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Semiclassical statistical mechanical theory for thermodynamics of hard body fluids

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Abstract : The simple theory is developed to derive the thermodynamic properties of the semiclassical fluid of hard convex body (HCB) molecules interacting *via* the hard Gaussian overlap potential. Analytic expressions are given and calculations are made for the thermodynamic properties and virial coefficients for the HCB fluids. The agreement with the Monte-Carlo data is good in all cases. The first order quantum corrections are also studied. The quantum effects increase with increase of packing fraction and depends on the shape parameter K.

Keywords : Hard body fluid, equation of state, quantum corrections

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1. Introduction

The purpose of the present work is to develop a theory for calculating the quantum corrections to the thermodynamic properties of fluid of hard-body molecules, which is of current interest, because many of the properties of real fluids are determined by the repulsive interactions between their molecules, which can be modelled by means of hard bodies of similar shape [1]. Moreover, such hard body fluids are most convenient reference systems in framing a perturbation theory for real fluids of non-spherical molecules. The simplest hard body fluids are hard convex body (HCB) fluids, such as hard ellipsoid of revolution (HER) and hard spherocylinder (HSC) and hard non-convex body fluid *i.e.* fused hard sphere and hard dumbbell (HDB) fluids. Considerable progress has been made in recent years in understanding the thermodynamic properties of the classical hard-body fluids [2–6], because they can model the shape of real molecules.

Although the influence of non-sphericity in the quantum effect is of considerable interest, it has not been investigated systematically. Using the decoupling approximation, Singh *et al* [4] have investigated the quantum effects for the HER fluid.

In this paper, we investigate the quantum corrections to the thermodynamic properties of the hard-body fluids at higher temperature. The usual procedure is based on the Hemmer-Jancovici (HJ) method [7,8] in which the expansion of the physical properties of interest is made about the classical value in term of the Ursell function. This approach has been extensively used for the hard sphere fluid in the semiclassical limit [9]. It may be extended to investigate the thermodynamic properties of the HCB fluid.

In the present paper, we employ the simple method to investigate the quantum corrections to the thermodynamic properties of the HCB fluids.

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In Section 2, we discuss the basic theory for calculating the thermodynamic properties of the HCB fluids in the semiclassical limit. The virial coefficient of the semiclassical HCB fluids are discussed in Section 3. Section 4 is confined to the classical HCB fluids. In Section 5, we derive expressions for the first order quantum correction to the free energy, equation of state and virial coefficients. The results are discussed there. The concluding remarks are given in Section 6.

2. Basic theory

We consider a molecular fluid of the hard convex body (HCB) molecules, which interact *via* the hard Gaussian overlap (HGO) potential defined as

$$u(r\omega_1\omega_2) = \infty, \quad r < \sigma(\omega_1\omega_2);$$

$$= 0, \quad r > \sigma(\omega_1\omega_2); \tag{1}$$

where $r = |r_1 - r_2|$ and ω_i represents the orientation of molecule i. Here, $\sigma(\omega_1\omega_2)$ is the distance of closest approach between two molecules and is expressed in terms of the Euler angles [10]

$$\sigma(\omega_1\omega_2) = \sigma_0[1 - \chi(\cos^2\theta_1 + \cos^2\theta_2$$

$$- 2\chi\cos\theta_1\cos\theta_2\cos\theta_{12})$$

$$\times (1 - \chi^2\cos^2\theta_{12})^{-1}]^{-1/2}. \tag{2}$$

Here $\sigma_0 = 2b$ is the width of a molecule and the shape parameter χ is defined as

$$\chi = (K^2 - 1)(K^2 + 1), \tag{3}$$

K being the length-to-breadth ratio of the molecule *i.e.* $K = 2a/2b$. This model is valid for oblate $(K < 1)$ as well as prolate $(K > 1)$ shape of arbitrary symmetry.

