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Thermodynamic Properties of Sutherland Fluids from an Analytical Perturbation Theory

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Analytical expressions are obtained for the thermodynamic properties of fluids with potentials consisting of a spherical hard core plus an attractive tail of the form $1/r^{\gamma}$ (Sutherland fluids). To this end, use is made of the Barker–Henderson perturbation theory together with an analytical expression for the first coordination shell of the radial distribution function of the reference hard-sphere fluid. This expression was derived previously on the basis of the analytical solution of the Percus–Yevick integral equation theory. The results are compared with available simulation data for a wide range of densities, temperatures, and values of the potential parameter γ. The overall agreement is good, and the accuracy is similar to that obtained using more accurate solutions for the radial distribution function of the hard-sphere fluid leading to nonanalytical expressions for the thermodynamic properties of the fluid considered.

KEY WORDS: Barker–Henderson perturbation theory; equation of state; hard-sphere fluid; radial distribution function; Sutherland potential.

1. INTRODUCTION

In the van der Waals model of fluids, the particles interact by means of a potential of the form

$$u(x) = \begin{cases} \infty, & x \leqslant 1 \\ -\varepsilon/x^{\gamma}, & x > 1 \end{cases} \tag{1}$$

which is also called the Sutherland potential [1]. In this expression, $x = r/\sigma$ is the distance in units of the hard-core diameter σ. This potential model

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closely mimics the Lennard–Jones potential, whose shape, in turn, reproduces qualitatively the shape of the potentials of real simple fluids.

On the other hand, perturbation theories for fluids with continuous potentials are based on obtaining the thermodynamic properties of the fluid from those of a reference fluid of hard-spheres (HS), with diameters depending on temperature and, eventually, on density [2, 3], by adding a temperature-dependent perturbation. However, it is to be noted that the results obtained from a perturbation theory can be very sensitive to the effective diameter of the reference fluid. This problem does not appear with a potential of the form of Eq. (1) in which the diameter of the particles is perfectly defined, in contrast with the case of a continuous potential such as the Lennard–Jones potential. Moreover, once we have set up a sufficiently accurate perturbation scheme for a Sutherland fluid, it is easy to extend it to Lennard–Jones fluids and even to real simple fluids. This could be achieved, for example, by means of changing the real fluid to an effective Sutherland fluid with parameters σ, ε, and γ appropriate for the fluid considered. One way to do this is to treat these parameters as adjustable parameters. This would allow us to use the expressions of the thermodynamic properties derived for the Sutherland potential to predict the properties of other kind of fluids.

In this paper, we obtain analytical expressions for the thermodynamic properties of Sutherland fluids as functions of the temperature, density, and value of the parameter γ, which determines the effective range of the potential. These expressions are derived from the second-order Barker–Henderson perturbation theory in combination with a simple expression for the first coordination shell of the radial distribution function (r.d.f.) of the hard-sphere reference fluid, derived previously [4]. The results are compared with available simulation data and with those obtained using more sophisticated expressions for the HS r.d.f.

2. THEORY

In order to obtain the thermodynamic properties of a fluid whose particles interact by means of a spherically symmetric potential, the Barker–Henderson perturbation theory [2] requires knowledge of the equation of state and the r.d.f. of a reference hard-sphere fluid. For this fluid, a great number of equations of state are available. Among them, the most frequently used is the Carnahan and Starling (CS) equation of state [5], which combines simplicity and accuracy:

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

where $\eta = \pi\rho\sigma^3/6$ is the packing fraction corresponding to the number density ρ for spheres of diameter σ.

With respect to the r.d.f., there are available analytical expressions for the r.d.f. [6–9] from the solution of the Percus–Yevick (PY) integral equation. However, it is known that the PY solution is not sufficiently accurate, particularly for radial distances close to contact. Therefore, a considerable number of procedures have been developed to improve the accuracy of the r.d.f. obtained from integral equation theories. In most cases, the resulting r.d.f. is nonanalytical, which makes its use impractical, particularly in the context of perturbation theories. For future reference, we mention here only the expressions for the r.d.f. of the HS fluid derived by Bravo Yuste and Santos [10] and by Tang and Lu [11], which are analytical, reasonably simple, and very accurate.

The problem is that, when used in perturbation theories, even the simplest expressions for the r.d.f. derived from integral equation theories, which are those which result from the PY theory, in general lead to non-analytical expressions for the thermodynamic properties of model fluids. In particular, this is the case for the Sutherland model that we are considering here.

