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# AN IMPROVED FIRST-ORDER PERTURBATION THEORY OF SIMPLE FLUIDS USING HIGH TEMPERATURE APPROXIMATION AND RANDOM PHASE APPROXIMATION

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In this paper, we have examined accuracy of an improved form of the first-order perturbation theory of simple fluids. Theory consists of the first-order perturbation theory of high temperature approximation and the random phase approximation. Inclusion of the random phase approximation enhances applicability of the perturbation theory to much wider ranges of temperatures and densities, especially to low densities. Comparisons are made between theoretical predictions and accurate computer simulation results for pressure, residual Helmholtz free energy, residual internal energy and vapor/liquid phase equilibria of Lennard-Jones fluids. In general, theoretical predictions are in very good agreement with simulation results. The random phase approximation is responsible for predicting accurate Gibbs ensemble Monte Carlo simulation results for vapor/liquid phase equilibria using the same theory in both vapor and liquid phases.

*Keywords:* Computer simulation; random phase approximation; simple fluids

## 1. INTRODUCTION

In recent years, there has been renewed interest in accurately calculating thermodynamic properties and phase equilibria of simple fluids because of their application as the reference system in perturbation theories of molecular fluids and fluid mixtures [1–4], and also in the

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theory of associating fluids [5, 6]. They are often used to describe thermodynamic properties and structures of molecular fluids in an effective way. Among the various theoretical approaches now available [7], perturbation theory is one of the most accurate predictive methods for calculating thermodynamic properties of fluids and fluid mixtures.

Perturbation theory approach is based on the premise that the local structure in dense fluids is determined primarily by strong, short-range repulsive forces and that the structure is only slightly modified by weak, long-range attractive forces. Therefore, in perturbation theories the hard sphere fluid is taken as the reference and the weak attractive forces are taken as the perturbation. This approach has been exploited in different forms of perturbation theories of simple fluids [8–14].

One of the most reliable forms of the first-order perturbation theory of simple fluids was presented by Verlet and Weis [11]. In this theory, the Lennard-Jones (LJ) pair potential was divided into a reference part and a perturbation part using Weeks-Chandler-Andersen (WCA) criteria [10]. Reference part of the Helmholtz free energy was represented by the hard sphere fluid plus a first order contribution to the free energy of the reference fluid, which contains blip-integral. Perturbation part of the free energy was represented by the first-order term using high-temperature approximation [10]. However, in their calculations, Verlet and Weis [11] introduced several approximations in evaluating properties of the reference fluid and the first-order perturbation term of the full free energy. Therefore, that theory could not predict simulation results for thermodynamic properties accurately. Problem became more severe in dealing with nonideal fluid mixtures. Later, this theory was modified by Shukla *et al.* [13]. In this modified form of the perturbation theory, properties of the reference fluid and the first-order contribution to the free energy were determined more accurately. This theory was applied extensively to binary fluid mixtures [13]. However, this theory was also based on the high temperature approximation and involved some approximations in evaluating the properties of the reference fluid and also of the first-order perturbation term. Consequently, although it offered a significant improvement over the previous versions, it was not adequate enough to predict thermodynamic properties of the pure fluids at all conditions. Moreover, it could not describe the composition dependence of the excess properties in fluid mixtures adequately.

Subsequently, Shukla [14] presented an improved form of the above first-order perturbation theory of fluid mixtures (which can be directly applied to the pure fluids), again based on high temperature approximation. In this theory, properties of the reference fluid were determined accurately, and the reference term and the first-order perturbation term in the expansion of free energy were also evaluated accurately. The hard sphere diameter was determined in such a way that the blip-integral appearing in the first-order reference term vanished identically. Consequently, the reference free energy reduced to that of the hard sphere fluid. Properties of the hard sphere fluid were then calculated using an accurate equation of state [15]. Values of the hard sphere distribution function inside the core as well as outside the core were obtained accurately [14]. This theory, involved no approximations in calculating properties of the reference fluid or those of the first-order perturbation term. Extensive comparisons of theoretical results with computer simulation results showed that this form of the perturbation theory could describe thermodynamic properties of several highly nonideal fluid mixtures reliably, and it represented a significant improvement over the previous form of the first-order perturbation theory.

However, such a first-order perturbation theory of high temperature approximation is accurate only at high densities and cannot be accurate at low densities, because at low densities attractive forces play significant role. Therefore, this theory in its present form cannot describe adequately, for example, the vapor/liquid phase equilibria of the fluids.

In recent years, computer simulation technique has provided extensive and accurate results for thermodynamic properties, in general, and for the vapor/liquid phase equilibria, in particular, against which the accuracy of the theory can be tested unambiguously using the same potential function [16–18].

Purpose of the present investigation is to further modify the first-order perturbation theory of high temperature approximation [14] by incorporating in it the random phase approximation (RPA) [19] such that (1) it can describe thermodynamic properties of simple fluids over the much wider ranges of temperature and density, especially at sufficiently low densities, and (2) it can predict vapor/liquid phase equilibria of pure fluids accurately using the same theoretical equation in both vapor and liquid phases.

The paper is organized as follows. In Section 2, we describe briefly the modified perturbation theory and its generalization to low densities. Section 3 provides details on how to determine thermodynamic properties of the reference fluid and that of the full system. In Section 4, we present comparisons of theoretical predictions with simulation results for the pressure, Helmholtz free energy, internal energy and vapor-liquid phase equilibria. Finally, conclusions of our findings are presented in Section 5.

