Thermodynamic properties of simple multi-Yukawa fluids: a variational approach

J.N. Herrera[a,*], A.Y. Salazar-Govea[b], A. Cruz- Vera[a], and E. González-Jiménez[a]
[a]Benemérita Universidad Autónoma de Puebla, Facultad de Ciencias Físico-Matemáticas,
Apartado Postal 1152, Puebla, Pue., México, 72000, México.
[b]Universidad Tecnológica de la Mixteca, Instituto de Agroindustrias,
Carretera a Acatlima K.M. 2.5, Huajuapán de León, Oaxaca, 69000, México,
[*]e-mail: nherrera@fcfm.buap.mx

The perturbation theory of dense fluids interacting according to an intermolecular potential represented as a linear combinations of m-Yukawa functions, whose reference interaction is the hard-sphere potential, allows setting an equation of state in terms of the ratio λ of the corresponding species molecular sizes. In this work we determine λ by solving numerically the non-linear equation that results from the minimization of the system Helmholtz free energy. The resulting values of λ are density and temperature dependent, and are in quantitative agreement with those from the development of Mansoori and Canfield. The proposed method also provides the compressibility factor of the corresponding Lennard-Jones fluid, represented by the combination of a hard-sphere plus two Yukawa terms, in good agreement with the available values from Monte Carlo simulations.

Keywords: Perturbation theory; characteristic diameters; effective potential.

La teoría de perturbaciones para sistemas densos permite obtener la ecuación de estado de forma analítica para cuando la interacción inter-molecular de sus componentes es representada como una combinación lineal de potenciales tipo m-Yukawa y tomando como el potencial de referencia una interacción de esfera dura. Dicha ecuación de estado depende de la razón de los diámetros característicos moleculares. En este trabajo se determina esta razón de los diámetros empleando un método variacional. Esto significa que tomamos la condición de minimización de la energía libre de Helmholtz con respecto a un parámetro $\lambda = R/\sigma$. Esta condición da una ecuación no lineal para el parámetro, la cual se resuelva numéricamente. Las soluciones obtenidas muestran la dependencia de λ respecto a la temperatura reducida y de la densidad. Nuestros resultados para λ son comparables cualitativamente con los obtenidos por Monsoori y Canfield. Además se obtiene el factor de compresibilidad para un fluido de esferas duras más dos términos Yukawa el cual representa un fluido tipo Lennard Jones, obtenemos un buen acuerdo con los resultados de Monte Carlo.

Descriptores: Teoría de perturbaciones; diámetros característicos; potencial efectivo.

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1. Introduction

Classical theories of fluids are based on the statistical mechanics ensemble formalism that allows the description of the thermodynamic behavior of diverse systems [1,2]. The common denominator for all these theories is the need for an intermolecular potential to describe the particle interactions as well as the resulting correlation functions and thermodynamic properties of interest. A successful approximation for the description of these interactions models hinges around the splitting of the interactions into short- and long-range contributions [1-5]. Typically, the first term is described in terms of either a hard- or soft-sphere, involving always a dominant repulsive contribution to account properly for the ever-present excluded volume effects [2]. The second term might include an attractive and a repulsive contribution because, according to the experimental evidence, the corresponding potential of mean force exhibits a non-periodic oscillatory radial dependence impossible to represent with just only one type of interaction.

Based on these observations, the first developments on the perturbation theory of fluids in the second half of the past century invoked the splitting of the total intermolecular potential into one represented by a hard-sphere (as a reference) and the corresponding perturbation around the reference. Among these theories [1] we have Barker-Henderson's (BH) [4] and Weeks-Chandler-Andersen's [5]. Just recently Guérin, [6] developed a perturbation approach for the thermodynamic properties of hard-sphere fluids based on a double-Yukawa potential, *i.e.*, one repulsive and the other attractive, following the first-order perturbation scheme of Tang and Lu [7]. This approximation is the first order mean spherical approximation (MSA), first order in $g(r)$, but second order in the thermodynamic properties. While Guérin's equation of state is analytic, it is parametric in the size-ratio , where R is the 'equivalent diameter' or hard-sphere diameter (an crucial parameter in any perturbation approach), while σ is the distance at which the total potential becomes zero.

