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Quantum Mechanical Scaled Particle Theory of Hard Spheres at High Temperature

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The leading term of the high-temperature quantum corrections to the scaled particle theory of the hard sphere fluid have been obtained. This provides approximate corrections to the pressure, surface tension, and reversible work to create a spherical cavity $W(r)$ of the quantum mechanical hard sphere fluid. A number of exact identities valid for the classical hard sphere fluid are shown to apply also to the quantum mechanical hard sphere fluid, including the fluctuation relation between $W(r)$ and the probability of finding a cavity of radius at least r.

KEY WORDS: Fluctuation relation; surface tension; equation of state; quantum corrections; hard sphere fluid; scaled particle theory.

1. INTRODUCTION

Unlike molecules with continuously differentiable intermolecular potential, the leading quantum mechanical correction in the high temperature for the free energy and pressure of a hard sphere (HS) fluid is linear and not quadratic in the thermal wavelength. In particular, if a is the HS diameter and ρ the number density, Hemmer(1) and Jancovici(2,3) showed that the pressure of

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the quantum mechanical HS fluid p can be written ($\beta = 1/kT$)

$$p = p_c + \lambda a \, \partial p_c/\partial a \tag{1}$$

neglecting higher order terms in the (dimensionless) scaled thermal wavelength

$$\lambda = h[2 \cdot 2^{1/2} a (2\pi mkT)^{1/2}]^{-1}$$

with p_c the pressure of the corresponding classical HS fluid at density ρ and diameter a. (In general, the subscript c on the symbol for any physical entity denotes the physical entity of the corresponding classical HS fluid). Since

$$\beta p_c/\rho = 1 + 4\eta g_c(a) \tag{2}$$

where $\eta = \pi \rho a^3/6$ and $g_c(a) = g_c(a, \rho)$ is the classical contact radial distribution function, one can write (1)

$$\beta p/\rho = 1 + 4\eta g_c(a) + 12\eta\lambda g_c(a) + 4\eta\lambda a(\partial g_c/\partial a)(a) \tag{3}$$

again neglecting higher order terms in λ. As yet no exact limiting relation is available between the quantum and classical properties, similar to (1) or (3), for the surface tension $\sigma_0(a)$ or the reversible work to form a spherical cavity $\Omega(r)$ of radius r, $W(r) = W(r, a, \rho)$, of a HS fluid. Even if such expressions were to be available, they, as well as (1) or (3), are simply schematics for providing approximate expressions to the properties of the quantal HS fluid since the properties of the corresponding classical HS fluid are known only approximately.

In this paper we provide approximate expressions for the pressure, surface tension, and $W(r)$ of the quantal HS fluid by a straightforward extension of the simple scaled particle (SP) theory.(4) The SP theory focuses attention on the conditional probability of finding a spherical cavity $\Omega(r)$ in the HS fluid, $G(r)$, which is in turn related to the probability of finding a spherical cavity of at least radius r, $p_0(r)$, by(4)

$$-dp_0(r)/dr = p_0 4\pi r^2 \rho G(r) \tag{4}$$

Using (1), we shall obtain a simultaneous approximation for p, $W(r)$, and σ_0 by a suitable approximation for $G(r)$ rather than by directly substituting an approximate $g_c(a)$ into (1), etc. In order to accomplish this, we shall have to relate p to $G(a)$ and $p_0(r)$ to $W(r)$. The latter step we carry out in the next section. In Section 3 we introduce our approximate $G(r)$ and deduce the approximate p, σ_0, and $W(r)$. Finally, in the last section we discuss our results by comparing the low-density expansion of our results with available theory.

In the classical scaled particle theory the relation between the pressure p and $G_c(a)$ is obtained, by virtue of (2), from the fact that(4)

$$G_c(a) = g_c(a) \tag{5}$$

a relation which no longer holds for the quantal HS fluid. Instead we will show below that

$$\beta p/\rho = 1 + 4\eta(1 + 3\lambda)G(a) \tag{6}$$

up to linear terms in λ. To show this, $G(a)$ is only to be expanded for small λ keeping only the first-order term in λ, that is,

$$G(a) = G_c(a) + \lambda\, \partial G_c(a)/\partial a \tag{7}$$

and substituted in (3) with (5).

