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# Analytic Equations of State for the Generalized Lennard-Jones Fluid Based on the Ross Variational Perturbation Theory and the Percus-Yevick Radial Distribution Function of Hard Spheres

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**Abstract** Analytic expressions for the equation of state and thermodynamic properties have been derived for a generalized Lennard-Jones fluid, based on the Ross variational perturbation theory and the analytic Percus-Yevick (PY) expression for the radial distribution function of hard spheres. It is shown that the variational procedure is absolutely convergent and the calculations are convenient and fast. Numerical calculations have been made within wide temperature and density ranges. The results show that the precision is equivalent to the non-analytic modified Weeks-Chandler-Anderson (mWCA) and complete analytic mean spherical approximation (MSA) theories as compared with computer simulation results. It is concluded that the analytic theory can be applied to research practical fluids within wide temperature and density ranges.

**Keywords** Analyticity · Equation of state · Thermodynamic quantities · Variational

## 1 Introduction

Perturbation theories such as the Barker-Henderson [1], Weeks-Chandler-Anderson (WCA) [2], and Ross theories [3] are most frequently used in research for the thermodynamic properties of fluids both at normal conditions and conditions with high temperature and high density. Kang et al. [4] have modified the WCA (mWCA) theory to make it applicable to fluids at high temperature and pressure conditions without the need of a variational procedure. Lado et al. [5,6] also proposed an optimized reference hypernetted chain (RHNC) theory. Talbot et al. [7] tested the Ross, mWCA, and

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RHNC theories for predicting the equilibrium properties of spherical fluids. They [7] found that the Ross and mWCA theories give very good results for the thermodynamic properties, but not for the structure. The RHNC theory requires more computer time, but yields satisfactory results both for thermodynamic properties and structure. If one's interest is restricted to the thermodynamic properties, then it is sufficient to use the Ross or mWCA theories, and there is no need for computer simulations of classical systems of particles interacting with spherical potentials. Recently, Vortler et al. [8] also tested the mWCA and RHNC theories for exp-6 fluids within wider temperature and pressure ranges; their conclusion is in accordance with that of Talbot et al. [7].

Among the most accurate perturbation theories, the Ross theory has been widely used to research shock-compressed properties of materials [9,10]. Its main disadvantage lies in the variational procedure being too time-consuming and very inconvenient in shock-compression calculations and melting problems. Tang et al. [11–13] have developed a mean spherical approximation (MSA) theory. However, the MSA theory also has some disadvantages even more severe than the Ross theory. Firstly, the MSA theory is inapplicable to fluids with high temperatures and densities [13], and at other conditions, the theory gives results comparable with the Ross theory or even worse. Secondly, the MSA theory needs to map the LJ potential with a double-Yukawa (DY) potential [11]. For the Ross theory, if it can provide an analytic EOS, it may have more advantages than many other non-variational perturbation theories. In our previous work [14,15], we have derived analytic expressions for equation of state (EOS) and thermodynamic properties for the LJ fluid based on the Ross theory by the aid of a semi-empirical analytic radial distribution function of hard spheres (HS-RDF). Although the numerical results in [15] are in good agreement with the Monte Carlo (MC) simulations and the original non-analytic Ross theory, the semi-empirical parameterized HS-RDF in [14,15] has no strict physical foundation, and is reliable just for the parameterized density region of the hard-sphere fluid. In addition, Foiles and Ashcroft [16] derived an analytic expression of the Helmholtz free energy for the DY pure fluid and mixture based on a variational theory. They [16] did not derive the analytic expressions for the equation of state and other thermodynamic properties, and also studied the properties of LJ mixtures by mapping the LJ potential with a DY potential.