## 2. THEORY

In this section, we briefly review the form of intermolecular interactions and the perturbation theory of high temperature approximation together with the random phase approximation. We consider a pure fluid, in which intermolecular interactions are represented by the Lennard-Jones (LJ) pair potential given by

$$u^{\text{LJ}}(r) = 4\varepsilon [(\sigma/r)^{12} - (\sigma/r)^6] \quad (1)$$

where  $\sigma$  and  $\varepsilon$  are size and energy parameters in the pair potential, respectively, and  $r$  is the interatomic separation distance.

Following the WCA criteria [10], the pair potential  $u^{\text{LJ}}(r)$  is divided into a reference part  $u^0(r)$  and a perturbation part  $u^p(r)$ ,

$$u^0(r) = \begin{cases} u^{\text{LJ}}(r) + \varepsilon & \text{for } r \leq R_m \\ 0 & \text{for } r > R_m \end{cases} \quad (2)$$

$$u^p(r) = \begin{cases} -\varepsilon & \text{for } r \leq R_m \\ u^{\text{LJ}}(r) & \text{for } r > R_m \end{cases} \quad (3)$$

where  $R_m = 2^{1/6} \sigma$  is the distance to the minimum in the LJ pair potential.

According to the first-order perturbation theory [14], the residual Helmholtz free energy of the pure fluid is written as

$$\frac{A^{\text{res}}}{NkT} = \frac{A^{0,\text{res}}}{NkT} + \frac{A^1}{NkT} \quad (4)$$

where,  $A^{0,\text{res}}$  is the residual free energy of the reference fluid, and  $A^1$  is the first-order perturbation contribution to the free energy.  $N$  is total number of molecules,  $T$  is temperature, and  $k$  being Boltzmann's constant. We now expand the reference fluid free energy,  $A^{0,\text{res}}$ , about the hard sphere fluid using blip-function expansion and obtain

$$\frac{A^{0,\text{res}}}{NkT} = \frac{A^{\text{HS},\text{res}}}{NkT} + \frac{A^{0,1}}{NkT} \quad (5)$$

where,  $A^{\text{HS},\text{res}}$  is the free energy of hard sphere fluid, and  $A^{0,1}$  is the first-order term of the reference fluid given by

$$\frac{A^{0,1}}{NkT} = 2\pi\rho \Delta B \quad (6)$$

with the blip-integral,  $\Delta B$ ,

$$\Delta B = \int_d^{R_m} [1 - \exp(-u^0/kT)] g^{\text{HS}}(r) r^2 dr - \int_0^d \exp(-u^0/kT) y^{\text{HS}}(r) r^2 dr \quad (7)$$

In order to make the correction term  $A^{0,1}$  in eqn. (7) vanish identically and make the theory accurate, the hard sphere diameter is determined such that

$$\Delta B = 0 \quad (8)$$

Consequently, the free energy of the reference fluid (eqn. 5) reduces to that of the hard sphere fluid

$$\frac{A^{0,\text{res}}}{NkT} = \frac{A^{0,\text{HS}}}{NkT} \quad (9)$$

Now, the first-order term of the free energy,  $A^1$ , is expressed in terms of two contributions, one arising from the high temperature approximation (HTA) [14] and another arising from the random phase

approximation (RPA) [19],

$$\frac{A^1}{NkT} = \frac{A_{\text{HTA}}^1}{NkT} + \frac{A_{\text{RPA}}^1}{NkT} \quad (10)$$

where  $A_{\text{HTA}}^1$  is given by [14]

$$\begin{aligned} \frac{A_{\text{HTA}}^1}{NkT} = (2\pi\rho/kT) & \left\{ -\varepsilon \int_0^d \exp(-u^0(r)/kT) y^{\text{HS}}(r) r^2 dr \right. \\ & - \int_d^{R_m} [\varepsilon \exp(-u^0(r)/kT) + u^{1J}(r)] g^{\text{HS}}(r) r^2 dr \\ & \left. + \int_d^\infty u^{1J}(r) g^{\text{HS}}(r) r^2 dr \right\} \quad (11) \end{aligned}$$

and  $A_{\text{RPA}}^1$  is given by [19]

$$\frac{A_{\text{RPA}}^1}{NkT} = (2(2\pi)^3 \rho)^{-1} \left\{ \int (u^p(q) S(q)/kT) - \ln [1 + u^p(q) S(q)/kT] \right\} d\bar{q} \quad (12)$$

In eqn. (12),  $u^p(q)$  is the fourier transform of  $u^p(r)$

$$u^p(q) = \rho \int u^p(r) \exp(-i\bar{q} \cdot \bar{r}) d\bar{r} \quad (13)$$

and  $S(q)$  is the fourier transform of  $g^{\text{HS}}(r)$ ,

$$S(q) = 1 + \rho \int [g^{\text{HS}}(r) - 1] \exp(-i\bar{q} \cdot \bar{r}) d\bar{r} \quad (14)$$

In the above equations,  $\rho (= N/V)$  is number density,  $V$  is total volume,  $g^{\text{HS}}(r)$  and  $y^{\text{HS}}(r)$  are radial distribution function and background correlation function of the hard sphere fluid, respectively. Using eqns. (9) and (10) into eqn. (4), the residual Helmholtz free energy of the whole system is given by

$$\frac{A^{\text{res}}}{NkT} = \frac{A^{\text{HS.res}}}{NkT} + \frac{A_{\text{HTA}}^1}{NkT} + \frac{A_{\text{RPA}}^1}{NkT} \quad (15)$$

Eqn. (15) defines the free energy of the full system and is an improved form of the perturbation theory, henceforth referred to as PTH. The RPA term in Eqn. (15) is responsible for extending the applicability of the PTH over a wider range of temperature and density. When the RPA term is ignored, eqn. (15) reduces to the perturbation theory of high temperature approximation, here called PTH-HTA. In order to achieve sufficient numerical accuracy, calculation of the free energy are performed numerically. The advantage of this theory is that it can be directly extended to mixtures without invoking any mixing rules.