2. THE REVERSIBLE WORK $W(r)$

In this section we shall demonstrate first that the classical fluid holds also for a corresponding quantum mechanical fluid. Specifically we will show that

$$p_0(r) = \exp[-\beta W(r)] \tag{8}$$

where $W(r)$ is the quantum mechanical reversible work to create a spherical cavity (a region devoid of molecular centers) $\Omega(r)$ in the quantum mechanical fluid. To prove (8), we will employ de Boer's treatment (Ref. 5, p. 337) of the canonical ensemble. The Slater sum for N molecules in a volume V is

$$W_{N,V}(\mathbf{r}_1,\ldots,\mathbf{r}_N) = N!\,(\lambda 2\sqrt{2}a)^{3N} \sum_i [\exp(-\beta E_i^{(N,V)})]|\Psi_i^{(N,V)}|^2 \tag{9}$$

where $E_i^{(N,V)}$ and $\Psi_i^{(N,V)}$ are the ith eigenvalue and eigenstate of a complete eigenset. The desired probability $p_0(r)$ of finding a spherical cavity $\Omega(r)$ of radius r not containing any molecule center in $\Omega(r)$ is

$$p_0(r) = \frac{\int_{V-\Omega(r)} W_{N,V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\, d\mathbf{r}^N}{\int_V W_{N,V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\, d\mathbf{r}^N} \tag{10}$$

with $d\mathbf{r}^N = d\mathbf{r}_1 \cdots d\mathbf{r}_N$. Introducing the Ursell functions $U_{l,V}(\mathbf{r}_1,\ldots,\mathbf{r}_l)$ defined by

$$W_{1,V}(\mathbf{r}_1) \equiv U_{1,V}(\mathbf{r}_1), \qquad W_{2,V}(\mathbf{r}_1,\mathbf{r}_2) = U_{2,V}(\mathbf{r}_1,\mathbf{r}_2) + U_{1,V}(\mathbf{r}_1)U_{1,V}(\mathbf{r}_2) \tag{11}$$

etc., we can write

$$\begin{aligned} \int_V W_{N,V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\, d\mathbf{r}^N &= S\prod_l a_l^{m_l}(V)/m_l! \\ \int_{V-\Omega} W_{N,V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\, d\mathbf{r}^N &= S\prod_l a_l^{m_l}(V,\Omega)/m_l! \end{aligned} \tag{12}$$

where the summation S must be carried out over all possible divisions of the N molecules into m_1 groups of one, m_2 groups of two,..., m_l groups of l, etc., molecules, with $\sum_l lm_l = N$ and

$$
\begin{aligned}
a_l(V) &\equiv (l!)^{-1} \int_V U_{l,V}(\mathbf{r}_1,\dots,\mathbf{r}_l)\, d\mathbf{r}^l \\
a_l(V,\Omega) &\equiv (l!)^{-1} \int_{V-\Omega} U_{l,V}(\mathbf{r}_1,\dots,\mathbf{r}_l)\, dr^l
\end{aligned}
\tag{13}
$$

where V is the arbitrary volume containing the N molecules.

In the thermodynamic limit ($N \to \infty$, $V \to \infty$, and $N/V = \rho$, finite) we find

$$p_0(r) = \exp\left[\sum_l a_l(V-\Omega) - \sum_l a_l(V)\right] \tag{14}$$

with the limiting form of the a_l

$$a_l(V) = Vb_l \qquad \text{and} \qquad a_l(V-\Omega) = (V-\Omega)b_l$$

where

$$b_l = \lim_{V\to\infty} (1/Vl!) \int_V U_{l,V}(\mathbf{r}_1,\dots,\mathbf{r}_l)\, d\mathbf{r}^l \tag{15}$$

The canonical partition function can be expressed as

$$Q_{N,V} = S \prod_{\Sigma lm_l = N} (Vb_l)^{m_l}/m_l! \tag{16}$$

with the usual canonical definition of the Helmholtz free energy F. Comparing (14) and (16), we can rewrite (14) as

$$p_0(r) = \exp[-\beta F(V-\Omega) + \beta F(V)] \tag{17}$$

where $F(V-\Omega) - F(V)$ is the reversible work $W(r)$ to create the spherical cavity $\Omega(r)$. Thus the validity of (8) is established.

