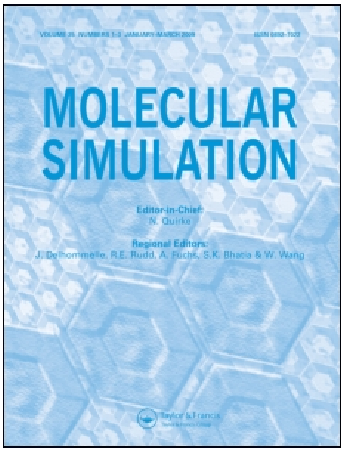

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Theory and Computer Simulation of the First- and Second-order Perturbative Contributions to the Free Energy of Square-well Fluids

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We have performed extensive MC simulations in the NVT ensemble of the first- and second-order perturbative contributions, F_1 and F_2, to the free energy of square-well (SW) fluids for wide ranges of densities and potential widths. These data are used to test the accuracy of theoretical calculations performed within the framework of the Barker–Henderson perturbation theory. For F_2 the performance of several approximations is analyzed.

Keywords: Perturbation theory; Computer simulation; Helmholtz free energy; Statistical mechanics

INTRODUCTION

In the Barker–Henderson perturbation theory [1], the thermodynamic properties of a fluid are expressed as power series of the inverse of the temperature, with the zero-order term giving the contribution due to a reference fluid suitably chosen. For systems with spherically symmetrical potentials, the appropriate reference fluid is the hard-sphere (HS) fluid, whose thermodynamic properties are well know both from theory as well as from computer simulation.

The Barker–Henderson theory has been successfully applied to fluids with molecules interacting by means of a variety of potential models. The theory is particularly simple to apply to fluids with square-well (SW) potentials of the form

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

where σ is the diameter of the particles, $-\epsilon$ the potential depth, and $\lambda\sigma$ the potential width.

When applied to this model of fluids, the theory has proved to be accurate for predicting the equation of state, except perhaps at very low temperatures. Less accurate are the results obtained for the excess internal energy [2,3]. This property is intimately related to the second order perturbative contribution F_2 to the free energy. This contribution has been studied both from theory as well as from computer simulation, for a potential width $\lambda = 1.5$ [4–7]. However, to the best of our knowledge, studies for other potential widths have not been reported.

The aim of this paper is to analyze the performance of the Barker–Henderson second order perturbation theory for SW fluids with potential widths λ ranging from 1.1 to 2.0. To this end, we have performed MC simulations on the reference HS system to determine the first- and second-order perturbative contributions F_1 and F_2 to the Helmholtz free energy. They are presented in "Monte Carlo simulations" section. These results are used to compare with the corresponding theoretical calculations. The second-order Barker–Henderson perturbation theory is summarized in "Perturbation theory" section. For the second-order contribution to the free energy three different approximations have been considered, namely the so-called *macroscopic compressibility* (mc) and *local compressibility* (lc) approximations [1], as well as a more refined approximation [6]. The latter is presented in "A more defined approximation for the second-order term" section. Finally, the results are discussed in the last section.

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TABLE I Monte Carlo simulations of the first-order perturbative contribution F_1/NkT to the Helmholtz free energy of a square-well fluids

ρ^*	$\lambda = 1.1$	$\lambda = 1.2$	$\lambda = 1.3$	$\lambda = 1.4$	$\lambda = 1.5$	$\lambda = 1.6$	$\lambda = 1.7$	$\lambda = 1.8$	$\lambda = 1.9$	$\lambda = 2.0$
0.10	−0.078	−0.170	−0.276	−0.397	−0.534	−0.689	−0.862	−1.055	−1.270	−1.508
0.20	−0.178	−0.380	−0.607	−0.861	−1.142	−1.454	−1.800	−2.182	−2.606	−3.078
0.30	−0.305	−0.638	−1.000	−1.393	−1.819	−2.284	−2.792	−3.353	−3.975	−4.672
0.40	−0.467	−0.953	−1.460	−1.991	−2.555	−3.157	−3.811	−4.532	−5.339	−6.257
0.50	−0.673	−1.333	−1.988	−2.649	−3.329	−4.046	−4.822	−5.684	−6.668	−7.816
0.60	−0.937	−1.789	−2.584	−3.350	−4.117	−4.916	−5.786	−6.776	−7.944	−9.350
0.70	−1.274	−2.325	−3.235	−4.069	−4.882	−5.728	−6.672	−7.791	−9.175	−10.900
0.80	−1.703	−2.943	−3.924	−4.773	−5.585	−6.445	−7.451	−8.730	−10.405	−12.542
0.90	−2.246	−3.635	−4.618	−5.420	−6.185	−7.033	−8.116	−9.641	−11.739	−14.378

MONTE CARLO SIMULATIONS

A potential of the form (1) can be split in the form

$$u(r) = u_0(r) + \epsilon u_1^*(r) \tag{2}$$

where $u_0(r)$ is the HS potential and $\epsilon u_1^*(r)$ the perturbative contribution. For a fluid whose particles interact by means of a potential of this kind, the thermodynamic properties can be expressed as an expansion in power series of the inverse of the reduced temperature $T^* = kT/\epsilon$. In particular, the free energy may be expressed in the form

$$\frac{F}{NkT} = \frac{F_0}{NkT} + \sum_{i=1}^{\infty} \frac{F_i}{NkT} \frac{1}{T^{*i}} \tag{3}$$

where F_0 is the Helmholtz free energy of the reference HS fluid and the coefficients F_i depends only on the packing fraction $\eta = \pi\rho\sigma^3/6$ of the reference HS fluid. The first-order term for a SW fluid is given in Refs. [4,7]

$$\frac{F_1}{NkT} = -\frac{\langle M \rangle_0}{N} \tag{4}$$

where $\langle M \rangle_0$ is the average number of pairs in the reference system separated by a distance ranging between σ and $\lambda\sigma$.