### 3. DETERMINATION OF THERMODYNAMIC PROPERTIES

In order to perform perturbation theory calculations, accurate values of the properties of the hard sphere fluid are required. Properties of the hard sphere fluid are determined using the procedure as described in detail elsewhere [14]. Free energy and chemical potential of the hard sphere fluid are obtained by an accurate equation of state [15]. Distribution functions of the hard sphere fluid are determined following the accurate method as described before [14]. Using only a single parameter in defining the distribution function inside the core ( $r < d$ ), this method gives the values of distribution functions at contact and also of  $g^{\text{HS}}(r)$  and  $y^{\text{HS}}(r)$ , accurately. These values are then used in eqns. (7) and (8) to determine the hard sphere diameter numerically. Once the properties of hard sphere fluid are known, free energy is evaluated from eqn. (15) together with eqns. (9), (11) and (12). To make numerical calculations sufficiently accurate, each  $g^{\text{HS}}$  is generated to  $6d$  at intervals of  $0.0125\text{\AA}$ . Numerical integrations are performed using 40-point Gauss quadrature formula. In numerical integrations, the cutoff distance  $r_c$  is always greater than  $6d$ . For  $r_c > 6d$ , the usual long-range corrections to thermodynamic properties are employed, with  $g^{\text{HS}} = 1$ . In determining the hard sphere diameters,  $g^{\text{HS}}(r)$  and  $y^{\text{HS}}(r)$  are computed to  $R_m$  and  $d$  respectively, using an interval of  $0.01\text{\AA}$ .

Other thermodynamic quantities are obtained numerically using the standard thermodynamic relationships. For example, pressure,  $P$ , residual internal energy,  $U^{\text{res}}$ , and residual chemical potential  $\mu^{\text{res}}$ , are



obtained from the following relations,

$$\frac{P}{\rho kT} = 1 + \rho^* \left( \partial \frac{(A^{\text{res}}/NkT)}{\partial \rho^*} \right), \quad (16)$$

$$\frac{U^{\text{res}}}{NkT} = -T^* \left( \partial \frac{(A^{\text{res}}/NkT)}{\partial T^*} \right), \quad (17)$$

$$\frac{\mu^{\text{res}}}{kT} = \frac{A^{\text{res}}}{NkT} + \rho^* \left( \partial \frac{(A^{\text{res}}/NkT)}{\partial \rho^*} \right) \quad (18)$$

with the reduced quantities,  $T^* = kT/\varepsilon$  and  $\rho^* = \rho\sigma^3$ . Numerical differentiations of the free energy are performed using a 7-point Lagrange polynomial.

It should be mentioned here that thermodynamic properties of simple pure Lennard-Jones fluids can be also determined reliably using the recently suggested equations of state [20, 21], because they are obtained by fitting several parameters to the accurate simulation results. These recent equations of state represent a significant improvement over the previously developed and the most commonly used equation of state for the LJ fluid due to Nicolas *et al.* [22]. However, equations of state cannot be used directly to calculate properties of the mixtures unless one invokes a mixing rule in the theory. Even today, mixing rules based on a rigorous theory are not available, and the ad-hoc mixing rules become usually inadequate in describing thermodynamic properties of highly nonideal fluid mixtures. On the other hand, the present form of perturbation theory can be directly extended to mixtures without any mixing rules.

#### 4. RESULTS AND DISCUSSION

In this section, we compare our theoretical predictions with computer simulation (CS) results for thermodynamic properties and phase equilibria. We have performed calculations for numerous fluids under different conditions. Since it is impossible to present all those results here, only a few selected results will be reported under extreme conditions. The purpose here is to check how accurately PTH can describe

simulation results for the pure fluids over a range of temperature and density. As mentioned in the previous section, KN EOS can represent simulation results accurately over a wide range of temperature and density of the pure fluids. Therefore, in our comparisons below we will frequently use KN EOS to represent simulation results.

Figure 1 presents a comparison between PTH predictions and simulation results [23] for the pressure as a function of density, at a subcritical temperature of the pure LJ fluid,  $T^* = kT/\epsilon = 0.928$ . In general, PTH agrees with simulation very well over the entire range of the fluid density,  $\rho^* = \rho\sigma^3$ . Also included in the figure are values of pressure determined from PTH-HTA. It is seen that the RPA term contributes substantially at low densities ( $\rho^* < 0.7$ ) at this temperature. Our results at other isotherms show that the effect of the RPA term decreases at higher temperatures, and this contribution becomes negligible at sufficiently high densities and high temperatures, as expected. At sufficiently low densities, RPA contribution improves the

