# SOME EXPLICIT RESULTS FOR THE MEAN SPHERICAL APPROXIMATION FOR MIXTURES OF YUKAWA FLUIDS

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*Dedicated to Professor William R. Smith on the occasion of his 65th birthday.*

The mean spherical approximation (MSA) is of interest because it produces an integral equation that yields useful analytical results for a number of fluids. One such case is the Yukawa fluid, which is a reasonable model for a simple fluid. The original MSA solution for this fluid, due to Waisman, is analytic but not explicit. Ginoza has simplified this solution. However, Ginoza's result is not quite explicit. Some years ago, Henderson, Blum, and Noworyta obtained explicit results for the thermodynamic functions of a single-component Yukawa fluid that have proven useful. They expanded Ginoza's result in an inverse-temperature expansion. Even when this expansion is truncated at fifth, or even lower, order, this expansion is nearly as accurate as the full solution and provides insight into the form of the higher-order coefficients in this expansion. In this paper Ginoza's implicit result for the case of a rather special mixture of Yukawa fluids is considered. Explicit results are obtained, again using an inverse-temperature expansion. Numerical results are given for the coefficients in this expansion. Some thoughts concerning the generalization of these results to a general mixture of Yukawa fluids are presented.

**Keywords**: Fluid mixtures; Yukawa potential; Mean spherical approximation; Peturbation expansion; Thermodynamic functions.

Our understanding of single-component simple fluids is well developed. Perturbation theory, which is an inverse-temperature expansion, has been very useful. Second-order perturbation theory[1–3] gives a good description of the thermodynamic functions of such fluids. Additionally, the mean spherical approximation[4] (MSA) has proven to be very useful. The MSA is particularily useful for fluids with a hard core. However, this is not a severe restriction since the repulsive part of the intermolecular potential is quite

steep and the difference between a hard and soft core is small and can be treated using a temperature-dependent effective hard sphere diameter, as suggested by Barker and Henderson[2] (BH).

The zeroth- and first-order perturbation terms of a single-component fluid can be obtained using results for a hard-sphere fluid. Even the second-order perturbation term can be obtained with reasonable accuracy by means of a compressibility approximation of BH [1]. Second-order perturbation theory gives good results for a pure fluid.

The solution of the MSA for a single-component Yukawa fluid, where the interaction potential is given by

$$u(R) = \begin{cases} \infty, & R < \sigma \\ -\dfrac{\varepsilon\sigma}{R}\exp\left[-\dfrac{z(R-\sigma)}{\sigma}\right], & R \geq \sigma \end{cases} \tag{1}$$

where $R$ is the separation of a molecular pair, $\sigma$ is the molecular diameter, $\varepsilon$ gives the strength of the attractive interaction, and $z$ is the decay parameter, was obtained by Waisman[5]. The Yukawa fluid is a reasonable model for a simple nonelectrolyte fluid. Waisman's solution is implicit and involves six simultaneous nonlinear equations in six unknowns. Waisman's solution has been simplified over the years. Ginoza[6] has reported the most simple result. However, his solution is still implicit. Henderson, Blum, and Noworyta[7] (HBN) have obtained explicit results by means of an inverse-temperature expansion, similar to perturbation theory, that was taken to fifth order. For the pure fluid, even an inverse-temperature expansion that is truncated at second order gives good results. The zeroth- and first-order terms in an inverse-temperature expansion obtained from the MSA are very accurate. The second-order term in an inverse-temperature expansion as given by the MSA term is approximate but agrees well with the BH simulation results for this second-order term and with their compressibility approximation.

