

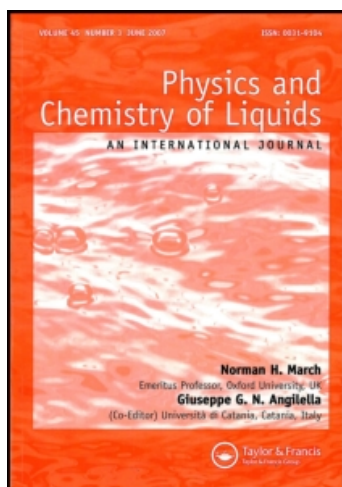
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### Equation of State for Soft Reference System

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## EQUATION OF STATE FOR SOFT REFERENCE SYSTEM

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We present an analytical equation of state for soft reference system such as liquid alkali metals. Thermodynamic properties—Excess entropy and diffusion coefficient have been calculated for liquid alkali metals using this equation of state. The calculated values of the self diffusion constant are compared with those corresponding to a hard-sphere fluid which shows that the softness plays a significant role in reducing diffusion.

KEY WORDS: Pair correlation function at hard sphere contact, softness in pair potential.

### 1 INTRODUCTION

Since the equation of state is one of the most fundamental characteristic of condensed matter, the search for accurate equation of state for hard sphere fluid continues being an open question. The equations of state can be obtained from integral equation theory proposed by Thiele and Wertheim<sup>1,2</sup>, solution of the Percus–Yevick equation (PY). However, Percus–Yevick solution fails to predict the high density “Monte Carlo” experimental data with enough accuracy. The PY approximation leads to a slight overestimate of the height of the main peak in the structure factor  $S(q)$  and tends to predict a large space between successive peaks. In recent past, several workers<sup>3–5</sup> have tried to correct Percus–Yevick solution, such approach is known as hard sphere Yukawa reference system. In this system the Yukawa potential is repulsive and therefore give rise to a “softening” of the potential. Equation of state (EOS) can also be related with the radial distribution function by a value when the spheres are in contact. Nevertheless, in spite of the evident simplicity of this (H.S.) system, there is no exact solution for the EOS at high or moderate densities. The majority of the equations of state proposed for representing the behaviour of the hard sphere fluid can be divided into two forms, independently for its dimensionality. The first one is in the analytical form such as PY-compressibility, PY-virial and Carnahan–starling EOS, having pole at  $\eta = 1$ . The second one determined by the coefficients  $B_i$  in the infinite virial series expansion of the compressibility factor in powers of the density. The objective of the present work is to give simple analytical EOS which represents the behaviour of the systems having soft repulsive pair

potential such as liquid alkali metals. This EOS has also been used to calculate thermodynamic properties of liquid alkali metals.

## 2 VARIOUS EQUATIONS OF STATES

At present, several equations of state (EOS) are available for a system of hard sphere which stem from different theories and methods.

The virial series seems to converge slowly and therefore require the infinite virial series expansion coefficients of the compressibility factor  $Z$  in powers of the density  $\rho = N/V$ . It can be written as<sup>6</sup>

$$Z = \frac{P}{\rho kT} = 1 + \sum_{i=2}^{\infty} B_i \rho^{i-1} \quad (1)$$

substituting various values of  $B_i$  available in the literature<sup>7</sup>, we get

$$\begin{aligned} Z = 1 + 4\eta + 10\eta^2 + 0.28695(4\eta)^3 + 0.110252(4\eta)^4 + 0.0389(4\eta)^5 \\ + 0.0137(4\eta)^6 + 0.0045166(4\eta)^7 + 0.0014954(4\eta)^8 + 0.0004997(4\eta)^9 \end{aligned} \quad (2)$$

where  $\eta$  is the packing fraction. The equation of state is also directly related with radial distribution function  $g(r)$ , as

$$\frac{P}{\rho kT} = 1 + \frac{2}{3} \pi \sigma^3 \rho g(\sigma) = 1 + 4\eta g(\sigma) \quad (3)$$

where  $g(\sigma)$  is the pair distribution function of hard sphere at contact. From Eqs. (2) and (3), we get

$$\begin{aligned} g(\sigma) = 1 + 2.5\eta + 0.28695(4\eta)^2 + 0.110252(4\eta)^3 + 0.0389(4\eta)^4 \\ + 0.0137(4\eta)^5 + 0.0045166(4\eta)^6 + 0.0014954(4\eta)^7 \\ + 0.0004997(4\eta)^8 \end{aligned} \quad (4)$$

