First-Order Perturbative Contribution to the Compressibility Factor of Square-Well Fluids from Monte Carlo and Integral Equation Theory

Julio Largo and José R. Solana*

Departamento de Físsica Aplicada, Universidad de Cantabria, 39005 Santander, Spain

Received: March 11, 2004; In Final Form: April 29, 2004

We have determined by Monte Carlo NVT simulations the zero- and first-order terms in the expansion of the compressibility factor of square-well fluids in the power series of the inverse of the reduced temperature for different densities and well widths. In addition, the values of the compressibility factor obtained from the perturbative expansion, truncated beyond the first-order term, are compared with those obtained directly by MC simulations performed on the SW system, which we reported previously (Largo, J.; Solana, J. R. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2003**, *67*, 066112). The aim is to establish the limits of validity of this truncated expansion in terms of densities, temperatures, and potential widths. We have found that this approximation is very accurate for any value of the potential width, density, and temperature, except perhaps for small potential widths at very low temperatures. Moreover, the values of the first-order contribution are compared with those obtained from the Tang and Lu (Tang, Y.; Lu, B. C.-Y. *J. Chem. Phys.* **1994** *100*, 6665) perturbation theory based on the integral equation theory as well as with those from the Barker−Henderson perturbation theory. The aim is twofold: on one hand, to establish whether the pressure route used in the Tang−Lu theory provides better accuracy than the energy route used in the Barker−Henderson theory and on the other hand to determine whether the Tang−Lu theory, which is more complicated, is advantageous compared to the Barker−Henderson theory. We have found that the Barker−Henderson perturbation theory is advantageous compared to the Tang−Lu theory with regard to the calculation of the thermodynamic properties, whereas the contrary is true for structural properties.

I. Introduction

Among the most successful theories of the liquid state are perturbation theories, which express the thermodynamic and structural properties of fluids as a series expansion in terms of a suitably chosen parameter. In this expansion, the zero-order term corresponds to the contribution of a reference fluid to these properties, and the higher order terms are successive corrections. The usefulness of this procedure depends on the rate of convergency of the series because usually only the lower-order terms can be determined. Thus, for example, the virial expansion of the equation of state can be considered to be a perturbative expansion with the ideal gas as the reference system, the density as the perturbative parameter, and a poor rate of convergency, which makes this procedure inappropriate at high densities. More frequently, the inverse of the reduced temperature $T^* = kT/\epsilon$, where ϵ is an energy parameter and k is the Bolzmann constant, is used as the perturbative parameter, and for fluids having spherically symmetrical intermolecular potentials, the hard-sphere (HS) fluid is used as the reference system. This gives a better rate of convergence of the perturbative expansion and is the case of the perturbation theories that are considered here.

Perhaps the simplest model of a fluid having not only repulsive but also attractive interactionsis the square-well (SW) fluid, in which particles interact by means of a potential of the form

$$u(r) = \begin{cases} \infty & \text{if } r < \sigma \\ -\epsilon & \text{if } \sigma \leq r \leq \lambda\sigma \\ 0 & \text{if } r > \lambda\sigma \end{cases} \tag{1}$$

* Corresponding author. E-mail: ramon.solana@unican.es. Phone: 942 20 14 47. Fax: 942 20 14 02.

where σ is the diameter of the particles, $-\epsilon$ is the potential depth, and λ is the range of the potential in units of the diameter σ. Despite its simplicity, the SW fluid is particularly suitable for testing the quality of a theory because of the considerable sensitivity of the calculated properties of this fluid to the accuracy of the theory.

Henderson and co-workers[1−6] developed the Barker−Henderson (BH) perturbation theory for SW fluids, including different refinements, and performed an extensive analysis of its performance. Many others authors carried out additional refinements and analyses of the same theory. An alternative procedure, which combines the perturbative series with integral equation theories to determine the terms in the series, has been also profusely used.[6−12]

Although perturbation theories, such as the Barker−Henderson theory, provide accurate results for the equation of state of SW fluids for wide ranges of densities and temperatures, most of the calculations have been performed for the potential width $\lambda = 1.5$. This is because, within this particular range of the potential, the SW potential mimics the potential of some other simple fluids. However, SW fluids with narrower potential ranges have recently been the subject of considerable interest to model the interactions between colloidal particles.[13−17] Therefore, it is desirable to establish the limits of validity of a perturbative expansion of the thermodynamic and structural properties without any theoretical approximation. With this aim, we have obtained by Monte Carlo (MC) simulations the zero- and first-order terms in the expansion of the compressibility factor in the power series of the inverse of the temperature for SW fluids of variable width. These data are reported in the next section. The truncated series is then compared in the same section with the MC results for the compressibility factor of

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SW fluids with λ ranging from 1.1 to 2.0, reported previously,[18] to determine the temperature, density, and potential width ranges for which the first-order perturbation theory obtained by MC simulations (MC-P), provides enough accuracy.

Once the range of applicability of the first-order truncated expansion is established, it is desirable to determine whether the well-known Barker–Henderson perturbation theory[1] is able to reproduce accurately the first-order term and whether a more recently proposed approximation, namely, the perturbation theory of Tang and Lu[12] (TL) based on integral equations, provides some advantage with respect to the simpler BH approximation. To this end, in section III we summarize the BH and TL perturbation theories and introduce some refinements to the former. The performance of these theories is analyzed in section IV, and the results are discussed in the same section.

II. Monte Carlo Simulations of the Zero- and First-Order Perturbative Terms of the Compressibility Factor

The procedure to determine, by means of MC, the zero- and first- order terms in the expansion of the pair correlation function (pcf) and the compressibility factor of a SW fluid in power series $\beta\epsilon = 1/T^*$, where T^* is the reduced temperature, has been developed by Smith et al.[4,6] They consider an intermolecular pair potential of the form

$$u(r) = u_0(r) + \epsilon u_1^*(r) \quad (2)$$

in which $u_0(r)$ is the hard-sphere (HS) potential and $u_1^*(r)$ is the perturbative contribution. Note that the SW potential (1) may be expressed in the form of eq 2. Then, the pcf can be expressed as a series expansion of the form

$$g(r) = \sum_{n=0}^{\infty} (\beta\epsilon)^n g_n(r) \quad (3)$$

where $g_0(r)$ is the pcf of a hard-sphere fluid and $g_n(r)$ is the perturbative contribution of order n.