The quantity of central importance for constructing the theory of quantum fluid is the Slater sum [4,9]. In the semiclassical limit (*i.e.* at high temperature) where the quantum effects are small, the Slater sum of the HCB fluid in analogy to the hard sphere (HS) fluid [9] may be written as [11]

$$W_N = W_N^c W_N^m, \tag{4}$$

where

$$W_N^c(x_1, x_2, ..., x_N) = \exp\left| -\beta\sum_{i<j} u(x_i x_j)\right| \tag{5}$$

is the Boltzmann factor and W_N^m is a function which measures the deviation from the classical behaviour. Like the HS fluid, W_N^m of the HCB fluid can be expressed in terms of the 'modified' Ursell functions U_l^m . Thus,

$$W_N^m(x_1, x_2, ..., x_N) = 1 + \sum_{i<j} U_2^m(x_i x_j)$$

$$+ \sum_{i<j<k} U_3^m(x_i x_j x_k)\sum_{i<j} + \sum_{k<l} U_2^m(x_i x_j)U_2^m(x_k x_l) + ... \tag{6}$$

Substituting eq. (6) in eq. (4), we obtain the expression for W_N

$$W_N(x_1, x_2, ..., x_N) = \exp\left| -\beta\sum u(x_i x_j)\right|$$

$$1 + \sum_{i<j} U_2^m(x_i x_j)\sum_{i<j<k} U_3^m(x_i x_j x_k) + ... \tag{7}$$

The U_l^m can, in principle, be found from the solution of the quantum mechanical 1-body problem. Unfortunately, the actual calculation is too involved to be feasible. It is only for system of hard spheres [9] that U_2^m and U_1^m have been evaluated. The first order quantum correction comes only for U_2^m. In the analogous way, U_2^m for the HCB fluid can be written as

$$U_2^m(x_1 x_2) \equiv U_2^m(r\omega_1\omega_2)$$

$$= -\exp\left[-(2\pi/\lambda^2)(r - \sigma(\omega_1\omega_2))^2\right] + O(\lambda^2), \tag{8}$$

where $\delta(x)$ is the Dirac δ-function.

In quantum statistical mechanics, the chemcial potential μ can be written as

$$\beta\mu = -\ln[Q_{N+1}/Q_N], \tag{9}$$

where Q_N is the canonical partition function of molecular fluid of N molecules, defined as

$$Q_N = \left[N!\lambda^{3N}q^{-N}\right]^{-1}\int...\int W_N(x_1, x_2, x_N)\prod_{i=1}^{N} dx_i \tag{10}$$

where

$$dx_i = (4\pi)^{-1}dr_i d\omega_i. \tag{11}$$

Substituting eqs. (7) and (10) in eq. (9), one obtains an expression for the chemical potential of the HCB fluid. The result is

$$\beta\mu = \beta\mu^c - (1/2)\rho\int dr < \left[2g_N^c(x_1 x_2)\right.$$

$$+ \rho\partial g_N^c(x_1 x_2)/\partial\rho\left]U_2^m(r\omega_1\omega_2) >_{\omega_1\omega_2} + O(\lambda^2), \tag{12}$$

where μ^c and $g_N^c(x_1 x_2)$ are, respectively, the chemical

potential and pair distribution function (PDF) of the classical HCB fluid and $\rho = N/V$ is the number density (N is the total number of molecules in volume V). Here

$$< (...) >_{\omega_1 \omega_2} = (4\pi)^{-2} \int d\omega_1 \int d\omega_2 (...). \tag{13}$$

In deriving eq. (12), the use has been made of the relation

$$\rho^2 \left[g^c_{N+1}(x_1 x_2) - g^c_N (x_1 x_2) \right]$$

$$= (\partial / \partial N) \left[\rho^2 g^c_N (x_1 x_2) \right]$$

$$= (1/V)(\partial / \partial \rho) \left[\rho^2 g^c_N (x_1 x_2) \right]. \tag{14}$$

(We drop the subscript N from now onwards in the paper)

Other thermodynamic properties can be obtained from the chmical potential. Thus, the Helmholtz free energy is given by

$$\beta A / N = (\beta A^C / N) - (1/2)\rho \int dr$$

$$\left\langle g^c (x_1 x_2) U_2^m (x_1 x_2) \right\rangle_{\omega_1 \omega_2} + O(\lambda^2) \tag{15}$$

and the equation of state is

$$\beta P / \rho = (\beta P^C / \rho) - (1/2)\rho \int dr$$

$$\left\langle \left[g^c (x_1 x_2) + \rho \partial g^c (x_1 x_2)/\partial \rho \right] U_2^m (x_1 x_2) \right\rangle_{\omega_1 \omega_2}, \tag{16}$$

where A^C and P^C are, respectively, the Helmholtz free energy and pressure of the classical HCB fluid.

