On equivalence of high temperature series expansion and coupling parameter series expansion in thermodynamic perturbation theory of fluids

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Abstract

The coupling parameter series expansion and the high temperature series expansion in the thermodynamic perturbation theory of fluids are shown to be equivalent if the interaction potential is pairwise additive. As a consequence, for the class of fluids with the potential having a hardcore repulsion, if the hard-sphere fluid is chosen as reference system, the terms of coupling parameter series expansion for radial distribution function, direct correlation function and Helmholtz free energy follow a scaling law with temperature. The scaling law is confirmed by application to square-well fluids.
I. INTRODUCTION

Perturbation series for Helmholtz free energy of a fluid at a given temperature and density was first written down by Zwanzig[1]. The basic idea is to split the total potential energy($V$) of the fluid containing $N$-particles into a reference part($V_{ref}$) and a perturbation part ($V_{per}$). Assuming that $V_{per}$ is small, the term $exp(-\beta V_{per})$ in the canonical partition function of the fluid is expanded in a series of $-\beta V_{per}$. Where $\beta = 1/k_b T$; $k_b$ being Boltzmann constant and $T$ being temperature. This results in a cumulant expansion for Helmholtz free energy. The series is also known as high temperature series expansion(HTSE). The perturbation series of Zwanzig is general in the sense that it doesn’t restrict to pairwise additive interactions between the fluid particles. However, if the interactions are pairwise additive, Zwanzig showed that the first order term in the series depends on radial distribution function(RDF) of the reference system and the second order term depends on correlation functions up to fourth order. An approximation to the second order term was obtained by Barker and Henderson[2]. It was not possible to calculate beyond second order as the higher order correlation functions are unknown.

The perturbation series for the Helmholtz free energy can be derived in alternative ways[3, 4] using coupling parameter or strength parameter ($\lambda$) which defines the strength of perturbation. The total potential energy of an imaginary fluid is written as, $V_{\lambda} = V_{ref} + \lambda V_{per}$. $\lambda = 0$ gives the reference fluid potential energy and $\lambda = 1$ gives potential energy of the fluid under consideration. One way of arriving at the perturbation series is to differentiate the Helmholtz free energy of the imaginary system w.r.t. $\lambda$. The derivative depends on ensemble average of $V_{per}$ w.r.t. the imaginary fluid i.e., $<V_{per}>_{\lambda}$. $<V_{per}>_{\lambda}$ is expanded as a Taylor series around $\lambda = 0$ and then the equation is integrated within the limits $\lambda = 0$ and $\lambda = 1$. This is called as $\lambda$-expansion and the terms are exactly the same as the HTSE.

Another way of obtaining the series, which works only in the case of a pairwise additive potential between the particles, is as follows: The Helmholtz free energy of the system is expanded as a Taylor series in $\lambda$ around $\lambda = 0$. In the case of a pairwise additive potential, it turns out that the Taylor series of Helmholtz free energy depends on the Taylor series of the pair correlation function with respect to $\lambda$ at $\lambda = 0$. This expansion of Helmholtz free energy is referred as coupling parameter series expansion(CPSE). In order to calculate $n^{th}$ order term in this expansion, $(n - 1)^{th}$ derivative of pair correlation function is supposed to be
known. The first order term in the CPSE can be directly seen to be equal to first order perturbation term in HTSE. The method to calculate higher order terms (including the second order term in an accurate way) was not known for a long time. In 2006, Zhou\(^7\) developed a numerical method to calculate the higher order derivatives of RDF using the integral equation theory (IET). Zhou’s method was, however, computationally intensive and the calculated derivatives have numerical fluctuations and require further smoothing procedures. Recently, we developed a much simpler method which doesn’t have those problems\(^5, 6\). The ability to calculate higher order terms, which was not possible with the earlier HTSE enormously improved the accuracy of predictions of the theory.

