PERTURBATION EXPANSION FOR FLUID USING HARD CORE WITH ATTRACTIVE PART REFERENCE POTENTIAL: I. GENERAL FORMALISM

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In this paper, we develop a perturbation expansion for hard-core with an attractive part reference potential and the formula for a reasonable choice of its parameters. Our formalism is a modification of the Barker–Henderson one applied in the case of the hard-sphere reference system. We also discuss a possible use of our method, mainly owing to the existence of Waisman's analytical solution for hard-core with the Yukawa part potential.

1. Introduction

Perturbation methods now provide a comprehensive theory of classical fluids [1, 2]. In these methods the hard-sphere system is used as the reference potential because for such a system there exist extensive simulation data [3] and the analytical solution of the Percus–Yevick equation [4] is known [5]. Moreover, this solution is fairly exact.

Commonly in the perturbation theory of the Barker–Henderson type two terms up to T^{-2}, where T is the temperature, are retained. Use of a potential closer to the real one (i.e. having, besides the hard core, also an attractive part) as a reference potential should be more practical because of faster convergence of the perturbation series. Probably, to a reasonable approximation in this case, terms of an order higher than first one may be neglected. The problem was that properties of any such type of system have not been satisfactorily known up to recent times.

However, recently Waisman [6] obtained an analytical solution for hard core with the Yukawa tail potential in the mean-spherical-approximation (MSA). A system with the same potential was next analyzed in detail by Henderson, Stell and Waisman [7]. It seems that when taking advantage of this potential as a reference system the use of our method is particularly simple and gives good prospects.

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2. Perturbation expansion in series of inverse temperature

We consider the total potential to be a sum of two-particle potentials in the form

$$u(r) = u_0(r)+\lambda u_1(r), \quad 0 \leqslant \lambda \leqslant 1, \tag{1}$$

where $u_0(r)$ stands for the reference potential part and $u_1(r)$ is treated as a perturbation. The configurational part of free energy can be expanded in the Taylor series in λ; after $\lambda = 1$ is set which recovers the original potential. This technique was first applied by Zwanzig [8]. The procedure is as follows:

$$\frac{\Delta A}{N} = \frac{\Delta A_0}{N} + \frac{\langle u_1\rangle_0}{N} + \int_0^1 d\lambda \frac{\langle u_1\rangle_\lambda - \langle u_1\rangle_0}{N}, \tag{2}$$

where ΔA_0 is the contribution to free energy from the reference potential, $U_1 = \sum_{i<j} u_1(r_{ij})$ and $\langle\ldots\rangle_{\lambda,0}$ denotes mean value using a system interacting through potential $u_\lambda(r)$ and $u_0(r)$, respectively. Next, $U_1(\boldsymbol{r}^N)$ is expanded in λ and integrated term by term which leads to

$$\frac{\Delta A}{N} = \frac{\Delta A_0}{N} + \beta \frac{\langle u_1\rangle_0}{N} - \frac{\beta^2}{2} \frac{\langle u_1^2\rangle_0 - \langle u_1\rangle_0^2}{N} + \ldots . \tag{3}$$

As a matter of fact, it is the expansion in $\beta(\beta = 1/kT)$

$$\Delta A = \sum_{n=0}^{\infty} \beta^n A_n. \tag{4}$$

The first term of this expansion contains the radial distribution function of the reference system, $g_0(r)$

$$\frac{\beta A_1}{N} = \tfrac{1}{2}\varrho \int dr g_0(r) u_1(r), \tag{5}$$

where ϱ is a number density. The second term contains the four and three-body correlation function which are very difficult to handle.

Using the hard-sphere reference system one cannot make the expansion directly because no part of original potential agrees with the hard-sphere one. Actually the expansion is a two-stage one. First the original potential is divided into two part, one being a reference part, $u_0(r)$, and the other a perturbation one, $u_1(r)$. Then properties of the reference system are approximated by a properly chosen trial hard-sphere system, $u_{\mathrm{HS}}(r)$, which is used in perturbation expansion directly [1, 2].