3. Virial equation of state

In the low density limit, the equation of state is given by

$$\beta P \Big/ \rho = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1}, \tag{17}$$

where B_n is the n-th viral coefficient. The PDF $g^c(x_1 x_2)$ may be expanded in powers of ρ [12]

$$g^c(x_1 x_2) = \exp[-\beta u(x_1 x_2)] \left[1 + \sum_{n \geq 1} \rho^n a^c_n (x_i x_j) \right], \tag{18}$$

where the coefficients $a^c_n(x_1 x_2)$ is the cluster integral of the classical molecular fluid, involving n field points and two base points. Thus,

$$a^c_1 (x_1 x_2) = \int \left\langle f^c (x_1 x_3) f^c (x_2 x_3) \right\rangle_{\omega_3} dr_3, \tag{19}$$

where

$$f^c (x_i x_j) = \exp[-\beta u(x_1 x_3)] - 1 \tag{20}$$

is the Mayer function.

When eq. (18) is substituted in eq. (16), the seccand third virial coefficient can be written as

$$B_2 = B_2^c - (1/2)\int \left\langle \exp[-\beta u(x_1 x_2)] U_2^m(x_1 x_2) \right\rangle_{\omega_1 \omega_2} dr, \tag{21}$$

$$B_3 = B_3^c - \int \left\langle \exp[-\beta u(x_1 x_2)] a^c_1 (x_1 x_2) U_2^m(x_1 x_2) \right\rangle_{\omega_1 \omega_2} dr, \tag{22}$$

where B_2^c and B_3^c are, respectively, the second and third viral coefficient for the classical molecular fluid.

4. Thermodynamics of classical hard convex-body fluids

The equation of state for classical HCB fluid may be written as

$$\beta P^C / \rho = 1 - (1/6)\beta \rho \int dr$$

$$\left\langle r g^c (r\omega_1 \omega_2)(\partial u(r\omega_1 \omega_2)/\partial r) \right\rangle_{\omega_1 \omega_2}$$

$$= 1 + (2\pi /3)\rho \left\langle \sigma^3 (\omega_1 \omega_2) g^c (\sigma(\omega_1 \omega_2)) \right\rangle_{\omega_1 \omega_2}. \tag{23}$$

This can be expressed in the form [5]

$$\beta P^C / \rho = 1 + (1/6)\rho(S + 4\pi R^2) \sigma^{av} g^{cav} (\sigma^{av}), \tag{24}$$

whre $g^{cav}(s^{av})$ si the averaged contact value of the classical PDF and $s^{av} = <r.u>$, whre the angular bracket denotes the average and u is the unit vector normal to the surface at the contact point. Here S is the surface of the molecule and R its mean radius of curvature.

Eq. (24) can be solved to give the Maeso-Solana (MS) equation of state of the HCB fluid in the form [5]

$$\beta P^C / \rho = 1 + \alpha(\beta P^C_{HS}/\rho - 1), \tag{25}$$

where P^C_{HS} is the pressure of the classical HS fluid, given by [13]

$$\beta P^C_{HC}/\rho - 1 = 4\eta g^C_{HC}(\sigma_{HC}) = 2\eta(2-\eta)/(1-\eta)^3. \tag{26}$$

Here, α is the shape factor defined as [2]

$$\alpha = RS/3V_m \tag{27}$$

and $\eta = \rho V_m$ is the packing fraction, where V_m is the volume of a molecule. We assume that the hard sphere with volume $V_m = (\pi/6)\sigma_{HS}^3$ is equal to that of the HCB molecule.

Using the relation

$$\beta A_{EX}^c \Big/ N = \int_0^\eta (\beta P^c/\rho - 1) d\eta'/\eta', \tag{28}$$

the excess free energy for the classical HCB fluid is given by

$$\beta A_{EX}^c/N = [\eta(4-3\eta)/(1-\eta)^2]\alpha. \tag{29}$$

Using the decoupling approximation [14], Singh-Singh-Sinha (SSS) [4] expression for the equation of state and excess free energy for the classical HCB fluid have been derived as

$$\beta P^c/\rho = 1 + [\beta P_{HS}^c/\rho - 1] F_1(x) \tag{30}$$

and

$$N = 1 + [\eta(4-3\eta)/(1-\eta)^2] F_1(x), \tag{31}$$

where

$$F_1(x) = (1-\chi)^{-1/2} [1 - (1/6)\chi^2$$
$$- (1/40)\chi^4 - (1/112)\chi^6 - ...]. \tag{32}$$

Eqs. (25) and (30) are identical in form. They differ only in coefficients α and $F_1(x)$.