The situation is less satisfactory for a mixture. The zeroth- and first-order perturbation terms can be determined from results for hard-sphere mixtures. However, little is known about the higher-order perturbation terms of a mixture of simple fluids. The MSA has proven very useful, even for specialized mixtures. For example, the solution of the MSA has been obtained for an electrolyte (a mixture of charged particles)[8], even for the case where the components have different diameters[9]. Additionally, Ginoza[6] has used the MSA to obtain implicit results for a simple nonelectrolyte fluid mixture of molecules that interact via the Yukawa intermolecular potential

$$u_{ij}(R) = \begin{cases} \infty, & R < \sigma_{ij} \\ -\dfrac{\varepsilon_{ij}\sigma_{ij}}{R}\exp\left[-\dfrac{z_{ij}(R-\sigma_{ij})}{\sigma_{ij}}\right], & R > \sigma_{ij} \end{cases} \qquad (2)$$

where $R$ is the separation of the centers of a pair of molecules, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\sigma_i$ is the molecular diameter of a molecule of species $i$. The parameter $\varepsilon_{ij}$ is the strength of the attractive interaction of an $ij$ pair at contact. The parameter $z_{ij}$ determines the range of the potential. There is probably little need for this range or decay parameter to differ for different molecular pairs. It is the counterpart of the index 6 in the Lennard–Jones (LJ) 12-6 potential, which usually does not vary with molecular species. Thus, we may safely assume that $z_{ij} = z$. The value $z = 1.8$ mimics[10] a LJ 12-6 potential and seems appropriate for most liquids.

Ginoza's result was obtained for the case of a factorizable mixture, where $z_{ij} = z$, $\sigma_{ij} = \sigma$ and

$$\varepsilon_{ij}^{LB} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \ . \qquad (3)$$

Equation (3) is one of the well-known Lorentz–Berthelot mixing rules.

As is the case for the single-component fluid, Ginoza's result is analytic but implicit. It is worth examining the case of a mixture of Yukawa fluids in order to obtain a useful theory of mixtures and finding explicit expressions that yield results for a mixture and some understanding of higher-order perturbation terms in an inverse-temperature series. Unfortunately, the restriction to equal-size molecules and Eq. (3) is a limitation. However, there is reason to believe that a perturbational inverse-temperature expansion may converge less well for a mixture of equal-size molecules than for a mixture of unequal-size molecules or even a pure fluid because molecules of different $\varepsilon_{ii}$ may be interchanged with no change in the repulsive energy. Thus, knowledge of the higher-order terms may be especially valuable for such an equal size mixture. Here, Ginoza's result is considered and explicit results using an inverse-temperature expansion are obtained. Approximations that may be useful for more general mixtures of simple fluids are considered.

### EXPLICIT FORMULAE

We consider an $m$-component mixture of Yukawa fluids, all with the same decay parameter, $z$, and of equal diameter, $\sigma$. The species differ only in the

strength of the attractive interaction, $\varepsilon_{ij}$, where Eq. (*3*) is satisfied. The concentration of species $i$ is $x_i = N_i/N$, where $N_i$ is the number of particles of species $i$ and $N = \Sigma_i N_i$ is the total number of molecules. Obviously, $\Sigma_i x_i = 1$. Define,

$$K = \beta \sum_{i=1}^{m} x_i \varepsilon_{ii} \tag{4}$$

where $\beta = 1/kT$ with $k$ and $T$ being the Boltzmann constant and temperature, respectively. Further, define the two average energies

$$\bar{\varepsilon} = \sum_{i=1}^{m} x_i \varepsilon_{ii} \tag{5}$$

and

$$\langle \varepsilon \rangle^{\text{LB}} = \sum_{i=1}^{m} x_i x_j \varepsilon_{ij}^{\text{LB}} . \tag{6}$$

The superscript LB denotes that Eq. (*3*) has been used to compute the cross interaction. In the case of a pure Yukawa fluid, $\bar{\varepsilon} = \langle \varepsilon \rangle^{\text{LB}} = \varepsilon$. For the pure fluid, $K = \beta\varepsilon$. Because of Eq. (*3*),

$$\langle \varepsilon \rangle^{\text{LB}} = \left( \sum_{i=1}^{m} x_i \sqrt{\varepsilon_{ii}} \right)^2 . \tag{7}$$

