\epsilon)_c$ depends upon the choice of parameter α, whereas space filling ratio $(\eta)_c$ is independent of the choice of parameter α.

In this paper we have introduced a universality assumption, in thermodynamic radial distribution function $G(R)$, for the contact values of the RDF of a hard-sphere LJ mixture with arbitrary number of components and arbitrary m. Continuity conditions allow us to fix the values of the universal function $G(R)$ at $R = 0$ in terms of the contact value of RDF. This implies that reasonable m-parameter form of $G(R)$ as a function of R can provide a very good approximate representation of $g(\sigma)$ regardless of the number of components, provided a good EOS for the multicomponent fluid system is used.

We have illustrated one possibility with $m = 0.83$ for LJ fluid. In a special case (see Table 2, Table 3), they reduce to the HS results, while for $m = 0.75$ they represent an improvement over the Z (CS) values, in quantitative agreement with the simulation results for hard sphere mixtures. The relationship between the thermodynamic properties and the contact values of the RDF in hard-core fluids is in principle so straightforward that the importance of explicit and suitable approximations for the latter need to be hardly emphasized.

In multi-component hard-core systems it is certainly true that a more accurate contact value of the RDF leads directly to a better EOS. Our results in an earlier paper[12] indicate that [Table 3 compared the EOS for a binary mixture of hard spheres (R_1, R_2) with $x_1 = x_2 = 0.5$ mol, $R_2/R_1 = 3.0$, and Table 4 compared the ΔZ of a binary mixture of hard spheres with $x_1 = x_2 = 0.5$ mol, $R_2/R_1 = 3.0$ on page 491], due to the fact that for HS mixtures the EOS or equivalently the compressibility factor, involves a summation over species in which the different contact values are included, one does obtain a more accurate EOS. In fact, as exemplified in the case of hard-sphere mixtures, it is possible to obtain an exact EOS with $m = 0.75$ using the contact values of the RDF. In any event, in specific applications, it is only the contact values of the RDF that are required. In this respect, it is fair to conclude that our new proposals provide in general a reasonably accurate approximation to $G(R)$ as compared to the available simulation data! We hope the availability of the new explicit expressions for the contact values of the RDF of hard-core mixtures in terms of properly terminated expressions of probability distribution function and thermodynamic work done may serve as a further motivation to carry out yet more simulations of these systems.

A thorough study of the EOS for the LJ model was reported by Barker *et al.*,[16] using the Percus–Yevick energy equation route. They calculated the Helmholtz free energy of the system and then obtained other thermodynamic properties by using a numerical approach. The Barker–Henderson theory has the advantage of using the well-studied hard sphere potential as the reference system. It has the disadvantage that it is accurate only at low temperatures. The agreement with machine simulation result is good for Barker–Henderson second-order approximation, and in fact it is superior to the Percus–Yevick energy equation approach.[7] This has the effect of making the hard sphere diameter dependant on density as well as on temperature. At higher temperature, Weeks *et al.*[3] used Percus–Yevick values for the hard sphere system. Unfortunately, the replacement of the Percus–Yevick reference RDF by a more accurate one worsens the agreement with computer simulation results. Results for the old variational theory are best at lower tem-

perature, but tend to overestimate the values of Z at higher temperatures.

5. Conclusion

It is easy to estimate routine thermodynamic properties for a liquid mixture[17] with the help of simple additive rules as given below

$$h(p,1)=\theta_p,\quad h(p,2)=\zeta_p,\quad h(p,3)=\mu_p,\quad p=0,1,2.$$

Furthermore, the formulations of the analytic EOSs of pure liquid and liquid mixtures introduced in the present paper are simple enough to be used for different applications and they are accurate enough to take a place next to the scaled particle theory.

At the interface between HS and LJ potential $r=\sigma$ we have observed the impact of α on potential $u_1(r)$ and function $f_1(\alpha)$

$$u(\sigma)=u_1(\sigma)=4\epsilon\alpha^6(\alpha^6-1),\quad f_1(\alpha)=-\frac{4}{3}\alpha^6(\alpha^6-3).$$

As shown in Table 7, we have observed that for $\alpha^6=3/2$ we obtained the best EOS for LJ fluid and it is shown in Table 2.

Table 7. Variation of α on EOS for LJ fluid.