The Lennard-Jones (12-6) (represented by LJ) potential is the most popular one in research for thermodynamic properties of fluids at low and moderate density ranges. In this paper, it will be shown that the analytic expressions for the EOS and thermodynamic properties of the LJ fluid can be derived based on the Ross theory and the Percus-Yevick (PY) expression for radial distribution functions of hard spheres (HS-RDF) [17,18]. There is no need of other approximations or the aid of a Yukawa-type potential. The applicability of the analytic formalism is the same as the original non-analytic Ross theory. For the convenience of applications, we would develop the analytic formalism for a generalized LJ (GLJ) fluid. The results for the LJ fluid can be included as a special case. In Sect. 2, the analytic expression for the radial distribution function for hard spheres is developed. In Sect. 3, the analytic EOS is developed. In Sect. 4, the numerical results are compared with Monte Carlo (MC) simulation data and the original non-analytic EOS, and the conclusion is presented in the same section.

## 2 Fundamental Formalism of the Ross Variational Perturbation Theory

In terms of the Ross perturbation theory [3], the Helmholtz free energy is expressed as follows

$$\frac{F}{NkT} = \frac{F_0}{NkT} + \frac{F_1}{NkT} + \frac{F_{12}(\eta)}{NkT} \tag{1}$$

where $F_0$ is the free energy of a reference hard-sphere system [19], and

$$\frac{F_1}{NkT} = 2\pi\rho\beta \int_d^\infty \varphi(r)g(r)r^2 \mathrm{d}r \tag{2}$$

is the first-order perturbation. $\phi(r)$ is the potential function, $g(r)$ is the HS-RDF. $F_{12}(\eta)$ is a function making Eq. 1 reproduce the MC inverse 12th-power results [3].

$$\frac{F_{12}(\eta)}{NkT} = -\left(\eta/2 + \eta^2 + \eta^4/2\right) \tag{3}$$

where $\eta = \pi\rho d^3/6$, $d$ is the hard-sphere diameter, and $\eta$ is employed as the variational parameter that minimizes the right side of Eq. 1. Namely, $\eta$ should be determined by

$$\frac{\partial}{\partial\eta}\left(\frac{F}{NkT}\right)_{T,\rho} = \frac{\partial}{\partial\eta}\left(\frac{F}{NkT}\right)_{T,\eta_\mathrm{e}} = 0 \tag{4}$$

The integral in Eq. 2 can be transformed to the following form,

$$\frac{F_1}{NkT} = 12\eta\beta \int_1^\infty \varphi(x)g(x)x^2 \mathrm{d}x = 12\eta\beta \int_0^\infty \Phi(t)G(t)\mathrm{d}t \tag{5}$$

where $x = r/d$ is the radial coordination reduced by the hard sphere diameter. $\Phi\,(t)$ is the inverse Laplace transformation of $x\phi(x)$ [20];

$$\Phi(t) = L^{-1}\left[x\phi(x)\right] \tag{6}$$

$G(t)$ is the Laplace transformation of $[rg(r)]$. The PY expression for $G(t)$ and $G(t)$ derivatives with respect to $\eta$ and $t$ are given in the Appendix.

## 3 Analytic Equation of State for the Generalized Lennard-Jones Fluids

The GLJ potential has the following form:

$$\varphi(r) = \varepsilon_0 \sum_{i=0}^{m} C_i (r_\mathrm{e}/r)^{n_i} \tag{7}$$

**Table 1** Comparison of the reduced Helmholtz energy $F/NkT$, the compressibility factor $PV/NkT$, and the reduced excess internal energy $U/NkT$ for the LJ fluid at normal conditions: Monte Carlo simulation (MC) [21]; calculated from the mWCA theory in this work by Kang et al. (K) [4]; from the analytic MSA approach (T) [11]; and from the Ross theory in this work (S)