Another possibility is the choice of equation of state with a pole,  $\eta = 1$ . Several theoretical equations of state for the hard sphere fluid predict a pole at  $\eta = 1$  for example Percus-Yevick compressibility and PY-virial equations of state<sup>8</sup>

$$Z_c = \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2} \quad (5)$$

and

$$Z_v = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \quad (6)$$

where suffixes  $c$  and  $v$  refer to the compressibility and virial equation respectively. Multiplying Eqs. (5) and (6) by factors  $\frac{1}{3}$  and  $\frac{2}{3}$  respectively and adding them, we obtain the well known Carnahan-Starling equation of state<sup>9</sup>

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (7)$$

which can also be reproduced in terms of second virial coefficient as<sup>10</sup>

$$Z = 1 + 4\eta + 4\eta \left[ \frac{8(8 - 4\eta)}{(4 - 4\eta)^3} - 1 \right] \quad (8)$$

and the value of  $g(\sigma)$  is obtained as

$$g(\sigma) = \left( 1 - \frac{\eta}{2} \right) / (1 - \eta)^3 \quad (9)$$

Another set of equations of state are those which can be obtained by improving Percus–Yevick equation of state analytically. One such we obtained from Hard Sphere Yukawa direct correlation function ( $dcf$ ) proposed by Colot *et al.*<sup>5</sup> They postulated a semi-empirical expression for  $dcf$  of a HS fluid which they obtained by mixing the  $dcf$  of Percus–Yevick with the  $dcf$  of the Yukawa tail producing the simple Fourier-transformed  $dcf$  as

$$C(q) = aC_{PY}(q) + [24\eta b/(q^2 + d^2)] \left[ \cos q + \frac{d}{q} \sin q \right] \quad (10)$$

where  $a$  and  $b$  are the functions of the packing fraction<sup>5</sup>. The long-wavelength limit of the structure factor is given by

$$[S(0)]^{-1} = \beta \left[ \frac{dP}{d\rho} \right] = \left[ 1 - aC_{PY}(0) - \frac{24\eta b(1 + d)}{d^2} \right] \quad (11)$$

By integrating Eq. (11), we get the expression for the equation of state for the HSY system

$$\frac{P}{\rho kT} = 1 - a + \frac{a(1 + \eta + \eta^2)}{(1 - \eta)^3} - \frac{12b(1 + d)\eta}{d^2} \quad (12)$$

If we substitute  $a = 1$  and  $b = 0$ , we get Eq. (6). For the calculations of thermodynamic properties of liquid metals, we have included perturbation  $\phi_1(q)$  in Random Phase approximation as

$$C(q) = C_{PYT}(q) - \beta\phi_1(q) \quad (13)$$

For  $\phi_1(q)$ , the Fourier transform of Cummings potential is used and the final result is

$$Z(\eta) = \frac{P}{\rho k T} = 1 - a + \frac{a(1 + \eta + \eta^2)}{(1 - \eta)^3} - \frac{12b(1 + d)}{d^2} \eta - \frac{12\eta(x_1 a_1 + x_2 a_2)}{(a_1^2 + a_2^2)} \quad (14)$$

where  $x_1, x_2, a_1$  and  $a_2$  are the parameters of Cummings potential<sup>11,12</sup>. The value of  $g(\sigma)$  is calculated in this case as

$$g(\sigma) = \frac{1}{4\eta} \left[ \frac{P}{\rho k T} - 1 \right] \quad (15)$$

Similarly, Zhou and Stell<sup>13</sup> proposed an equation of state. We know that the contributions to the pair correlation function  $h(r)$  and *dcf*  $C(r)$  that have come to be known as the bridge function  $b(r)$  and tail function  $d(r)$ . These play an essential role in improving the hypernetted chain (HNC) and Percus–Yevick approximation. Zhou and Stell<sup>13</sup> applied the zero-separation theorem to obtain these functions and proposed an equation of state as

$$Z = (1 - \theta)P_c^{\text{PY}} + \theta P_v^{\text{PY}} \quad (16)$$

where  $P_c^{\text{PY}}$  and  $P_v^{\text{PY}}$  are the pressures obtained from the compressibility equation and the virial equation in PY approximation respectively. They have proposed  $\theta = \frac{1}{4} + \frac{1}{2}\eta$  as the best approximation. Hence

$$\frac{P}{\rho k T} = \frac{-6\eta^4 - 3\eta^3 + 4\eta^2 + 4\eta + 4}{4(1 - \eta)^3} \quad (17)$$