To determine the two lower-order terms $g_0(r)$ and $g_1(r)$, Barker et al.[1,4] divide the intermolecular distances into equal intervals (r_0, r_1), ...,(r_i, r_{i+1}), ... Then, if N_i is the number of intermolecular distances in the interval (r_i, r_{i+1}), they obtain

$$g_0(r_{i+1/2}) = \frac{3\langle N_i\rangle_0}{2\pi N\rho(r_{i+1}^3 - r_i^3)} \quad (4)$$

and

$$g_1(r_{i+1/2}) = -\frac{3\sum_j \{\langle N_i N_j\rangle_0 - \langle N_i\rangle_0\langle N_j\rangle_0\}u_1^*(r_j)}{2\pi N\rho(r_{i+1}^3 - r_i^3)} \quad (5)$$

In these expressions, angular brackets mean an average, and the subscript 0 means that the average is performed in the reference system. Therefore, eqs 4 and 5 relate the zero- and first-order terms in the perturbative expansion of the pcf of the fluid with a spherical hard-core potential to $\langle N_i\rangle_0$ and $\langle N_i N_j\rangle_0 - \langle N_i\rangle_0\langle N_j\rangle_0$, that is, the average number of pairs of particles of the reference HS fluid separated by a given distance and the fluctuations of that number. These averages can be obtained

TABLE 1: Monte Carlo Results for the Zeroth-Order Perturbative Contribution to the Compressibility Factor of an SW Fluid

ρ^*	Z_0	g_0
0.10	1.2399	1.1452
0.20	1.5542	1.3231
0.30	1.9687	1.5417
0.40	2.5239	1.8190
0.50	3.2748	2.1723
0.60	4.2988	2.6251
0.70	5.7300	3.2263
0.80	7.7655	4.0379
0.90	10.7248	5.1592

TABLE 2: Monte Carlo Results for the First-Order Perturbative Contribution to the Compressibility Factor of a SW Fluid with $\lambda = 1.1'$

ρ^*	Z_1	g_{10}	$g_{1\lambda^-}$	$g_{1\lambda^+}$
0.10	−0.0851	1.0597	1.0464	−0.0551
0.20	−0.2235	1.1398	1.0941	−0.1631
0.30	−0.4216	1.1697	1.1171	−0.2659
0.40	−0.7325	1.2138	1.1341	−0.4347
0.50	−1.1704	1.1982	1.1329	−0.6070
0.60	−1.8084	1.1793	1.1484	−0.8188
0.70	−2.6779	1.0302	1.1249	−1.0215
0.80	−3.9049	0.7883	1.1051	−1.2381
0.90	−5.4117	0.4212	1.0684	−1.4051

by MC simulations in the reference HS system. Smith et al.[4] reported values of $g_1(r)$ calculated in this way for $\lambda = 1.5$.

When the expansion (3) truncated at the level of the first-order term, that is,

$$g(r) \approx g_0(r) + \frac{g_1(r)}{T^*} \quad (6)$$

is introduced into the pressure equation for the SW fluid

$$Z = \frac{pV}{NkT} = \frac{2}{3}\pi\rho\sigma^3\{g(\sigma^+) - \lambda^3[g(\lambda\sigma^-) - g(\lambda\sigma^+)]\} \quad (7)$$

the zero- and first- order terms of the expansion of the compressibility factor in the power series of the inverse of the reduced temperature

$$Z \approx Z_0 + \frac{Z_1}{T^*} \quad (8)$$

are readily obtained in the form

$$Z_0 = \frac{p_0 V}{NkT} = 1 + \frac{2}{3}\pi\rho\sigma^3 g_0(\sigma^+) \quad (9)$$

and

$$Z_1 = \frac{p_1 V}{NkT} = \frac{2}{3}\pi\rho\sigma^3\{g_1(\sigma^+) - \lambda^3[g_1(\lambda\sigma^-) - g_1(\lambda\sigma^+)]\} \quad (10)$$