Now, following Ginoza, define $z_i = \sqrt{\beta\varepsilon_{ii}/K}$. This is more transparently written as

$$z_i = \sqrt{\frac{\varepsilon_{ii}}{\bar{\varepsilon}}} . \tag{8}$$

Thus, we have the three equations

$$\sum_{i=1}^{m} x_i = 1 \tag{9}$$

$$\sum_{i=1}^{m} z_i x_i = \bar{z} \tag{10}$$

and

$$\sum_{i=1}^{m} z_i^2 x_i = 1 . \tag{11}$$

Equation (*10*) is the definition of $\bar{z}$. Note that the $z_i$ and $\bar{z}$ are unrelated to the decay parameter $z$ in the Yukawa potential, which is always constant and independent of concentration. Note that $K = \beta \langle \varepsilon \rangle^{LB} / \bar{z}^2$ or $\bar{z}^2 = \langle \varepsilon \rangle^{LB} / \bar{\varepsilon}$. We have used the notation of Ginoza, rather than inventing a new notation.

Ginoza showed that

$$\Gamma(\Gamma + z) = -\frac{6K\eta}{\sigma} D_2 (\Gamma) \tag{12}$$

where $\eta = \pi \rho \sigma^3 / 6$ and $\rho = N/V$, where $V$ is the volume that the fluid occupies.

$$D_n (\Gamma) = \sum_i x_i X_i^n \tag{13}$$

and

$$X_i = \frac{z_i - \bar{z}}{1 + \Gamma \phi_0} + \frac{\bar{z}}{\Phi_0 (1 + \psi \Gamma)} \tag{14}$$

where

$$\phi_0 = \frac{1 - \exp(-z)}{z} . \tag{15}$$

There is a misprint in Eq. (*4*) of the HBN paper[7]. Equation (*12*) is the correct expression. All numerical results in the HBN paper are correct.

$\Phi_0$ is given by Eq. (*7*) of HBN and $\Phi_1$ is given by

$$\Phi_1 = \frac{1 - \exp(-z)}{z} - \frac{12\eta}{1 - \eta} \frac{1 - z/2 - (1 + z/2) \exp(-z)}{z^3} . \tag{16}$$

Finally, $\psi$ is given by

$$\psi = \frac{\Phi_1}{\Phi_0} \tag{17}$$

or

$$\psi = z^2 (1 - \eta)^2 \, \frac{1 - \exp(-z)}{\exp(-z) \, L(z) + S(z)} - 12\eta(1 - \eta) \frac{1 - z/2 - (1 + z/2)\exp(-z)}{\exp(-z) \, L(z) + S(z)} \, . \quad (18)$$

The polynomials $L(z)$ and $S(z)$ are defined by Eqs (9) and (10) of the HBN paper and are the Wertheim polynomials[11]. We note the misprint in Eq. (7) of HBN [7]. All numerical calculations in the HBN paper were performed with the correct formulae. The above notation is that of HBN and essentially that of Ginoza.

Equation (12) can be simplified to give

$$\Gamma(\Gamma + z) = -\frac{6K\eta}{\sigma} \left[ \frac{1 - \bar{z}^2}{(1 + \Gamma\phi_0)^2} + \frac{\bar{z}^2}{\Phi_0^2 \, (1 + \Gamma\psi)^2} \right]. \quad (19)$$

Results could be obtained by numerical solution of Eq. (19) for $\Gamma$. Following HBN, explicit results can be obtained by means of an expansion in powers of $K$,

$$\Gamma = \sum_{n=1}^{\infty} K^n \Gamma_n \, . \quad (20)$$

We have obtained the $\Gamma_n$ to fifth order. In displaying our results, it is convenient to define

$$\gamma_n = (1 - \bar{z}^2)\phi_0^n + \frac{\bar{z}^2}{\Phi_0^2}\psi^n \, . \quad (21)$$