Introducing (8) into (4), we can write

$$\beta\, dW(r) = \rho G(r) 4\pi r^2\, dr \tag{18}$$

The macroscopic meaning$^{(4)}$ of $dW(r)$ as the reversible work to increase the cavity from radius r to $r + dr$ allows us to break $dW(r)$ into a bulk term $p\, dv$ ($dv = 4\pi r^2\, dr$) and a surface contribution $\sigma(r)\, dS$ ($dS = 8\pi r\, dr$),

$$\beta\, dW(r) = \beta p\, dv + \beta\sigma(r)\, dS \tag{19}$$

The quantal surface tension of the HS fluid $\sigma(r)$ against a spherical cavity of radius r is defined by (19). The usual surface tension $\sigma_0(a)$ of the quantum HS fluid follows from $\sigma(r)$ in the limit as $r \to \infty$, i.e., when the cavity becomes an infinite flat surface. Substituting (19) into (18) allows us to relate $G(r)$ to p and $\sigma(r)$,

$$G(r) = \beta p/\rho + 2\beta\sigma(r)/\rho r \tag{20}$$

In the remaining part of this section we draw attention to certain exact relations satisfied by $G(r)$ for $r \leqslant a/2$ which are identical to those satisfied by $G_c(r)$. We have the following exact conditions on $G(r)$:

$$G(r) = G_c(r) = (1 - 4\pi r^2\rho/3)^{-1} \qquad \text{for} \quad r \leqslant a/2 \tag{21}$$

$$(\partial G/\partial r)_{r=a/2} = 6\eta[a(1 - \eta)^2]^{-1} \tag{22}$$

and

$$\begin{aligned}(\partial^2 G/\partial r^2)_{r=a/2} = {} & 24\eta[a^2(1 - \eta)^2]^{-1} + 72\eta^2[a^2(1 - \eta)^3]^{-1} \\ & - 48\eta G(a)[a^2(1 - \eta)]^{-1}\end{aligned} \tag{23}$$

These equalities can be obtained directly from (10) as in the case of the classical SP theory. We multiply the integrand of the numerator in (10) by $\prod_j [1 - E'(\mathbf{R} - \mathbf{r}_j)]$ and extend its limit of integration from $V - \Omega(r)$ to V, to obtain

$$\begin{aligned}p_0(r) = 1 & - \frac{\sum_j \int_V E'(\mathbf{R} - \mathbf{r}_j) W_{N,V}(\mathbf{r}_1,\dots, \mathbf{r}_N)\, d\mathbf{r}^N}{\int_V W_{N,V}(\mathbf{r}_1,\dots, \mathbf{r}_N)\, d\mathbf{r}^N} \\ & + \sum_{j,k}{}' \frac{\int_V E'(\mathbf{R} - \mathbf{r}_j) E'(\mathbf{R} - \mathbf{r}_k) W_{N,V}(\mathbf{R}_1,\dots, \mathbf{r}_N)\, d\mathbf{r}^N}{\int_V W_{N,V}(\mathbf{r}_1,\dots, \mathbf{r}_N)\, d\mathbf{r}^N}\end{aligned} \tag{24}$$

where $E'(\mathbf{R} - \mathbf{r}_j)$ is unity when the jth HS molecule center is inside a sphere of radius $\mathbf{r}_j$ located at $\mathbf{R}$ and is zero otherwise. Thus only the first and second terms in (24) do not vanish for $r < a/2$, since then no two particle centers can simultaneously be accommodated on the cavity boundary. Thus.

$$p_0(r) = 1 - \rho\tfrac{4}{3}\pi r^3 \tag{25}$$

as long as $r < a/2$, which together with (4) yields (21). The other two relations are obtained directly from (24) by evaluating the second and third derivatives at $r = a/2$ (of Ref. 4).