On the one hand, the R parameter in BH's perturbation theory is obtained from the integration of the Mayer function, and thus, it depends on the temperature [4]. On the other hand, Guérin's theory keeps a constant value of λ for the determination of the thermodynamics properties of various systems, whose predictions are in good agreement with the cor-

responding Monte Carlo (MC) simulation counterparts, even though the used λ values have no physical justification.

In the present work we start with the analytical results from Guérin, and after invoking the Gibbs-Bogolioubov (GB) condition, we determine the value of λ that minimizes the system's Helmholtz free energy [8]. This procedure, that we call VMSA, results in an equation non-linear on the λ-parameter, indicates that λ depends on the system density and temperature as well on the intermolecular potential parameters. The resulting thermodynamic properties from VMSA are in good agreement with those from MC simulations at low and intermediate densities, while exhibiting significant deviations for high densities as expected for this kind of variational approaches [9]. Moreover, the VMSA predictions are similar to those of Mansoori-Canfield, while involving a simpler calculation of the λ parameter [9,12].

In Sec. 2 we present the relevant expressions of Guérin's approach for the thermodynamic properties of the HSMY fluids and the variational approximation for the λ parameter; while in Sec. 3 we apply our analytical results to illustrate the behavior of the λ with the system density and temperature, as well as the behavior of the isothermal compressibility for a real system.

2. Thermodynamic properties of HSMYF and VMSA

Let us consider a mono-disperse fluid whose effective potential is represented by the hard-sphere interaction, HS, plus a linear combination of Yukawa terms (MYHS):

$$u(r) = \infty, \quad \text{for} \quad r < \lambda\sigma, \tag{1a}$$

and

$$u(r) = \varepsilon\varphi\left(\frac{r}{\sigma}\right) = \varepsilon\varphi(x), \quad \text{when} \quad x > \lambda \tag{1b}$$

where $x = r/\sigma$ and $\varphi(x)$ is given by:

$$\varphi(x) = \frac{c}{x}\Sigma_i^m(-1)^i \exp[-\alpha_i(x-1)] \tag{1c}$$

In Eqs. (1a-c) m is the number of Yukawa terms, α_i and ε are the size and energy parameters representing the inverse of the range and the magnitude of the interactions, respectively, $\lambda = R/\sigma$, where R is the effective hard-sphere diameter, σ is defined by the condition u(σ)=0 [6], and the constant c is determined such that $\varphi(x)$=-1.

Following the recently proposed perturbation approach by Tang and Lu, we expand the radial distribution function as $g(r) = g_0 + g_1$, where the first contribution is the radial distribution function of the reference hard-sphere fluid, while the second becomes the perturbation contribution [7]. Consequently, the Helmholtz free energy of the system can be split into the following three terms [6]:

$$a = a_0 + a_1 + a_2 \tag{2}$$

with

$$a_0 = \frac{4\eta - 3\eta^2}{(1-\eta)^2},$$

$$a_1 = 2\pi\rho\beta \int_\sigma^\infty g_0(r)u(r)r^2 dr$$

and

$$a_2 = \pi\rho\beta \int_\sigma^\infty g_1(r)u(r)r^2 dr \tag{3}$$

In Eq. (3) η is the packing factor, *i.e.*, $\eta = \pi\rho\sigma^3\lambda^3/6$, a_0 is the Helmholtz free energy from Carnahan-Starling (CS) equation of state, while a_1 and a_2 are the first order perturbation terms when $g(r)$ is split into $g_0(r)$ and $g_1(r)$, respectively.

When we apply these equations to the MYHS potential the resulting expressions for the integrals of $rg_0(r)$ and $rg_1(r)$ become [7]:

$$G_0(s) = \int_R^\infty rg_0(r)e^{-sr}dr \quad G_1(s) = \int_R^\infty rg_1(r)e^{-sr}dr \tag{4}$$