Our results for the $\Gamma_n$ are

$$\Gamma_1 = -\frac{6\eta}{z}\gamma_0 \quad (22)$$

$$\Gamma_2 = \frac{12\eta}{z}\gamma_1\Gamma_1 - \frac{\Gamma_1^2}{z} \quad (23)$$

$$\Gamma_3 = \frac{12\eta}{z}\left(\gamma_1\Gamma_2 - \frac{3}{2}\gamma_2\Gamma_1^2\right) - \frac{2\Gamma_1\Gamma_2}{z} \quad (24)$$

$$\Gamma_4 = \frac{12\eta}{z}\left(\gamma_1\Gamma_3 - 3\gamma_2\Gamma_1\Gamma_2 + 2\gamma_3\Gamma_1^3\right) - \frac{2\Gamma_1\Gamma_3}{z} - \frac{\Gamma_2^2}{z} \quad (25)$$

and

$$\Gamma_5 = \frac{12\eta}{z}\left(\gamma_1\Gamma_4 - 3\gamma_2(\Gamma_1\Gamma_3 + \Gamma_2^2) + 6\gamma_3\Gamma_1^2\Gamma_2 - \frac{5}{2}\gamma_4\Gamma_1^2\right) - \frac{2\Gamma_1\Gamma_4}{z} - \frac{2\Gamma_2\Gamma_3}{z} . \quad (26)$$

Now that $\Gamma$ has been determined, we can turn to the thermodynamics. The energy is obtained from

$$\beta\Delta E = -K\sum_{i=1}^{m} x_i z_i[-\Gamma X_i + (\alpha_0 + \alpha_1\Gamma)D_1] \quad (27)$$

where $\Delta E$ is the excess energy over that of the ideal gas mixture ($3NkT/2$) and $\alpha_0$ and $\alpha_1$ are given by Eqs (18) and (19) of HBN [7]. Equation (27) can be simplified to

$$\beta\Delta E = K\frac{\Gamma}{1+\Gamma\phi_0}(1-\bar{z}^2) - \bar{z}^2\frac{\alpha_0 + (\alpha_1 - 1)\Gamma}{\Phi_0[1+\Gamma\psi]} . \quad (28)$$

It is convenient to define

$$\bar{\alpha} = \alpha_1 - 1 - \alpha_0\psi \quad (29)$$

and

$$\delta_n = (1-\bar{z}^2)\phi_0^n - \frac{\bar{z}^2}{\Phi_0}\bar{\alpha}\psi^n . \quad (30)$$

Expanding in powers of $K$ yields

$$\Delta E = \sum_{n=1}^{\infty} K^n E_n \quad (31)$$

with

$$\frac{E_1}{NkT} = -\bar{z}^2\frac{\alpha_0}{\Phi_0} = -\bar{z}^2\frac{zL(z)}{\exp(-z)L(z) + S(z)} \quad (32)$$

$$\frac{E_2}{NkT} = \delta_0\Gamma_1 \quad (33)$$

$$\frac{E_3}{NkT} = \delta_0 \Gamma_2 - \delta_1 \Gamma_1^2 \tag{34}$$

$$\frac{E_4}{NkT} = \delta_0 \Gamma_3 - 2\delta_1 \Gamma_1 \Gamma_2 + \delta_2 \Gamma_1^3 \tag{35}$$

and

$$\frac{E_5}{NkT} = \delta_0 \Gamma_4 - \delta_1 (\Gamma_2^2 + 2\Gamma_1 \Gamma_3) + 3\delta_2 \Gamma_1^2 \Gamma_2 - \delta_3 \Gamma_1^4 \ . \tag{36}$$

The leading term $E_0$ is, of course, zero since $\Delta E$ is the excess energy. The excess Helmholtz energy is obtained from

$$\Delta A = \sum_{n=0}^{\infty} K^n A_n \tag{37}$$

with

$$\frac{A_0}{NkT} = \eta \frac{4 - 3\eta}{(1 - \eta)^2} \tag{38}$$

together with

$$A_n = \frac{1}{n} E_n \tag{39}$$

for $n > 0$. Equation (38) results from the Carnahan–Starling expression for the hard-sphere pressure. The entropy of mixing term must be included in the ideal gas term.