In a previous paper [4], we derived a simple expression for the first coordination shell for the r.d.f. of the HS fluid. This will allow us to obtain analytical expressions for the thermodynamic properties of the van der Waals fluids, as we will see later. The expression for $g_1(x)$ is

$$g_1(x) = \frac{1}{x^2} \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} I_{nm} \frac{n(x-1.5)^{n-1}}{(1-\eta)^{n+1}} \eta^m \tag{3}$$

where I_{nm} are constants. This result was obtained on the basis of the analytical expression for the PY r.d.f. in the form derived by Chang and Sandler [9]. The procedure consisted in performing a double-series expansion of the analytical expression of $g_1(x)$, in terms of both the packing fraction η and the reduced distance x. This is very tedious and not as simple as it might appear at first sight, but the final expression, Eq. (3), is simple enough and suitable for our purposes. Values of the coefficients I_{nm} up to $n=8$ and $m=16$ were reported in the same paper. This is sufficient to obtain values of $g_1(x)$ which are in close agreement with those obtained from the starting expression.

The procedure could be applied to the second coordination shell, to obtain $g_2(x)$. However, this would result in a more complicated expression for the r.d.f. and, consequently, for the thermodynamic properties obtained by means of a perturbation theory. Instead, we consider only the first coordination shell of the r.d.f. of the HS fluid and add a tail correction consistent with assuming $g(x) = 1$ for the second- and higher-order shells, as for the ideal gas. We have found that, for the fluids we are studying here, this is sufficient to obtain good overall results for the thermodynamic properties. Therefore, we take

$$g(x) = \begin{cases} g_1(x), & 1 \leqslant x \leqslant 2 \\ 1, & x > 2 \end{cases} \tag{4}$$

where $g_1(x)$ is given by Eq. (3), which we rewrite in the form

$$g(x) = \frac{1}{x^2} \sum_{n=1}^{\infty} G_n(\eta)(x - 1.5)^{n-1} \tag{5}$$

with

$$G_n(\eta) = \frac{n}{(1-\eta)^{n+1}} \sum_{m=0}^{\infty} I_{nm} \eta^m \tag{6}$$

Once a suitable expression for $g(x)$ is available, it can be used in combination with the Barker–Henderson perturbation theory [2] to obtain the thermodynamic properties of the fluid. This theory expresses the free energy as a power series in the inverse of the reduced temperature $T^* = kT/\varepsilon$, where ε is the energy parameter of the potential. Up to second order, the result is

$$\frac{F}{NkT} = \frac{F_0}{NkT} + \frac{F_1}{NkT}\frac{1}{T^*} + \frac{F_2}{NkT}\frac{1}{T^{*2}} \tag{7}$$

where the subscript 0 refers to the hard-sphere reference fluid,

$$F_1 = 12\eta \int_0^{\infty} g(x)\, u(x)\, x^2\, dx \tag{8}$$

and, in the so-called "local compressibility" approximation,

$$F_2 = -\frac{36}{\pi}\frac{\eta kT}{\sigma^3}\left(\frac{\partial \eta}{\partial p}\right)_0 \frac{\partial}{\partial \eta}\left(\eta \int_0^{\infty} g(x)\, u^2(x)\, x^2\, dx\right) \tag{9}$$

If we introduce expression Eq. (4), together with Eqs. (5) and (6), and denote

$$I_1 = \sum_{n=1}^{\infty} G_n \int_1^2 (x - 1.5)^{n-1}\, u^*(x)\, dx + \int_2^{\infty} u^*(x)\, x^2\, dx \tag{10}$$

$$I_2 = \sum_{n=1}^{\infty} G_n \int_1^2 (x - 1.5)^{n-1}\, u^{*2}(x)\, dx + \int_2^{\infty} u^{*2}(x)\, x^2\, dx \tag{11}$$

then Eqs. (8) and (9) can be expressed in the form

$$\frac{F_1}{NkT} = 12\eta I_1 \tag{12}$$

and

$$\frac{F_2}{NkT} = -\frac{36}{\pi}\frac{\eta kT}{\sigma^3}\left(\frac{\partial\eta}{\partial p}\right)_0 \frac{\partial}{\partial\eta}(\eta I_2) = -\frac{36}{\pi}\frac{\eta kT}{\sigma^3}\left(\frac{\partial\eta}{\partial p}\right)_0 \left(I_2 + \eta\,\frac{\partial I_2}{\partial\eta}\right) \tag{13}$$