Within the PY approximation, Wertheim [9] derived an analytical expression for $G_0(s)$ of hard-spheres of diameter R, *i.e.*,

$$G_0 = \frac{R^2 L(sR)e^{sR}}{(1-\eta)^2 Q(sR)s^2 R^2} \tag{5}$$

with

$$Q(z) = \frac{S(z) + 12\eta L(z)e^{-z}}{(1-\eta)^2 z^3}$$

$$L(z) = \left(1 - \frac{\eta}{2}\right)z + 1 + 2\eta$$

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

Moreover, Tang and Lu derived the corresponding $G_1(s)$ expression for a mono-disperse fluid represented by an interaction potential that comprises two Yukawa terms (with identical interaction magnitude) and a hard-sphere core of diameter R [10]. However, the inclusion of different interaction amplitudes for the two Yukawa terms (m=2) with equal diameter is straightforward, so that for that case we have that:

$$G_1(s) = \frac{R^2\beta k \exp(-sR)}{(sR+\gamma)Q^2(sR)Q^2(\gamma)}. \tag{7}$$

From the previous expressions we can obtain the explicit contributions to the reduced Helmholtz free energy, Eq. (2), in the following form [6]:

$$a_{11} = \frac{12\eta}{(1-\eta)^2} \frac{c}{\lambda T^*} \Sigma_i (-1)^i \frac{\exp(\alpha_i(1-\lambda))}{(\alpha_i \lambda)^2} \frac{L(\alpha_i \lambda)}{Q(\alpha_i \lambda)} \quad (8a)$$

$$a_{12} = -12\eta g_0(R) \frac{c}{\lambda T^*} \Sigma_i \frac{(-1)^i}{(\alpha_i \lambda)^2} K_i \quad (8b)$$

$$a_{21} = -6\eta \left(\frac{c}{\lambda T^*}\right)^2$$
$$\times \Sigma_{i,j} \frac{(-1)^{i+j}}{(\alpha_i \lambda + \alpha_j \lambda)} \frac{\exp[(\alpha_i + \alpha_j)(1-\lambda)]}{Q^2(\alpha_i \lambda)} \quad (8c)$$

$$a_{22} = 6\eta \left(\frac{c}{\lambda T^*}\right)^2$$
$$\times \left[\Sigma_i (-1)^i \frac{\exp[\alpha_i(1-\lambda)]}{Q^2(\alpha_i \lambda)}\right] \left[\Sigma_j \frac{(-1)^j}{(\alpha_j \lambda)^2} K_j\right] \quad (8d)$$

where $\lambda = R/\sigma$, $T^* = k_B T/\varepsilon$, k_B is the Boltzmann constant and T is the absolute temperature, while $L(z)$ and $Q(z)$ are given by the Eq. (6), and K_i is given by the following expression,

$$K_i = (1 + \alpha_i \lambda) \exp[\alpha_i(1-\lambda)] - (1 + \alpha_i) \quad (9)$$

The thermodynamic definition of the excess internal energy is given by the expression:

$$u = \frac{U - U^{id}}{N k_B T} = \beta \frac{\partial a}{\partial \beta} \quad (10)$$

By differentiation of the Helmholtz free energy with respect to density we obtain the corresponding compressibility factor Z, *i.e.*,

$$Z = Z_0 + Z_1 + Z_2 \quad (11)$$

Where Z_0 is given by the Carnahan - Starling:

$$Z_0 = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}$$

and invoking the following relationship,

$$Z_i = Z_{i1} + Z_{i2}, \quad Z_{ij} = \eta \frac{\partial(a_{ij})}{\partial \eta} \quad (12)$$

we have that:

$$Z_{11} = a_{11} + 12\eta^2 \frac{c}{\lambda T^*} \Sigma_i (-1)^i \frac{\exp[\alpha_i(1-\lambda)]}{(\alpha_i \lambda)^2}$$
$$\times \left[\frac{\alpha_i \lambda(5+\eta)/2 + 2(2+\eta)}{(1-\eta)^3 Q(\alpha_i \lambda)} - \frac{L(\alpha_i \lambda) Q'_\eta(\alpha_i \lambda)}{(1-\eta)^2 Q^2(\alpha_i \lambda)}\right] \quad (13a)$$

$$Z_{12} = a_{12} - 6\eta^2 \frac{5+\eta}{(1-\eta)^3} \frac{c}{\lambda T^*} \Sigma_i \frac{(-1)^i}{(\alpha_i \lambda)^2} K_i \quad (13b)$$