The second-order term in the expansion (3) can be expressed as the fluctuation of M around his average value [4,7]

$$\frac{F_2}{NkT} = -\frac{1}{2N} \langle [M - \langle M \rangle_0]^2 \rangle_0 \tag{5}$$

where subscript zero indicates that the averages are performed on the reference HS system. Higher order momenta of the distribution of pairs lead to higher order terms in the expansion (3).

We have performed MC simulations in the NVT ensemble of a system consisting of 512 hard spheres initially placed in a regular configuration. The systems was 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 2.5×10^5 cycles by counting the number of pairs within the potential well after each cycle. The acceptance ratio was settled to about 50%. Potential wells in the range $1.1 \leq \lambda \leq 2.0$ and reduced densities $\rho^* = \rho\sigma^3$ from 0.1 to 0.9 where considered. Results are shown in Tables I and II. Several independent runs were performed in order to estimate the accuracy of the simulations from the standard deviation. The estimated error in F_1/NkT is beyond the third decimal figure of the data reported in Table I, whereas the estimated error in F_2/NkT is always lower than 1%. Our results for $\lambda = 1.5$ are in good agreement with those available in Refs. [4–7].

PERTURBATION THEORY

In the Barker–Henderson perturbation theory, the first-order contribution to the free energy of a SW fluid can be expressed in the form [1]

$$\frac{F_1}{NkT} = 2\pi\rho \int_{\sigma}^{\infty} u_1^*(r) g_0(r) r^2 \mathrm{d}r, \tag{6}$$

where $g_0(r)$ is the radial distribution function (r.d.f.) of the HS reference fluid. The second order term in

TABLE II MC simulations of the second-order perturbative contribution F_2/NkT to the Helmholtz free energy of a square-well fluids

ρ^*	$\lambda = 1.1$	$\lambda = 1.2$	$\lambda = 1.3$	$\lambda = 1.4$	$\lambda = 1.5$	$\lambda = 1.6$	$\lambda = 1.7$	$\lambda = 1.8$	$\lambda = 1.9$	$\lambda = 2.0$
0.10	−0.037	−0.074	−0.113	−0.152	−0.194	−0.238	−0.285	−0.334	−0.388	−0.448
0.20	−0.077	−0.141	−0.197	−0.245	−0.292	−0.337	−0.383	−0.434	−0.490	−0.552
0.30	−0.119	−0.197	−0.249	−0.287	−0.322	−0.357	−0.395	−0.437	−0.485	−0.543
0.40	−0.163	−0.236	−0.270	−0.292	−0.317	−0.348	−0.388	−0.430	−0.479	−0.541
0.50	−0.205	−0.257	−0.270	−0.284	−0.309	−0.342	−0.378	−0.422	−0.479	−0.553
0.60	−0.242	−0.260	−0.257	−0.277	−0.309	−0.339	−0.374	−0.426	−0.491	−0.598
0.70	−0.269	−0.251	−0.245	−0.275	−0.307	−0.337	−0.381	−0.440	−0.536	−0.673
0.80	−0.281	−0.229	−0.242	−0.273	−0.283	−0.313	−0.384	−0.455	−0.583	−0.758
0.90	−0.276	−0.214	−0.234	−0.250	−0.245	−0.299	−0.406	−0.492	−0.675	−0.795

the mc approximation is given by

$$\frac{F_2}{NkT} = -\pi\rho kT\left(\frac{\partial\rho}{\partial p}\right)_0\int_\sigma^\infty [u_1^*(r)]^2 g_0(r) r^2\,\mathrm{d}r \qquad (7)$$

and in the lc approximation

$$\frac{F_2}{NkT} = -\pi\rho kT\int_\sigma^\infty [u_1^*(r)]^2\left\{\frac{\partial[\rho g_0(r)]}{\partial p}\right\}_0 r^2\,\mathrm{d}r. \qquad (8)$$

For a SW fluid it is convenient to define the *coordination number* N_c^HS of the reference HS fluid in the form

$$N_\mathrm{c}^\mathrm{HS} = 24\eta\int_1^\lambda g_0(r^*) r^{*2}\,\mathrm{d}r^*. \qquad (9)$$

where $r^* = r/\sigma$ is the reduced distance. N_c^HS represents the average number of particles in the reference HS fluid whose center lies within a distance λ from the center of a given particle.