We have performed MC simulations in the NVT ensemble for a system consisting of 512 hard spheres that were initially placed in a regular configuration. The systems were allowed to equilibrate for 5×10^4 cycles, each of them consisting of an attempt move per particle, after which the averages involved in eqs 4 and 5 were calculated from the next 10^5 cycles. The acceptance ratio was settled to about 50%. From these data, we have calculated the corresponding values of Z_0 and Z_1 from eqs 9 and 10. They are listed in Tables 1–11. The values of Z_0
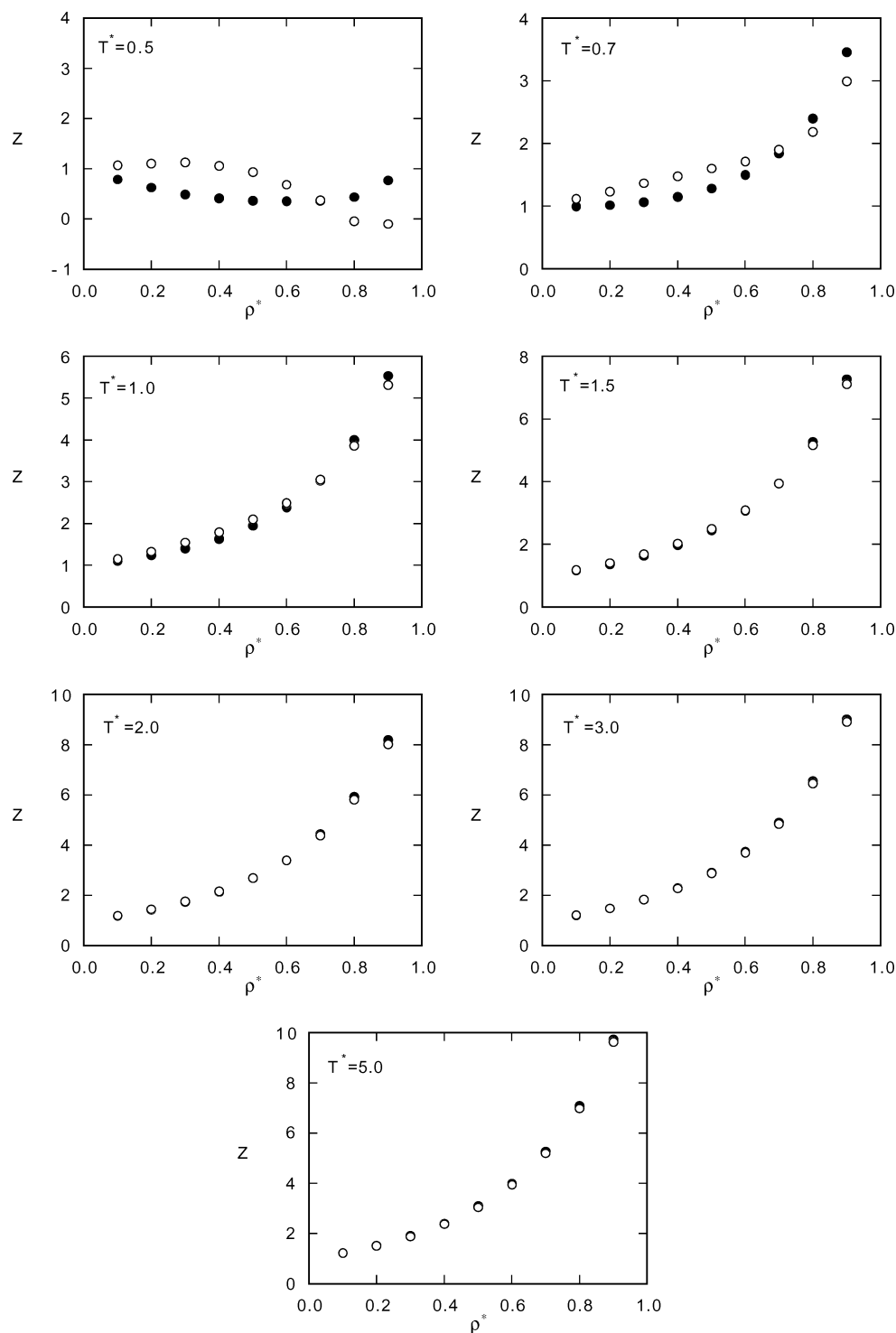
Figure 1. Comparison of the Monte Carlo perturbation theory (MC-P) (○) with the MC simulations (●) for the compressibility factor of a square-well fluid with well width $\lambda = 1.1$.

listed in Table 1 are in good agreement with those found in the literature.[19]

The values of Z obtained by MC-P using eq 8 and the MC values of Z_0 and Z_1 are compared in Figures 1−3 with the values of Z for the SW fluid reported previously[18] as a function of the reduced density ρ^* for different reduced temperatures T^* and potential widths $\lambda = 1.1$, 1.5, and 2.0. Similar results are obtained for other potential widths. From these Figures, it is clear that the MC-P procedure, truncated at the level of the first-order term, works very well, except perhaps at the lowest temperatures for the lowest potential widths.

TABLE 3: Monte Carlo Results for the First-Order Perturbative Contribution to the Compressibility Factor of an SW Fluid with $\lambda = 1.2'$

ρ^*	Z_1	g_{10}	$g_{1\lambda^-}$	$g_{1\lambda^+}$
0.10	−0.1881	0.9698	0.9716	−0.1093
0.20	−0.4757	0.9346	0.9461	−0.2520
0.30	−0.8674	0.8520	0.8741	−0.4178
0.40	−1.4343	0.6782	0.8161	−0.5671
0.50	−2.0744	0.5102	0.7626	−0.6790
0.60	−2.9468	0.2283	0.7174	−0.7718
0.70	−3.9852	−0.0917	0.7201	−0.8000
0.80	−5.2015	−0.5518	0.7089	−0.7683
0.90	−6.4170	−0.9955	0.7028	−0.6911

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TABLE 4: Monte Carlo Results for the First-Order Perturbative Contribution to the Compressibility Factor of an SW Fluid with $\lambda = 1.3'$

ρ^*	Z_1	g_{10}	$g_{1\lambda^-}$	$g_{1\lambda^+}$
0.10	−0.3143	0.8899	0.9181	−0.1700
0.20	−0.7275	0.7654	0.8089	−0.3299
0.30	−1.2567	0.5952	0.7136	−0.4677
0.40	−1.9729	0.3084	0.6588	−0.5535
0.50	−2.8237	0.0283	0.6440	−0.5962
0.60	−3.7493	−0.3397	0.6145	−0.5889
0.70	−4.6620	−0.6167	0.6128	−0.5539
0.80	−5.5472	−0.9845	0.5641	−0.4947
0.90	−5.9101	−1.1770	0.4732	−0.4182

TABLE 5: Monte Carlo Results for the First-Order Perturbative Contribution to the Compressibility Factor of an SW Fluid with $\lambda = 1.4'$

ρ^*	Z_1	g_{10}	$g_{1\lambda^-}$	$g_{1\lambda^+}$
0.10	−0.4199	0.8017	0.8327	−0.1901
0.20	−0.9799	0.5999	0.7169	−0.3543
0.30	−1.6802	0.3568	0.6427	−0.4619
0.40	−2.5387	0.0120	0.6028	−0.5059
0.50	−3.4253	−0.3049	0.5685	−0.5124
0.60	−4.2933	−0.5899	0.5542	−0.4759
0.70	−4.9808	−0.8102	0.5141	−0.4287
0.80	−5.4038	−0.9409	0.4322	−0.4002
0.90	−5.2817	−0.9163	0.3459	−0.3413

TABLE 6: Monte Carlo Results for the First-Order Perturbative Contribution to the Compressibility Factor of an SW Fluid with $\lambda = 1.5'$