In order to proceed further, we must make assumptions about the behavior of $G(r)$ between $r = a/2$ and $r = a$; this we do in the next section.

3. THE BASIC APPROXIMATION FOR $G(r)$

We have previously shown[6] that a formal expression for $G(r)$ for $r \geqslant a/2$ which is not inconsistent with (20)–(23) is provided by the form

$$\begin{aligned}G(r) = {} & \beta p/\rho + 2\beta\sigma_0 a/\rho r + \beta\delta/\rho r^2 \\ & + [(2r/a) - 1]^2 E(2r - a)\Gamma/(r/a)^n, \qquad n \geqslant 2\end{aligned} \tag{26}$$

where $E(x) = 1$ or 0 according as $x > 0$ or $x < 0$; p, σ_0 δ and Γ are suitable functions of $a^3\rho$; and n is an adjustable parameter. Actually p will be the pressure, σ_0 the surface tension, etc. in the SP type approximation. The first three terms in (26) account for the correct macroscopic behavior(4) and the last term is introduced to take account of the microscopic behavior.(6) For convenience we can rewrite (26) as

$$G(r) = P + \Sigma/r + \Delta/r^2 + [(2r/a) - 1]^2 E(2r - a)\Gamma/(r/a)^n, \qquad n \geqslant 2 \tag{27}$$

with the abbreviations

$$P = \beta p/\rho, \qquad \Sigma = 2\beta\sigma_0/\rho, \qquad \Delta = \beta\delta/\rho$$

P, Σ, Δ, and Γ represent four functions of ρa^3 which have to be determined using the four conditions (6) and (21)–(23), namely

$$\begin{aligned} G(a) &= P + \Sigma + \Delta + \Gamma = (P - 1)/4\eta(1 + 3\lambda) \\ G(a/2) &= P + 2\Sigma + 4\Delta = (1 - \eta)^{-1} \\ (\partial G/\partial a)(a/2) &= 2\Sigma + 8\Delta = -3\eta/(1 - \eta)^2 \\ \frac{\partial^2 G}{\partial a^2}\left(\frac{a}{2}\right) &= 2\Sigma + 12\Delta + \frac{2\Gamma}{\zeta} \\ &= \frac{3\eta}{(1 - \eta)^l} + \frac{9\eta^2}{(1 - \eta)^3} - \frac{3/2G(a)}{(1 - \eta)(1 + 3\lambda)} \\ \zeta &\equiv 2^{1-n} \qquad (n \geqslant 2) \end{aligned} \tag{28}$$

The equations (28) are valid to linear terms in λ only, so that the simultaneous solution of (28) can be written

$$P = P_c + 3\lambda P_\lambda, \qquad \Sigma = \Sigma_c + 3\lambda\Sigma_\lambda, \qquad \Delta = \Delta_c + 3\lambda\Delta_\lambda, \\ \Gamma = \Gamma_c + 3\lambda\Gamma_\lambda \tag{29}$$

where the entities with subscript c are the classical ones and those with subscript λ are the first-order high-temperature quantum mechanical correction divided by 3λ. After straightforward algebra we find

$$\begin{aligned} P_c &= [1 + 5\eta\zeta + 8\zeta\eta^2 + (5\zeta - 1)\eta^3]D^{-1}(\eta, \zeta) \\ P_\lambda &= \eta(1 - \eta)^2(1 - \eta + \eta\zeta) \\ &\quad \times [4 + (6 + 14\zeta)\eta + (2\zeta - 9)\eta^2 + (2\zeta - 1)\eta^3]D^{-2}(\eta, \zeta) \end{aligned} \tag{30}$$

$$\begin{aligned} \Sigma_c &= -\tfrac{3}{2}\eta[1 + 5\zeta\eta - (1 - 4\zeta)\eta^3]D^{-1}(\eta, \zeta) \\ \Sigma_\lambda &= -\eta(1 - \eta)^2(1 - \eta + \eta\zeta) \\ &\quad \times [4 + (6 + 14\zeta)\eta + (2\zeta - 9)\eta^2 + (2\zeta - 1)\eta^3]D^{-2}(\eta, \zeta) \end{aligned} \tag{31}$$