Then, from Eq. (6)

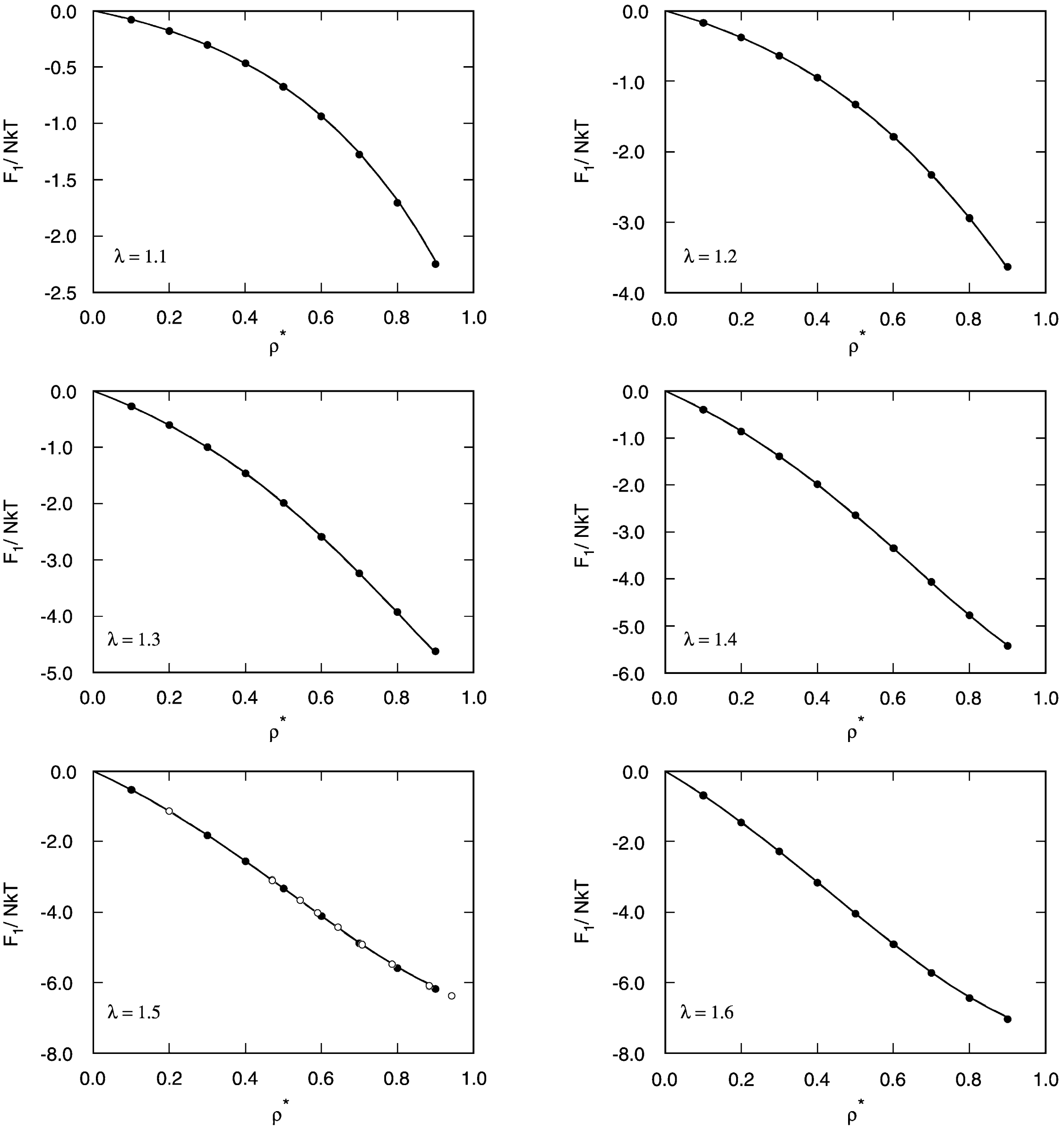
$$\frac{F_1}{NkT} = -\frac{1}{2}N_\mathrm{c}^\mathrm{HS}, \qquad (10)$$

and in the mc approximation, from Eq. (7)

$$\frac{F_2}{NkT} = -\frac{kT}{\sigma^3}\frac{3}{2\pi}\left(\frac{\partial\eta}{\partial p}\right)_0 N_\mathrm{c}^\mathrm{HS}. \qquad (11)$$

whereas in the lc approximation, from Eq. (8)

$$\frac{F_2}{NkT} = -\frac{kT}{\sigma^3}\frac{3\eta}{2\pi}\left(\frac{\partial\eta}{\partial p}\right)_0\frac{\partial N_\mathrm{c}^\mathrm{HS}}{\partial\eta}. \qquad (12)$$