In a few recent papers\(^8–12\), it has been argued that the HTSE and CPSE are actually different beyond the first order term. It also has been stated that, only in the special case of hard sphere reference system and only for reduced temperature equal to 1, the two series are equal. However, the conclusions were not based on any rigorous results and the arguments were heuristic. Apart from this, a function having two different series expansions contradicts the uniqueness of power series expansion. This raises questions about the validity of the conclusions made in the papers\(^8–12\). In view of this, we re-examine the equivalence of CPSE and HTSE and prove rigorously that both the expansions are equivalent. Even though this result is not very surprising, the equivalence of CPSE and HTSE leads to interesting scaling relations in the case of fluids with interaction potential having a hardcore repulsion(for example, the square well (SW) fluid) if the hardcore repulsive part is taken as reference. For such fluids, the HTSE becomes a power series in \(\beta\). Hence, the terms of CPSE also scale with powers of \(\beta\). As a consequence, once the terms of CPSE are calculated along a particular isotherm for such fluids, the structure and thermodynamic properties of those fluids at other temperatures can be obtained using the scaling relations.

In section II, we prove the equivalence of CPSE and HTSE and in section III we describe the consequences of the equivalence of HTSE and CPSE. The paper is concluded in section IV.

II. THE HTSE AND THE CPSE

Consider a fluid of \(N\) interacting particles in a volume \(\Omega\) at reduced temperature \(T\). Reduced units (\(\epsilon/k_B = \sigma = 1\), where \(\epsilon\) is the well depth and \(\sigma\) is hard sphere diameter) are
used throughout the paper. The Zwanzig’s expansion or HTSE for Helmholtz free energy $F$ of the system is given by

$$F = F_{\text{ref}} + \sum_{n=1}^{\infty} \frac{\omega_n}{n!} (-\beta)^{n-1}$$  \hspace{1cm} (1)

where

$$\omega_1 = \langle V_{\text{per}} \rangle_0$$  \hspace{1cm} (2)

$$\omega_2 = \langle V_{\text{per}}^2 \rangle_0 - \langle V_{\text{per}} \rangle_0^2$$  \hspace{1cm} (3)

$$\omega_3 = \langle V_{\text{per}}^3 \rangle_0 - 3\langle V_{\text{per}} \rangle_0^2\langle V_{\text{per}} \rangle_0 + 2\langle V_{\text{per}} \rangle_0^3$$  \hspace{1cm} (4)

$$\omega_s = s! \sum_{\{n_j\}} (-1)^{\Sigma n_j - 1} (\Sigma n_j - 1)! \prod_{j=1}^{\infty} \frac{1}{n_j!} \left( \frac{\langle V_{\text{per}} \rangle_0^{j}}{j!} \right)^{n_j}$$  \hspace{1cm} (5)

The subscript 0 implies that the averages are with respect to the reference system ensemble. In the Eq.(5), the $\{n_j\}$ implies that the summation is a multiple sum over all possible $n_j$’s such that the constraint $\sum_{n=1}^{\infty} n_j = s$ is satisfied. Here $n_j$’s are positive integers. It can be seen that for all $j > s$, $n_j$’s are zero. Above series for $F$ doesn’t require a pairwise additive interaction potential. However, in the case of a spherically symmetric pairwise additive potential $u(r)$, the $\omega_1$ simplifies to

$$\omega_1 = \frac{2\pi N^2}{\Omega} \int_0^\infty u_{\text{per}}(r)g_0(r)r^2dr$$  \hspace{1cm} (6)

where $u_{\text{per}}(r)$ is the perturbation part of $u(r)$ when separated as $u(r) = u_{\text{ref}}(r) + u_{\text{per}}(r)$. $g_0(r)$ is the radial distribution function of the reference system. $r$ is the radial distance from the origin. $\omega_2$ has been shown to depend on correlation functions up to fourth order. An approximation to $\omega_2$ has been derived by Barker and Henderson [2].

In the $\lambda$-expansion [4] and the CPSE, as mentioned in the introduction, an imaginary fluid is considered with total potential energy given by $V_{\lambda} = V_{\text{ref}} + \lambda V_{\text{per}}$. Differentiating $F(\lambda)$ w.r.t. $\lambda$ and integrating between limits $\lambda = 0$ to $\lambda = 1$ gives

$$F = F_{\text{ref}} + \int_0^1 \langle V_{\text{per}} \rangle_\lambda d\lambda$$  \hspace{1cm} (7)