| $kT/\varepsilon$ | $\rho\sigma^3$ | $F/NkT$ | | | | $PV/NkT$ | | | | $U/NkT$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | MC | K | T | S | MC | K | T | S | MC | K | T | S |
| 0.75 | 0.10 | −0.81 | | −0.72 | −0.59 | 0.23 | | 0.33 | 0.39 | −1.53 | | −1.07 | −0.77 |
| | 0.20 | −1.48 | | −1.37 | −1.21 | −0.29 | | −0.25 | −0.28 | −2.53 | | −1.99 | −1.62 |
| | 0.30 | −2.11 | | −1.98 | −1.86 | −0.78 | | −0.82 | −0.98 | −3.44 | | −2.87 | −2.54 |
| | 0.40 | −2.68 | | −2.58 | −2.53 | −1.20 | | −1.35 | −1.64 | −4.28 | | −3.77 | −3.53 |
| | 0.50 | −3.23 | | −3.15 | −3.18 | −1.69 | | −1.75 | −2.15 | −4.97 | | −4.69 | −4.57 |
| | 0.60 | −3.74 | | −3.66 | −3.77 | −2.05 | | −1.86 | −2.32 | −5.81 | | −5.64 | −5.65 |
| | 0.70 | −4.17 | −4.15 | −4.08 | −4.26 | −1.71 | −1.88 | −1.45 | −1.88 | −6.76 | −6.68 | −6.57 | −6.72 |
| | 0.80 | −4.47 | −4.46 | −4.34 | −4.57 | −0.53 | −0.56 | −0.22 | −0.48 | −7.71 | −7.66 | −7.44 | −7.70 |
| | 0.84 | −4.54 | −4.52 | −4.38 | −4.62 | 0.37 | 0.32 | 0.60 | 0.45 | −8.05 | −8.01 | −7.75 | −8.06 |
| 1.15 | 0.10 | −0.39 | | −0.37 | −0.32 | 0.61 | | 0.65 | 0.67 | −0.75 | | −0.62 | −0.50 |
| | 0.20 | −0.73 | | −0.70 | −0.65 | 0.35 | | 0.36 | 0.33 | −1.35 | | −1.20 | −1.04 |
| | 0.30 | −1.05 | | −1.01 | −0.99 | 0.12 | | 0.10 | 0.03 | −1.95 | | −1.76 | −1.63 |
| | 0.40 | −1.33 | | −1.30 | −1.31 | −0.09 | | −0.09 | −0.25 | −2.48 | | −2.34 | −2.25 |
| | 0.50 | −1.59 | | −1.55 | −1.60 | −0.13 | | −0.14 | −0.34 | −3.02 | | −2.92 | −2.90 |
| | 0.60 | −1.79 | | −1.74 | −1.84 | 0.07 | | 0.06 | −0.14 | −3.60 | | −3.51 | −3.55 |
| | 0.65 | −1.84 | | −1.81 | −1.92 | 0.31 | | 0.31 | 0.11 | −3.87 | | −3.80 | −3.87 |
| | 0.75 | −1.88 | | −1.85 | −1.99 | 1.17 | | 1.21 | 1.09 | −4.46 | | −4.34 | −4.46 |
| | 0.85 | −1.78 | | −1.74 | −1.87 | 2.86 | | 2.87 | 2.89 | −4.93 | | −4.80 | −4.95 |