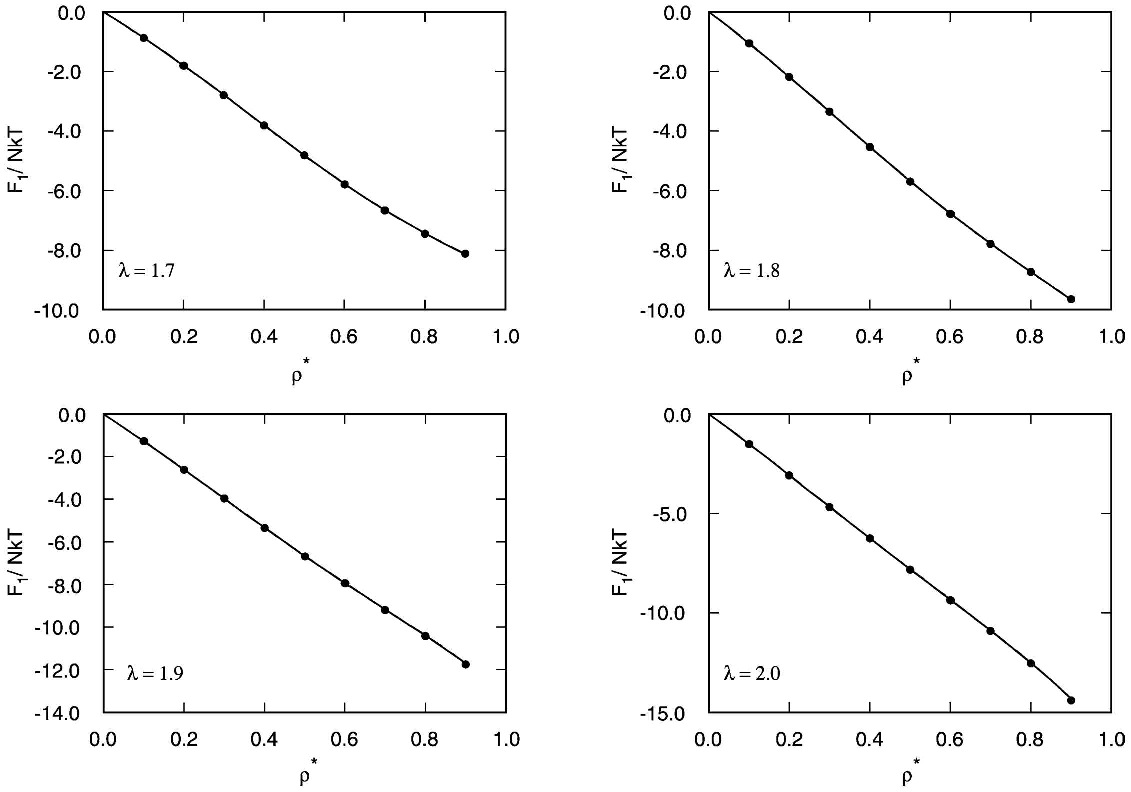


FIGURE 1 First order perturbative contribution F_1/NkT to the Helmholtz free energy of square-well fluids. Points: simulation data from this work (filled circles) and from Refs. [4–6] (open circles). Curves: Barker–Henderson perturbation theory.

The derivative $(\partial \eta/\partial p)_0$ can be determined from the equation of state of the HS reference fluid. To this end, we can use the Carnahan–Starling (CS) equation [8]

$$Z^{\mathrm{HS}} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}. \tag{13}$$

The fundamental quantity involved in Eqs. (6)–(8) is the coordination number $N_{\mathrm{c}}^{\mathrm{HS}}$, which in turn can be obtained from the p.c.f. through Eq. (9). A procedure to obtain accurate expressions of the r.d.f. of the HS fluid consistent with any prescribed equation of state, and in particular the CS equation, has been developed by Bravo Yuste *et al.* [9,10]. However, explicit expressions were not reported by these authors. Therefore, in Appendix 1 we include the analytical expressions of the r.d.f. and the coordination number which result from their procedure when the CS equation is used.

A MORE REFINED APPROXIMATION FOR THE SECOND-ORDER TERM

A more refined expression for the second-order contribution to the Helmholtz free energy is [6],

$$\frac{F_2}{NkT} = -\frac{1}{4}\rho J_1 - \frac{1}{2}\rho^2 J_2 - \frac{1}{8}\rho^3(2J_3+4J_4+J_5) \tag{14}$$

where

$$J_1 = \int [u_1^*(\vec{r}_1,\vec{r}_2)]^2 g_0(\vec{r}_1,\vec{r}_2)\mathrm{d}\vec{r}_2 \tag{15}$$

$$J_2 = \int\int u_1^*(\vec{r}_1,\vec{r}_2)g_0(\vec{r}_1,\vec{r}_2)u_1^*(\vec{r}_2,\vec{r}_3)g_0(\vec{r}_2,\vec{r}_3) \times h_0(\vec{r}_1,\vec{r}_3)\mathrm{d}\vec{r}_2\mathrm{d}\vec{r}_3 \tag{16}$$

$$J_3 = \int\int\int u_1^*(\vec{r}_1,\vec{r}_2)g_0(\vec{r}_1,\vec{r}_2)u_1^*(\vec{r}_3,\vec{r}_4)g_0(\vec{r}_3,\vec{r}_4)h_0(\vec{r}_1,\vec{r}_3) \times h_0(\vec{r}_2,\vec{r}_4)\mathrm{d}\vec{r}_2\mathrm{d}\vec{r}_3\mathrm{d}\vec{r}_4 \tag{17}$$

$$J_4 = \int\int\int u_1^*(\vec{r}_1,\vec{r}_2)g_0(\vec{r}_1,\vec{r}_2)u_1^*(\vec{r}_3,\vec{r}_4)g_0(\vec{r}_3,\vec{r}_4) \times h_0(\vec{r}_1,\vec{r}_3)h_0(\vec{r}_1,\vec{r}_4)h_0(\vec{r}_2,\vec{r}_4)\mathrm{d}\vec{r}_2\mathrm{d}\vec{r}_3\mathrm{d}\vec{r}_4 \tag{18}$$

and

$$J_5 = \int\int\int u_1^*(\vec{r}_1,\vec{r}_2)g_0(\vec{r}_1,\vec{r}_2)u_1^*(\vec{r}_3,\vec{r}_4)g_0(\vec{r}_3,\vec{r}_4)h_0(\vec{r}_2,\vec{r}_3) \times h_0(\vec{r}_1,\vec{r}_3)h_0(\vec{r}_1,\vec{r}_4)h_0(\vec{r}_2,\vec{r}_4)\mathrm{d}\vec{r}_2\mathrm{d}\vec{r}_3\mathrm{d}\vec{r}_4 \tag{19}$$

with $h_0(r) = g_0(r) - 1$.