Series number	α^6	u_1/ϵ	f_1
1	1/2	−1	5/3
2	2/2	0	8/3
3	3/2	3	9/3
4	4/2	8	8/3
5	5/2	15	5/3
6	6/2	24	0/3

Though it is customary to use HS as a reference system, it need not be so, as shown here in the case of LJ system (Tables 2 and 3). The hard-sphere fluid need not be an excellent reference system for the properties of liquids, although firm conclusions could not be reached because of the presence of adjustable parameters in the HS approach itself. Computer simulation results can be obtained easily by introduction of ge which leads to close EOS for HS with $m=0.75$ and LJ fluid for $m=0.83$ respectively.

Appendix A: Appendix for mixture

$$A_0=\frac{(F_0+F_1\eta+F_2\eta^2)}{(G_0+G_1\eta)(1-\eta)^2},\qquad \text{(A1)}$$

where

$$\begin{aligned}
F_0&=0,\\
F_1&=-3\theta_0[-2m\theta_0\mu_0+2m\zeta_0^2-\zeta_0^2]\\
&\quad-3\theta_0[-2\zeta_0^2-4m\theta_0\mu_0+4m\zeta_0^2]ge\\
&\quad-3\theta_0[-2m\theta_0\mu_0+2m\zeta_0^2-\zeta_0^2]ge^2,\\
F_2&=-6\mu_0m\theta_0^2-3\theta_0[4m\theta_0\mu_0-8m\zeta_0^2]ge\\
&\quad-3\theta_0[2m\theta_0\mu_0-4m\zeta_0^2]ge^2,\\
G_0&=2\mu_0[-2m\zeta_0+\zeta_0+2m\theta_0^2-2\theta_0^2]\\
&\quad+2\mu_0[2\zeta_0+4m\theta_0^2-4\theta_0^2-4m\zeta_0]ge\\
&\quad+2\mu_0[-2m\zeta_0+\zeta_0+2m\theta_0^2-2\theta_0^2]ge^2,\\
G_1&=2\mu_0[-8m\theta_0^2+8m\zeta_0]ge+8\mu_0mge^2\zeta_0,\\
A_1&=\frac{(F_0+F_1\eta)}{(G_0+G_1\eta)},
\end{aligned}\qquad \text{(A2)}$$

where

$$\begin{aligned}
F_0&=-\theta_0[-\theta_0f_2\beta\zeta_2+\zeta_0f_2\beta\theta_2+f_2\beta\zeta_2m\theta_0+\zeta_0f_1\theta_1\\
&\quad-2\zeta_0f_2\beta\theta_2m+\theta_0f_1\zeta_1m-\theta_0f_1\zeta_1\\
&\quad-2\zeta_0f_1\theta_1m]\beta-\theta_0[2f_2\beta\zeta_2m\theta_0-4\zeta_0f_1\theta_1m\\
&\quad+2\zeta_0f_1\theta_1-2\theta_0f_2\beta\zeta_2+2\theta_0f_1\zeta_1m-2\theta_0f_1\zeta_1\\
&\quad+2\zeta_0f_2\beta\theta_2-4\zeta_0f_2\beta\theta_2m]\beta ge\\
&\quad-\theta_0[-\theta_0f_2\beta\zeta_2+\zeta_0f_2\beta\theta_2+f_2\beta\zeta_2m\theta_0\\
&\quad+\zeta_0f_1\theta_1-2\zeta_0f_2\beta\theta_2m+\theta_0f_1\zeta_1m\\
&\quad-\theta_0f_1\zeta_1-2\zeta_0f_1\theta_1m]\beta ge^2,\\
F_1&=-\theta_0[4\theta_0f_1\zeta_1m+4f_2\beta\zeta_2m\theta_0]\beta\\
&\quad-\theta_0[8\zeta_0f_2\beta\theta_2m+8\zeta_0f_1\theta_1m]\beta ge\\
&\quad-\theta_0[4\zeta_0f_2\beta\theta_2m+4\zeta_0f_1\theta_1m]\beta ge^2,\\
G_0&=\zeta_0[-2m\zeta_0+\zeta_0+2m\theta_0^2-2\theta_0^2]\\
&\quad+\zeta_0[2\zeta_0+4m\theta_0^2-4\theta_0^2-4m\zeta_0]ge\\
&\quad+\zeta_0[-2m\zeta_0+\zeta_0+2m\theta_0^2-2\theta_0^2]ge^2,\\
G_1&=\zeta_0[-8m\theta_0^2+8m\zeta_0]ge+4\zeta_0^2mge^2,\\
B_0&=\frac{(F_0+F_1\eta+F_2\eta^2)}{(G_0+G_1\eta)(1-\eta)^2},
\end{aligned}\qquad \text{(A3)}$$