| | 0.92 | −1.56 | | −1.52 | −1.65 | 4.72 | | 4.68 | 4.81 | −5.18 | | −5.05 | −5.20 |
| 1.35 | 0.10 | −0.30 | −0.22 | −0.28 | −0.25 | 0.72 | 0.77 | 0.74 | 0.75 | −0.58 | −0.41 | −0.51 | −0.42 |
| | 0.20 | −0.56 | | −0.52 | −0.50 | 0.50 | | 0.52 | 0.50 | −1.12 | | −0.99 | −0.88 |
| | 0.30 | −0.80 | −0.69 | −0.75 | −0.75 | 0.35 | 0.31 | 0.35 | 0.27 | −1.55 | −1.35 | −1.47 | −1.37 |
| | 0.40 | −1.00 | | −0.95 | −0.98 | 0.27 | | 0.25 | 0.12 | −2.04 | | −1.95 | −1.89 |
| | 0.50 | −1.16 | −1.10 | −1.12 | −1.18 | 0.30 | 0.18 | 0.29 | 0.14 | −2.50 | −2.40 | −2.44 | −2.43 |
| | 0.55 | −1.22 | | −1.18 | −1.26 | 0.41 | | 0.39 | 0.23 | −2.74 | | −2.69 | −2.70 |
| | 0.70 | −1.29 | | 1.25 | −1.36 | 1.17 | | 1.23 | 1.12 | −3.47 | | −3.39 | −3.47 |
| | 0.80 | −1.19 | | −1.15 | −1.27 | 2.42 | | 2.46 | 2.43 | −3.89 | | −3.80 | −3.91 |
| | 0.90 | −0.91 | −0.91 | −0.87 | −0.98 | 4.58 | 4.49 | 4.52 | 4.60 | −4.19 | −4.20 | −4.11 | −4.22 |
| | 0.95 | −0.67 | −0.68 | −0.64 | −0.75 | 6.32 | 5.96 | 5.97 | 6.08 | −4.23 | −4.30 | −4.21 | −4.31 |
| 2.74 | 0.10 | −0.03 | | −0.03 | −0.04 | 0.97 | | 0.98 | 0.97 | −0.22 | | −0.22 | −0.20 |
| | 0.20 | −0.05 | −0.03 | −0.05 | −0.06 | 0.99 | 0.99 | 0.99 | 0.96 | −0.44 | −0.40 | −0.43 | −0.41 |
| | 0.30 | −0.05 | | −0.04 | −0.07 | 1.04 | | 1.05 | 1.01 | −0.65 | | −0.64 | −0.63 |
| | 0.40 | −0.00 | 0.00 | −0.00 | −0.05 | 1.20 | 1.18 | 1.20 | 1.14 | −0.86 | −0.83 | −0.86 | −0.85 |
| | 0.55 | 0.06 | | 0.11 | 0.05 | 1.65 | | 1.66 | 1.60 | −1.17 | | −1.16 | −1.18 |
| | 0.70 | 0.37 | 0.37 | 0.37 | 0.30 | 2.64 | 2.57 | 2.60 | 2.57 | −1.42 | −1.45 | −1.43 | −1.45 |
| | 0.80 | 0.65 | 0.64 | 0.65 | 0.57 | 3.60 | 3.62 | 3.67 | 3.65 | −1.56 | −1.58 | −1.55 | −1.58 |
| | 0.90 | 1.04 | 1.03 | 1.05 | 0.97 | 5.14 | 5.15 | 5.25 | 5.20 | −1.62 | −1.62 | −1.61 | −1.62 |