The subscript $\lambda$ in the above equation implies that the average is w.r.t. the ensemble with potential energy $V_{\lambda}$. Expanding $\langle V_{\text{per}} \rangle_\lambda$ around $\lambda = 0$ in a Taylor series and substituting
\( \lambda = 1 \), we get the HTSE. In the case of pairwise additive potentials, above Eq.(7) can be re-written in terms of pair correlation function \( \rho^{(2)}(1, 2) \) of the imaginary system i.e.,

\[
F = F_{\text{ref}} + \frac{1}{2} \int_0^1 d\lambda \int_\Omega d1 d2 u_{\text{per}}(1, 2) \rho^{(2)}_\lambda(1, 2) \tag{8}
\]

Following Hansen\[4\], we denote the position vector \( \vec{r}_i \) of \( i \)th particle by \( i \) to simplify notation. \( d1 \) denotes the volume element \( d\vec{r}_1 \) around \( \vec{r}_1 \). Expanding \( \rho^{(2)}_\lambda(1, 2) \) in a Taylor series around \( \lambda = 0 \) and substituting in above Eq.(8), we get the CPSE for \( F \) given by

\[
F = F_{\text{ref}} + \frac{1}{2} \int_0^1 d\lambda \int_\Omega d1 d2 u_{\text{per}}(1, 2) \left( \rho^{(2)}_0(1, 2) + \lambda \frac{d\rho^{(2)}_\lambda}{d\lambda}(1, 2) \bigg|_0 + \frac{\lambda^2}{2!} \frac{d^2\rho^{(2)}_\lambda}{d\lambda^2}(1, 2) \bigg|_0 + \cdots \right) \tag{9}
\]

If the system is homogeneous and isotropic, \( \rho^{(2)}_\lambda(1, 2) \) becomes equal to \( \rho^2 g_\lambda(|1 - 2|) \) and the integral in Eq.(9) simplifies. Here \( \rho \) is the density of the system and \( g_\lambda(r) \) is the RDF of the imaginary system.

**A. Equivalence of HTSE and CPSE**

It can be easily seen that first order terms in both the series are same; as mentioned above, in a homogeneous system, \( \rho^{(2)}_\lambda(1, 2) \) becomes equal to \( \rho^2 g_\lambda(|1 - 2|) \) and

\[
\frac{1}{2} \int_0^1 d\lambda \int_\Omega d1 d2 u_{\text{per}}(1, 2) \rho^{(2)}_0(1, 2) = \omega_1 \tag{10}
\]

In order to see the equivalence of second term of CPSE with that of HTSE, consider the definition of \( \rho^{(2)}_\lambda(1, 2) \) i.e.,

\[
\rho^{(2)}_\lambda(1, 2) = N(N - 1) \frac{1}{Z_N(\lambda)} \int_\Omega d\vec{r}^{(N-2)} \exp(-\beta V_\lambda) \tag{11}
\]

where

\[
Z_N(\lambda) = \int_\Omega d\vec{r}^{(N)} \exp(-\beta V_\lambda) \tag{12}
\]

Here \( \int_\Omega d\vec{r}^{(N)} \) implies \( \int_\Omega d1 d2 \cdots dN \)

Now,

\[
\frac{d\rho^{(2)}_\lambda}{d\lambda} = \frac{N(N - 1)}{Z_N(\lambda)} \int_\Omega d\vec{r}^{(N-2)} \exp(-\beta V_\lambda) \int d\vec{r}^{(N-2)} \exp(-\beta V_\lambda) \left( -\frac{N(N - 1)}{Z_N(\lambda)} \int_\Omega d\vec{r}^{(N-2)} \exp(-\beta V_\lambda) \int d\vec{r}^{(N-2)} \exp(-\beta V_\lambda) \right) \tag{13}
\]
Substituting the above equation in second order term of CPSE we get,

\[
\frac{1}{2} \int_0^1 d\lambda \int_\Omega d1d2u_{per}(1,2)\lambda \frac{d\rho^{(2)}}{d\lambda}(1,2) \bigg|_0 = \frac{N(N-1)}{2Z_N(0)} \int_\Omega d\tau^{N}(-\beta V_{per})exp(-\beta V_{ref})u_{per}(1,2) - \frac{N(N-1)}{2Z^2_N(0)} \int_\Omega d\tau^{N}u_{per}(1,2)exp(-\beta V_{ref}) \\
\times \int_\Omega d\tau^{N}(-\beta V_{per})exp(-\beta V_{ref})
\]