ρ^*	Z_1	g_{10}	$g_{1\lambda^-}$	$g_{1\lambda^+}$
0.10	−0.5705	0.7434	0.8202	−0.2072
0.20	−1.2688	0.4851	0.6975	−0.3437
0.30	−2.0999	0.1787	0.6069	−0.4363
0.40	−3.0553	−0.1781	0.5684	−0.4594
0.50	−3.8798	−0.4523	0.5173	−0.4465
0.60	−4.7045	−0.6858	0.4971	−0.4090
0.70	−5.2110	−0.7301	0.4425	−0.3943
0.80	−5.1752	−0.6579	0.3644	−0.3559
0.90	−4.7183	−0.4168	0.3158	−0.3024

TABLE 7: Monte Carlo Results for the First-Order Perturbative Contribution to the Compressibility Factor of an SW Fluid with $\lambda = 1.6'$

ρ^*	Z_1	g_{10}	$g_{1\lambda^-}$	$g_{1\lambda^+}$
0.10	−0.7313	0.6991	0.7974	−0.2257
0.20	−1.6091	0.3821	0.6559	−0.3752
0.30	−2.5912	0.0614	0.5908	−0.4310
0.40	−3.5404	−0.2663	0.5451	−0.4217
0.50	−4.5046	−0.4553	0.5111	−0.4280
0.60	−5.1221	−0.5289	0.4615	−0.4045
0.70	−5.4260	−0.4881	0.4229	−0.3615
0.80	−5.2443	−0.2214	0.3986	−0.3115
0.90	−4.7243	0.1896	0.4001	−0.2581

TABLE 8: Monte Carlo Results for the First-Order Perturbative Contribution to the Compressibility Factor of an SW Fluid with $\lambda = 1.7'$

ρ^*	Z_1	g_{10}	$g_{1\lambda^-}$	$g_{1\lambda^+}$
0.10	−0.9058	0.6558	0.7746	−0.2392
0.20	−1.9287	0.3174	0.6316	−0.3702
0.30	−3.0165	0.0005	0.5645	−0.4128
0.40	−4.0462	−0.2517	0.5284	−0.4034
0.50	−4.9462	−0.3054	0.4948	−0.4044
0.60	−5.5628	−0.2685	0.4602	−0.3861
0.70	−5.7609	−0.0710	0.4319	−0.3534
0.80	−5.7877	0.3537	0.4433	−0.3318
0.90	−5.5660	0.8264	0.4384	−0.3308

TABLE 9: Monte Carlo Results for the First-Order Perturbative Contribution to the Compressibility Factor of an SW Fluid with $\lambda = 1.8'$

ρ^*	Z_1	g_{10}	$g_{1\lambda^-}$	$g_{1\lambda^+}$
0.10	−1.1056	0.6228	0.7558	−0.2561
0.20	−2.3116	0.2679	0.6271	−0.3651
0.30	−3.5138	0.0380	0.5508	−0.4147
0.40	−4.7090	−0.1764	0.5242	−0.4093
0.50	−5.5184	−0.0810	0.4937	−0.3960
0.60	−6.2743	0.1398	0.4863	−0.3938
0.70	−6.6124	0.4042	0.4737	−0.3690
0.80	−7.2644	0.8710	0.4995	−0.3932
0.90	−8.7179	1.2195	0.5680	−0.4341

TABLE 10: Monte Carlo Results for the First-Order Perturbative Contribution to the Compressibility Factor of an SW Fluid with $\lambda = 1.9'$

ρ^*	Z_1	g_{10}	$g_{1\lambda^-}$	$g_{1\lambda^+}$
0.10	−1.3139	0.6023	0.7585	−0.2439
0.20	−2.7048	0.2859	0.6258	−0.3573
0.30	−4.1214	0.0968	0.5689	−0.4015
0.40	−5.4611	0.0232	0.5270	−0.4267
0.50	−6.4061	0.2358	0.5186	−0.4076
0.60	−7.4898	0.4806	0.5254	−0.4137
0.70	−8.7077	0.7818	0.5708	−0.4091
0.80	−10.2808	1.0820	0.6232	−0.4292
0.90	−12.9625	1.0019	0.6875	−0.4611

TABLE 11: Monte Carlo Results for the First-Order Perturbative Contribution to the Compressibility Factor of an SW Fluid with $\lambda = 2.0'$

ρ^*	Z_1	g_{10}	$g_{1\lambda^-}$	$g_{1\lambda^+}$
0.10	−1.5924	0.5950	0.7627	−0.2620
0.20	−3.0870	0.3619	0.6139	−0.3526
0.30	−4.8103	0.2295	0.5736	−0.4121
0.40	−6.3386	0.2633	0.5606	−0.4181
0.50	−7.7594	0.5572	0.5697	−0.4262
0.60	−9.1529	0.8538	0.5949	−0.4222
0.70	−10.8885	1.1728	0.6289	−0.4461
0.80	−14.0066	1.1599	0.6797	−0.5102
0.90	−18.2924	0.8065	0.6746	−0.6393

III. Barker−Henderson and Tang−Lu Perturbation Theories

III.1 Barker−Henderson Perturbation Theory. In perturbation theory, the Helmholtz free energy can be expressed as a power series in the inverse of the reduced temperature in the form

$$\frac{F}{NkT} = \frac{F_0}{NkT} + \sum_{n=1}^{\infty} \frac{F_n}{NkT} \frac{1}{T^{*n}} \qquad (11)$$

where F_0 is the Helmholtz free energy of the reference HS fluid and the coefficient F_n is the perturbative contribution of order n that depends only on the packing fraction $\eta = \pi \rho \sigma^3/6$ of the reference HS fluid.