**Table 1** continued

| $kT/\varepsilon$ | $\rho\sigma^3$ | $F/NkT$ | | | | $PV/NkT$ | | | | $U/NkT$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | MC | K | T | S | MC | K | T | S | MC | K | T | S |
| | 1.00 | 1.58 | 1.57 | 1.61 | 1.52 | 7.39 | 7.37 | 7.56 | 7.37 | −1.53 | −1.56 | −1.58 | −1.56 |
| | 1.08 | 2.16 | | 2.21 | 2.09 | 9.58 | | 10.15 | 9.65 | −1.39 | | −1.44 | −1.41 |
| AAD | | | 0.028 | 0.113 | 0.055 | | 0.132 | 0.059 | 0.084 | | 0.110 | 0.072 | 0.083 |

**Table 2** Same as Table 1, but the fluid is at high temperature and density

| $kT/\varepsilon$ | $\rho\sigma^3$ | $F/NkT$ | | | $PV/NkT$ | | | $U/NkT$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | EX | S | K | EX | S | K | EX | S | K |
| 100 | 0.2 | 0.21 | 0.20 | 0.21 | 1.22 | 1.22 | 1.22 | 0.036 | 0.034 | 0.04 |
| | 0.4 | 0.45 | 0.43* | 0.45 | 1.51 | 1.50 | 1.51 | 0.085 | 0.081 | 0.09 |
| | 0.5 | 0.58 | 0.56 | 0.58 | 1.68 | 1.67 | 1.68 | 0.115 | 0.111 | 0.12 |
| | 0.666 | 0.82 | 0.80 | 0.82 | 2.00 | 2.01 | 2.03 | 0.175 | 0.173 | 0.18 |
| | 1 | 1.39 | 1.38 | 1.40 | 2.95 | 2.96 | 2.98 | 0.361 | 0.358* | 0.37 |
| | 1.333 | 2.13 | 2.12* | 2.15 | 4.36 | 4.40 | 4.39 | 0.648 | 0.652 | 0.66 |
| | 1.4 | 2.31 | 2.30 | 2.32 | 4.76 | 4.76 | 4.75 | 0.734 | 0.729 | 0.74 |
| | 2 | 4.36 | 4.36 | 4.37 | 9.50 | 9.57* | 9.51 | 1.767 | 1.779 | 1.78 |
| | 2.222 | 5.38 | 5.39 | 5.38 | 12.10 | 12.26 | 12.19 | 2.346 | 2.385 | 2.39 |
| | 2.38 | 6.22 | 6.24* | 6.24 | 14.46 | 14.56 | 14.50 | 2.887 | 2.909 | 2.90 |
| | 2.5 | 6.92 | 6.95 | 6.95 | 16.29 | 16.54 | 16.49 | 3.304 | 3.365* | 3.37 |
| 20 | 0.2 | | 0.23 | 0.14 | 1.27 | 1.26 | 1.27 | −0.005 | −0.010 | −0.004 |
| | 0.4 | | 0.52* | 0.55 | 1.67 | 1.65 | 1.67 | 0.009 | 0.001 | 0.01 |
| | 0.5 | | 0.70* | 0.72 | 1.93 | 1.92 | 1.95 | 0.026 | 0.018 | 0.03 |
| | 0.666 | | 1.04* | 1.07 | 2.51 | 2.52* | 2.54 | 0.083 | 0.074 | 0.09 |
| | 1 | | 1.98 | 2.02 | 4.46 | 4.49 | 4.48 | 0.348 | 0.343 | 0.35 |
| | 1.333 | | 3.43 | 3.46 | 8.00 | 8.09 | 8.03 | 0.942 | 0.958 | 0.96 |
| | 1.765 | | 6.45 | 6.46 | 16.68 | 16.75 | 16.69 | 2.65 | 2.65 | 2.65 |
| 5 | 0.2 | | 0.12 | 0.14 | 1.17 | 1.15 | 1.15 | −0.202 | −0.200 | −0.19 |
| | 0.5 | | 0.46* | 0.51 | 1.82 | 1.82 | 1.85 | −0.474 | −0.488 | −0.47 |
| | 0.666 | | 0.80 | 0.86 | 2.67 | 2.67 | 2.69 | −0.584 | −0.592 | −0.59 |
| | 1 | | 2.08 | 2.13 | 6.34 | 6.49 | 6.42 | −0.456 | −0.448 | −0.45 |
| | 1.279 | | 4.16 | 4.19 | 13.44 | 13.46 | 13.37 | 0.435 | 0.413 | 0.41 |
| | | | 0.013 | 0.015 | | 0.056 | 0.041 | | 0.013 | 0.012 |

"EX" denotes the exact calculations from Ref. [3]. Results from the mWCA theory are partly available; from the analytic MSA approach are unavailable; and the results from the analytic Ross theory labeled '*' are slightly different from those of the non-analytic Ross theory in Ref. [3]

The parameter $\varepsilon_0$ is the potential depth and $r_\mathrm{e}$ is the equilibrium distance. For the Lennard-Jones (12–6) potential,

$$\varphi(r) = \varepsilon_0 \left[ (r_\mathrm{e}/r)^{12} - 2(r_\mathrm{e}/r)^6 \right] \tag{8}$$

We have

$$m = 2, \quad n_1 = 6, \quad n_2 = 12, \quad C_1 = -2, \quad C_2 = 1 \tag{9}$$

Introducing the following notation,

$$\lambda = (r_\mathrm{e}/d) = (\eta_\mathrm{e}/\eta)^{1/3}, \quad \eta_\mathrm{e} = \pi \rho r_\mathrm{e}^3/6 \tag{10}$$

$$\frac{\partial \lambda}{\partial \eta} = -\frac{\lambda}{3\eta}, \quad \text{and} \quad \frac{\partial \lambda}{\partial \eta_\mathrm{e}} = \frac{\lambda}{3\eta_\mathrm{e}} \tag{11}$$