(14)

Consider the first term in the RHS of the above equation. It can be seen that the integral remains invariant if (1, 2) is replaced by any other possible pair and there are exactly \(N(N−1)/2\) possible pairs. The same argument holds for the second term on the RHS of above Eg. (14). Thus the above equation becomes,

\[
\frac{1}{2} \int_0^1 d\lambda \int_\Omega d1d2u_{per}(1,2)\lambda \frac{d\rho^{(2)}}{d\lambda}(1,2) \bigg|_0 = \frac{1}{Z_N(0)} \int_\Omega d\tau^{N}(-\beta V_{per})exp(-\beta V_{ref})V_{per} - \frac{1}{Z^2_N(0)} \int_\Omega d\tau^{N}V_{per}exp(-\beta V_{ref}) \\
\times \int_\Omega d\tau^{N}(-\beta V_{per})exp(-\beta V_{ref}) \\
= -\beta \langle V^2_{per} \rangle_0 + \beta \langle V_{per} \rangle_0^2 \\
= -\beta \omega_2/2
\]

(15)

Now to prove the equivalence of a general term of CPSE to that of HTSE, we first define the following:

\[
P_0 = P = \int_\Omega d3..dNexp(-\beta V_{\lambda}) \\
P_1 = \frac{dP}{d\lambda} = \int_\Omega d3..dN(-\beta V_{per})exp(-\beta V_{\lambda}) \\
P_2 = \frac{d^2P}{d\lambda^2} = \int_\Omega d3..dN(-\beta V_{per})^2exp(-\beta V_{\lambda}) \\
\ldots \\
P_s = \frac{d^sP}{d\lambda^s} = \int_\Omega d3..dN(-\beta V_{per})^sexp(-\beta V_{\lambda})
\]

(16)
and
\[ Z_0 = Z_N(\lambda) = \int_\Omega d1..dN \exp(-\beta V_\lambda) \]
\[ Z_1 = \frac{dZ_N(\lambda)}{d\lambda} = \int_\Omega d1..dN (-\beta V_{\text{per}}) \exp(-\beta V_\lambda) \]
\[ Z_2 = \frac{d^2Z_N(\lambda)}{d\lambda^2} = \int_\Omega d1..dN (-\beta V_{\text{per}})^2 \exp(-\beta V_\lambda) \]
\[ \vdots \]
\[ Z_s = \frac{d^sZ_N(\lambda)}{d\lambda^s} = \int_\Omega d1..dN (-\beta V_{\text{per}})^s \exp(-\beta V_\lambda) \] (17)

Here \( d1 \) implies \( d\vec{r}_1 \) and so on. It can be easily seen that

\[
\frac{1}{N(N-1)r_\lambda^2(1,2)} = \frac{P_0}{Z_0} \]
\[
\frac{1}{N(N-1)} \frac{d\rho_\lambda^2(1,2)}{d\lambda} = \frac{P_1}{Z_0} - \frac{P_0}{Z_0^2} Z_1 \]
\[
\frac{1}{N(N-1)} \frac{d^2\rho_\lambda^2(1,2)}{d\lambda^2} = \frac{P_2}{Z_0} - 2 \frac{P_1}{Z_0} Z_1 + 2 \frac{P_0}{Z_0^2} Z_1^2 - \frac{P_0}{Z_0} Z_1^2 \] (18)

To get the \( s^{\text{th}} \) (\( s \geq 1 \)) derivative of \( \rho_\lambda^2(r_1, r_2) \), the \( s^{\text{th}} \) derivative of \( \frac{P_0}{Z_0} \) is required which in turn requires the the \( s^{\text{th}} \) derivative of \( \frac{1}{Z_0} \). Since \( Z_0 \) is a well behaved function, it can be expected that \( s^{\text{th}} \) derivative of \( \frac{1}{Z_0} \) w.r.t. \( \lambda \) exits. The \( s^{\text{th}} \) derivative of \( \frac{1}{Z_0} \) is \([13]\)