The pressure and chemical potentials can be obtained by straightforward differentiation of $A$. In particular, the pressure is given by

$$pV = \eta \frac{\partial A}{\partial \eta} \ . \tag{40}$$

We note that $\phi_0$ and $\bar{z}^2$ are independent of density. The derivatives of $\Phi_0$, $\phi$, $\alpha_0$, and $\alpha_1$ with respect to $\eta$ are exactly the same as for the pure Yukawa fluid. Further,

$$\frac{\partial \gamma_n}{\partial \eta} = \frac{\bar{z}^2}{\Phi_0^2} \psi^n \left( \frac{n}{\psi} \frac{\partial \psi}{\partial \eta} - \frac{2}{\Phi_0} \frac{\partial \Phi_0}{\partial \eta} \right) \tag{41}$$

and

$$\frac{\partial \delta_n}{\partial \eta} = -\frac{\bar{z}^2}{\Phi_0} \bar{\alpha} \psi^n \left( \frac{n}{\psi} \frac{\partial \psi}{\partial \eta} - \frac{1}{\Phi_0} \frac{\partial \Phi_0}{\partial \eta} + \frac{1}{\bar{\alpha}} \frac{\partial \bar{\alpha}}{\partial \eta} \right). \tag{42}$$

We now give the derivatives of the $\Gamma_1$ through $\Gamma_4$.

$$\frac{\partial \Gamma_1}{\partial \eta} = -\frac{6}{z} \left( \gamma_0 + \eta \frac{\partial \gamma_0}{\partial \eta} \right) \tag{43}$$

$$\frac{\partial \Gamma_2}{\partial \eta} = \frac{12}{z} \left( \gamma_1 \Gamma_1 + \eta \left\{ \frac{\partial \gamma_1}{\partial \eta} \Gamma_1 + \gamma_1 \frac{\partial \Gamma_1}{\partial \eta} \right\} \right) - \frac{2\Gamma_1}{z} \frac{\partial \Gamma_1}{\partial \eta} \tag{44}$$

$$\frac{\partial \Gamma_3}{\partial \eta} = \frac{12}{z} \left( \gamma_1 \Gamma_2 - \frac{3}{2} \gamma_2 \Gamma_1^2 \right) +$$
$$+ \frac{12\eta}{z} \left( \frac{\partial \gamma_1}{\partial \eta} \Gamma_2 + \gamma_1 \frac{\partial \Gamma_2}{\partial \eta} - \frac{3}{2} \frac{\partial \gamma_2}{\partial \eta} \Gamma_1^2 - 3\gamma_2 \Gamma_1 \frac{\partial \Gamma_1}{\partial \eta} \right) - \tag{45}$$
$$- \frac{2}{z} \left( \frac{\partial \Gamma_1}{\partial \eta} \Gamma_2 + \Gamma_1 \frac{\partial \Gamma_2}{\partial \eta} \right)$$

and

$$\frac{\partial \Gamma_4}{\partial \eta} = \frac{12}{z} \left( \gamma_1 \Gamma_3 - 3\gamma_2 \Gamma_1 \Gamma_2 + 2\gamma_3 \Gamma_1^3 \right) +$$
$$+ \frac{12\eta}{z} \left( \frac{\partial \gamma_1}{\partial \eta} \Gamma_3 + \gamma_1 \frac{\partial \Gamma_3}{\partial \eta} - 3 \frac{\partial \gamma_2}{\partial \eta} \Gamma_1 \Gamma_2 - 3\gamma_2 \frac{\partial \Gamma_1}{\partial \eta} \Gamma_2 - 3\gamma_2 \Gamma_1 \frac{\partial \Gamma_2}{\partial \eta} + \tag{46}\right.$$
$$\left. + 2 \frac{\partial \gamma_3}{\partial \eta} \Gamma_1^3 + 6\gamma_3 \Gamma_1^2 \frac{\partial \Gamma_1}{\partial \eta} \right) - \frac{2}{z} \left( \frac{\partial \Gamma_1}{\partial \eta} \Gamma_3 + \Gamma_1 \frac{\partial \Gamma_3}{\partial \eta} + \Gamma_2 \frac{\partial \Gamma_2}{\partial \eta} \right).$$

The expression for the derivative of $\Gamma_5$ is even more lengthy and is not given as it is not necessary to obtain $p_5$.