$$Z_{21} = a_{21} + 12\eta^2 \left(\frac{c}{\lambda T^*}\right)^2 \Sigma_{i,j} (-1)^{i+j}$$
$$\times \frac{\exp[(\alpha_i + \alpha_j)(1-\lambda)]}{(\alpha_i \lambda + \alpha_j \lambda)} \frac{Q'_\eta(\alpha_i \lambda) Q(\alpha_j \lambda) Q'_\eta(\alpha_j \lambda)}{Q^3(\alpha_i \lambda) Q^3(\alpha_j \lambda)} \quad (13c)$$

$$Z_{22} = a_{22} - 12\eta^2 \left(\frac{c}{\lambda T^*}\right)^2$$
$$\times \left[\Sigma_i (-1)^i \exp[\alpha_i(1-\lambda)] \frac{Q'_\eta(\alpha_i \lambda)}{Q^3(\alpha_i \lambda)}\right]$$
$$\times \left[\Sigma_j \frac{(-1)^j}{(\alpha_j \lambda)^2} K_j\right] \quad (13d)$$

Where Q'_η denotes the derivative of Q with respect to η. The compressibility factor given by Eq. (11) has an explicit analytical form in terms of the intermolecular potential parameters, with the exception of λ that should be determined through (at least) three possible routes [9,11,13]: by (i) using Barker-Henderson equation, [4], (ii) invoking an expression derived by Verlet and Weiss (VW), [13], and (iii) applying a variational method subject to the Gibbs Bogolioubov criteria, [8,9,12].

The first method translates into the following expression for λ:

$$\lambda = \int_0^1 \left[1 - e^{-\beta \varepsilon \varphi_{DY}(x)}\right] dx \quad (14)$$

which means that the calculated value of λ is explicitly dependent on the system temperature, where the integration is performed numerically [6].

The second route to λ uses molecular simulation results and the BH theory to adjust the following expression, this adjusts was obtained by Verlet-Weis (VW) [13]:

$$\lambda = \frac{0.3837 + 1.068/T^*}{0.42931.0/T^*} \quad (15)$$

From Eq. (15) becomes evident the temperature dependence of the λ parameter. Even though Eq. (15) was derived from the BH perturbation terms, there is a significant difference between the behavior of this expression and that from the BH (first) route, *i.e.*, in that the slopes of the corresponding curves are convex for the VW [13] and concave for the BH [4] routes, respectively. Note also that in both routes the reduced diameter decreases with increasing temperature, and λ does not depend on the system density [4,13].

The third method, the so-called VMSA involves the minimization of the Helmholtz free energy with respect to λ, using $\eta = \pi \rho^* \lambda^3/6$. From Eqs. (2) and (8a-d) the Helmholtz free energy can be considered as a density functional so that the minimization condition can be written as:

$$\left(\frac{\partial a}{\partial \lambda}\right)_{\rho^*, T^*} = 0 \quad (16)$$

and consequently, in the alternative form:

$$\left(\frac{\partial a}{\partial \lambda}\right)_{\eta, T^*} + \left(\frac{\partial a}{\partial \eta}\right)_{\rho^*, T^*} \left(\frac{\partial \eta}{\partial \lambda}\right)_{\rho^*, T^*}$$
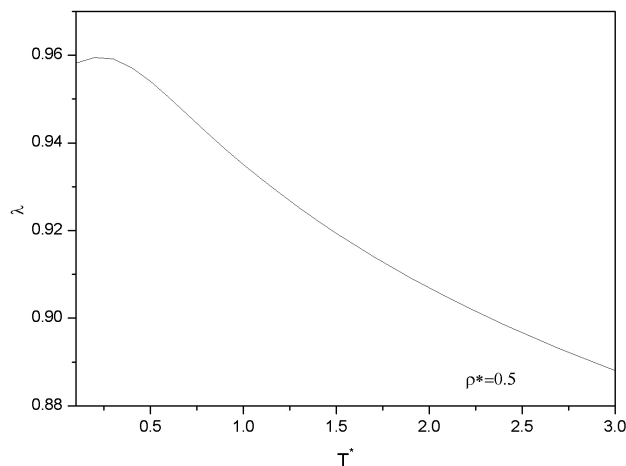$$= \left(\frac{\partial a}{\partial \lambda}\right)_{\eta, T^*} + \frac{3z}{\lambda} = 0 \quad (17)$$

FIGURE 1. Temperature dependence of the reduced diameter λ for $\rho* = 0.5$ from the numerical solution of Eq. (17).