\[
\frac{d^s}{d\lambda^s} \left( \frac{1}{Z_0} \right) = s! \sum_{\{n_j\}} (-1)^\alpha \alpha! \prod_{j=1}^{\infty} \frac{1}{n_j!} \left( \frac{Z_j}{j!} \right)^{n_j} \]
\[
\alpha = \sum_{j=1}^{\infty} n_j \] (19)

where \( \sum_{\{n_j\}} \) is again a multiple sum over \( n_j \)’s such that the constraint \( \sum_{j=1}^{\infty} jn_j = s \) is satisfied. Using Leibnitz formula for calculating the \( s^{\text{th}} \) derivative of a product of two functions we get

\[
\frac{1}{N(N-1)} \frac{d^s\rho_\lambda^2(1,2)}{d\lambda^s} = \sum_{r=0}^{s} \frac{s!}{(s-r)!r!} P_{s-r} \frac{d^r}{d\lambda^r} \left( \frac{1}{Z_0} \right) \] (20)

The \( (s+1)^{\text{th}} \) term in CPSE(Eq.(9)) is,

\[
\Gamma_{s+1} = \frac{1}{(s+1)!} \frac{1}{2} \int_\Omega d1d2 u_{\text{per}}(1,2) \frac{d^s\rho_\lambda^2(1,2)}{d\lambda^s} \bigg|_0 \] (21)
Substituting Eq.\(\text{(20)}\) in Eq.\(\text{(21)}\) and after some algebra, the \((s+1)\)th term in CPSE becomes

\[
\Gamma_{s+1} = \frac{1}{(s+1)!} \sum_{r=0}^{s} \frac{s!}{(s-r)!} \left\langle \frac{(-\beta V_{\text{per}})^{s-r+1}}{-\beta} \right\rangle_0 \sum_{\{n_j\}} (-1)^{\alpha'} \frac{1}{n_j!} \prod_{j=1}^{\infty} \frac{\left\langle \frac{(-\beta V_{\text{per}})^{j}}{j!} \right\rangle_0^{n_j}}{j!} \tag{22}
\]

\[
= \frac{1}{(s+1)!} \frac{-1}{\beta} \sum_{r=0}^{s} \frac{s!}{(s-r)!} \sum_{\{n_j\}} (-1)^{\alpha'} \frac{1}{n_j!} \prod_{j=1}^{\infty} \frac{\left\langle \frac{(-\beta V_{\text{per}})^{j}}{j!} \right\rangle_0^{n_j}}{n_j!} \frac{(n_{s-r+1}+1)(s-r+1)}{(n_{s-r+1}+1)!} \left(\frac{(-\beta V_{\text{per}})^{s-r+1}}{(s-r+1)!} \right\rangle_0^{n_{s-r+1}+1} \tag{23}
\]

Now consider a set of \(\{n'_j\}\)s such that, for all \(j \neq s-r+1\), \(n'_j = n_j\) and for \(j = s-r+1\), \(n'_j = n_j + 1\). Then,

\[
\sum_{j=1}^{\infty} j n'_j = \sum_{j=1}^{\infty} j n_j + (s-r+1) = s+1 \tag{24}
\]

and

\[
\alpha' = \sum_{j=1}^{\infty} n'_j = \sum_{j=1}^{\infty} n_j + 1 = \alpha + 1 \tag{25}
\]

Using Eq.\(\text{(24)}\) and Eq.\(\text{(25)}\) in Eq.\(\text{(23)}\), we get,

\[
\Gamma_{s+1} = \frac{1}{(s+1)!} \frac{-1}{\beta} \sum_{r=0}^{s} (n'_{s-r+1})(s-r+1)s! \sum_{\{n'_j\}} (-1)^{(\alpha'-1)}(\alpha' - 1)! \frac{1}{n'_j!} \prod_{j=1}^{\infty} \frac{\left\langle \frac{(-\beta V_{\text{per}})^{j}}{j!} \right\rangle_0^{n'_j}}{n'_j!} \left(\frac{(-\beta V_{\text{per}})^{s-r+1}}{(s-r+1)!} \right\rangle_0^{n_{s-r+1}+1} \tag{26}
\]

where \(n'_j\)'s satisfy the constraint of Eq.\(\text{(24)}\). It can be seen easily that \(\sum_{r=0}^{s} (n'_{s-r+1})(s-r+1) = s+1\), as all \(n_j\)'s for \(j > s+1\) must be zero for the constraint of Eq.\(\text{(24)}\) to be satisfied.