The expression for $p_0$ is obtained from Eq. (*38*) and is

$$\frac{p_0 V}{NkT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \tag{47}$$

The higher-order $p_n$ are

$$\frac{p_1 V}{NkT} = -\eta \frac{\bar{z}^2}{\Phi_0} \left( \frac{\partial \alpha_0}{\partial \eta} - \frac{\alpha_0}{\Phi_0} \frac{\partial \Phi_0}{\partial \eta} \right) \tag{48}$$

$$\frac{p_2 V}{NkT} = \frac{\eta}{2} \left( \frac{\partial \delta_0}{\partial \eta} \Gamma_1 + \delta_0 \frac{\partial \Gamma_1}{\partial \eta} \right) \tag{49}$$

$$\frac{p_3 V}{NkT} = \frac{\eta}{3} \left( \frac{\partial \delta_0}{\partial \eta} \Gamma_2 + \delta_0 \frac{\partial \Gamma_2}{\partial \eta} - \frac{\partial \delta_1}{\partial \eta} \Gamma_1^2 - 2\delta_1 \Gamma_1 \frac{\partial \Gamma_1}{\partial \eta} \right) \tag{50}$$

$$\frac{p_4 V}{NkT} = \frac{\eta}{4} \left( \frac{\partial \delta_0}{\partial \eta} \Gamma_3 + \delta_0 \frac{\partial \Gamma_3}{\partial \eta} - 2 \left\{ \frac{\partial \delta_1}{\partial \eta} \Gamma_1 \Gamma_2 + \delta_1 \frac{\partial \Gamma_1}{\partial \eta} \Gamma_2 + \delta_1 \Gamma_1 \frac{\partial \Gamma_2}{\partial \eta} \right\} + \right.$$
$$\left. + \frac{\partial \delta_2}{\partial \eta} \Gamma_1^3 + 3\delta_2 \Gamma_1^2 \frac{\partial \Gamma_1}{\partial \eta} \right) \tag{51}$$

and

$$\frac{p_5 V}{NkT} = \frac{\eta}{5} \left( \frac{\partial \delta_0}{\partial \eta} \Gamma_4 + \delta_0 \frac{\partial \Gamma_4}{\partial \eta} - \frac{\partial \delta_1}{\partial \eta} \left\{ \Gamma_2^2 + 2\Gamma_1 \Gamma_3 \right\} - \right.$$
$$- 2\delta_1 \left\{ \Gamma_2 \frac{\partial \Gamma_2}{\partial \eta} + \frac{\partial \Gamma_1}{\partial \eta} \Gamma_3 + \Gamma_1 \frac{\partial \Gamma_3}{\partial \eta} \right\} +$$
$$+ 3 \left\{ \frac{\partial \delta_2}{\partial \eta} \Gamma_1^2 \Gamma_2 + \delta_2 \left[ 2\Gamma_1 \Gamma_2 \frac{\partial \Gamma_1}{\partial \eta} + \Gamma_1^2 \frac{\partial \Gamma_2}{\partial \eta} \right] \right\} -$$
$$\left. - \frac{\partial \delta_3}{\partial \eta} \Gamma_1^4 - 4\delta_3 \Gamma_1^3 \frac{\partial \Gamma_1}{\partial \eta} \right). \tag{52}$$

Thus, the pressure is given by

$$p_n = \sum_{n=0}^{\infty} K^n p_n . \tag{53}$$

The Gibbs' energy is obtained from

$$G = A + pV . \tag{54}$$

We have checked all our expressions explicitly and using Mathematica. Further, the derivatives were checked by comparison of results of a Fortran program based on the explicit formulae with the Mathematica results. A futher check was obtained by comparison, both analytically and numerically, of the results given here with those for the single-component fluid obtained by HBN for the case where all $\varepsilon_{ij}$ are equal and for the case of a binary mixture with $x_1 = 0$ and $x_2 = 0$.