$$\begin{aligned} \Delta_c &= \tfrac{3}{4}\eta^2[1 + (3\zeta - 1)\eta]D^{-1}(\eta, \zeta) \\ \Delta_\lambda &= \tfrac{1}{4}\eta(1 - \eta)^2(1 - \eta + \eta\zeta) \\ &\quad \times [4 + (6 + 14\zeta)\eta + (2\zeta - 9)\eta^2 + (2\zeta - 1)\eta^3]D^{-2}(\eta, \zeta) \end{aligned} \tag{32}$$

$$\begin{aligned}\Gamma_c &= -\tfrac{3}{4}\eta^2\zeta(2 + \eta)D^{-1}(\eta, \zeta)\\ \Gamma_\lambda &= -\tfrac{1}{4}\zeta\eta(1 - \eta)^2\\ &\quad \times [8 + (40\zeta - 8)\eta + 12\zeta\eta^2 + \eta^3 + (2\zeta - 1)\eta^4]D^{-2}(\eta, \zeta)\end{aligned} \tag{33}$$

where

$$D(\eta, \zeta) = (1 - \eta)^2[1 + (5\zeta - 2)\eta + (-2\zeta + 1)\eta^2]$$

From (28), writing $G(a) = G_c(a) + 3\lambda G_\lambda(a)$, we have, using (30)–(33),

$$\begin{aligned}G_c(a) &= [4 + (20\zeta - 6)\eta + (3 - 4\zeta)\eta^2 + (2\zeta - 1)\eta^3]D^{-1}(\eta, \zeta)\\ G_\lambda(a) &= \eta(16 - 22\zeta) - \eta^2(34 + 64\zeta + 86\zeta^2)\\ &\quad + (21 - 66\zeta - 62\zeta^2)\eta^3 + (-2 + 7\zeta - 6\zeta^2)\eta^4\\ &\quad + (1 - 4\zeta - 4\zeta^2)\eta^5\end{aligned} \tag{34}$$

Finally from (27) and (19) we obtain on integration the reversible work for forming the cavity $\Omega(r)$,

$$\beta W(a) = \tfrac{4}{3}\pi r^3 \rho P + 2\pi\rho r^2\Sigma + 4\pi\rho r\Delta + 4\pi\rho\gamma(r) \tag{35}$$

with

$$\gamma(r) = \Gamma\int_0^r [(2r/a) - 1]^2 E(2r - a)a^n\, dr/r^{n-2}$$

4. DISCUSSION

Equations (30)–(35) provide ths sought-for leading terms of the high-temperature quantum mechanical correction to the SP theory of the HS fluid. We now have a simultaneous set of approximate relations for the pressure, surface tension, and reversible work of cavity formation which contain a single undetermined parameter n or $\zeta = 2^{1-n}$. To assess the approximations made for the quantal corrections for the pressure we can compare the first few terms of the η expansion of P_λ given by (30) with that obtained by substituting $G_c(a) = g_c(a)$ given by (34) into (3). We find

$$P_\lambda/\eta = 4 + 20\eta + (57 - 18\zeta)\eta^2 + \cdots \qquad \text{[Eqs. (3) and (34)]} \tag{36}$$

$$P_\lambda/\eta = 4 + (26 - 22\zeta)\eta + (81 - 222\zeta + 134\zeta^2)\eta^2 \qquad \text{[Eq. (30)]} \tag{37}$$

The second terms of (36) and (37) become identical for $\zeta = 3/11$ or $n \simeq 2.84$. This also agrees with the leading term of the high-temperature quantum correction to the second virial coefficient of the HS fluid [Eqs. (40) and (41) in Ref. 3 and further references therein].

Finally, although there is no available exact expansion to compare Σ_λ from (31), we should note that $P_\lambda/\Sigma_\lambda = -1$.

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