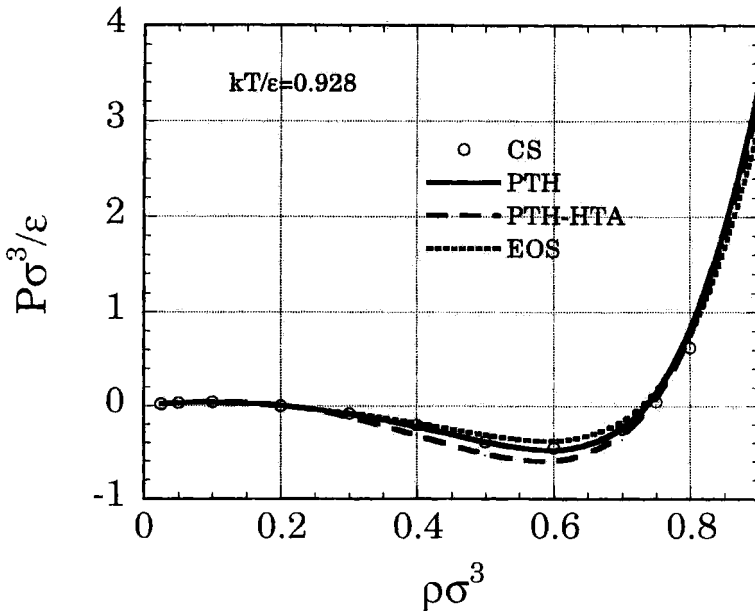


FIGURE 1 Pressure of pure LJ fluids as a function of density at a subcritical temperature from theory and computer simulation [23].

PTH results significantly. Also shown in the figure are values of the pressure obtained from KN EOS. As can be seen, both PTH and KN EOS agree well with simulation. We note that the effect of RPA is not seen at lower densities because we are comparing the total pressure, which is dominated by the ideal term. Thus, RPA effect is concealed by the ideal contribution to the pressure.

In order to demonstrate the effect of RPA in PTH more clearly, Figure 2 compares the results for residual Helmholtz free energy at a slightly higher temperature,  $kT/\epsilon = 1$ , over a range of density. In this comparison, it is assumed that simulation results can be given by KN EOS, i.e.,  $CS=KN$  EOS. As can be seen, PTH agrees very well with KN EOS. The comparison of PTH-HTA results with PTH results show clearly that the RPA contribution is significant at lower densities ( $\rho\sigma^3 < 0.7$ ), suggesting that the effect of attractive forces is very pronounced at low densities. Similar comparisons are made in Figures 3 and 4 for pressure and residual internal energy, respectively,

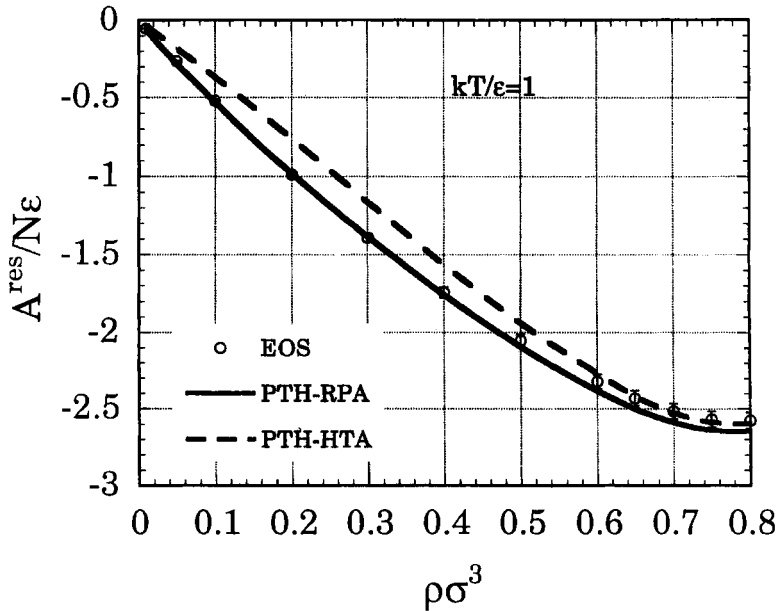


FIGURE 2 Pressure of pure LJ fluids as a function of density at a subcritical temperature from theory and equation of state [21].

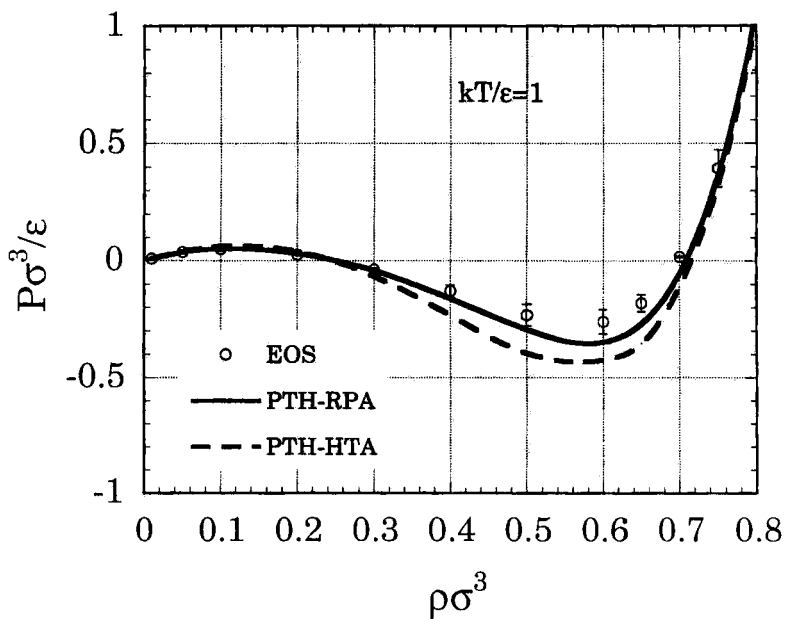


FIGURE 3 Residual internal energy of pure LJ fluids as a function of density at a subcritical temperature from theory and equation of state [21].