Expanding eq. (25) in power of ρ and equating it to the virial equation of state, we obtain expression for B_2^c and B_3^c of the HCB as

$$B_2^c = 4\alpha V_m, \tag{33a}$$

$$B_3^c = 10\alpha V_m^2, \tag{33b}$$

where V_m is the volume of a molecule. We assume that the hard spheres with volume $V_m = (\pi/6)\sigma_{HS}^3$ is equal to that of the HCB molecule.

The equation of state of the classical HCB fluid is given by Boublik [2,3] using the improved scaled particle theory as

$$\beta P^c/\rho = (1-\eta)^{-1} + 3\alpha\eta(1-\eta)^{-2} + \alpha^2\eta^2(3-\eta)(1-\eta)^{-3}. \tag{34}$$

This gives the excess free energy of the classical HCB fluid

$$\beta A_{EX}^c/N = (\alpha^2 - 1)\ln(1-\eta)$$

$$+ (3\alpha - \alpha^2)(1-\eta)^{-1} + \alpha^2(1-\eta)^{-2} - 3\alpha. \tag{35}$$

Expanding eq. (34) in power of ρ, expressions for B_2^c and B_3^c in this case, are given by [2]

$$B_2^c = (1+3\alpha)V_m, \tag{36a}$$

$$B_3^c = (1+6\alpha+3\alpha^2)V_m^2. \tag{36b}$$

Comparing eqs. (33) and (36), we find that both B_2^c and B_3^c differ. However, both eqs. (33) and (36) give exact results for the hard sphere ($\alpha = 1$).

For the geometry of the HER, α is obtained from eq. (27). The theory developed for the HER fluid can be employed for the hard dumbbel (HDDB) fluid. For this, it is assumed that $\sigma_{HDB} = \sigma_{HER}$ and $V_{HDR} = V_{HER}$. This gives

$$(\pi/6)\sigma_{HDB}^3 [1 + 3 1^*/2 - 1^{*3}/2] = (\pi/6)K\sigma_{HER}^3$$

leading to

$$K = 1 + 3 1^*/2 - 1^{*3}/2, \tag{37}$$

where $1^* = 1/\sigma$ is the site-site elongation. For homonuclear diatomic fluid, the parameter α is explicitly given by [2].

$$\alpha = (1+1^*)(2+1^*)/(2+3 1^* - 1^{*3}). \tag{38}$$

The values of B_2^c/V_m and B_3^c/V_m^2 for the classical HER fluid obtained under different methods are compared with the 'exact' result [2] in Table 1 for different values of K. They increase with increase of K. The agreement is good except for large value of K. The results obtained from eq. (36) are better than those obtained from eq. (33).

The values of equation of state, $\beta P^c/\rho$ for the classical HER fluid obtained under different conditions are compared with Monte-Carlo (MC) [2,3] values in Table 2 for different K. They are comparable at low values of η and are in good agreement with the MC

Table 1. Virial coefficients of classical prolate HER fluid.

K	B_2^c/V_m			B_3^c/V_m^2		
	Present	Boublik	Exact	Present	Boublik	Exact
	[eq. (33a)]	[eq. (36a)]		[eq. (33b)j]	[eq. (36b)]	
1.25	4.071	4.053	4.053	10.178	10.215	10.18
1.50	4.238	4.178	4.178	10.595	10.724	10.69
2.00	4.718	4.538	4.538	11.795	12.250	12.09
2.75	5.614	5.211	5.211	14.036	15.331	14.81
3.00	5.938	5.454	5.454	14.846	16.519	15.85

Table 2. Equation of state $\beta P^c/\rho$ for classical HER fluid for different values of K.