The GLJ potential in Eq. 7 can be reformulated as

$$\phi(x) = \varepsilon_0 \sum_{i=0}^{m} C_i (\lambda/x)^{n_i} \tag{12}$$

By the aid of the mathematical formula,

$$L^{-1}\left[ (x+\lambda)^{-n-1} \right] = \frac{t^n}{n!} \mathrm{e}^{-\lambda t} \tag{13}$$

the inverse Laplace transformation of $x\phi(x)$ can be derived as

$$\Phi(t) = L^{-1}\left[ x\phi(x) \right] = \lambda^2 \varepsilon_0 \sum_{i=0}^{m} \frac{C_i}{(n_i - 2)!} (\lambda t)^{n_i - 2} \tag{14}$$

$$\Phi'_\lambda(t) = \frac{2\Phi(t)}{\lambda} + \lambda \varepsilon_0 \sum_{i=0}^{4} \frac{C_i}{(n_i - 3)!} (\lambda t)^{n_i - 2} \tag{15}$$

The substitution of Eq. 14 into Eq. 5 yields

$$\frac{F_1}{NkT} = 12\eta\beta \int_1^\infty \varphi(x) g(x) x^2 \mathrm{d}x = 12\eta\beta \int_0^\infty \Phi(t) G(t) \mathrm{d}t \tag{16}$$

The compressibility factor can be derived as follows:

$$\frac{PV}{NkT} = 1 + \rho\frac{\partial}{\partial\rho}\left(\frac{F}{NkT}\right)_T = 1 + \eta_e\frac{\partial}{\partial\eta_e}\left(\frac{F}{NkT}\right)_T$$
$$= 1 + \eta_e\frac{\partial}{\partial\eta_e}\left(\frac{F}{NkT}\right)_{T,\eta} + \frac{\partial}{\partial\eta}\left(\frac{F}{NkT}\right)_{T,\eta_e}\eta_e\frac{\partial\eta}{\partial\eta_e}$$

From Eq. 4, the third term in the equation equals zero, and we obtain

$$\frac{PV}{NkT} = 1 + \eta_e\frac{\partial}{\partial\eta_e}\left(\frac{F}{NkT}\right)_{T,\eta} = 1 + \eta_e\frac{\partial}{\partial\eta_e}\left(\frac{F_1}{NkT}\right)_{T,\eta} \tag{17}$$

$$\frac{PV}{NkT} = 1 + 4\lambda\eta\beta\int_0^\infty \Phi'_\lambda(t)G(t)\mathrm{d}t \tag{18}$$

The equation for the internal energy is

$$\frac{U}{NkT} = \beta\frac{\partial}{\partial\beta}\left(\frac{F}{NkT}\right)_\rho = \beta\frac{\partial}{\partial\beta}\left(\frac{F}{NkT}\right)_\eta + \frac{\partial}{\partial\eta}\left(\frac{F}{NkT}\right)_{T,\eta_e}\beta\frac{\partial\eta}{\partial\beta}$$

From Eq. 4, the second term also equals zero, and the equation is changed as

$$\frac{U}{NkT} = \beta\frac{\partial}{\partial\beta}\left(\frac{F}{NkT}\right)_\eta = \beta\frac{\partial}{\partial\beta}\left(\frac{F_1}{NkT}\right)_\eta = \frac{F_1}{NkT} \tag{19}$$

With the substitution of Eqs. 3 and 16 into Eq. 1, and Eq. 1 into Eq. 4, the equation to determine $\eta$ can be derived as

$$\frac{4-2\eta}{(1-\eta)^3} - \frac{1}{2} - \frac{45}{4}\eta^2 + \frac{\partial}{\partial\eta}\frac{F_1}{NkT} = 0 \tag{20}$$

$$\frac{\partial}{\partial\eta}\frac{F_1}{NkT} = \frac{1}{\eta}\left(\frac{F_1}{NkT}\right) + 12\eta\beta\int_0^\infty\left[(-\lambda/3\eta)\,\Phi'_\lambda(t)\,G(t) + \Phi(t)\,G'_\eta(t)\right]\mathrm{d}t$$
$$= \frac{1}{\eta}\left(\frac{F_1}{NkT} - \frac{PV}{NkT} + 1\right) + 12\eta\beta\int_0^\infty \Phi(t)\,G'_\eta(t)\,\mathrm{d}t \tag{21}$$

Although Eq. 20 is a nonlinear algebraic equation, by using the Newtonian iteration approach, its solution is insensitive to the initial value and is absolutely convergent.