where

$$\begin{aligned}
F_0&=0,\\
F_1&=[-3\theta_0\zeta_0^2+6\mu_0\theta_0^2-3\zeta_0\mu_0]\\
&\quad+[-6\theta_0\zeta_0^2+12\mu_0\theta_0^2-6\zeta_0\mu_0]ge\\
&\quad+[-3\theta_0\zeta_0^2+6\mu_0\theta_0^2-3\zeta_0\mu_0]ge^2,\\
F_2&=[3\zeta_0\mu_0-6\mu_0\theta_0^2]+[-12\mu_0\theta_0^2+12\theta_0\zeta_0^2+6\zeta_0\mu_0]ge\\
&\quad+[12\theta_0\zeta_0^2+3\zeta_0\mu_0-6\mu_0\theta_0^2]ge^2,\\
G_0&=2\mu_0[-2m\zeta_0+\zeta_0+2m\theta_0^2-2\theta_0^2]\\
&\quad+2\mu_0[2\zeta_0+4m\theta_0^2-4\theta_0^2-4m\zeta_0]ge
\end{aligned}$$

$$+ 2\mu_0[-2m\zeta_0 + \zeta_0 + 2m\theta_0^2 - 2\theta_0^2]ge^2,$$
$$G_1 = 2\mu_0[-8m\theta_0^2 + 8m\zeta_0]ge + 8m\mu_0\zeta_0 ge^2,$$
$$B_1 = \frac{(F_0 + F_1\eta)}{(G_0 + G_1\eta)}, \tag{A4}$$

where

$$\begin{aligned}
F_0 &= -\beta[f_1\zeta_1\zeta_0 - 2\zeta_0 f_2\beta\theta_2\theta_0 + f_2\beta\zeta_2\zeta_0 - 2\zeta_0 f_1\theta_1\theta_0] \\
&\quad - 2\beta[f_1\zeta_1\zeta_0 - 2\zeta_0 f_2\beta\theta_2\theta_0 + f_2\beta\zeta_2\zeta_0 \\
&\quad - 2\zeta_0 f_1\theta_1\theta_0]ge - \beta[f_1\zeta_1\zeta_0 - 2\zeta_0 f_2\beta\theta_2\theta_0 \\
&\quad + f_2\beta\zeta_2\zeta_0 - 2\zeta_0 f_1\theta_1\theta_0]ge^2, \\
F_1 &= -\beta[-4f_1\zeta_1\zeta_0 + 8f_2\beta\zeta_2\theta_0^2 - 4f_2\beta\zeta_2\zeta_0 \\
&\quad + 8f_1\zeta_1\theta_0^2] + [-\beta(-4f_1\zeta_1\zeta_0 + 8f_2\beta\zeta_2\theta_0^2 \\
&\quad - 4f_2\beta\zeta_2\zeta_0 + 8f_1\zeta_1\theta_0^2) - \beta(8\zeta_0 f_2\beta\theta_2\theta_0 \\
&\quad + 8\zeta_0 f_1\theta_1\theta_0 - 4f_2\beta\zeta_2\zeta_0 - 4f_1\zeta_1\zeta_0)]ge \\
&\quad - \beta[8\zeta_0 f_2\beta\theta_2\theta_0 + 8\zeta_0 f_1\theta_1\theta_0 \\
&\quad - 4f_2\beta\zeta_2\zeta_0 - 4f_1\zeta_1\zeta_0]ge^2, \\
G_0 &= 2\zeta_0[-2m\zeta_0 + \zeta_0 + 2m\theta_0^2 - 2\theta_0^2] \\
&\quad + 2\zeta_0[2\zeta_0 + 4m\theta_0^2 - 4\theta_0^2 - 4m\zeta_0]ge \\
&\quad + 2\zeta_0[-2m\zeta_0 + \zeta_0 + 2m\theta_0^2 - 2\theta_0^2]ge^2, \\
G_1 &= 2\zeta_0[-8m\theta_0^2 + 8m\zeta_0]ge + 8\zeta_0^2 mge^2,
\end{aligned}$$
$$Z_0 = \frac{(F_0 + F_1\eta + F_2\eta^2)}{(G_0 + G_1\eta)(1-\eta)^2}, \tag{A5}$$