K		MS eq. (25)	SSS eq. (30)	Boublik eq. (34)	MC
1.25	0.207	2.515	2.513	2.515	2.53
	0.366	5.777	5.772	5.792	5.72
	0.430	8.421	8.413	8.454	8.53
	0.471	10.903	10.893	10.955	11.10
	0.510	14.148	14.134	14.229	14.40
2.00	0.197	2.618	2.606	2.619	2.65
	0.371	6.729	6.685	6.931	7.05
	0.487	13.875	13.776	14.639	14.00
	0.550	21.645	21.487	23.148	21.90
	0.596	30.936	30.706	33.385	31.50
2.75	0.190	2.817	2.797	2.830	2.76
	0.335	6.924	6.266	6.697	6.26
	0.427	11.022	10.912	12.134	11.00
	0.479	15.462	15.303	17.407	15.30
	0.545	24.540	24.282	28.421	24.70
3.00	0.184	2.826	2.805	2.843	2.84
	0.253	4.148	4.113	4.288	4.13
	0.357	7.551	7.477	8.194	7.34
	0.453	13.713	13.571	15.610	13.90
	0.545	25.899	25.619	30.861	24.80

Table 3. Equation of state $\beta P^c/\rho$ for classical hard dumbbell fluid for different values of 1^*.

1^*	η	MS eq. (25)	SSS eq. (30)	Boublik eq. (34)	MC
0.2	0.1047	1.563	1.566	1.562	1.56
	0.2094	2.546	2.552	2.545	2.59
	0.3142	4.345	4.359	4.352	4.45
	0.4187	7.876	7.903	7.906	8.02
	0.4712	10.924	10.964	10.979	11.17
0.4	0.1047	1.593	1.591	1.588	1.59
	0.2094	2.626	2.623	2.626	2.64
	0.3142	4.519	4.512	4.549	4.59
	0.4189	8.233	8.218	8.355	8.42
	0.4712	11.439	11.418	11.666	11.67
0.6	0.1047	1.642	1.619	1.631	1.63
	0.2094	2.761	2.697	2.765	2.78
	0.3142	4.812	4.674	4.892	4.95
	0.4189	8.836	8.551	9.150	9.23
	0.4712	12.309	11.829	12.874	12.87
0.8	0.1047	1.717	1.639	1.699	1.70
	0.2094	2.967	2.754	2.984	3.01
	0.3142	5.257	4.797	5.438	5.48
	0.4189	9.751	8.804	10.424	10.54
	0.4712	13.630	12.263	14.824	14.88
1.0	0.1047	1.830	1.647	1.804	1.79
	0.2094	3.276	2.776	3.330	3.36
	0.3142	5.927	4.844	6.314	6.40
	0.4189	11.126	8.901	12.497	12.64
	0.4712	15.615	12.404	18.017	18.06

data. At high density, Boublik results are not so good. One may employ the MS or SSS expression to obtain $\beta P^c/\rho$ for the classical HER fluid.

Next, we calculate the equation of state $\beta P^c/\rho$ for the classical HDB fluid using different methods. They are compared with the MC data [2] in Table 3 for different of 1^*. They are in good agreement for low values of η and/or low values of 1^*. However Boublik method is relatively good for higher value of η and/or higher value of 1^*.

In the following section, we employ the MS theory to estimate tha thermodynamics of the semiclassical hard-body fluids.

5. Quantum correction to thermodynamics

Substituting eq. (8) in eq. (15), the first order quantum correction to the free energy of the HCB fluid is given by

$$\beta(A - A^c)/N = (\pi/\sqrt{2})\rho$$

$$\times \left\langle \sigma^2(\omega_1\omega_2)g^C(\sigma(\omega_1\omega_2))\right\rangle_{\omega_1\omega_2} \lambda. \quad (39)$$

It can be expressed in the form [5]

$$\beta(A - A^c)/N = (1/2\sqrt{2})\rho(S + 4\pi R^2)g^{cav}(\sigma^{av})\lambda. \quad (40)$$

For the hard sphere (HS) molecules with diameter σ_{HS}, eq. (40) gives [9]

$$\beta(A_{HS} - A_{HS}^c)/N = (\pi/\sqrt{2})\rho\sigma_{HS}^2 g_{HS}^c(\sigma_{HD})\lambda. \quad (41)$$