FIGURE 2. Reduced density dependence of the parameter λ for several reduced temperatures according to the numerical solution of Eq. (17).

The explicit form of Eq. (17) can be obtained by invoking Eqs. (2) and (11) after a lengthy algebraic manipulation whose result is a non-linear expression for the λ parameter and explicit in the system density and the potential parameters. Because the non-linearity of equation (17), *i.e.*, containing exponentials and polynomials terms of λ, the choice of the physically meaningful root is based on the fact that here we use the hard-sphere fluid as our perturbation reference, and consequently, the root to chose is that closest to one. However, in practice this is not an issue because there is only one root that satisfies the non-linear equation. Note also that neither Eqs. (16)-(17) nor the general expressions for the free energy and compressibility factors contains restrictions for the size of this root, *i.e.*, $\lambda > 1$ or $\lambda < 1$. Note however that the restrictions for the characteristic particles diameters in the system have been discussed by Guérin [6].

3. Results

In this work we apply the new approach to the study of fluids interacting with a hard-sphere plus a double Yukawa potential, *i.e.*,

$$u(r) = \varepsilon\varphi(x) = \varepsilon\frac{c}{x}\Sigma_i^m(-1)^i \exp[-\alpha_i(x-1)] \quad (18)$$

for which we have results from literature for comparison purposes [6,12]. In Fig. 1 we plot the solution of Eq. (17) as a function of the system temperature for $m = 2$ along the reduced isochore $\rho* = 0.5$, for a fluid represented by an effective Lennard - Jones potential, where the perturbation involves the parameters $\alpha_1 = 2.6509$, $\alpha_2 = 14.8105$ and $c = 2.0053$ [6,14]. According to this figure, the dependence of λ at low densities exhibits a slope similar to that predicted by BH, however, as the density is increased the fluid behaves as that described by Verlet - Weiss [13]

In Fig. 2 we plot the density dependence of λ 'parameterized' by the system's reduced temperature. Note that the observed behavior is similar to that predicted by Mansoori
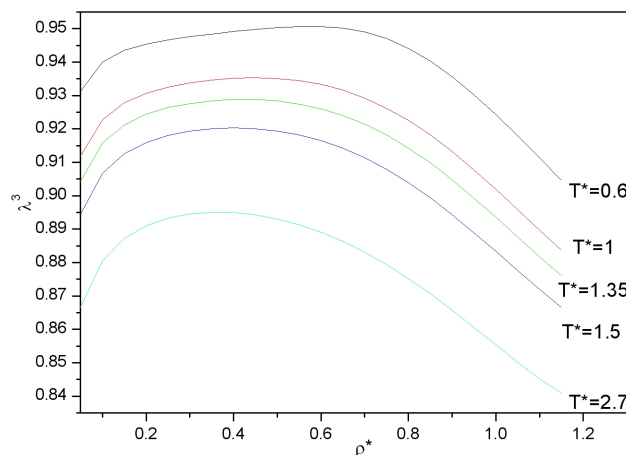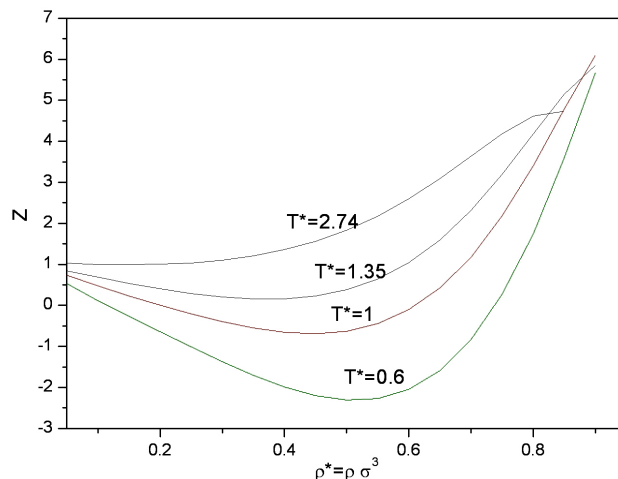