In the Barker−Henderson perturbation theory, the first-order contribution is given by[1,6]

$$\frac{F_1}{NkT} = 2\pi\rho \int_0^\infty u_1^*(r)\, g_0(r) r^2\, \mathrm{d}r \qquad (12)$$

The same authors propose two different approximations for the second-order term. Thus, in the macroscopic compressibility (mc) approximation

$$\frac{F_2}{NkT} = -\pi\rho kT \left(\frac{\partial\rho}{\partial p}\right)_0 \int_0^\infty [u_1^*(r)]^2\, g_0(r) r^2\, \mathrm{d}r \qquad (13)$$
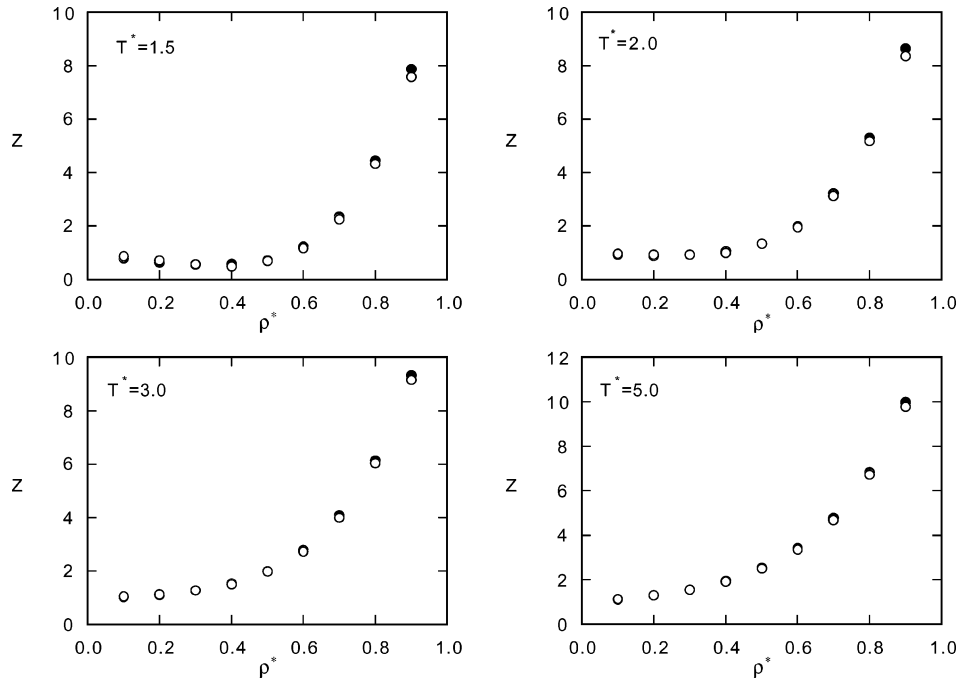
Figure 2. Comparison of the Monte Carlo perturbation theory (MC−P) (○) with the MC simulations (●) for the compressibility factor of a square-well fluid with well width $\lambda = 1.5$.
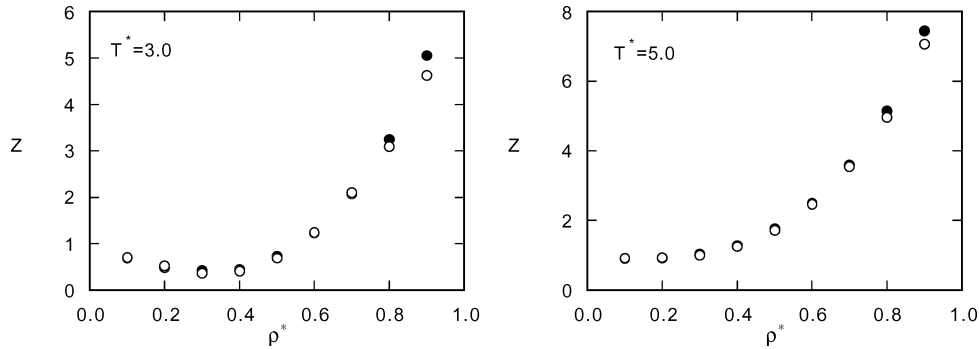

Figure 3. Comparison of the Monte Carlo perturbation theory (MC−P) (○) with the MC simulations (●) for the compressibility factor of a square-well fluid with well width $\lambda = 2.0$.

and in the local compressibility (lc) approximation

$$\frac{F_2}{NkT} = -\pi\rho kT \int_0^\infty [u_1^*(r)]^2 \left\{ \frac{\partial[\rho g_0(r)]}{\partial p} \right\}_0 r^2 \, dr \qquad (14)$$

Smith et al.[3] developed an alternative, and more rigorous although much more cumbersome, numerical procedure to determine F_2. A MC procedure to obtain F_1 and F_2 was developed by Barker and Henderson[2] and used to calculate these perturbative contributions for an SW fluid with $\lambda = 1.5$. On the basis of these MC calculations, they reported[5] a parametrization for F_2.

For a SW fluid, the perturbative contributions (12−14) can be expressed in a more convenient way by means of the coordination number N_c^{HS} of the reference HS fluid

$$N_c^{HS} = 24\eta \int_1^\lambda g_0(x) x^2 \, dx \qquad (15)$$

which represents the average number of particles in the reference HS fluid whose center lies at a reduced distance $x = r/\sigma$ lower than λ from the center of a given particle.

In terms of this coordination number, eqs 12−14 transform into

$$\frac{F_1}{NkT} = -\frac{1}{2} N_c^{HS} \qquad (16)$$

$$\frac{F_2}{NkT} = -\frac{kT}{\sigma^3} \frac{3}{2\pi} \left(\frac{\partial\eta}{\partial p}\right)_0 N_c^{HS} \qquad (17)$$

and

$$\frac{F_2}{NkT} = -\frac{kT}{\sigma^3} \frac{3\eta}{2\pi} \left(\frac{\partial\eta}{\partial p}\right)_0 \frac{\partial N_c^{HS}}{\partial\eta} \qquad (18)$$

respectively, where $\eta = (\pi/6)\rho\sigma^3$ is the packing fraction.