If we consider the HS with equal molar volume $V_m = (\pi/6)\sigma_{HS}^3$ of the HCB molecule and at the same density ρ, then from eqs. (40) and (41), we get

$$(A - A^c)/(A_{HS} - A_{HS}^c) = (1/2)(S + 4\pi R^2)/\pi\sigma_{HS}^2)$$

$$\times (g^{cav}(\sigma^{av})/g_{HS}^c(\sigma_{HS})). \quad (42)$$

This can be expressed as

$$(A - A^c)/(A_{HS} - A_{HS}^c) = (1/2)(\alpha + (4/3)\pi R^3/V_m)$$

$$\times (\sigma_{HS}/2R)(g^{cav}(\sigma^{av})/g_{HS}^c(\sigma_{HS})). \quad (43)$$

If we approximate $\sigma_{HS} \approx \sigma^{av}$ [5], then

$$(\sigma_{HS}/2R)(g^{cav}(\sigma^{av})/g^c_{HS}(d_{HS}))$$

$$\approx (\sigma^{av}/2R)(g^{cav}(\sigma^{av})/g^c_{HS}(\sigma^c_{HS})) \approx 1 \qquad (44)$$

and

$$(1/2)(\alpha + ((4/3)\pi R^3/V_m)) \approx \alpha \qquad (45)$$

which is accurate for the HCB fluid with not too large values of α. So the final form of the free energy, correct to the first order quantum correction, is given by

$$A - A^C = \alpha(A_{HS} - A^c_{HS}). \qquad (46)$$

When eq. (41) is used, we get

$$\beta A/N = \beta A^C/N + 3\sqrt{2}\alpha\eta g^c_{HS}(\sigma_{HS})(\lambda/\sigma_{HS}), \qquad (47)$$

where σ_{HS} is the effective diameter of the HS molecule and is given by $\sigma_{HS} = K^{1/3}\sigma_0$ and $g^c_{HS}(\sigma_{HS})$ is the radial distribution function (RDF) of the classical HS fluid, given by [12]

$$g^c_{HS}(\sigma_{HS}) = (1 - \eta/2)/(1 - \eta)^2, \qquad (48)$$

where

$$\eta = (\pi/6)\rho\sigma^3_{HS} = (\pi/6)\rho K\sigma^3_0.$$

Finally, eq. (47) can be expressed as

$$\beta A/N = (\beta A^C/N) + A^*_1(\lambda/\sigma_0), \qquad (49)$$

where

$$A^*_1 = 3\sqrt{2}(\alpha/K^{1/3})[\eta(1 - \eta/2)/(1 - \eta)^3]. \qquad (50)$$

Using eq. (16), the equation of state of the HCB fluid, correct to the first order quantum correction, is given by

$$\beta P/\rho = (\beta P^C/\rho) + P^*_1(\lambda/\sigma_0), \qquad (51)$$

where

$$P^*_1 = 3\sqrt{2}(\alpha/K^{1/3})[\eta(1 + \eta - \eta^2/2)/(1 - \eta)^4]. \qquad (52)$$

When eq. (25) is used, eqs. (49) and (51) can be rewritten as

$$\beta A/N = [1 + (\lambda/2\sqrt{2})(\partial/\partial\sigma_{HS})](\beta A^C/N) \qquad (53)$$

and

$$\beta P/\rho = [1 + (\lambda/2\sqrt{2})(\partial/\partial\sigma_{HS})](\beta P^C/\rho). \qquad (54)$$

Thus, the leading quantum correction to the thermodynamic properties of the HCB fluid like those of the HS fluid [9], can be obtained by replacing the actual

diameter σ_{HS} by an effective diameter $(\sigma_{HS} + 2^{-3/2}\lambda)$, provided eq. (25) is used.

When eq. (17) is substituted in eq. (51), we obtain expressions for the first few virial coefficient of the semiclassical HCB fluid as

$$B_2 = B^c_2[1 + (3/2\sqrt{2})(\lambda/\sigma_{HS})], \qquad (55)$$

$$B_3 = B^c_3[1 + (3/2)(\lambda/\sigma_{HS})], \qquad (56)$$

where B^c_2 and B^c_3 are given by eqs. (33a) and (33b) respectively. Eqs. (55) and (56) can also be expressed as

$$B_n = [1 + (\lambda/2\sqrt{2})(\partial/\partial\sigma_{HS})]B^c_n. \qquad (57)$$

We assume that this theory holds also for the hard non-convex body fluid.