where

$$\begin{aligned}
F_0 &= [-2\mu_0\theta_0^2 - 2\mu_0 m\zeta_0 + 2\mu_0 m\theta_0^2 + \zeta_0\mu_0] \\
&\quad + [2\zeta_0\mu_0 - 4\mu_0\theta_0^2 - 4\mu_0 m\zeta_0 + 4\mu_0 m\theta_0^2]ge \\
&\quad + [-2\mu_0\theta_0^2 - 2\mu_0 m\zeta_0 + 2\mu_0 m\theta_0^2 + \zeta_0\mu_0]ge^2, \\
F_1 &= [2\zeta_0\mu_0 - 4\mu_0\theta_0^2 - 4\mu_0 m\zeta_0 + 4\mu_0 m\theta_0^2] \\
&\quad + [4\zeta_0\mu_0 - 8\mu_0\theta_0^2]ge \\
&\quad + [4\mu_0 m\theta_0^2 + 2\zeta_0\mu_0 - 4\mu_0\theta_0^2]ge^2, \\
F_2 &= [6\mu_0 m\zeta_0 - 3\zeta_0\mu_0 + 6\mu_0\theta_0^2 - 6\mu_0 m\theta_0^2] \\
&\quad + [4\mu_0 m\zeta_0 + 12\mu_0\theta_0^2 - 4\mu_0 m\theta_0^2 \\
&\quad - 6\zeta_0\mu_0 - 12\theta_0\zeta_0^2]ge \\
&\quad + [2\mu_0 m\zeta_0 + 12m\theta_0\zeta_0^2 - 12\theta_0\zeta_0^2 + 6\mu_0\theta_0^2 \\
&\quad - 3\zeta_0\mu_0 - 6\mu_0 m\theta_0^2]ge^2, \\
G_0 &= \mu_0[-2m\zeta_0 + \zeta_0 + 2m\theta_0^2 - 2\theta_0^2] \\
&\quad + \mu_0[2\zeta_0 + 4m\theta_0^2 - 4\theta_0^2 - 4m\zeta_0]ge \\
&\quad + \mu_0[-2m\zeta_0 + \zeta_0 + 2m\theta_0^2 - 2\theta_0^2]ge^2, \\
G_1 &= \mu_0[-8m\theta_0^2 + 8m\zeta_0]ge + 4\mu_0 mge^2,
\end{aligned}$$
$$Z_1 = \frac{(F_0 + F_1\eta)}{(G_0 + G_1\eta)}, \tag{A6}$$

where

$$\begin{aligned}
F_0 &= 0, \\
F_1 &= -4\beta[f_2\beta\zeta_2\zeta_0 - 2f_1\zeta_1\theta_0^2 \\
&\quad + 2f_1\zeta_1\theta_0^2 m - 2f_2\beta\zeta_2 m\zeta_0 + f_1\zeta_1\zeta_0 \\
&\quad + 2f_2\beta\zeta_2\theta_0^2 m - 2f_1\zeta_1 m\zeta_0 - 2f_2\beta\zeta_2\theta_0^2] \\
&\quad - 4\beta[2f_2\beta\zeta_2\theta_0^2 m - 2\zeta_0 f_2\beta\theta_2\theta_0 \\
&\quad - 2f_2\beta\zeta_2 m\zeta_0 + 2f_1\zeta_1\theta_0^2 m - 2\zeta_0 f_1\theta_1\theta_0 \\
&\quad - 2f_2\beta\zeta_2\theta_0^2 + 2f_1\zeta_1\zeta_0 + 2f_2\beta\zeta_2\zeta_0 \\
&\quad - 2f_1\zeta_1 m\zeta_0 - 2f_1\zeta_1\theta_0^2]ge \\
&\quad - 4\beta[2\zeta_0 f_1\theta_1\theta_0 m - 2\zeta_0 f_1\theta_1\theta_0 - 2\zeta_0 f_2\beta\theta_2\theta_0 \\
&\quad - f_1\zeta_1 m\zeta_0 + 2\zeta_0 f_2\beta\theta_2\theta_0 m + f_2\beta\zeta_2\zeta_0 \\
&\quad + f_1\zeta_1\zeta_0 - f_2\beta\zeta_2 m\zeta_0]ge^2, \\
G_0 &= \zeta_0[-2m\zeta_0 + \zeta_0 + 2m\theta_0^2 - 2\theta_0^2] \\
&\quad + \zeta_0[2\zeta_0 + 4m\theta_0^2 - 4\theta_0^2 - 4m\zeta_0]ge \\
&\quad + \zeta_0[-2m\zeta_0 + \zeta_0 + 2m\theta_0^2 - 2\theta_0^2]ge^2, \\
G_1 &= \zeta_0[-8m\theta_0^2 + 8m\zeta_0]ge + 4\zeta_0^2 mge^2.
\end{aligned}$$