For a SW fluid, the second order term (14) has no analytical solution. The term J_1 is easy to calculate because for the SW potential is proportional to the first order term F_1. The second integral can be determined in either of two ways

$$J_2 = 4\pi\int_0^\infty u_1^*(r)g_0(r)\gamma(r)r^2\mathrm{d}r \tag{20}$$

or

$$J_2 = 4\pi\int_0^\infty h_0(r)\gamma'(r)r^2\mathrm{d}r \tag{21}$$

where

$$\gamma(x) = \frac{2\pi}{x}\int_0^\infty u_1^*(y)g_0(y)y\mathrm{d}y\int_{|x-y|}^{x+y} h_0(z)z\mathrm{d}z \tag{22}$$

and

$$\gamma'(x) = \frac{2\pi}{x}\int_0^\infty u_1^*(y)g_0(y)y\mathrm{d}y\int_{|x-y|}^{x+y} u_1^*(z)g_0(z)z\mathrm{d}z. \tag{23}$$

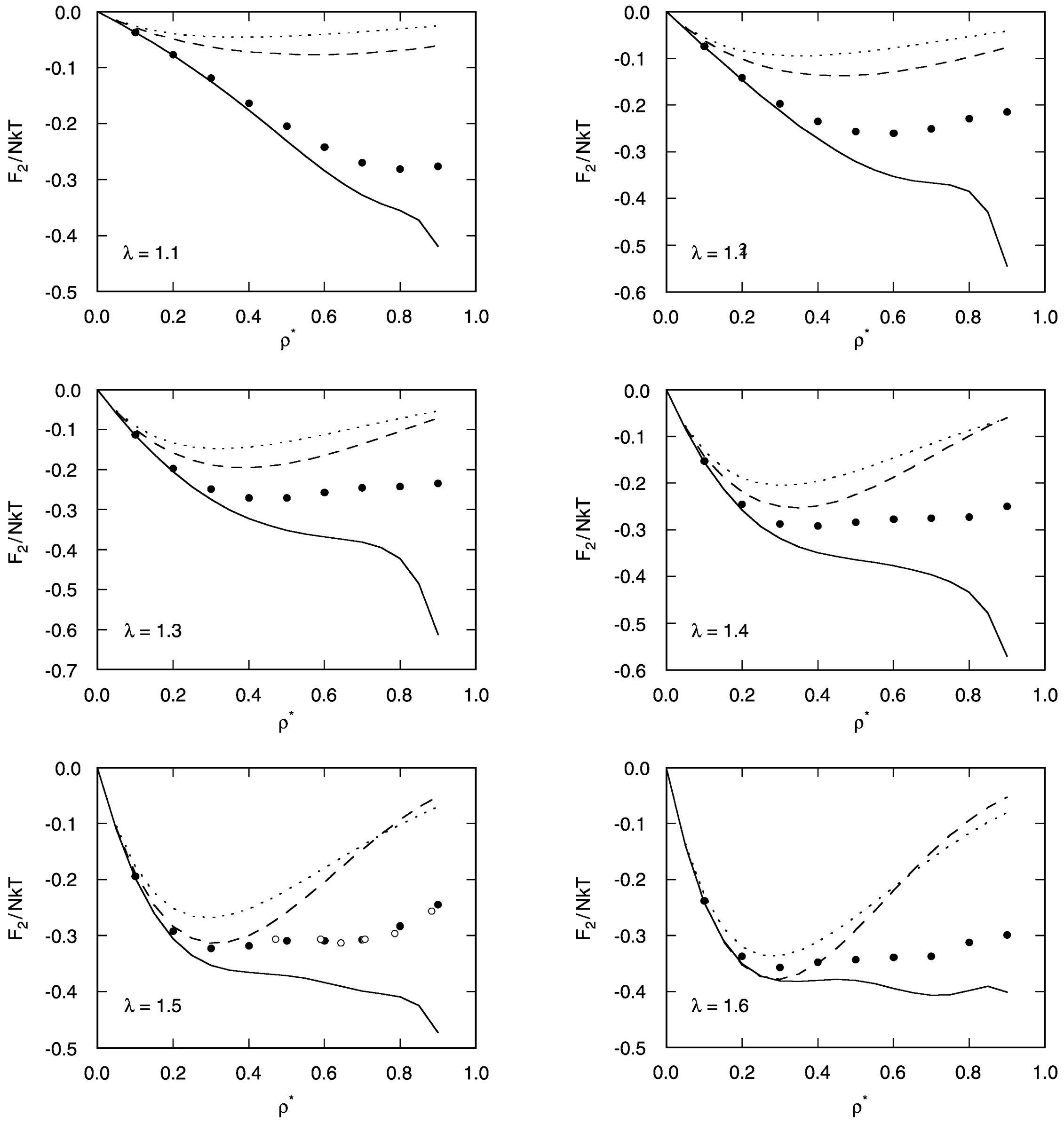
Using these auxiliary functions we can rewrite J_3 and J_4 in the form,

$$J_3 = 4\pi\int_0^\infty [\gamma(r)]^2 r^2\mathrm{d}r \tag{24}$$

and

$$J_4 = 4\pi\int_0^\infty h_0(r)[\gamma(r)]^2 r^2\mathrm{d}r. \tag{25}$$

The most difficult integration is that of J_5. It is performed by expanding the integrand in series of