## 4 Numerical Results and Discussion

By using the expressions derived above, we have calculated the configurational free energy $F/NkT$, the compressibility factor $PV/NkT$, and the excess internal energy $U/NkT$ for the LJ fluid at normal conditions and with high temperature and density. The results are listed in Tables 1 and 2. In the two tables, we also list the Monte Carlo (MC) simulation data [21] and the results of mWCA theory by Kang et al. [4], both based on the LJ potential. The average absolute deviation (AAD) is shown in the last row of the two tables, for comparison. The results of the MSA approach from Tang [13] by the aid of the DY potential are also listed in Table 1.

Table 1 shows that the mWCA, MSA, and Ross theories give equivalently good results as compared with the MC simulation results. The AAD of $F/NkT$, $PV/NkT$, and $U/NkT$ at normal condition are 0.028, 0.132, and 0.110 from the mWCA theory; 0.113, 0.059, and 0.072 from the MSA approach [12]; and 0.055, 0.084, and 0.083 from the Ross theory, respectively. Table 2 shows that the results at the condition of high temperature and density calculated from the Ross and mWCA theories are in good agreement with each other, and also in good agreement with the MC data. The AAD of $F/NkT$, $PV/NkT$, and $U/NkT$ are 0.015, 0.041, and 0.012 for the mWCA theory and 0.013, 0.056, and 0.013 for the Ross theory, respectively. Noting that it seems impossible to develop an analytic EOS from the mWCA theory, and that the numerical calculation is fairly inconvenient for the mWCA theory, which must use the complicated expression for the HS-RDF in the coordinate space, the analytic EOS from the Ross theory is simpler and the numerical calculation is fast and convenient. Additionally, the analytic EOS from the MSA by Tang [13–15] also is complicated as compared with the present simple analytic EOS, even with the aid of a DY potential.

In summary, we have shown that by using the analytic expression of the radial distribution function of hard spheres previously developed, it is possible to establish a simple analytic EOS for fluids with a continuous GLJ potential based on the Ross variational perturbation theory. The main thermodynamic quantities can be analytically derived, the obtained expressions are surprisingly simple, and the variational calculations are absolutely convergent. It is the next step for us to develop an analytic EOS for the DY potential or other potentials by the same procedure. The work is underway.

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## Appendix

$$G(t) = \frac{tL(t)}{Q(t)} \tag{A1}$$

$$L(t) = (1 + \eta/2)\,t + (1 + 2\eta) \tag{A2}$$

$$Q(t) = 12\eta L(t) + S(t)\,\mathrm{e}^{t} \tag{A3}$$

$$S(t) = (1-\eta)^2 t^3 + 6\eta(1-\eta)\,t^2 + 18\eta^2 t - 12\eta(1+2\eta) \tag{A4}$$

$$Q'_{\eta}(t) = 12L(t) + 12\eta L'_{\eta}(t) + S'_{\eta}(t)\,\mathrm{e}^{t} \tag{A5}$$

$$Q'_{t}(t) = 12\eta L'_{t}(t) + S'_{t}(t)\,\mathrm{e}^{t} + S(t)\,\mathrm{e}^{t} \tag{A6}$$

$$G'_{\eta}(t) = G(t)\,L^{-1}(t)\,L'_{\eta}(t) - G^{2}(t)\,[tL(t)]^{-1}\,Q'_{\eta}(t) \tag{A7}$$

$$G'_{t}(t) = G(t)\left[t^{-1} + L^{-1}(t)\,L'_{t}(t)\right] - G^{2}(t)\,[tL(t)]^{-1}\,Q'_{t}(t) \tag{A8}$$

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