Appendix B: Appendix for pure

$$z_0 = \frac{(F_0 + F_1\eta + F_2\eta^2)}{(G_0 + G_1\eta)(1-\eta)^2}, \tag{B1}$$

where

$$\begin{aligned}
F_0 &= -ge^2 - 2ge - 1, \\
F_1 &= -2 - 4ge + (-2 + 4m)ge^2, \\
F_2 &= 3 - 6ge + (-9 + 8m)ge^2, \\
G_0 &= -ge^2 - 2ge - 1, \\
G_1 &= 4mge^2, \quad z_1 = \frac{(F_0 + F_1\eta)}{(G_0 + G_1\eta)},
\end{aligned} \tag{B2}$$

where

$$\begin{aligned}
F_0 &= 0, \\
F_1 &= -4\beta\epsilon(-f_2\beta\epsilon - f_1) - 4\beta\epsilon[-2f_1 - 2f_2\beta\epsilon]ge \\
&\quad - 4\beta\epsilon[-f_1 - f_2\beta\epsilon + f_2\beta\epsilon m + f_1 m]ge^2, \\
G_0 &= -ge^2 - 2ge - 1, \quad G_1 = 4mge^2, \\
a_0 &= \frac{(F_0 + F_1\eta + F_2\eta^2)}{(G_0 + G_1\eta)(1-\eta)^2},
\end{aligned} \tag{B3}$$

where

$$\begin{aligned}
F_0 &= 0, \quad F_1 = 3 + 6ge + 3ge^2, \\
F_2 &= 6mge^2 + 12mge - 6m, \\
G_0 &= -2ge^2 - 4ge - 2, \quad G_1 = 8mge^2, \\
a_1 &= \frac{(F_0 + F_1\eta)}{(G_0 + G_1\eta)},
\end{aligned} \tag{B4}$$

where

$$F_0 = \beta\epsilon m(f_1 + f_2\beta\epsilon) + 2\beta\epsilon m[f_1 + f_2\beta\epsilon]ge$$

$$+\beta\epsilon m[f_1+f_2\beta\epsilon]ge^2,$$
$$F_1=-4\beta\epsilon m(f_1+f_2\beta\epsilon)-8\beta\epsilon m[f_1+f_2\beta\epsilon]ge$$
$$-4\beta\epsilon m[f_1+f_2\beta\epsilon]ge^2,$$
$$G_0=-ge^2-2ge-1,\quad G_1=4mge^2,$$
$$b_0=\frac{(F_0+F_1\eta+F_2\eta^2)}{((G_0+G_1\eta)(1-\eta)^2)},\tag{B5}$$

where

$$F_0=0,\quad F_1=0,\quad F_2=-3+6ge+9ge^2,$$
$$G_0=-2ge^2-4ge-2,\quad G_1=8mge^2,$$
$$b_1=\frac{(F_0+F_1\eta)}{(G_0+G_1\eta)},\tag{B6}$$

where

$$F_0=\beta\epsilon(f_1+f_2\beta\epsilon)+2\beta\epsilon[f_1+f_2\beta\epsilon]ge$$
$$+\beta\epsilon[f_1+f_2\beta\epsilon]ge^2,$$
$$F_1=-4\beta\epsilon(f_1+f_2\beta\epsilon)-8\beta\epsilon[f_1+f_2\beta\epsilon]ge$$
$$-4\beta\epsilon[f_1+f_2\beta\epsilon]ge^2,$$
$$G_0=-2ge^2-4ge-2,\quad G_1=8mge^2.$$

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