Thus Eq.\(\text{(26)}\) becomes

\[
\Gamma_{s+1} = (-\beta)^s \sum_{\{n'_j\}} (-1)^{(\alpha'-1)}(\alpha' - 1)! \prod_{j=1}^{\infty} \frac{1}{n'_j!} \left\langle \frac{(-\beta V_{\text{per}})^{j}}{j!} \right\rangle_0^{n'_j} \left(\frac{(\omega_{s+1})}{(s+1)!}\right) \tag{27}
\]

\[
= (-\beta)^s \frac{(\omega_{s+1})}{(s+1)!} \tag{28}
\]

which is nothing but \((s+1)\)th order term in HTSE.

\[\text{III. FLUIDS WITH HARDCORE REPULSION}\]

Consider a homogeneous fluid with particles interacting via a pairwise additive spherically symmetric potential. Let the potential \(u(r)\) have a hardcore repulsion(\(u_{\text{ref}}(r)\)) and a slowly
varying attractive part \( u_{\text{per}}(r) \) whose value is small compared to \( k_bT \) so that it can be treated as a perturbation. i.e.,

\[
u(r) = \infty \quad r \leq r_0 \\
= u_{\text{per}}(r) \quad r > r_0
\]

(29)

If the hardcore part is taken as the potential of the reference system, the ensemble averages w.r.t. the hard-sphere reference system become independent of temperature. As a result, the \( \omega_i \)'s in Equations(3-5) become independent of temperature. Hence the HTSE becomes a power series in \( \beta = 1/k_bT \). This result is well known[4]. Since it has now been shown that the terms of CPSE are equivalent to those of HTSE, the terms of CPSE also scale with powers of \( \beta \). \( s^\text{th} \) term of the series is proportional to \( \beta^{s-1} \) as can be seen from Eq.(28).

It can also be seen that the derivatives of RDF and the direct correlation function(DCF) also scale with powers of \( \beta \). Consider \( s^\text{th} \) derivative of \( \rho_\lambda(1,2) \). It can be seen from Eq.(20) that each term in the summation in the R.H.S. depends upon the following term:

\[
\frac{P_{s-r}}{Z_0^{s-r}} \prod_{j=1}^{\infty} Z_j^{n_j}
\]

(30)

which can be re-written as follows

\[
\frac{P_{s-r}}{Z_0^{s-r}} \prod_{j=1}^{\infty} Z_j^{n_j} = \frac{P_{s-r}}{Z_0} \prod_{j=1}^{\infty} \left[ \frac{Z_j}{Z_0} \right]^{n_j}
\]

\[
= \frac{P_{s-r}}{Z_0} \beta^s \langle \langle -V_{\text{per}} \rangle_0 \rangle_0^n \langle \langle -V_{\text{per}} \rangle_0 \rangle_0^{n_2} \langle \langle -V_{\text{per}} \rangle_0 \rangle_0^{n_3} \ldots \rangle
\]

(31)

When evaluated at \( \lambda = 0 \) with \( u_{\text{ref}}(r) \) as that of hard-sphere, it can be seen from the Eq.(16) that \( P_{s-r} \) depends on \( \beta^{s-r} \). Since the averages in above Eq.(31) become independent of temperature, the total dependence on \( \beta \) of each term in the R.H.S. of Eq.(20) would be \( \beta^s \). Thus,

\[
\left. \frac{d^s \rho_\lambda^{(2)}(1,2)}{d\lambda^s} \right|_{\lambda=0} = \left. \rho^2 \frac{d^s g_\lambda(r)}{d\lambda^s} \right|_{\lambda=0} \propto \beta^s
\]

(32)

Also, since \( \left. \frac{d^s g_\lambda(r)}{d\lambda^s} \right|_{\lambda=0} \propto \beta^s \), its fourier transform also would be proportional to \( \beta^s \) i.e.,

\[
\left. \frac{d^s \hat{g}_\lambda(k)}{d\lambda^s} \right|_{\lambda=0} = \left. \frac{d^s \hat{h}_\lambda(k)}{d\lambda^s} \right|_{\lambda=0} \propto \beta^s
\]