The compressibility factor can be obtained from eq 11 in the form

$$Z = \frac{pV}{NkT} = \left(\frac{pV}{NkT}\right)_0 + \eta \frac{\partial}{\partial\eta}\left[\frac{F}{NkT} - \frac{F_0}{NkT}\right] =$$

$$Z_0 + Z_1 \frac{1}{T^*} + Z_2 \frac{1}{T^{*2}} + \dots \quad (19)$$

where from eq 16

$$Z_1 = \frac{p_1 V}{NkT} = -\frac{\eta}{2} \frac{\partial N_c^{HS}}{\partial \eta} \tag{20}$$

and from eqs 17 and 18

$$Z_2 = \frac{p_2 V}{NkT} = -\frac{kT}{\sigma^3} \frac{3}{2\pi} \eta \frac{\partial}{\partial \eta} \left[\left(\frac{\partial \eta}{\partial p} \right)_o N_c^{HS} \right] \tag{21}$$

and

$$Z_2 = \frac{p_2 V}{NkT} = -\frac{kT}{\sigma^3} \frac{3}{2\pi} \eta \frac{\partial}{\partial \eta} \left[\eta \left(\frac{\partial \eta}{\partial p} \right)_o \frac{\partial N_c^{HS}}{\partial \eta} \right] \tag{22}$$

respectively, for the mc and lc approximations. For the compressibility factor Z_0 of the HS reference system, we can use the Carnahan–Starling (CS) equation

$$Z^{HS} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \tag{23}$$

which can also be used to obtain the derivative $(\partial \eta / \partial p)_0$.

III.2 Simplified Expressions for the Coordination Number of the Hard-Sphere Fluid. The coordination number of the HS reference fluid can be determined from any suitable expression of the pcf for that fluid. Thus, for example, Chang and Sandler[21] have reported an analytical expression for N_c^{HS} based on the Percus–Yevick (PY) theory for the pcf. A more accurate analytical expression for the pcf that is compatible with any prescribed analytical equation of state of the HS fluid can be obtained from a procedure developed by Bravo Yuste et al.[22,23] The corresponding expression of N_c^{HS} has been reported previously.[24] In any case, these expressions can be simplified by means of a procedure developed by Tang and Lu.[12]

They start from an arbitrary function $f(x)$ whose Laplace transform is of the form

$$F^L(s) = \int_1^\infty x f(x) e^{-sx} dx \tag{24}$$

Then, using the Hilbert transform to split $F^L(t)$ into two parts, one of them in the range $[1, \lambda]$, it holds[12] that

$$\int_1^\lambda f(x) x^2 dx = -\frac{dF^L(s)}{ds}\bigg|_{s=0} + Res\left[F^L(s) \frac{\lambda s - 1}{s^2} e^{\lambda s} \right] \tag{25}$$

where Res represents the summation of residues produced by all singularities in the function $F^L(s)$.

We will use eq 25 to simplify the calculation of the coordination number N_c^{HS} both in the PY as well as in the Bravo Yuste et al.[22,23] theories. We are interested in the first coordination shell of the HS fluid, that is, $1 \le x \le 2$. In this region, the Laplace transform of $xg(x)$ is

$$L[xg(x)] = tF(t)e^{-t} \tag{26}$$

where

$$F(t) = -\frac{1}{12\eta} \frac{L(t)}{S(t)} \tag{27}$$

with

$$L(t) = 1 + \sum_{j=1}^l L_j t^j \tag{28}$$

and

$$S(t) = 1 + \sum_{k=1}^m S_k t^k \tag{29}$$

Then, using eqs 24 and 25, with

$$f(x) = g(x) \tag{30}$$

and

$$F^L(s) = sF(s)e^{-s} = -\frac{s}{12\eta} \frac{L(s)}{S(s)} e^{-s} \tag{31}$$

we obtain

$$\int_1^\lambda g(x) x^2 dx = -\frac{d}{ds}\left[-\frac{s}{12\eta} \frac{L(s)}{S(s)} e^{-s} \right]\bigg|_{s=0} + Res\left[-\frac{s}{12\eta} \frac{L(s)}{S(s)} e^{-s} \frac{\lambda s - 1}{s^2} e^{\lambda s} \right]$$

$$= \frac{1}{12\eta} + Res\left[-\frac{1}{12\eta} \frac{L(s)}{S(s)} \frac{\lambda s - 1}{s} e^{(\lambda-1)s} \right] \tag{32}$$

where the residue of a function in a pole of order n is given by

$$Res_n[f(s)] = \frac{1}{(n-1)!} \lim_{s \to t}\left\{ \frac{d^{n-1}}{ds^{n-1}}[(s-t)^n f(s)] \right\} \tag{33}$$

The polynomial $S(t)$ has s roots t_i, $i = 1,..., s$ giving rise to singularities. The residue in eq 32, is of order 1 if $x \le 2$ so that

$$N_c^{HS} = 2 - 2 \sum_{i=1}^s \frac{L(t_i)(\lambda t_i - 1)}{S'(t_i) t_i} e^{(\lambda-1)t_i} \tag{34}$$

It is obvious that eq 34 is considerably simpler than eq 15 because in the former we do not need to know explicitly the pcf $g(r)$ or carry out the integration of eq 15. More important, in the context of the Barker–Henderson perturbation theory, is that the derivatives of the coordination number that appear in eqs 20–22 are easily performed from eq 34 in the form

$$\frac{\partial N_c^{HS}}{\partial \eta} = \frac{\partial}{\partial \eta}\left[2 - 2 Res\left[\frac{L(s)}{S(s)} \frac{\lambda s - 1}{s} e^{(\lambda-1)s} \right] \right]$$

$$= -2 Res\left[\frac{\partial}{\partial \eta}\left(\frac{L(s)}{S(s)} \right) \frac{\lambda s - 1}{s} e^{(\lambda-1)s} \right]$$

$$= -2 Res\left[\left[\frac{Lr(s) S(s) - L(s) Sr(s)}{S^2(s)} \right] \frac{\lambda s - 1}{s} e^{(\lambda-1)s} \right] \tag{35}$$

where $Lr(s) = \partial L(s)/\partial \eta$ and $Sr(s) = \partial S(s)/\partial \eta$. Now, the residues are of order 2 so that, denoting

$$A(s) = (Lr(s) S(s) - L(s) Sr(s)) \frac{\lambda s - 1}{s} \tag{36}$$

and $A'(s) = \partial A(s)/\partial s$, expression 35 transforms into

$$\frac{\partial N_c^{HS}}{\partial \eta} = -2\sum_{i=1}^{s}\left[\frac{A'(t_i) + (\lambda - 1)A(t_i)}{S'^2(t_i)} - \frac{S''(t_i)\,A(t_i)}{S'^3(t_i)}\right]e^{(\lambda-1)t_i} \tag{37}$$

