

Simple equilibrium theory for equation of state of hard convex body fluids

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Abstract : Using the physical interpretation of the reciprocal of activity, an expression is derived for the equation of state of hard convex body fluids. The theory is applied to evaluate the equation of state of hard ellipsoid of revolution, hard dumbbells and prolate hard spherocylinders. In all these cases, the agreement with simulation results is fairly good.

Keywords : Hard convex-body fluid, reciprocal of activity, equation of state.

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1. Introduction

A fluid of hard non-spherical molecules 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. Moreover, such hard body fluids are the most convenient reference systems in framing a perturbation theory for real molecular fluids whose molecules interact *via* non-spherical pair potentials. The simplest hard body fluids are the hard convex body (HCB) fluids, such as hard ellipsoid of revolution (HER) fluids, hard dumbbell (HDB) fluids, and hard spherocylinder (HSC) fluids. They have been extensively studied [1], because they can model the shape of the real molecules. An approach based on a physical interpretation of the reciprocal of activity has been employed for hard sphere fluid [2]. This simple approach was extended for a fluid of hard D-spheres with different values of D [3]. This approach can be extended to the HCB fluid.

In this present paper, we extend this approach to derive the equation of state of the HCB fluids.

2. Basic theory

We consider a molecular fluid of N molecules in a volume V at temperature T . The chemical potential of the molecular fluid can be obtained from the partition function Q_N as

$$\begin{aligned} \mu(\rho, T) &= -kT(\partial \ln Q_N / \partial N)_{T, V} \\ &= -kT \ln [Q_{N+1} / Q_N], \end{aligned} \quad (1)$$

where the partition function Q_N for a linear molecular fluid is given by

$$Q_N = (N! \lambda^{3N} q^{-N})^{-1} \int \dots \int \exp[-\beta U_N] \prod_{i=j}^N dx_i, \quad (2)$$

where

$$dx_i = (4\pi)^{-1} dr_i d\omega_i, \quad (3)$$

and

$$U_N = \sum_{i < j} u(x_i, x_j). \quad (4)$$

$u(x_i, x_j)$ is the pair interaction potential between molecules

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i and j . Here, $x_i \equiv (r_i, \omega_i)$ is the vector describing both the position r_i of the center of mass and the orientation ω_i of molecule i . Further in eq. (2), λ is the thermal wavelength defined as

$$\lambda = (2\pi\hbar^2\beta/m)^{1/2},$$

q is the single particle rotational partition function and $\beta = (kT)^{-1}$, where k is the Boltzman constant.

Substituting eq. (2) in eq. (1), we get

$$\mu(\rho, T) = \mu_{id}(\rho, T) - kT \ln a^{-1}(\rho, T), \quad (5)$$

where

$$\begin{aligned} \mu_{id}(\rho, T) = & -kT \ln(V\lambda^{-3}q/N) \\ & -kT \ln(\lambda^{-3}q/P). \end{aligned} \quad (6)$$

Here, μ_{id} is the chemical potential of an ideal gas of density ρ and temperature T , and a is the activity relative to that of the ideal gas at the same density and temperature.

We write

$$\begin{aligned} U_{N+1} &= U_N + \sum_i u(x_i, x_{N+1}) \\ &= U_N + 2u_{N+1}, \end{aligned} \quad (7)$$

where

$$U_{N+1} = \left(\frac{V}{2}\right) \sum u(x_i, x_{N+1}) \quad (8)$$

is the potential energy of the $(N+1)$ -th molecule within the fluid. Then a^{-1} can be expressed as [2,3]

$$Va^{-1} = \int dx_{N+1} \exp[-2\beta u_{N+1}]. \quad (9)$$

In order to perform the integration of eq. (9), the N particles of the system are first fixed in a most likely configuration, then the $(N+1)$ -th particle wanders throughout the whole system. Other thermodynamic properties can be expressed in terms of a^{-1} . Thus the pressure of the molecular fluid is

$$P/\rho kT = 1 - \ln a^{-1}(\rho, T) + \rho^{-1} \int_0^\rho \ln a^{-1}(\rho', T) d\rho'. \quad (10)$$