(33)

where \( h_\lambda(r) = g_\lambda(r) - 1 \) is the total correlation function and \( \hat{h}_\lambda(k) \) is its fourier transform. The Ornstein-Zernike equation for the imaginary fluid in fourier space is given by[4].
\[ h_\lambda(k) = \frac{c_\lambda(k)}{1 - \rho c_\lambda(k)} \] (34)

Using similar arguments given in the case of \( \frac{d^n g_\lambda(r)}{d\lambda^n} \bigg|_{\lambda=0} \), it can be seen that

\[ \frac{d^n c_\lambda(r)}{d\lambda^n} \bigg|_{\lambda=0} \propto \beta^n \] (35)

Thus from the above discussion, it can be seen that, for the class of fluids with hardcore repulsion, apart from the Helmholtz free energy series, the Taylor series for \( c(r) \) and \( g(r) \) obtained by expanding around \( \lambda = 0 \) also becomes power series in \( \beta \). As a result, if the coefficients of the series are obtained along one isotherm, then the whole phase diagram can be obtained provided the series converges. To obtain the coefficients of the series which are related to the derivatives of \( g_\lambda(r) \) and \( c_\lambda(r) \) at \( \lambda = 0 \), few recently developed methods are available as discussed in the introduction[5–7].

To test the scaling relations derived above, we applied the method discussed in Ref. [6] to square well(SW) fluids. The calculation method used is exactly the same as in Ref. [6] and hence is not repeated here. We obtained the derivatives of \( g(r) \) of SW fluid of width 0.25 at various reduced temperatures(T) and plotted \( T^n \frac{d^n g_\lambda(r)}{d\lambda^n} \bigg|_0 \) for \( n = 1, 2, 3 \) and 6 in Fig. (1).

It can be seen from Fig. (1) that the curves corresponding to each derivative at different temperatures are coinciding after scaling. Also we obtained the first three coefficients of the HTSE for SW fluids of width 1.2 and 2.0 using the same method of Ref. [6]. In the case of SW fluid of width 1.2, the coefficients of HTSE are obtained by calculating the terms of CPSE at \( T = 0.7 \) and scaling with temperature according to \( T^n \Gamma_{n+1} \) where \( \Gamma_n \) is \( n^{th} \) order term in the CPSE for Helmholtz free energy per particle. In the same way, the coefficients of HTSE for SW fluid of width 2.0 are obtained by calculating the terms of CPSE at \( T = 2.0 \) followed by scaling. The results are compared with simualtion data[8] in Fig(2) and Fig(3). It can be seen that there is an excellent match between simulation data and present calculations which confirms the scaling relations.

IV. CONCLUSION

We have shown rigorously that the CPSE and HTSE are equivalent when the interaction potential is pairwise additive. As a result, we have shown that for fluids with interaction
FIG. 1. (Color Online) Scaled derivatives of $g(r)$ of SW fluid of width 0.25 at reduced density $\rho = 0.8$ at various reduced temperatures. Solid line: $T = 0.9$, hollow squares: $T = 0.6$, crosses: $T = 1.5$.

FIG. 2. (Color Online) First three coefficients of HTSE for SW fluid of width 1.2. Lines are present results, symbols are simulation data [8]. $a_1, a_2$, and $a_3$ are first three coefficients of HTSE for Helmholtz free energy per particle respectively.
FIG. 3. (Color Online) First three coefficients of HTSE for SW fluid of width 2.0. Lines are present results, symbols are simulation data. \(a_1, a_2\) and \(a_3\) are first three coefficients of HTSE for Helmholtz free energy per particle respectively.

potential having a hardcore repulsion, if the hard-sphere fluid is taken as the reference system, the terms of CPSE and the derivatives of RDF and DCF w.r.t. the coupling parameter follow a scaling relation with temperature. We also have confirmed the scaling relations through applications to square well fluids. Thus, for such fluids, if the derivatives of RDF are known along an isotherm, the structural and thermodynamic properties can be obtained at any other temperature provided the series is convergent at that temperature.

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