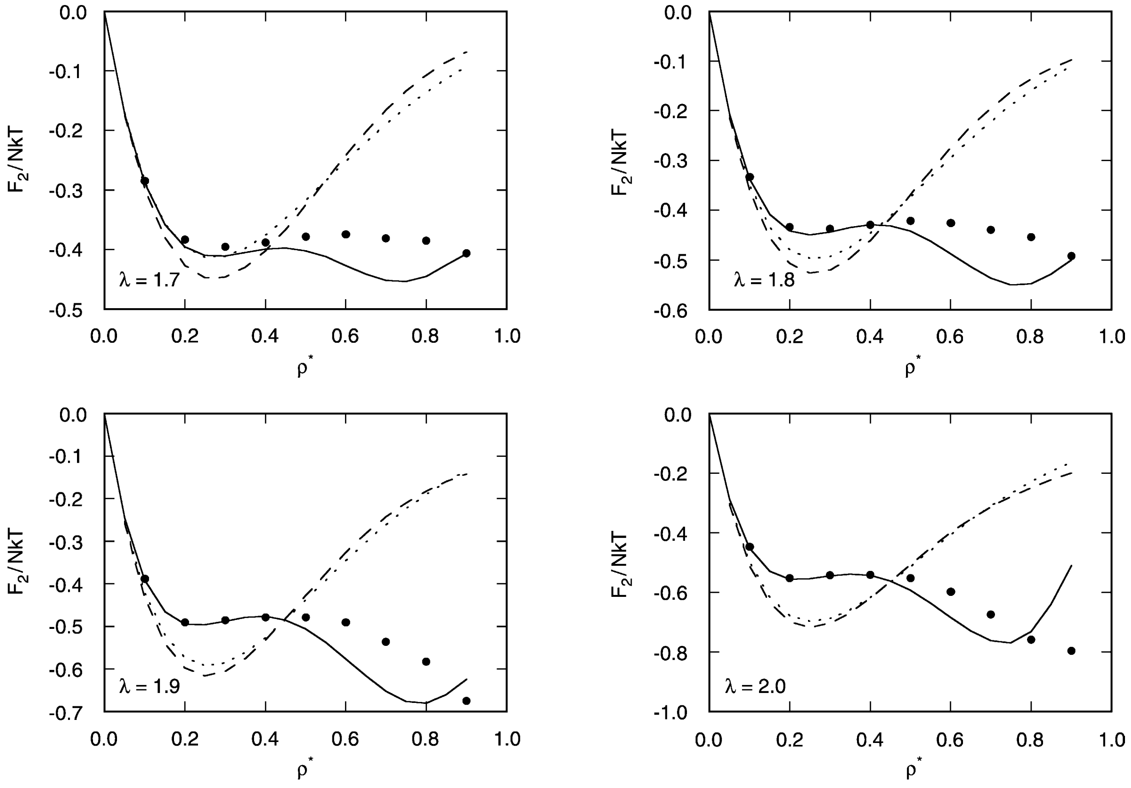


FIGURE 2 Second order perturbative contribution F_2/NkT to the Helmholtz free energy of square-well fluids. Points: simulation data from this work (filled circles) and from Refs. [4–6] (open circles). Curves: Barker–Henderson perturbation theory in the refined version (continuous curves), in the local compressibility approximation (dashed curves), and in the macroscopic compressibility approximation (dotted curves).

Legendre polynomials [11], with the result

$$J_5 = 64\pi^3 \sum_{l=0} [(2l+1)^2]^{-1} \int_0^\infty r_{12}^2 u_1^*(\vec{r}_1,\vec{r}_2) g_0(\vec{r}_1,\vec{r}_2) \mathrm{d}r_{12} \times \int_0^\infty r_{13}^2 h_0(\vec{r}_1,\vec{r}_3) A_l(r_{12},r_{13}) \mathrm{d}r_{13} \times \int_0^\infty r_{14}^2 h_0(\vec{r}_1,\vec{r}_4) A_l(r_{12},r_{14}) B_l(r_{13},r_{14}) \mathrm{d}r_{14}, \quad (26)$$

where

$$A_l(r_{12},r_{13}) = \frac{1}{2}(2l+1)\int_0^\pi h_0(\vec{r}_2,\vec{r}_3) P_l(\cos(\theta_{23}))\sin(\theta_{23})\mathrm{d}\theta_{23} \quad (27)$$

and

$$B_l(r_{12},r_{13}) = \frac{1}{2}(2l+1)\int_0^\pi u_1^*(\vec{r}_2,\vec{r}_3) \times g_0(\vec{r}_2,\vec{r}_3) P_l(\cos(\theta_{23}))\sin(\theta_{23})\mathrm{d}\theta_{23}, \quad (28)$$

with the condition

$$r_{23}^2 = r_{12}^2 + r_{13}^2 - 2r_{12}r_{13}\cos(\theta_{23}). \quad (29)$$

Details on the calculations are given in Appendix 2.[†] For $\lambda = 1.5$ our results are in complete agreement with those obtained Smith *et al.* [6]. The small difference are attributed to the different r.d.f. (the Percus–Yevick one) used in their calculations.

RESULTS AND DISCUSSION

The calculated values of F_1 are compared in Fig. 1 with simulation data for the values of λ considered. One can see that the accuracy of the perturbation theory is excellent for the whole ranges of densities and potential widths.