Barker and Henderson accomplished such a type of expansion after introducing a modified potential function [9]

$$\tilde{v}(d, \mu, \alpha, \gamma; r) = \begin{cases} u[d+(r-d)/\alpha], & d+(r-d)/\alpha < \mu, \\ 0 \quad\quad\quad\quad\quad , & \mu, < d+(r-d)/\alpha < d+(\mu-d)/\alpha, \\ \gamma u(r) \quad\quad\quad , & \mu < r. \end{cases} \tag{6}$$

For $\alpha = \gamma = 0$ the potential defined by Eq. (6) becomes the hard-sphere potential of diameter d, for $\alpha = \gamma = 1$ we have the original potential. The parameter α characterizes the

steepness of modified potential in the repulsive region while γ describes its depth in the attractive region. Their procedure lies in the expansion of the configurational integral in α and γ about the point $\alpha = \gamma = 0$, which corresponds to the hard-sphere potential. In the result they obtained

$$\frac{\beta A}{N} = \frac{\beta A_0}{N} - \alpha 2\pi\varrho d^2 g_0(d)\left[d + \int_0^{\mu} dz\{\exp[-\beta u(z)] - 1\}\right]$$

$$+\gamma 2\pi\varrho\beta \int_{\mu}^{\infty} dr r^2 g_0(r) u(r) + \text{higher order terms.} \tag{7}$$

The parameters μ and d are defined as follows

$$u(\mu) = 0, \tag{8a}$$

$$d = \int_0^{\mu} dr\{1 - \exp[-\beta u(r)]\}. \tag{8b}$$

Such a choice is unique and although it is not essential to the procedure, it gives the best results.

It is widely known that Barker-Henderson's expansion is successful because real potentials are steep for $r < \mu$ and effects caused by the attractive part of the potential on the structure of liquid are small.

3. Expansion using hard-core with attractive part reference potential

We are going to obtain a method giving the unique way of choosing appropriate parameters of hard core with attractive part reference potential. We define a modified potential as

$$v(d, \mu, \alpha, \gamma, \zeta; r) = \begin{cases} u[d + (r-d)/\alpha] & , \ d + (r-d)/\alpha < \mu, \\ (1-\zeta) u_{\text{ref}}(r) & , \ \mu < d + (r-d)/\alpha < d + (\mu - d)/\alpha, \\ \gamma u(r) + (1-\zeta) u_{\text{ref}}(r), & \ \mu < r, \end{cases} \tag{9}$$

where $u_{\text{ref}}(r)$ denotes the reference potential. In comparison to $\tilde{v}(r)$ (Eq. (6)) $v(r)$ comprises one parameter more, which takes into account the depth of the reference potential in the attractive region. For $\alpha = \gamma = \zeta = 0$ the modified potential becomes the reference one. For $\alpha = \gamma = \zeta = 1$ the original potential is reproduced.

To facilitate the evaluations we define function $\exp[-\beta v(r)]$ (we omit further the rest of the arguments for simplicity)

$$\exp[-\beta v(r)] = \left[1 - \theta\left(d + \frac{r-d}{\alpha} - \mu\right)\right] \exp\left[-\beta u\left(d + \frac{r-d}{\alpha}\right)\right]$$

$$+\theta\left(d + \frac{r-d}{\alpha} - \mu\right)\theta(\mu - r) \exp[-\beta(1-\zeta) u_{\text{ref}}(r)]$$

$$+\theta(r-\mu) \exp\{-\beta[\gamma u(r) + (1-\zeta) u_{\text{ref}}(r)]\}, \tag{10}$$

where $\theta(x)$ is the Heaviside step function. The configurational integral for a system of N particles is defined by the equation

$$Q_N = (N!)^{-1} \int d\boldsymbol{r}^N \exp\left[-\beta \sum_{i<j}^{N} v(r_{ij})\right]. \tag{11}$$