Similarly,

$$\frac{\partial^2 N_c^{HS}}{\partial \eta^2} = -2Res\left[\frac{\partial^2}{\partial\eta^2}\left[\frac{L(s)}{S(s)}\right]\frac{\lambda s - 1}{s}e^{(\lambda-1)s}\right] \tag{38}$$

Then, $B(s)$ is defined in the form

$$B(s) = (Lrr(s)\,S^2(s) - L(s)\,Srr(s)\,S(s) - 2Lr(s)\,Sr(s) + \\ 2L(s)\,Sr^2(s))\frac{\lambda s - 1}{s}e^{(\lambda-1)s} \tag{39}$$

where $Lrr(s) = \partial^2 L(s)/\partial\eta^2$ and $Srr(s) = \partial^2 S(s)/\partial\eta^2$. By taking the derivatives $B'(s) = \partial B(s)/\partial s$ and $B''(s) = \partial^2 B(s)/\partial s^2$, we arrive at

$$\frac{\partial^2 N_c^{HS}}{\partial \eta^2} = -\sum_{i=1}^{s}\{B''(t_i)\,S'^2(t_i) - 3B'(t_i)\,S''(t_i)\,S'(t_i) - B(t_i)\,S''' \\ (t_i)\,S'(t_i) + 3B(t_i)\,S''^2(t_i)\}/S'^5(t_i) \tag{40}$$

Equations 34, 37, and 40 can be used within the context of either the Percus−Yevick theory or the Bravo Yuste et al.[22,23] theory. In the former, $l = 1$, $m = 3$, and[25]

$$L_1^{PY} = \frac{1 + \frac{1}{2}\eta}{1 + 2\eta} \tag{41}$$

$$S_1^{PY} = -\frac{3}{2}\frac{\eta}{1 + 2\eta} \tag{42}$$

$$S_2^{PY} = -\frac{1}{2}\frac{1 - \eta}{1 + 2\eta} \tag{43}$$

and

$$S_3^{PY} = -\frac{(1 - \eta)^2}{12\eta(1 + 2\eta)} \tag{44}$$

In the Bravo Yuste et al.[22,23] theory, $l = 2$, $m = 4$, and

$$L_1 = L_1^{PY} + \frac{12\eta}{1 + 2\eta}\left(\frac{1}{2}L_2 - S_4\right) \tag{45}$$

$$S_1 = S_1^{PY} + \frac{12\eta}{1 + 2\eta}\left(\frac{1}{2}L_2 - S_4\right) \tag{46}$$

$$S_2 = S_2^{PY} + \frac{12\eta}{1 + 2\eta}\left(\frac{1 - 4\eta}{12\eta}L_2 + S_4\right) \tag{47}$$

$$S_3 = S_3^{PY} - \frac{12\eta}{1 + 2\eta}\left(\frac{1 - \eta}{12\eta}L_2 + \frac{1}{2}S_4\right) \tag{48}$$

$$L_2 = -3(Z^{HS} - 1)S_4 \tag{49}$$

and

$$S_4 = \frac{1 - \eta}{36\eta\left(Z - \frac{1}{3}\right)}\left\{1 - \left[1 + \frac{Z^{HS} - \frac{1}{3}}{Z^{HS} - Z^{PY}}\left(\frac{K_T^{HS}}{K_T^{PY}} - 1\right)\right]^{1/2}\right\} \tag{50}$$

For Z^{HS}, we can use any suitable equation of state for the HS fluid, such as the Carnahan−Starling equation (eq 23), and K_T^{HS} would be the corresponding isothermal compressibility, whereas Z^{PY} is the Percus−Yevick equation of state and K_T^{PY} the corresponding isothermal compressibility.

III.3 Tang−Lu Perturbation Theory. Tang and Lu[12,26] have developed a procedure to obtain an analytical expression of the pcf, and hence the equation of state, by combining the mean spherical approximation (MSA) with a perturbative expansion. They express[12] the Laplace transform of the pcf of the SW fluid in the form

$$g^L(s) = g_0^L(s) + \beta\epsilon g_1^L(s) + \cdots \tag{51}$$

where g_0^L is the Laplace transform of the hard-sphere pcf as given by the Percus−Yevick theory. They also reported[12] an analytical expression for the inverse Laplace transform of the first-order term $g_1^L(s)$ in the expansion (eq 51) up to $r = 2\sigma$. From that expression, one can easily find the first-order contribution Z_1 to the compressibility factor.

We note that the idea of combining a perturbative expansion with integral equation theory to obtain the terms in the expansion is not new. As stated previously, many authors have exploited this idea. Restricting ourselves to the SW fluid, perturbative contributions to the pcf have been obtained from the Percus−Yevick theory,[7,8] the Ivon−Born−Green equation,[9,11] the mean spherical approximation,[6] and the hypernetted chain approximation.[6,10] What is new in the TL[12,26] theory is that they have reported an analytical and relatively simple expression for the first-order perturbative contribution $g_1(r)$ to the pcf up to a distance $r = 2\sigma$, as stated before. This in turn allows us to obtain an analytical expression for the first-order perturbative contribution, Z_1, to the compressibility factor trough expression (eq 10). This, in principle, makes the TL theory for Z_1 of comparable difficulty and usefulness to the BH expression (eq 20). This is the main reason for having considered these two theories in this paper.