3. Hard ellipsoid fluid

We consider a hard ellipsoid of revolution (HER) fluid having the major and minor axes $(2a)$ and $(2b)$

respectively. We calculate a^{-1} for the HER fluid, generalising the theory for the hard spheres [2] and hard D-spheres [3]. a^{-1} is simply the probability that at a point $x = r\omega$ chosen at random the $(N+1)$ -th molecule could be inserted. This probability is a measure as the product of two terms $a^{-1} = P_1 P_2$. The first term is the unconditional probability P_1 that the randomly chosen point x does not overlap one of the N molecules within V i.e.

$$\begin{aligned} P_1 &= \left[V - N(\pi/6)(2a)(2b)^2 \right] / V \\ &= 1 - (\pi/6)\rho K\sigma^3, \end{aligned} \quad (11)$$

where $K = 2a/2b$ and $\sigma = 2b$ is the width of the molecule.

The second term is the conditional probability that no molecule will be in the additional volume in which the $(N+1)$ -th molecule is to be accommodated. That additional volume is

$$\begin{aligned} S &= (\pi/6)(4a)(4b)^2 - (\pi/6)(2a)(2b)^2 \\ &= (8\pi/6)K\sigma^3 - (\pi/6)K\sigma^3 = (7\pi/6)K\sigma^3. \end{aligned} \quad (12)$$

Then, the conditional probability P_2 that all N molecules lie outside this additional volume S is given by

$$\begin{aligned} P_2 &= \left[1 - (7\pi/6)K\sigma^3/(V - N\omega) \right]^N \\ &= \exp \left[- (7\pi/6)\rho K\sigma^3/(1 - \rho\omega) \right], \end{aligned} \quad (13)$$

where ω is an average volume per molecule and $(V - N\omega)$ is the free volume.

Then a^{-1} is given by

$$\begin{aligned} a^{-1} &= P_1 P_2 \\ &= \left[1 - (\pi/6)\rho K\sigma^3 \right] \exp \left[- (7\pi/6)\rho K\sigma^3/(1 - \rho\omega) \right]. \end{aligned} \quad (14)$$

The value of ω is the average volume occupied by a HER molecule in closed packed condition. It can be computed following the method of Andrews [2].

Thus,

$$\omega = \omega_L + (\rho/\rho_0)(\omega_H - \omega_L), \quad (15)$$

where ω_L and ω_H are low and high density values of ω , respectively and ρ_0 is the closed packed density. For the

HER fluid, $\rho_0 = \sqrt{2/K\sigma^3}$. It can be shown that

$$\omega_H = \rho_0^{-1} = K\sigma^3 / \sqrt{2} \quad (16)$$

and

$$\begin{aligned} \omega_L &= [3(2^4)(B_3/B_2^2) - 1]B_2/2^3(2^3 - 1) \\ &= [48(B_3/B_2^2) - 1]B_2/56, \end{aligned} \quad (17)$$

where B_2 and B_3 are the second and third virial coefficients of the HER fluid.

Finally, we obtain a simple expression of α^{-1} for the HER fluid

$$\begin{aligned} \alpha^{-1} &= (1 - (\pi/6)K\sigma^3\rho) \exp\left[-(7\pi/6)K\sigma^3\rho/(1 - \rho\omega_L \right. \\ &\quad \left. + (\rho/\rho_0)^2(\omega_L\rho_0 - 1))\right] \\ &= (1 - 0.7405z) \exp\left[-5.183z/(1 - Az + Bz^2)\right], \end{aligned} \quad (18)$$

where

$$z = \rho/\rho_0 = k\sigma^3/\sqrt{2}, \quad (19)$$

$$A = \omega_L\rho_0, \quad (20a)$$

$$B = A - 1. \quad (20b)$$

Substituting eq. (18) in eq. (10), we obtain an expression for the equation of state of HER fluid

$$\begin{aligned} P/\rho kT &= 5.1834z/(1 - Az + Bz) \\ &\quad - (1.3504/z) \ln(1 - 0.7405z) \\ &\quad - (C/z) \ln(1 - Az + Bz^2) \\ &\quad - (D/z) \ln((1 - Bz)/(1 - z)), \end{aligned} \quad (21)$$