The compressibility factor can be obtained from Eq. (7) in the form

$$\begin{aligned}\frac{pV}{NkT} &= \left(\frac{pV}{NkT}\right)_0 + \eta\,\frac{\partial}{\partial\eta}\left[\frac{F}{NkT} - \frac{F_0}{NkT}\right] \\ &= \left(\frac{pV}{NkT}\right)_0 + \frac{p_1 V}{NkT}\frac{1}{T^*} + \frac{p_2 V}{NkT}\frac{1}{T^{*2}}\end{aligned} \tag{14}$$

where

$$\frac{p_1 V}{NkT} = 12\eta\left(I_1 + \eta\,\frac{\partial I_1}{\partial\eta}\right) \tag{15}$$

and

$$\begin{aligned}\frac{p_2 V}{NkT} = -\frac{36\eta kT}{\pi\sigma^3}\Bigg\{&\left[\left(\frac{\partial\eta}{\partial p}\right)_0 + \eta\,\frac{\partial}{\partial\eta}\left(\frac{\partial\eta}{\partial p}\right)_0\right]\left(I_2 + \eta\,\frac{\partial I_2}{\partial\eta}\right) \\ &+ \eta\left(\frac{\partial\eta}{\partial p}\right)_0\left(2\,\frac{\partial I_2}{\partial\eta} + \eta\,\frac{\partial^2 I_2}{\partial\eta^2}\right)\Bigg\}\end{aligned} \tag{16}$$

The internal energy is given by

$$\frac{U}{NkT} = -T\,\frac{\partial}{\partial T}\left(\frac{F}{NkT}\right) = \frac{U_0}{NkT} + \frac{U_1}{NkT}\frac{1}{T^*} + \frac{U_2}{NkT}\frac{1}{T^{*2}} \tag{17}$$

with

$$\frac{U_1}{NkT} = \frac{F_1}{NkT} \tag{18}$$

and

$$\frac{U_2}{NkT} = \frac{2F_2}{NkT} \tag{19}$$

For a potential of the form of Eq. (1), with $\gamma > 3$, we have

$$I_1 = -\sum_{n=1}^{\infty} G_n(\eta) \left[\sum_{\substack{j=1 \\ j \neq n-\gamma}}^{n-1} \frac{(-1.5)^j \, (n-1)!}{(n-\gamma-j) \; j!(n-j-1)!} \, (2^{n-\gamma-j} - 1) \right.$$
$$\left. + \, \delta(n-\gamma-j) \, \frac{(-1.5)^j \, (n-1)!}{j!(n-j-1)!} \log 2 \right] + \frac{2^{3-\gamma}}{3-\gamma} \tag{20}$$

where $\delta(z)$ is the Kronecker delta function, whose value is 1 if and 0 otherwise,

$$I_2 = \sum_{n=1}^{\infty} G_n(\eta) \left[\sum_{\substack{j=1 \\ j \neq n-2\gamma}}^{n-1} \frac{(-1.5)^j \, (n-1)!}{(n-2\gamma-j) \; j!(n-j-1)!} \, (2^{n-2\gamma-j} - 1) \right.$$
$$\left. + \, \delta(n-2\gamma-j) \, \frac{(-1.5)^j \, (n-1)!}{j!(n-j-1)!} \log 2 \right] + \frac{2^{3-2\gamma}}{3-2\gamma} \tag{21}$$

$\partial I_1/\partial\eta$ and $\partial I_2/\partial\eta$ are given by Eqs. (20) and (21), respectively, by changing $G_n(\eta)$ to

$$\frac{\partial G_n(\eta)}{\partial\eta} = \frac{n+1}{1-\eta} \, G_n(\eta) + \frac{n}{(1-\eta)^{n+1}} \sum_{m=1}^{\infty} m I_{nm} \eta^{m-1} \tag{22}$$

Finally, $\partial^2 I_2/\partial\eta^2$ is given by Eq. (21), by changing $G_n(\eta)$ to

$$\frac{\partial^2 G_n(\eta)}{\partial\eta^2} = \frac{n+1}{(1-\eta)^2} \, G_n(\eta) + \frac{n+1}{1-\eta} \frac{\partial G_n(\eta)}{\partial\eta} + \frac{n(n+1)}{(1-\eta)^{n+2}} \sum_{m=1}^{\infty} m I_{nm} \eta^{m-1}$$
$$+ \frac{n}{(1-\eta)^{n+1}} \sum_{m=1}^{\infty} m(m-1) \, I_{nm} \eta^{m-2} \tag{23}$$