### EXTENSION TO MORE GENERAL MIXTURES OF YUKAWA FLUIDS

The results thus far are based on Ginoza's results for a factorizable mixture and thus are rigorous consequences of the MSA if the particles are of equal size and Eq. (*3*) is satisfied. However, Eq. (*3*) is not generally satisfied. One possibility would be to write

$$E = \sum_{n=1}^{\infty} \langle K \rangle^n \langle E \rangle_n \tag{55}$$

where

$$\langle K \rangle = \beta \langle \varepsilon \rangle \tag{56}$$

with

$$\langle \varepsilon \rangle = \sum_{ij=1}^{m} x_i x_j \varepsilon_{ij} \ . \tag{57}$$

Note that $\langle \varepsilon \rangle$ is equal to $\langle \varepsilon \rangle^{\text{LB}}$ only if Eq. (*3*) is satisfied. In general, the two quantities will differ.

From first-order perturbation theory we know that for a general mixture of Yukawa fluids of equal size,

$$\frac{\langle E \rangle_1}{NkT} = -\frac{\alpha_0}{\Phi_0} = -\frac{z\,L(z)}{\exp(-z)\,L(z) + S(z)} \ . \tag{58}$$

This suggests the approximation

$$\langle E \rangle_n = \frac{E_n}{\overline{z}^{2n}} \ . \tag{59}$$

Equation (*59*) is a valid consequence of the MSA whether or not Eq. (*3*) is satisfied. As long as Eq. (*3*) is satisfied, the change is only a formal change of notation. However, Eqs (*55*)–(*59*) are applicable to solutions for which Eq. (*3*) is not satisfied; they are no longer rigorous MSA results but a nonrigorous, but hopefully useful, modification. We refer to Eqs (*55*)–(*59*) as the modified MSA (M/MSA) equations.

For the Helmholtz energy,

$$\Delta A = \sum_{n=0}^{\infty} \langle K \rangle^n \langle A \rangle_n \tag{60}$$

with $A_0$ given by Eq. (*38*),

$$\langle A \rangle_n = \frac{\langle E \rangle_n}{n} \tag{61}$$

for the higher order $\langle A \rangle_n$. Similarly,

$$p = \sum_{n=0}^{\infty} \langle K \rangle^n \langle p \rangle_n \tag{62}$$

with

$$\langle p \rangle_n = \frac{p_n}{\overline{z}^{2n}} . \tag{63}$$

This leaves the question of a generalization to the case where the particles are of unequal size. Again the zeroth- and first-order terms can be written explicitly using known results for the Percus–Yevick (PY) thermodynamics and the Laplace transforms of the PY radial distribution functions of a hard-sphere mixture[12]. As we have mentioned, we expect that the expansions in $1/T$ will converge more quickly for mixtures of particles of unequal size. If this is the case, the lower-order terms in $1/T$ should dominate and the higher-order terms can be estimated using some average concentration-dependent diameter. We leave such a procedure for future work and concentrate here on the equal-size case, which is of less general interest for practical calculations but is of possibly greater theoretical interest because of the slower convergence of the $1/T$ series.

## RESULTS FOR A SIMPLE MIXTURE

As an application and illustration of these formulae, we report results for a binary mixture ($m = 2$) of equal-size molecules for which $\varepsilon_{11} = \varepsilon$ and $\varepsilon_{12} = \varepsilon_{22} = 0$. This mixture is qualitatively representative of mixtures involving helium, which has a comparatively small $\varepsilon_{\text{He,He}}$. Results for more general mixtures will be given in later publications.