The results for F_2/NkT are shown in Fig. 2 together with the corresponding simulation data. The figure shows that the macroscopic and the lc approximations are in poor agreement with simulation data for small potential widths. For intermediate widths,

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[†] The values of the integrals J_i, together with the values resulting for F_2, for the values of the potential width considered in this paper are available from the authors upon request.

these approximations give reasonable results up to densities of order of $\rho^* = 0.4$. For greater potential widths the accuracy of these approximations deteriorates again so that they are in close agreement with simulation data only at low densities.

Better overall agreement is provided by the refined approximation described in "A more refined approximation for the second-order term" section. This approximation is in qualitative agreement with simulation data up to high densities and is accurate up to densities of order of $\rho^* = 0.4$ for all potential widths considered. For higher densities, further refinements are needed in order to achieve complete agreement with simulation data. Furthermore, for low values of the potential width λ, even the second order perturbation theory may be insufficient to obtain the Helmholtz free energy of the system with enough accuracy. Unfortunately, higher order terms, beyond the second, are difficult to obtain.

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APPENDIX 1

The radial distribution function of the HS fluid which results from the procedures developed by Bravo Yuste *et al.* [9,10] using the Carnahan–Starling equation of state (13), in the first coordination shell $1 \le x \le 2$ can be expressed in the form

$$g(x) = \frac{1}{x}(a_1 e^{t_1(x-1)} + a_2 e^{t_2(x-1)} + a_3 \cos(b(x-1)) e^{a(x-1)} + a_4 \sin(b(x-1)) e^{a(x-1)}) \tag{30}$$

where:

$$a = -\frac{S_3}{4S_4} - y_p \tag{31}$$

$$b = -y_m(-I) \tag{32}$$

$$a_1 = -\frac{1}{12\eta}\frac{(1 + L_1 t_1 + L_2 t_1^2)t_1}{S_1 + 2S_2 t_1 + 3S_3 t_1^2 + 4S_4 t_1^3} \tag{33}$$

$$a_2 = -\frac{1}{12\eta}\frac{(1 + L_1 t_2 + L_2 t_2^2)t_2}{S_1 + 2S_2 t_2 + 3S_3 t_2^2 + 4S_4 t_2^3} \tag{34}$$

$$a_3 = -\frac{2}{12\eta}\frac{q1q2 + q3q4}{q2^2 + q4^2} \tag{35}$$

$$a_4 = -\frac{2}{12\eta}\frac{q_1 q_4 - q_3 q_2}{q_2^2 + q_4^2} \tag{36}$$

$$q_1 = (a + L_1 a^2 + L_2(a^2 - b^2)a - b(L_1 b + L_2 2ab)) \tag{37}$$

$$q_2 = (S_1 + 2S_2 a + 3S_3(a^2 - b^2) + 4S_4(a^3 - 3b^2 a)) \tag{38}$$

$$q_3 = (b + L_1 ab + L_2(a^2 - b^2)b + a(L_1 b + L_2 2ab)) \tag{39}$$

$$q_4 = (2S_2 b + 3S_3 2ab + 4S_4(3a^2 b - b^3)) \tag{40}$$

$$t_1 = -\frac{S_3}{4S_4} + yp - yn \tag{41}$$

$$t_2 = -\frac{S_3}{4S_4} + yp + yn \tag{42}$$

$$L_1 = \frac{3 + 6\eta - (\eta - 1)U}{6 + 12\eta} \tag{43}$$

$$L_2 = -\frac{1}{12K}(\eta - 2)(\eta - 1)(U - 3) \tag{44}$$

$$S_1 = \frac{1}{6}\left(-3 - \frac{(\eta - 1)U}{1 + 2\eta}\right) \tag{45}$$

$$S_2 = \frac{\eta - 1}{12K(1 + 2\eta)} \times (3(\eta - 2)(1 + 2\eta) + \eta(2\eta^2 - 2\eta - 3)U) \tag{46}$$

$$S_3 = \frac{1}{12K\eta(1 + 2\eta)} \times ((\eta - 1)^4(1 + 2\eta) - (\eta - 1)^2\eta(\eta^2 - \eta - 1)U) \tag{47}$$

$$S_4 = \frac{(1 - \eta)^4(U - 3)}{72K\eta} \tag{48}$$

$$U = \sqrt{\frac{3(1 + 2\eta)^2(7 - 5\eta + \eta^2)}{1 + 4\eta + (\eta - 2)^2\eta^2}} \tag{49}$$

$$K = \eta^3 - 3\eta - 1 \tag{50}$$

$$y_p = -\frac{1}{2}\sqrt{\frac{S_3^2}{4S_4^2} - \frac{2S_2}{3S_4} + y_r + \frac{F_0}{3S_4}} \tag{51}$$

$$y_r = \frac{S_2^2 - 3S_1 S_3 + 12S_4}{3S_4 F_0} \tag{52}$$

$$y_n = \frac{1}{2}\sqrt{\frac{S_3^2}{2\,S_4^2} - \frac{4\,S_2}{3\,S_4} - y_r - \frac{F_0}{3\,S_4} + \frac{-\frac{S_3^3}{S_4^3} + \frac{4\,S_2S_3}{S_4^2} - \frac{8\,S_1}{S_4}}{8y_p}} \quad (53)$$

$$F_0 = \frac{1}{\sqrt[2]{3}}(2\,S_2^3 - 9\,S_1S_2S_3 + 27\,S_3^2 + 27\,S_1^2S_4 - 72\,S_2S_4 + \sqrt{\left(-4(S_2^2 - 3\,S_1S_3 + 12\,S_4)^3 + (2\,S_2^3 - 9\,S_1S_2S_3 + 27\,S_3^2 + 27\,S_1^2S_4 - 72\,S_2S_4)^2\right)}^{\frac{1}{3}}. \quad (54)$$