On the other hand, taking Eq. (2) for the equation of state of the reference fluid, we have

$$\left(\frac{\partial\eta}{\partial p}\right)_0 = \frac{1}{kT} \frac{\pi\sigma^3}{6} \frac{(1-\eta)^4}{1+4\eta+4\eta^2-4\eta^3+\eta^4} \tag{24}$$

and

$$\frac{\partial}{\partial \eta}\left(\frac{\partial \eta}{\partial p}\right)_0 = \frac{1}{kT}\,\frac{\pi\sigma^3}{6}\,\frac{4(1-\eta)^3\,(-2-5\eta+\eta^2)}{(1+4\eta+4\eta^2-4\eta^3+\eta^4)^2} \tag{25}$$

With Eqs. (20) to (25), all quantities needed to obtain up to the second perturbative contributions to the equation of state and the internal energy of Sutherland fluids are completely determined.

3. RESULTS AND DISCUSSION

From the expressions derived in the previous section, and the values of I_{nm} up to $n=8$ and $m=16$ reported in a previous paper [4], we have obtained the compressibility factor $Z=pV/NkT$ and the internal energy of Sutherland fluids with $\gamma=6$, 12, 18, and 36 as a function of the packing fraction η. Results are compared in Figs. 1 and 2 with simulation data [12]. For $\gamma=6$, the agreement is very good for both thermodynamic quantities. In the remaining cases, the calculated values of the compressibility factor closely agree with simulation data at low to moderate densities, whereas at high densities some deviations appear, which increase for increasing values of γ. The situation in the case of the internal energy is similar, although the deviations between calculated results and simulation data start at lower densities. In any case, these deviations for high values of γ are of minor importance, because in real fluids the attractive contribution to the potential energy generally corresponds to values of γ close to 6.

We have considered the possibility of including higher-order perturbative contributions to these thermodynamic properties, in the way proposed by Praestgaard and Toxvaerd [13]. However, we have found that the results are hardly distinguishable from those obtained from the second order perturbation theory. We have also analyzed the effect of using more accurate analytical expressions for the r.d.f. of the hard-sphere fluid, such as those of Bravo Yuste and Santos [10] and Tang and Lu [11]. Both expressions give nearly identical results for the first and second shells of the r.d.f., and lead to nonanalytical expressions for the thermodynamic properties of Sutherland fluids. Therefore, we have considered the second of them because it is somewhat simpler to handle. The compressibility factor and the internal energy obtained using this expression up to the second shell in combination with the Barker–Henderson second order perturbation theory are also shown in Figs. 1 and 2. The results are very close to those obtained from the expressions derived in the previous section. Therefore, the reasons for the deviations between calculated values and simulation data