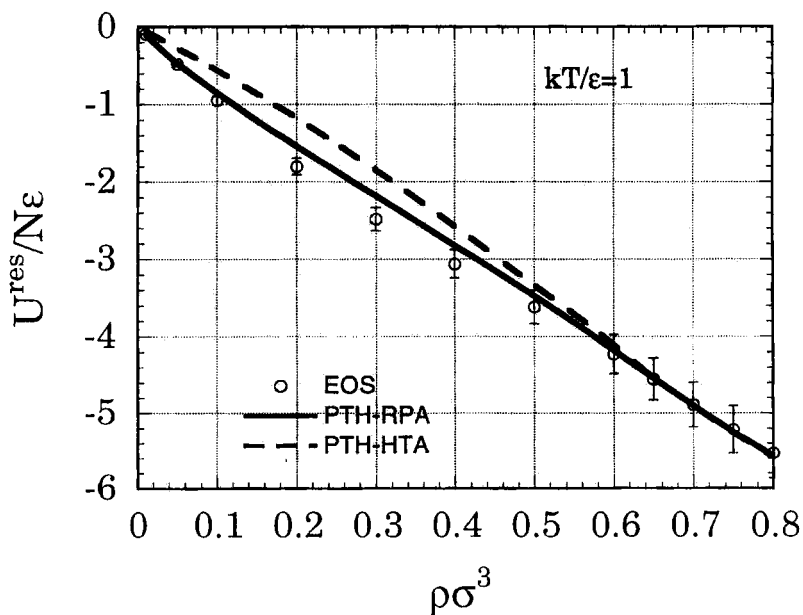


FIGURE 4 Pressure of pure LJ fluids as a function of density at three supercritical temperatures from theory and computer simulation [24, 25].

considered at  $kT/\varepsilon = 1$ . In all cases, PTH predictions compare very well with KN EOS results. The remaining discrepancy between PTH and KN EOS at the intermediate densities in Figures 3 and 4 is the result of simulation uncertainty. Even at the supercritical temperature, say,  $kT/\varepsilon = 1.35$ , where the fluid lies in the stable condition for all densities, PTH-RPA provided a significant improvement over PTH-HTA at very low densities.

So far, we compared PTH predictions with simulation results in the subcritical range of the temperature of the pure LJ fluid. In order to demonstrate the validity of PTH in supercritical conditions, Figures 5 and 6, respectively, present comparisons of pressure and residual internal energy as a function of density, each at three temperatures,  $kT/\varepsilon = 1.35$ , 1.988 and 2.74. Among these, the first and the last conditions have been investigated extensively using different theories [7]. Overall, theoretical predictions are seen to be in very good agreement with simulation results [24, 25] at all temperatures and densities. Even

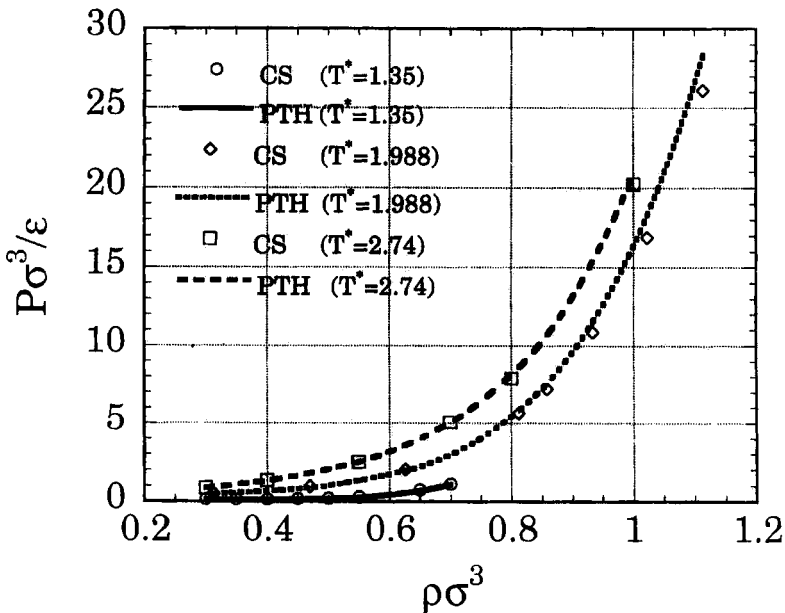


FIGURE 5 Residual internal energy of pure LJ fluids as a function of density at three supercritical temperature from theory and computer simulation [24, 25].