The expression for the coordination number N_c^{HS} which results from this r.d.f. together with Eq. (9) is

$$N_c^{HS} = 24\eta(I_1 + I_2 + I_3 + I_4), \quad (55)$$

with

$$I_1 = a_1\frac{(1 - t_1 + e^{(\lambda-1)t_1}(\lambda t_1 - 1))}{t_1^2} \quad (56)$$

$$I_1 = a_2\frac{(1 - t_2 + e^{(\lambda-1)t_2}(\lambda t_2 - 1))}{t_2^2} \quad (57)$$

$$I_3 = a_3\frac{a^2(1-a) - b^2(1+a)}{(a^2+b^2)^2} + a_3\frac{e^{(\lambda-1)a}((b^2 - a^2 + a(a^2+b^2)\lambda)\cos(b(\lambda-1)) + (-2ab + b(a^2+b^2)\lambda)\sin(b(\lambda-1)))}{(a^2+b^2)^2} \quad (58)$$

$$I_4 = a_4\frac{(a-2)ab + b^3}{(a^2+b^2)^2} + a_4\frac{e^{(\lambda-1)a}((2ab - b(a^2+b^2)\lambda)\cos(b(\lambda-1)) + (b^2 - a^2 + a(a^2+b^2)\lambda)\sin(b(\lambda-1)))}{(a^2+b^2)^2}. \quad (59)$$

APPENDIX 2

As stated before, the evaluation of the integrals J_i has been performed numerically,[†] in spite of the fact that J_1 can be obtained analytically. This allows us to estimate the quality of the numerical procedure by comparing their results with the analytical values obtained for J_1.

We have carried out the numerical integration taking an interval $\Delta r = 0.01\sigma$, or $\Delta r^* = 0.01$, and the value of the integrand in the center of each interval. For the r.d.f. of the HS system we used the analytical expression obtained from the procedure developed by Bravo Yuste *et al.* [9,10] with the CS equation. It is to be noted, however, that we need higher order coordination shells, not included in Appendix 1. Beyond $r^* = 6$ we have taken $g_0(r^*) = 1$.

To evaluate J_1, J_2, J_3, J_4 for a given density, the external integration was evaluated between $0 \le r^* \le 6$. For each values of r^* we evaluated the function $\gamma(x)$. This is a double integral that, for the particular case of a SW potential is given by

$$\gamma(x) = \frac{2\pi}{x}\int_{\sigma}^{\lambda\sigma}(-1)g_0(y)y\mathrm{d}y\int_{|x-y|}^{x+y}h_0(z)\mathrm{z}dz \quad (60)$$

with $h_0(z) = g_0(z) - 1$, so that $h_0(z) = -1$ for $z < 1$. Once the value of $\gamma(x)$ is known, the integrals $J_i i \le 4$ follow immediately.

The calculation of J_5, even for a potential as simple as the SW potential, is more cumbersome. We have to use an expansion of the integrand in terms of the Legendre polynomials, as stated before. The first step consisted in evaluating the Legendre coefficients $P_l(\cos(\theta))$ for $0 \le l \le 11$ and $0 \le \theta \le \pi$. We have performed the calculations for 100 values of θ equally spaced.

Once the $P_l(\cos(\theta)$ were evaluated, the next step was the calculation of the functions $A_l(r_{12}, r_{13})$ and $B_l(r_{12}, r_{13})$, using expressions (27) and (28), together with expression (29), for all values $0 \le r_{12} \le 6, 0 \le r_{13} \le 6, 0 \le \theta_{23} \le \pi$ needed to evaluate J_5. The detailed procedure followed to evaluate this integral is as follows. The expression to be evaluated is

$$
\begin{aligned}
J_5 = & 64\pi^3 \sum_{l=0} [(2l+1)^2]^{-1} \int_\sigma^{\lambda\sigma} r_{12}^2 (-1) g_0(r_{12}) \mathrm{d}r_{12} \\
& \times \int_0^\infty r_{13}^2 h_0(r_{13}) A_l(r_{12}, r_{13}) \mathrm{d}r_{13} \\
& \times \int_0^\infty r_{14}^2 h_0(r_{14}) A_l(r_{12}, r_{14}) B_l(r_{13}, r_{14}) \mathrm{d}r_{14}
\end{aligned}
$$

where functions $A_l(x, y)$ and $B_l(x, y)$ had been calculated before. Then, taking values of r_{12} between 1 and λ with intervals of 0.01, as mentioned before, $g_0(r_{12})$ was evaluated. For each value of r_{12} we took values of r_{13} between 0 and ∞ and calculated $h_0(r_{13})$ and $A_l(r_{12}, r_{13})$. In turn, for each of these pairs of r_{12}, r_{13} we took a value of r_{14} between 0 and ∞ and evaluated $h_0(r_{14})$, $A_l(r_{12}, r_{14})$ and $B_l(r_{13}, r_{14})$. In this way, J_5 was evaluated.