The $A_1$ for this mixture are shown in Fig. 1 for $x_2 = 0$ and $x_1 = x_2 = 0.5$. In Fig. 2 the higher-order $A_n$ are displayed. The $A_n$ are multiplied by $x_1^n$ to make them comparable in magnitude. It is seen that the inverse-temperature expansion is rapidly convergent in case of a pure fluid ($x_1 = 1$). For the pure fluid, the high-order $A_n$ are small at high densities because the hard cores are close together and particle fluctuations are inhibited. Convergence is not relevant for $x_2 = 1$ because all the perturbation terms are zero. On the other hand, for the mixture at $x_1 = 0.5$, although $A_1$, and to a lesser extent $A_2$ are the largest terms, the convergence is not rapid at small $T$. This is a result of the fact that for equal-size molecules particles of different attractive energy can be interchanged with no consequence in the repulsive energies. This means that care must be used with the inverse-temperature expansion for a mixture of equal-size molecules, at least in the
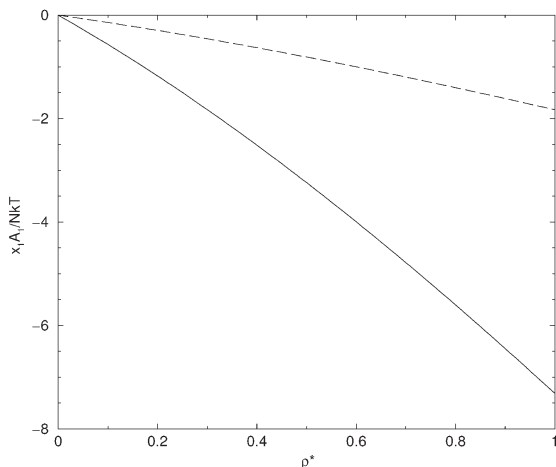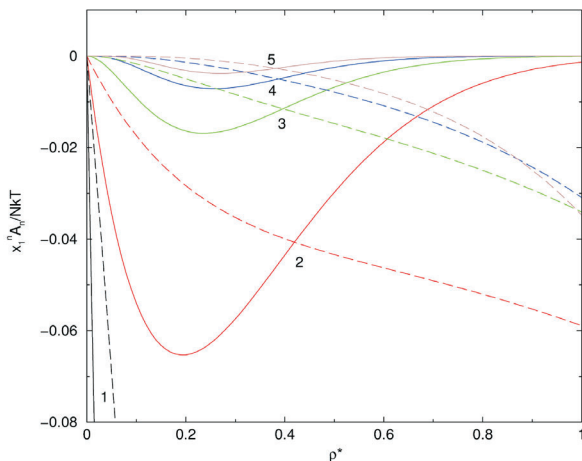


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Coefficient $A_1$ of a mixture of equal size Yukawa molecules for which $\varepsilon_{12} = \varepsilon_{22} = 0$ as a function of the density, $\rho^* = \rho\sigma^3$. The solid curve gives the values for $x_2 = 0$, that is a pure fluid of molecules of species 1 for which $\varepsilon_{11} \neq 0$, and the dashed curve gives the values for $x_1 = x_2 = 0.5$. The values of $A_1$ are multiplied by $x_1$ to give a better impression of its relative value. All quantities are dimensionless

case considered here, for temperatures smaller than about $\varepsilon_{11}/k$. The convergence should be more rapid with mixtures of unequal-size molecules.



FIG. 2

Coefficients $A_n$ of a mixture of equal size Yukawa molecules for which $\varepsilon_{12} = \varepsilon_{22} = 0$ as a function of the density $\rho^* = \rho\sigma^3$. The $A_n$ are multiplied by $x_1^n$ to give a better impression of their relative magnitudes. The numbers by the curves give the value of $n$. The solid and dashed curves have the same meaning as in Fig. 1. All quantities are dimensionless

### CONCLUSION

Expressions for the coefficients in an inverse-temperature expansion of the Helmholtz energy and pressure are given for the case of mixtures of Yukawa molecules of equal size. The convergence of this series is not rapid, at least for the case considered here. Nonetheless, the results can be applied to mixtures of such gases. If lower temperature results are desired, one could solve Eq. (*19*) numerically and use this result in Eq. (*28*) to obtain the energy. This alternative procedure is less attractive because it is numerical but will be investigated.

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