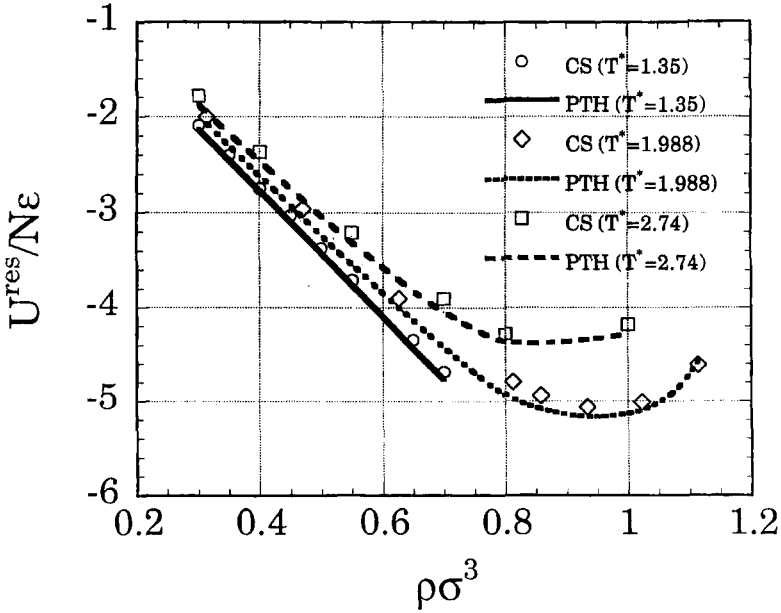


FIGURE 6 Residual Helmholtz free energy of pure LJ fluids as a function of density at a supercritical temperature from theory and equation of state [21].

at higher temperatures, PTH can describe accurately the free energy, pressure and internal energy over the entire range of the fluid density. A sample example of such a comparison is presented in Figures 7–9 for the residual Helmholtz free energy, pressure and residual internal energy, considered at a supercritical temperature  $kT/\epsilon = 3$ . We note that at this temperature,  $kT/\epsilon = 3$ , gas/gas phase equilibria have been obtained recently using the Gibbs ensemble Monte Carlo simulation [26]. Therefore, this comparison at  $kT/\epsilon = 3$  is important for the theory to be applied in calculating gas/gas phase equilibria in binary fluid mixtures.

Calculation of vapor/liquid equilibria using the first-order perturbation theory based on high temperature approximation has been a challenging problem, for such a theory is reliable at high densities only. Therefore, one has to use the virial equation of state to calculate properties of the vapor phase, and the perturbation theory to determine properties of the liquid phase. Because of the use of two different equations, the calculation of vapor/liquid equilibria of pure fluids

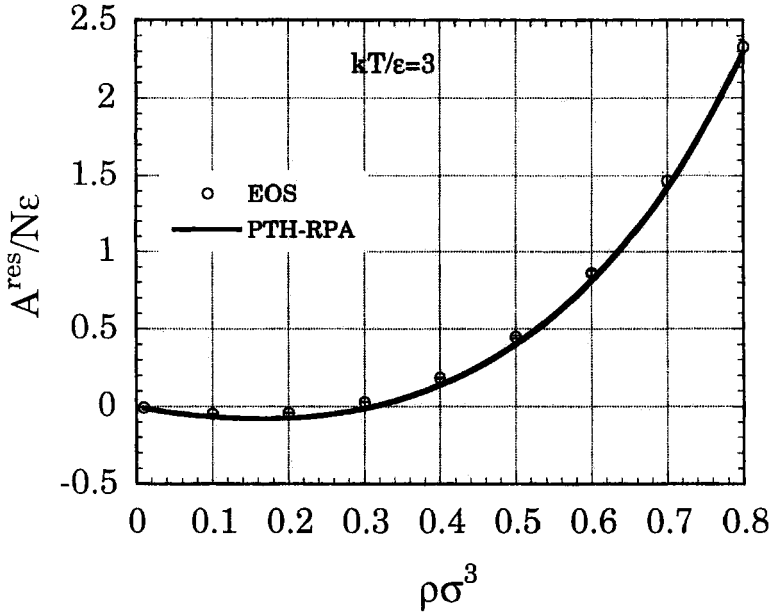


FIGURE 7 Residual Helmholtz free energy of pure LJ fluids as a function of density at a subcritical temperature from theory and equation of state [21].

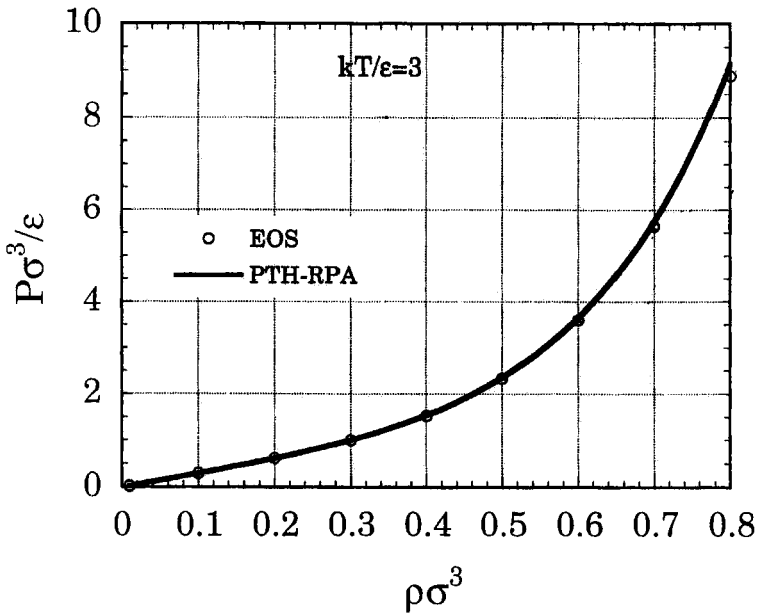


FIGURE 8 Pressure of pure LJ fluids as a function of density at a supercritical temperature from theory and equation of state [21].