Now we calculate (as Barker and Henderson did) the derivative of $\ln Q_N$ with respect to χ_k ($\chi_1 = \alpha$, $\chi_2 = \gamma$, $\chi_3 = \zeta$)

$$\frac{\partial \ln Q_N}{\partial \chi_k} = 2\pi N \varrho \int_0^\infty dr r^2 y(r) \frac{\partial}{\partial \chi_k} \{\exp[-\beta v(r)]\}, \tag{12}$$

where $g(r)$ corresponds to the radial distribution function of the system interacting through potential $v(r)$ and $y(r)$ is

$$y(r) = \exp[\beta v(r)]\, g(r). \tag{13}$$

Next, we calculate $\partial \ln Q_N/\partial \chi_k$ with respect to particular χ_k. For $\chi_1 = \alpha$ from Eq. (10) we get

$$\frac{\partial}{\partial \alpha}\{\exp[-\beta v(r)]\} = \frac{r-d}{\alpha^2}\,\delta\left(d+\frac{r-d}{\alpha}-\mu\right)\left\{\exp\left[-\beta u\left(d+\frac{r-d}{\alpha}\right)\right]\right.$$

$$\left. -\theta(\mu-r)\exp[-\beta(1-\zeta)u_{\mathrm{ref}}(r)]\right\} + \frac{\beta(r-d)}{\alpha^2}\left[1-\theta\left(d+\frac{r-d}{\alpha}-\mu\right)\right]\frac{d}{dr}u\left(d+\frac{r-d}{\alpha}\right). \tag{14}$$

Thus

$$\frac{\partial \ln Q_N}{\partial \alpha} = 2\pi N \varrho d_1^2(\mu-d)\{\exp[-\beta u(\mu)]-\exp[-\beta(1-\zeta)u_{\mathrm{ref}}(d_1)]\}y(d_1)$$

$$+\frac{2\pi N}{\alpha^2}\varrho\beta\int_0^\infty dr(r-d)\left[1-\theta\left(\frac{r-d_1}{\alpha}\right)\right]\left[\frac{d}{dr}u\left(d+\frac{r-d}{\alpha}\right)\right]\exp\left[-\beta u\left(d+\frac{r-d}{\alpha}\right)\right]y(r)r^2, \tag{15}$$

where $d_1 = d+\alpha(\mu-d)$. After introducing a new variable of integration defined by

$$z = d+(r-d)/\alpha \tag{16}$$

we obtain

$$\frac{\partial \ln Q_N}{\partial \alpha} = 2\pi N \varrho d_1^2(\mu-d)\{\exp[-\beta u(\mu)]-\exp[-\beta(1-\zeta)u_{\mathrm{ref}}(d_1)]\}y(d_1)$$

$$+2\pi N\varrho\beta\int_0^\mu dz(z-d)\frac{du(z)}{dz}\exp[-\beta u(z)]y[d+\alpha(z-d)]\,[d+\alpha(z-d)]^2. \tag{17}$$

In the limit as $\alpha, \gamma, \zeta \to 0$ we obtain

$$\left.\frac{\partial \ln Q_N}{\partial \alpha}\right|_{\alpha=\gamma=\zeta=0} = 2\pi N \varrho d^2 y_{\mathrm{ref}}(d)\,\{(d-\mu)\exp[-\beta u_{\mathrm{ref}}(d_+)] + \int_0^{\mu} dz \exp[-\beta u(z)]\}, \quad (18)$$

where $u_{\mathrm{ref}}(d_+)$ stands for the right-side limit of the reference potential at $r = d$. We may do this because $\alpha \in [0,1]$ and $\lim_{\alpha \to 0_+} u_{\mathrm{ref}}(d_1)$ implies $\lim_{\gamma \to d_+} u_{\mathrm{ref}}(r)$. On the other hand putting $y(d) = y(d_+)$ when $y(r)$ is discontinuous at $r = d$ involves only a certain interpretation, because as is seen from Eq. (17) the expression $y(d+\alpha(z-d))$ under the integral becomes in the limit $\alpha \to 0$ $y(d_+)$ or $y(d_-)$ according to z and is greater or smaller than d, respectively. This point will be discussed in detail in Sec. 4.