The reduced virial coefficients $B^*_2 = B_2/V_m$ and $B^*_3 = B_3/V^2_m$ for the HER fluid are shown in Figure 1 as a function of K for $\lambda/\sigma_0 = 0.0$ and 0.1. $\lambda/\sigma_0 = 0.0$ corresponds to the classical value. We find that the virial coefficients are minimum at $K = 1.0$ and increase as K deviates from unity.
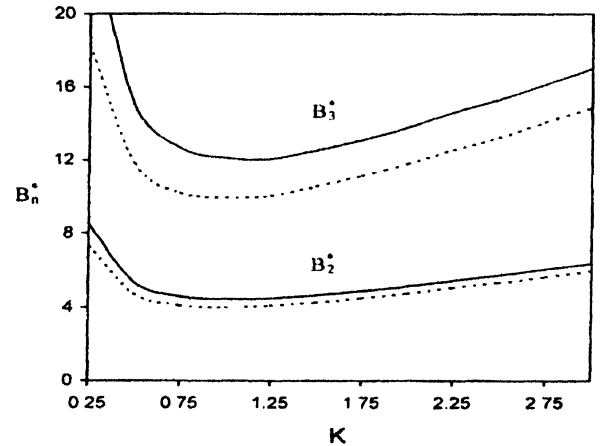

Figure 1. The reduced virial coefficients B^*_2 and B^*_3 of the HER fluid as a function of K at $\lambda/\sigma_0 = 0.0$ and 0.1. The thick line represents $\lambda/\sigma_0 = 0.1$ and the dotted line $\lambda/\sigma_0 = 0.0$.

The values of the first order coefficients A^*_1 and P^*_1 of the HER fluid reported in Table 4 show that they decrease first with increase of K and then begins to increase for $K \geq 2.0$. Further, they increase with the increase of packing fraction η.

The excess free energy $\beta A_{EX}/N$ and equation of state $\beta P/\rho$ of the HER fluid are reported in shown in Figures 2 and 3, respectively, as a function of K at $\eta = 0.1$ and 0.3 for $\lambda/\sigma_0 = 0.0$ and 0.1. These figures show that the

Table 4. Virial of the first order coefficients A_i^* and P_i^* for the HER fluid.

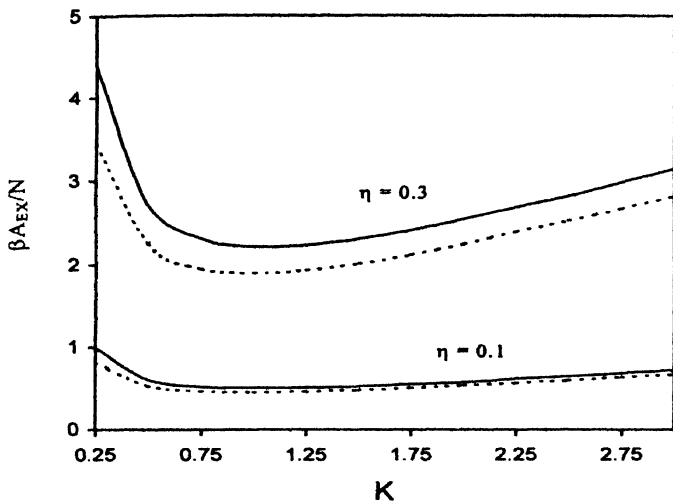| K_1 $\eta \rightarrow$	A_i^*			P_i^*		
	0.1	0.3	0.5	0.1	0.3	0.5
1/3	1.184	6.753	27.252	1.516	14.245	99.925
1/2	0.822	4.687	18.915	1.052	9.887	69.354
2/3	0.671	3.825	15.436	0.859	8.068	56.599
1 0	0.553	3.154	12.728	0.708	6.653	46.669
1 5	0.512	2.919	11.780	0.655	6.157	43.515
2.0	0.518	2.953	11.915	0.663	6.228	43.690
3 0	0.569	3.247	13.102	0.729	6.848	48.039