FIGURE 3. Reduced density dependence of the compressibility factor along several isotherms for a HS-2Yuk, with the parameters indicated in the text, we used the results obtained from Eq. (17).

and Canfield, [9], who used a similar variational method, even though, applied to a rather different free energy expression through a more involved procedure for the determination of λ. In contrast to the variational development of Mansoori and Canfield [9], the strong isothermal density dependence of the parameter λ in our results originates in the use of the perturbation theory of Tang and Lu, which hinges around the expansion of the radial distribution function.

In Fig. 3 we display the density dependence of the compressibility factor along several reduced temperatures for a 2-Yukawa fluid with parameters representing a HS+LJ potential, [11].

In Fig. 4 we compare the predicted reduced density dependence of the compressibility factor for the same system as in Figs. 2-3, along the isotherm $T^* = 1.35$, against Monte Carlo simulation results [12].

From these figures we can conclude that the proposed variational approach provides quantitative agreement with Monte Carlo simulation predictions within a range of fluid
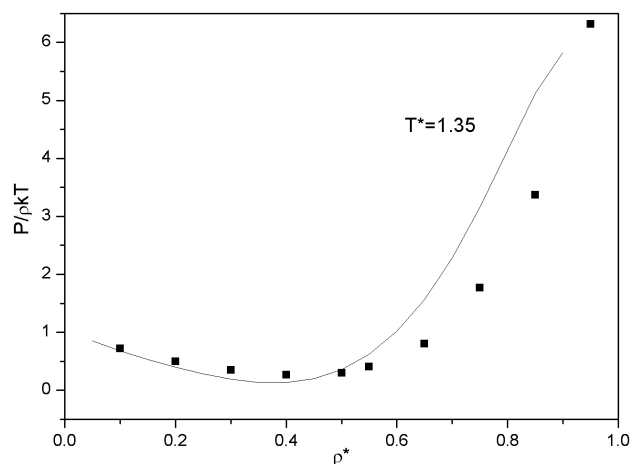
FIGURE 4. Comparison between the prediction based on Eq. (17) (solid line) and Monte Carlo simulation results (points, [12]) for the reduced density dependence of the isothermal compressibility.

densities. However, there are obvious significant deviations at higher densities, whose origin must be investigated to find ways to overcome the deficiencies, *e.g.*, either through the modification of the hard-sphere contribution to the compressibility factor or by introducing a higher order perturbation as already attempted elsewhere [12]. We should highlight that Fig. 1 shows the expected temperature dependence for the parameter λ, while Fig. 2 indicates that the density effect on λ becomes stronger with increasing density. Moreover, at densities $\rho* > 0.85$ Tang-Lu theory fails to predict accurately the fluid thermodynamic properties, and consequently, this condition can be used to establish the limit of validity for the VMSA approximation [7]. Note that this high-density behavior is typical for variational approximations [9,11]. In fact, there is a paper related to the content of the present manuscript, but It is somewhat different, [16].

4. Conclusions

The thermodynamic properties of a fluid represented as a hard-sphere plus an m-Yukawa type perturbation were expressed in terms of the λ parameter, which is determined by the VMSA theory. The resulting λ values indicate that they have a significant dependence on the system density and temperature; and are quantitatively in agreement with those from the perturbation theory of Barker and Henderson at low densities, while at higher densities they follow the functional dependence of Verlet-Weiss theory.

The proposed VMSA approach differs from the other two previously mentioned theories in that the resulting λ parameter depends not only on the system density and temperature, but also on the potential parameters defining the model. In this sense, our approximation is 'more complete' than the others because the effective diameter representing the system must depend on the system thermodynamic (temperature and density) state conditions. Therefore, we can also use equations of state for the description of the reference fluid other than the Carnahan-Starling (see *e.g.*, Ref. 12).

Finally, we could claim that the proposed approach completes formally the results from Guérin as well as Tang and Lu for the thermodynamic properties of a fluid represented as a hard-sphere plus m-Yukawa tails [6,7].

Acknowledgements

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