The derivatives of $\ln Q_N$ with respect to γ and ζ are calculated in a similar way with the result

$$\left.\frac{\partial \ln Q_N}{\partial \gamma}\right|_{\alpha=\gamma=\zeta=0} = -2\pi N \varrho \beta \int_{\mu}^{\infty} dr r^2 g_{\mathrm{ref}}(r) u(r), \quad (19)$$

$$\left.\frac{\partial \ln Q_N}{\partial \zeta}\right|_{\alpha=\gamma=\zeta=0} = 2\pi N \varrho \beta \int_{d}^{\infty} dr r^2 g_{\mathrm{ref}}(r) u_{\mathrm{ref}}(r). \quad (20)$$

Full expansion can be written as

$$\frac{\beta A}{N} = \frac{\beta A_{\mathrm{ref}}}{N} - \alpha 2\pi \varrho d^2 y_{\mathrm{ref}}(d)\,\{(d-\mu)\exp[-\beta u_{\mathrm{ref}}(d_+)] + \int_0^{\mu} dz \exp[-\beta u(z)]\}$$

$$+\gamma 2\pi \varrho \beta \int_{\mu}^{\infty} dr r^2 g_{\mathrm{ref}}(r) u(r) - \zeta 2\pi \varrho \beta \int_{d}^{\infty} dr r^2 g_{\mathrm{ref}}(r) u_{\mathrm{ref}}(r) + \ldots \quad (21)$$

In this formula A corresponds to the configurational free energy of the system, which interacts through potential $v(r)$ and A_{ref} through $u_{\mathrm{ref}}(r)$. Putting $\alpha = \gamma = \zeta = 1$ leads to the expression for free energy corresponding to the original potential $u(r)$.

We turn next to the choice of reference potential parameters. Following Barker and Henderson [9] the simpler choice of μ is

$$u(\mu) = 0. \quad (22)$$

Equating to zero the terms of the first order in Eq. (21) implies

$$d = \mu - \exp[\beta u_{\mathrm{ref}}(d_+)] \int_0^{\mu} dz \exp[-\beta u(z)], \quad (23)$$

$$\int_{d}^{\infty} dr g_{\mathrm{ref}}(r) r^2 [\theta(r-\mu) u(r) - u_{\mathrm{ref}}(r)] = 0, \quad (24)$$

and when neglecting the terms of the order higher than the first

$$\frac{\beta A}{N} = \frac{\beta A_{\mathrm{ref}}}{N}. \quad (25)$$

Eq. (9) does not state precisely what is the perturbation $u_1(r)$ in the region $d < r < \mu$, because the reference potential is the hard-core one. The most natural way is to specify $u_1(r)$ as

$$u_1(r) = u(r) - u_{\text{ref}}(r), \quad r > d. \tag{26}$$

However, the term containing $u(r)$ is integrated in Eq. (21) from the limit μ rather than d (analogically to Barker-Henderson theory) so the proper choice is

$$u_1(r) = \begin{cases} -u_{\text{ref}}(r) & , \ d < r < \mu, \\ u(r) - u_{\text{ref}}(r), & r > \mu. \end{cases} \tag{27}$$

Each potential having a hard core with an attractive part is described at least by three parameters: d, the diameter of hard core and the remaining two indicating the depth and range of the attractive part. Through Eqs. (23) and (24) we can specify two of them so unless the third one is not fixed from the beginning, it remains free. We have the possibility of making the best choice by using a variational method.