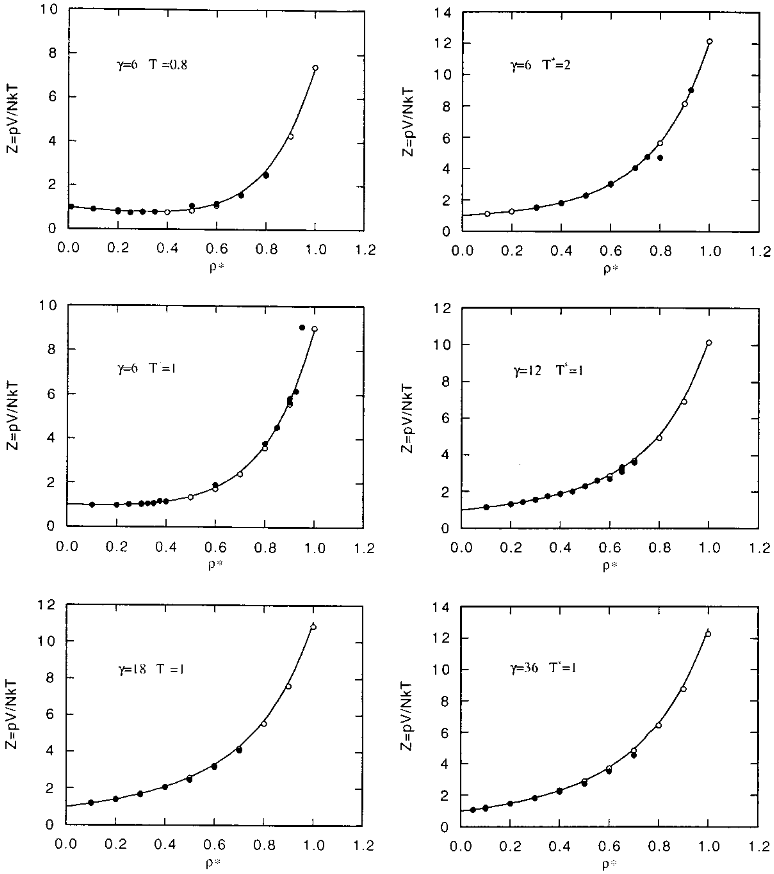

Fig. 1. Compressibility factor $Z = pV/NkT$ for Sutherland fluids as a function of the reduced density $\rho^* = \rho\sigma^3$ for several values of the exponent γ of the attractive part of the potential. Filled circles: Simulation data from Ref. 12. Solid lines: Eq. (14) with Eqs. (15)–(23). Open circles: Numerical results from BH second-order perturbation theory with the expression of Tang and Lu [11] for the r.d.f. of the hard-sphere reference fluid.

observed in these figures have to be attributed to the perturbation theory itself, rather than to the inaccuracy of the procedure we have developed.

In summary, we have shown that it is possible to obtain analytical expressions for the thermodynamic properties of Sutherland fluids from a second-order Barker–Henderson perturbation theory. To achieve this goal, the starting point consists in expressing the first shell contribution to the radial distribution function of the reference fluid of hard spheres as a power series in terms of the reduced radial distance x around $x = 1.5$ and in terms

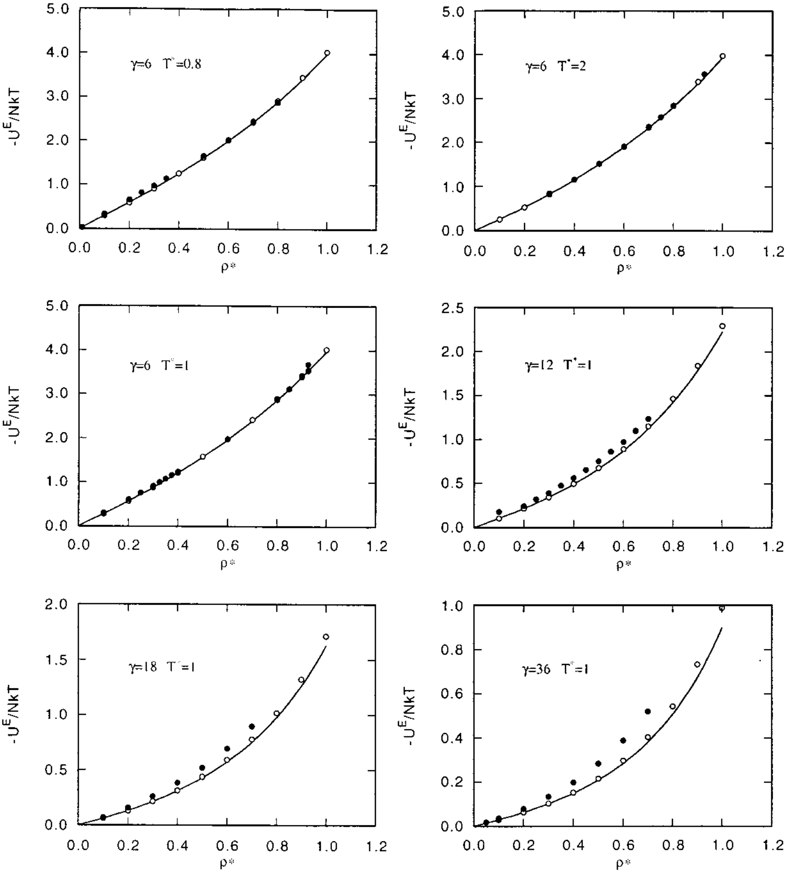

Fig. 2. As in Fig. 1 for the absolute value of the excess internal energy, $-U^E/NkT$. Solid lines: Eq. (17) with Eqs. (18), (19), and (20)–(22).

of the packing fraction η. For this purpose, the analytical expression of the r.d.f. resulting from the Percus–Yevick theory is to be preferred, because it is simpler than other analytical solutions of the r.d.f. of the HS fluid and provides practically the same accuracy when used in a Barker–Henderson perturbation scheme. For the second- and higher-order shell contributions, we have found that, for the fluids considered, a good approximation consists in taking $g(x)$, as in the ideal gas. The procedure could be extended to continuous potentials, such as the Lennard–Jones potential, by introducing a suitable temperature-dependent effective diameter. Alternatively, thermodynamic properties of fluids with continuous potentials could be obtained from those of an equivalent Sutherland fluid with its potential parameters suitably determined.

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