IV. Results and Discussion

In Figure 4, the results for the first-order perturbative contribution Z_1 to the compressibility factor, as obtained from the Barker−Henderson theory using either the PY[25] theory or the Bravo Yuste et al.[22,23] theory for the pcf of the hard-sphere reference fluid, are compared with those obtained from the TL[12,26] theory and with the MC results of Tables 2−11. The Figure shows that the BH theory with the PY pcf gives results hardly distinguishable on the scale of the Figure from the results given by the TL theory. This is perhaps a bit surprising because, as shown in the previous section, the former theory uses the energy route whereas the latter uses the virial route to obtain the equation of state, and it is known that different routes usually give different results. Moreover, we must take into account that the two theories have very different foundations.

Slightly better results at high densities are obtained with the BH theory with the Bravo Yuste et al. pcf. This might have been expected because it is known that the PY pcf for the HS fluid is not accurate enough at high densities for short distances in contrast to the Bravo Yuste et al. pcf. This fact, together with its greater simplicity, should make the BH perturbation theory preferable to the TL perturbation theory for many applications. In addition, there are a number of ways[1,3] to determine the second-order perturbative contribution to the equation of state and other thermodynamic properties within the context of the BH theory, whereas this is not the case for
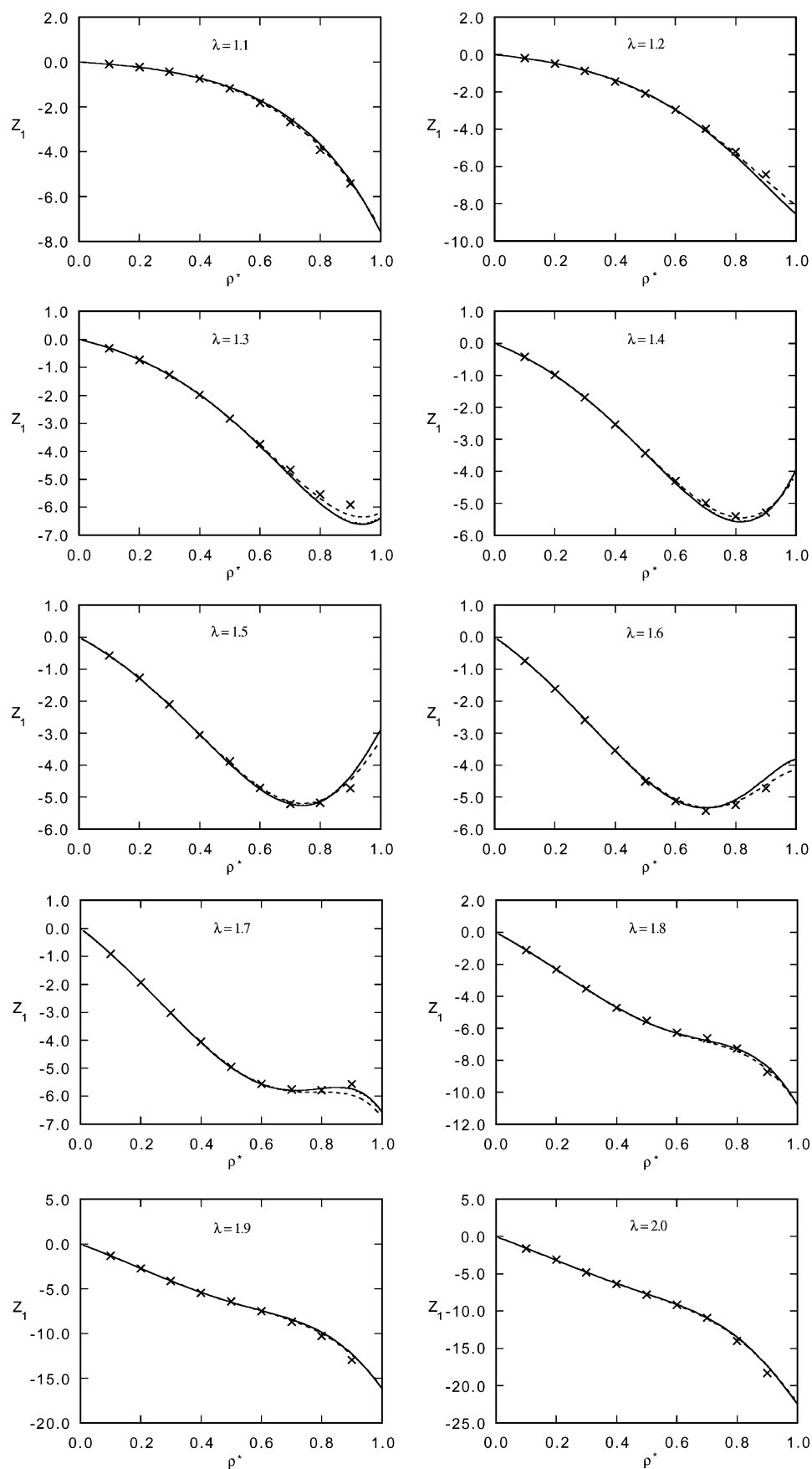
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Figure 4. Comparison of the Monte Carlo values for the first perturbative contribution Z_1 to the equation of state ($\times$) with the theoretical predictions of the Barker−Henderson perturbation theory with the Percus−Yevick pcf (continuous curves) and with the Bravo Yuste et al.[22,23] pcf (dashed curves), and the Tang and Lu perturbation theory[12,26] (dotted curves). Continuous and dotted curves are nearly indistinguishable from each other on the scale of the plot.

the TL theory; nevertheless, the TL theory has the advantage over the BH theory of providing an analytical expression for the first-order perturbative contribution to the pcf of the SW fluid. With this expression and the PY theory for the zero-order contribution, the truncated expansion (eq 6) provides reasonable results for the pcf of SW fluids[12,27] with values of the range, density, or temperature that are not too low. Therefore, if we are interested in the thermodynamic properties, the BH theory should be preferred, whereas if we are interested in the structural properties, the choice would be the TL theory. In any case, as is clear from Figures 1−3, at relatively low temperatures, the perturbative expansion (eq 19) of the compressibility factor, truncated at the level of the first-order term, will not suffice, independent of the theory used, to obtain accurate results.

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