It can be shown [10] that the last term in Eq. (3) is negative and

$$\frac{A}{N} \leqslant \frac{A_{\text{ref}}}{N} + \beta \frac{\langle u_1 \rangle_{\text{ref}}}{N}. \tag{28}$$

According to Eqs. (23) and (24) in our case

$$\frac{A}{N} \leqslant \frac{A_{\text{ref}}}{N} \tag{29}$$

and we can choose the parameter which is at our disposal, so that the right side of inequality (29) attains minimum.

The proposed expansion enables us to calculate free energy. One can easily evaluate the radial distribution function through the known virial-perturbation methods [2, 11] taking advantage of calculated parameters of the reference system.

4. Final remarks

Recently Waisman [6] obtained the analytical solution for potential

$$u(x) = \begin{cases} \infty & , x < 1, \\ -\varepsilon \exp\left[-z(x-1)\right]/x, & x > 1, \end{cases} \tag{30}$$

where $x = r/d$, in the mean spherical approximation. The problem is how exact are the results of the solution Waisman gave.

Results in perturbation theories depend both on the method of expansion and accuracy of a used reference system. It may turn out that the advantage of having a reference system

closer to the real potential in liquid in comparison to the standard hard-sphere system can be cancelled by defects of approximate solution in calculation of A_0. Then for example inequality (25) which holds for a true function may not be satisfied for an approximate function (A_{ref} may not attain a minimum for physical values of the parameters).

There is one further point worth considering. It regards function $y(r)$, the knowledge of which (at point $r = d$) is necessary in our formalism. When the hard-core system is considered one need not know $y(r)$ inside the hard-core region to calculate $g(r)$ and $c(r)$, where $c(r)$ is defined by the Zernike-Ornstein equation

$$g(r)-1 = c(r)+\varrho \int [g(\boldsymbol{r}')-1]c(|\boldsymbol{r}-\boldsymbol{r}'|)d\boldsymbol{r}'. \tag{31}$$

Inversely, knowledge of $g(r)$ and $c(r)$ is not sufficient to calculate $y(r)$ inside the hard-core region.

To illustrate this we introduce function $d(r)$ and $e(r)$ given by

$$c(r) = [e(r)-1]\, y(r)+d(r), \tag{32}$$

$$e(r) = \exp[-\beta u(r)]. \tag{33}$$

Henderson, Stell and Waisman [7] showed that when $e(r) = \exp[-\beta u_{\text{HC}}(r)]$ is assumed, where $u_{\text{HC}}(r)$ is the hard-core potential, and $d(r) = -\beta w(r)$, where $w(r)$ is a soft pair potential added to $u_{\text{HC}}(r)$, then MSA is obtained. Because $c(r)$ and $g(r)$ are specified uniquely in the whole range of r by the requirement $g(r) = 0$, $r < d$, and $c(r) = -\beta w(r)$, $r > d$, a change of $d(r)$ inside the hard-core region influence only $y(r)$ in the same region.

Assuming that $d(r) = -\beta w(r)$, $r < d$, one obtains a discontinuous $y(r)$ at $r = d$ because equation

$$g(d_+) = \beta\varepsilon - c(d), \tag{34}$$

which holds for the Yukawa potential [6], cannot be fulfilled together with the requirement of continuity of $y(r)$

$$g(d_+) = [\beta\varepsilon - c(d^-)] \exp(\beta\varepsilon). \tag{35}$$

This is a serious defect of MSA because the genuine function $y(r)$ is continuous even for potential with hard core.

One way to avoid the difficulties with the discontinuous function $y(r)$ is to assume that MSA refers only to functions $g(r)$ and $c(r)$. Then $y(r)$ inside the hard core is to our disposal and in particular we may make it continuous. An other way is to improve the MSA solution for Yukawa potential similarly as it was done in the case of the hard-sphere system [12]. Unfortunately the simulation data for the Yukawa potential are not yet known.

In a subsequent paper our method will be applied to calculation of properties of the Lennard-Jones fluid.

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