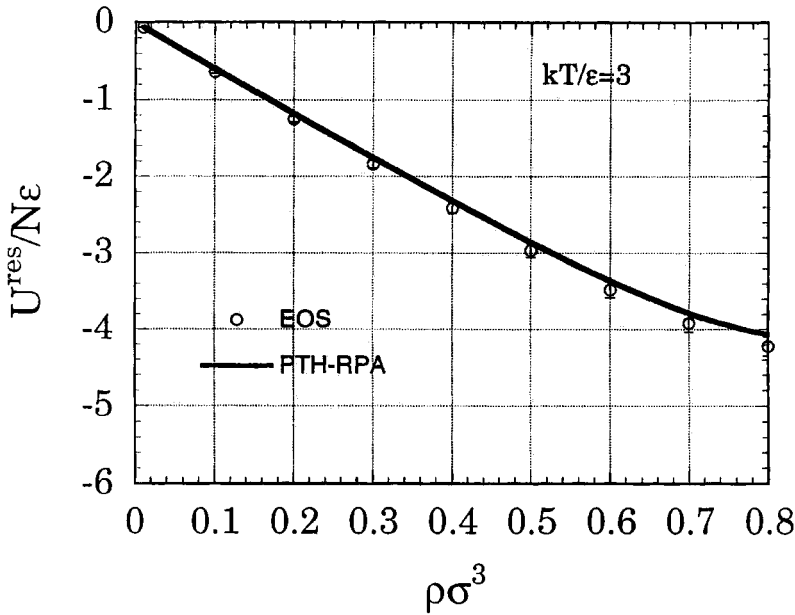


FIGURE 9 Residual internal energy of pure LJ fluids as a function of density at a supercritical temperature from theory and equation of state [21].

becomes inconsistent. This inconsistency becomes more pronounced in calculating the vapor/liquid equilibria in fluid mixtures. Since the present form of perturbation theory is found to be accurate for the entire range of the fluid densities, we used the same equation (eqn. (15)) for calculating properties of both vapor and liquid phases. The vapor/liquid equilibria were determined by satisfying the usual phase equilibrium criteria that at a given temperature pressure and chemical potential in the two phases should be equal. Results for vapor/liquid equilibria of pure LJ fluids are presented in Figure 10. PTH predictions are found to be in very good agreement with the recent simulation results [18,27], and they also agree with the predictions of KN EOS. These comparisons suggest that PTH can be applied to predict thermodynamic properties and phase equilibria of fluid mixtures with confidence.

Because PTH has been found to be reliable over a range of temperature and density, it would be interesting to compare critical parameters of the pure LJ fluid. Table I contains such a comparison. Table I shows that the values of both critical temperature and critical



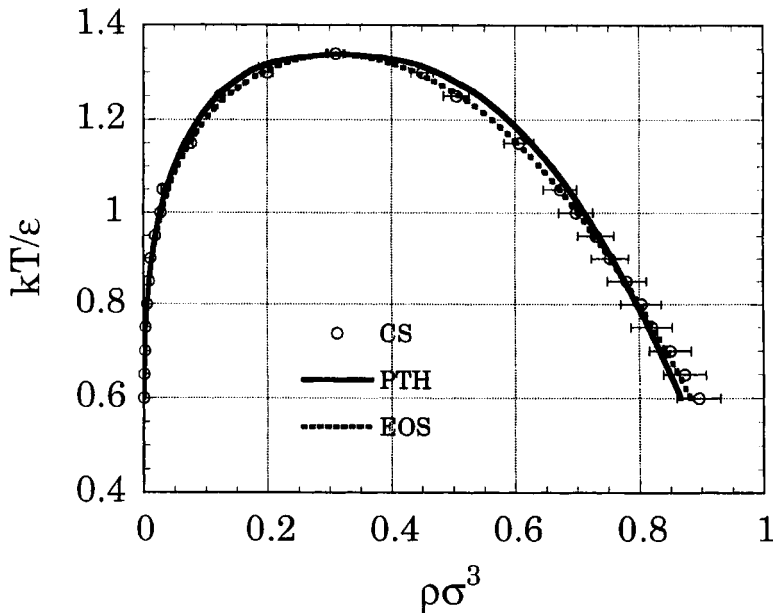


FIGURE 10 Vapor/liquid phase equilibria of pure LJ fluid from theory and computer simulation [18, 27].

TABLE I Critical parameters for the Lennard-Jones fluid

Property	CS	KN EOS <sup>3</sup>	JZG EOS <sup>4</sup>	PTH
$T_c^*$	1.316 <sup>1</sup> 1.281 <sup>2</sup>	1.339	1.313	1.330
$\rho_c^*$	0.304 <sup>1</sup> 0.320 <sup>2</sup>	0.311	0.310	0.309
$P\sigma^3/\epsilon$	—	0.141	0.129	0.141

<sup>1</sup>Smit [28]

<sup>2</sup>Panagiotopoulos [18]

<sup>3</sup>Kolafa and Nezbeda [21]

<sup>4</sup>Johnson *et al.* [20]

density calculated from PTH lie between those obtained from computer simulation [18, 28] and KN EOS. The critical pressure of PTH also compares very well with that of KN EOS.