where

$$C = 5.1834/2B,$$

$$D = 5.1834A/2B(1-B). \quad (22)$$

If the HER molecule be assumed to be the hard sphere molecule of the effective hard sphere

$$d = K^{1/3}\sigma^3,$$

then [1]

$$B_2 = (2\pi^3)K\sigma^3,$$

$$B_3 = (5/8)B_2^2. \quad (23)$$

and eq. (21) reduces to

$$\begin{aligned} P/\rho kT &= 5.1834z/(1 - 1.5340z + 0.5340z^2) \\ &\quad - (1.3504/z) \ln(1 - 0.7405z) \\ &\quad - (4.8534/z) \ln(1 - 1.5340z + 0.5340z^2) \\ &\quad - (15.977/z) \ln((1 - 1.5340z)/(1-z)) \end{aligned} \quad (24)$$

as given by Andrews [2] for the hard sphere fluid. However B_2 and B_3 for the HER fluid are given by [1]

$$B_2 = (1 + 3\alpha)V_m \quad (25a)$$

and

$$B_3 = (1 + 6\alpha + 3\alpha^2)V_m^2, \quad (25b)$$

where

$$V_m = (\pi/6)K\sigma^3$$

is the volume of a HER molecule and α is the shape factor defined by

$$\alpha = Rs/3V_m. \quad (26)$$

Here, R is the $(1/4\pi)$ -multiple of the mean curvature integral and s the surface integral. For hard sphere, $\alpha = 1$ while for all other convex bodies, $\alpha > 1$. For the HER fluid

$$\begin{aligned} A &= (0.7405/56)[48((1 + 6\alpha + 3\alpha^2)/(1 + 3\alpha^2) - 1) \\ &\quad [1 + 3\alpha]]. \end{aligned} \quad (27)$$

4. Applications

We apply the proposed theory to calculate the equation of state for some HCB fluids.

4.1. Hard ellipsoid of revolution :

Knowing α and K , one can calculate the coefficients A , B , C and D appearing in eq. (21)

We employ eqs. (21) and (24) to calculate the equation of state $P/\rho kT$ for the prolate ($K > 1$) and oblate ($K < 1$) HER fluids. When the equation of state is calculated as a function of η , the values of $P/\rho kT$ obtained by eq. (24) does not depend on K as K is associated in the expression of η , whereas the value of $P/\rho kT$ obtained by eq. (21) depends on K due to the presence of α in eq. (21). The values of the equation of state $P/\rho kT$ obtained

by eqs. (21) and (24), are compared with the exact simulation results [1] for $K > 1$ and $K < 1$ in Tables 1

Table 1. Equation of state, $P/\eta kT$ of the prolate HER fluids ($K > 1$)

K	η	Eq. (21)	Eq.(24)	Exact[1]
1.25	0.207	2.492	2.485	2.53
	0.282	3.628	3.611	3.71
	0.330	4.689	4.660	4.76
	0.366	5.742	5.699	5.72
	0.430	8.461	8.379	8.93
	0.447	9.448	9.350	9.37
2.00	0.1974	2.434	2.373	2.65
	0.2710	3.570	3.412	3.87
	0.3190	4.664	4.366	4.93
	0.3712	6.359	5.873	7.05
	0.4569	13.989	12.282	14.00
	0.5241	18.847	16.233	17.20
3.00	0.1885	2.427	2.275	2.78
	0.2958	4.512	3.850	5.31
	0.3560	6.670	5.384	7.35
	0.4712	15.920	11.001	14.70
	0.5236	25.662	17.333	21.30

Table 2. Equation of state, $P/\eta kT$ of the oblate HER fluid ($K < 1$).