Figure 2. The excess free energy, $\beta A_{Ex}/N$ of the HER fluid as a function of K for $\eta = 0.1$ and 0.3 at $\lambda/\sigma_0 = 0.0$ and 0.1. The keys are same as in Figure 1.
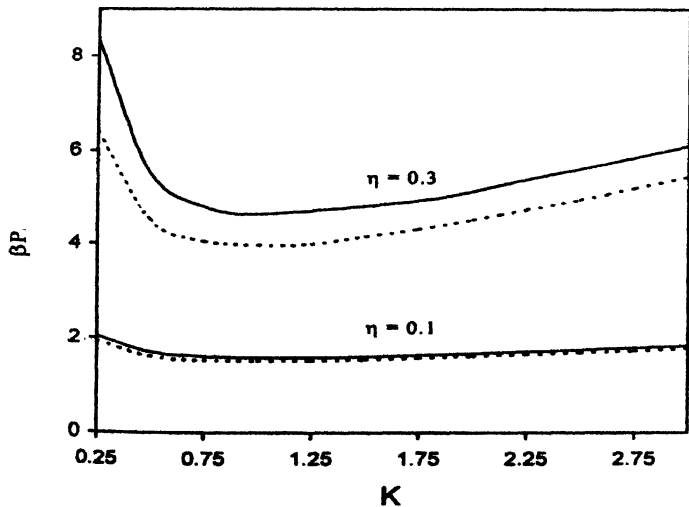

Figure 3. The equation of state $\beta P/\rho$, of the HER fluid as a function of K for $\eta = 0.1$ and 0.3 at $\lambda/\sigma_0 = 0.0$ and 0.1. The keys are same as in Figure 1.

thermodynamic properties at a given η are minimum at $K = 1.0$ and increase when K either increases or decreases.

In Table 5, we report the excess free energy $\beta A_{Ex}/N$ and equation of state $\beta P/\rho$ for the HDB at $\eta = 0.1$, 0.3 and 0.5 for $\lambda/\sigma_0 = 0.0$ and 0.1 for different values of 1^*. From this, we find that they increase with increase of η and 1^*.

Table 5. Excess free energy $\beta A_{Ex}/N$ and equation of state $\beta P/\rho$ for the hard dumbbell fluid.

		$\beta A_{Ex}/N$		$\beta P/\rho$	
		$\lambda/\sigma_0 = 0 0$	$\lambda/\sigma_0 = 0.1$	$\lambda/\sigma_0 = 0.0$	$\lambda/\sigma_0 = 0.1$
0.0	0.1	0.457	0.512	1.521	1.592
	0.3	1.898	2.213	3.974	4.639
	0.5	5.000	6.273	13.000	17.667
0.2	0.1	0.465	0.516	1.549	1.616
	0.3	1.933	2.228	4.047	4.669
	0.5	5.093	6.282	13.241	17.601
0.4	0.1	0.489	0.540	1.630	1.695
	0.03	2.034	2.324	4.258	4.871
	0.5	5.357	6.531	13.929	18.288
0.6	0.1	0.530	0.583	1.766	1.833
	0.3	2.203	2.504	4.612	5.248
	0.5	5.804	7.020	15.089	19.549
0.8	0.1	0.592	0.650	1.972	2.046
	0.3	2.460	2.788	5.151	5.842
	0.5	6.481	7.803	16.852	21.699

The percentage contribution of the quantum correction to the free energy and pressure of the HDB fluid at $\lambda/\sigma_0 = 0.1$ are given in Table 6. We find that the quantum correction increases with η and decreases with 1^*.

Table 6. Percentage of quantum correction to the free energy and pressure of hard dumbbell at $\lambda/\sigma_0 = 0.1$.

1^*	$[(A-A^c)/A^c] \times 100$		$[(P-P^c)/P^c] \times 100$	
	$\eta = 0.1$	$\eta = 0.3$	$\eta = 0.1$	$\eta = 0.3$
0.0	12.104	16.619	4.655	16.742
0.2	12.102	15.243	4.269	15.356
0.4	10.418	14.305	4.006	14.411
0.6	9.964	13.682	3.832	13.783
0.8	9.699	13.316	3.729	13.415
1.0	9.606	13.190	3.694	13.288

6. Concluding remarks

We have developed a simple theory to calculate the first order quantum corrections to the free energy, pressure and virial coefficients of the HCB fluid and applied it to

the HER and HDB fluids. The quantum corrections depend on K for the HER and I^* for the HDB. Further, the quantum correction for these systems, like those of the HS fluid, increase with the increase of η.

Only the leading term of U_2^m $(r\omega_1\omega_2)$ is known for the HCB fluid. Further, U_3^m is not known in general, except for HS fluid, so the second order quantum corrections is not considered here.

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