In order to further demonstrate the reliability of the present theory, we finally compare PTH with the recent integral equation theories. Table II compares results for the pressure obtained from different

TABLE II Comparison of PTH with the recent integral equation theories and computer simulation

$kT/\epsilon$	$\rho\sigma^3$	$\beta P/\rho$					PTH
		CS	PHNC1 <sup>†</sup>	PHNC2 <sup>†</sup>	HMSA <sup>†</sup>	RHNC <sup>†</sup>	
0.786	0.85	0.99	0.94	1.20	1.01	1.03	1.06
1.15	0.85	2.86	2.71	2.92	2.80	2.87	2.90
2.74	0.55	1.65	1.58	1.62	1.65	1.66	1.65
	1.10	10.17	9.87	10.14	9.92	10.20	10.12
5	0.2	1.17	-	-	-	-	1.17
	0.5	1.87	1.82	1.84	1.86	1.86	1.86
	1.279	13.44	13.08	13.45	13.03	13.35	13.49
20	0.2	1.27	-	-	-	-	1.27
	0.5	1.93	1.93	1.94	1.94	1.95	1.95
	1.765	16.68	16.42	16.68	16.35	16.64	16.81
100	0.2	1.22	-	-	-	-	1.22
	1.0	2.95	2.93	2.95	2.96	2.98	2.98
	2.5	16.29	16.23	16.46	16.21	16.44	16.26
AAD%			2.83	3.28	1.49	1.38	1.43

<sup>†</sup> Results of these theories are reported recently by Kang and Ree [29].  
 PHNC1 = Perturbative-hypernetted-chain based on the Martynov-Sarkisov integral equation  
 PHNC2 = Perturbative-hypernetted-chain based on modified Martynov-Sarkisov integral equation  
 HMSA = Hypernetted-chain mean spherical approximation  
 RHNC = Reference hypernetted-chain theory

TABLE III Comparison of PTH with the recent integral equation theories and computer simulation

$kT/\epsilon$	$\rho\sigma^3$	$\beta U^{res}/N$					PTH
		CS	PHNC1 <sup>†</sup>	PHNC2 <sup>†</sup>	HMSA <sup>†</sup>	RHNC <sup>†</sup>	
0.786	0.85	-7.70	-7.71	-7.67	-7.68	-7.68	-7.74
1.15	0.85	-4.93	-4.96	-4.92	-4.93	-4.93	-4.97
2.74	0.55	-1.17	-1.18	-1.17	-1.17	-1.17	-1.18
	1.10	-1.35	-1.41	-1.36	-1.39	-1.34	-1.36
5	0.2	-0.20	-	-	-	-	-0.21
	0.5	-0.47	-0.48	-0.48	-0.47	-0.47	-0.48
	1.279	0.44	0.35	0.41	0.34	0.41	0.41
20	0.2	-0.0050	-	-	-	-	-0.006
	0.5	0.03	0.03	0.03	0.03	0.03	0.03
	1.765	2.65	2.59	2.65	2.57	2.64	2.62
100	0.2	0.04	-	-	-	-	0.04
	1.0	0.36	0.36	0.36	0.36	0.37	0.37
	2.5	3.30	3.29	3.35	3.29	3.35	3.34
AAD%			3.12	1.18	2.92	1.25	1.90

<sup>†</sup> For definition of these theories, see Table II. Results for integral equation theories and simulation are from Kang and Ree [29].

recent integral equation theories with simulation. These theories are: perturbative-hypernetted-chain based on the Martynov-Sarkiso integral equation (PHNC1), perturbative-hypernetted-chain based on the modified Martynov-Sarkiso integral equation (PHNC2), hypernetted-chain mean spherical approximation (HMSA) and reference hypernetted-chain theory (RHNC). Their results are taken from the recent study [29]. In general, PTH performs better than PHNC1, PHNC2 and HMSA, and is almost equivalent to RHNC. Similar comparisons are made in Table III for internal energy. Again, PTH is very good in describing simulation results.

## 6. CONCLUSIONS

In this paper, we have presented a modified form of the first-order hard sphere perturbation theory, which consists of the first-order perturbation theory of high temperature approximation [14] and random phase approximation [19]. The RPA term is responsible in accounting for the effect of attractive forces at low densities. As a result, PTH represents a significant improvement over PTH-HTA. Our results for pressure, Helmholtz free energy, internal energy and vapor/liquid equilibria show that PTH is highly accurate in describing the properties of simple fluids from the vicinity of the triple point to the critical point, and also in the supercritical conditions. PTH is found to be in full agreement with the accurate KN EOS. Comparison of PTH with the recent integral equation theories shows that PTH is almost equivalent to RHNC theory in describing thermodynamic properties of LJ fluids.

These comparisons suggest that the modified form of the first-order perturbation theory is highly reliable in describing thermodynamic properties and vapor/liquid phase equilibria of simple fluids. In our future application, this theory will be used to predict thermodynamic properties and phase equilibria of fluid mixtures using the same theoretical equation in both vapor and liquid phases, without using any mixing rules.

## LIST OF SYMBOLS

$A$	Helmholtz free energy
CS	Computer simulation

EOS	Equation of state
$g$	Pair correlation function
HTA	High temperature approximation
JZG	Johnson-Zollweg-Gubbins EOS
KN	Kolafa and Nezbeda EOS
LJ	Lennard-Jones pair potential
$P$	Pressure
PTH	Perturbation Theory
RPA	Random phase approximation
$T$	Absolute temperature
$U$	Internal energy
$u$	Pair potential
$y$	Background correlation function

### Greek Letters

$\varepsilon$	Energy parameter in the pair potential
$\sigma$	Size parameter in the pair potential
$\mu$	Chemical potential

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