K	η	Eq. (21)	Eq. (24)	Exact[1]
0.8	0.214	2.528	2.521	2.49
	0.281	3.609	3.592	3.73
	0.370	5.876	5.832	5.67
	0.410	7.463	7.396	7.65
	0.493	12.994	12.834	12.80
	0.541	18.895	18.621	17.40
0.5	0.1969	2.428	2.368	2.66
	0.2680	3.512	3.360	3.91
	0.3163	4.593	4.326	4.97
	0.3510	5.626	5.235	5.96
	0.3937	7.22	6.702	7.98
	0.4660	11.970	10.615	12.40
0.333	0.5262	19.185	16.509	18.90
	0.1827	2.353	2.214	2.87
	0.2945	4.484	3.860	5.33
	0.3267	5.791	4.577	6.41
	0.4154	11.510	7.838	11.2
	0.4712	15.920	12.511	15.6

and 2, respectively. The results obtained by eqs. (21) and (24) are in good agreement at low η and/or values of K near unity.

The deviation increases with increase of η and/or deviation of K from unity. The values of $P/\rho kT$ obtained from eq. (21) are better when compared with the 'exact' data. Hence, we employ eq. (21) for further calculation of the equation of state of the HCB fluid.

4.2. Hard dumbbell fluid :

We consider the fluid of hard dumbbell (HDB) (with the site-site elongation $L^* = L/\sigma$). When applying the proposed theory, we first define the corresponding the HER for a given HDB such that $\sigma_{HER} = \sigma_{HDB}$ and $V_{HER} = H_{HDB}$ i.e

$$(\pi/6)k\sigma_{HER}^3 = (\pi/6)\sigma_{HDB}^3 [1 + 3L^*/2 - L^{*3}/2] \tag{28}$$

or,

$$K = 1 + 3L^*/2 - L^{*3}/2 \tag{28a}$$

and

$$\alpha = (1 + L^*)(2 + L^*)/(2 + 3L^* - L^{*3}). \tag{28b}$$

One obtains K and α for a given value of L^* . We employ eq. (21) to calculate the equation of state, $P/\rho kT$ of the HDB fluid. They are compared with the exact simulation data [1] in Table 3 for $L^* = 0.2, 0.4$ and 0.6 for different values of η . The agreement is fairly good except when L^* is large (i.e. $L^* = 0.6$) as well as η is large ($\eta \geq 0.35$).

Table 3. Equation of state, $P/\sigma kT$ of the HDB fluids.

η	$L^* = 0.2$		$L^* = 0.4$		$L^* = 0.6$	
	Theory	Exact	Theory	Exact	Theory	Exact
0.1047	1.554	1.56	1.557	1.59	1.563	1.63
9.1571	1.969	2.01	1.978	2.04	1.995	2.13
0.2094	2.521	2.59	2.542	2.69	2.578	2.78
0.2618	3.270	3.36	3.311	3.49	3.382	3.67
0.3142	4.303	4.45	4.378	4.59	4.509	4.95
0.3665	5.760	5.95	5.891	6.21	6.127	6.69
0.4185	7.890	8.02	8.119	8.42	8.534	9.23
0.4712	11.133	11.17	11.531	11.67	12.268	12.87

4.3. Prolate hard spherocylinder fluid :

Next, we apply the theory to calculate the equation of state for prolate hard spherocylinder (HSC) fluid. For this, we assume $\sigma_{HER} = \sigma_{HSC}$ and $V_{HER} = V_{HSC}$ i.e

$$(\pi/6)K\sigma_{HER}^3 = (\pi/12)(3\gamma - 1)\sigma_{HSC}^3$$

or

$$K = (3\gamma - 1)/2, \tag{29}$$

where γ is the ratio of maximum length ($L + \alpha$) and width α . For this, we obtain K and hence other parameters appearing in eq. (21). The values of $P/\rho kT$ of the prolate HSC fluid are compared with the 'exact' results [1] in Table 4. The agreement is very good.

Table 4. Equation of state, $P/\rho kT$ of the prolate HSC fluids.

γ	η	Theory	Exact
1.4	0.3142	4.347	4.42
1.6	0.2948	3.967	4.10
	0.3873	6.745	6.84

5. Concluding remarks

Using the physical interpretation of reciprocal of activity, we have given a simple expression for the equation of state of the HCB fluids. The results obtained for the HER, HDB and prolate HSC fluids are in good agreement when compared with the simulation data.

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