Recently, Maeso *et al.*<sup>7</sup> have proposed an equation of state expressed in the form of virial series as

$$Z = \left( 1 + \sum_{i=1}^6 p_i \eta^i \right) / (1 - \eta)^2 = \frac{1}{(1 - \eta)^2} [1 + 2\eta + 3\eta^2 + 2.3648\eta^3 + 1.4944\eta^4 + 1.7504\eta^5 + 4.672\eta^6] \quad (18)$$

### 3 RESULTS AND DISCUSSION

The calculated values of the equations of state described in Section 2 are tabulated in Table 1 for different values of packing fraction  $\eta$ . We find that all these equations

**Table 1** Values of various equations of state at different values of  $\eta$ .

$\eta$ Eq.	PY (6)	Ours (14)	Zhou Stell (17)	Virial (2)	CS (7)	Maeso et al. (18)
0.05	1.2275	1.2273	1.2274	1.2274	1.2274	1.2274
0.1	1.5226	1.5198	1.5214	1.5216	1.5213	1.5216
0.15	1.9092	1.8983	1.9038	1.9049 (1.9050)	1.9037	1.9050
0.20	2.4218	2.3911	2.4055	2.4084 (2.4096)	2.4063	2.4096
0.25	3.1111	3.0398	3.0694	3.0748 (3.0813)	3.0740	3.0811
0.30	4.0524	3.9907	3.9580	3.9621 (3.9873)	3.9737	3.9869
0.35	5.3618	5.0804	5.1628	5.1483 (5.2283)	5.2057	5.2286
0.40	7.2222	6.7100	6.8222	6.7356 (6.9554)	6.9259	6.9630
0.45	9.9323	9.0288	9.1518	8.8568 (9.3972)	9.3847	9.4392
0.50	14.000	12.4302	12.5000	11.6812 (12.8979)	13.000	13.0668
0.55	20.3290	17.6065	17.4536	15.4212 (17.9717)	18.5034	18.5438
0.60	30.625	25.8456	25.0562	20.3402 (25.3719)	27.25	27.1168

of state estimate almost same values up to  $\eta = 0.35$  beyond which they differ starting from the range of liquid metal densities to higher densities. Among these equations of state, PY approximation [Eq. 6] shows higher values while virial series drops to lower values at higher densities when calculated up to seven terms. This difference is more pronounced beyond  $\eta = 0.55$  beyond liquid metallic range. Bracketted values in the same column are the values when ten terms are included in virial series (Eq. 2). The Carnahan–Starling (Eq. 7) and Maeso *et al.* (Eq. 18) equations of state lie in between PY and the soft reference equations of state (Eqs. 14 and 17). Thus, we find that these equations of state differ significantly at higher densities and the equation of state of the substances having soft repulsive pair potential such as liquid alkali metals can neither be represented by PY approximation nor by C. S equation of state. However, Eq. (2) predicts almost same values at higher densities as those obtained by Eqs. (14 and 17), representing equations of state for substances having soft repulsive pair potential. The influence of softness and perturbation potential over PY approximation can be obtained by writing equation of state as<sup>14</sup>

$$\frac{P}{\rho kT} = 1 + 4\eta g(\sigma) - \rho Q(\rho) \quad (19)$$

where  $g(\sigma)$  is the pair correlation function at hard sphere contact for PY approxima-

tion. Equating Eq. (19) with our equation of state (Eq. 14), we find

$$\rho Q(\rho) = 4\eta \frac{(1 + \eta/2)}{(1 - \eta)^2} + a - \frac{a(1 + \eta + \eta^2)}{(1 - \eta)^3} + \frac{12b(1 + d)}{d^2} \eta + \frac{12\eta(x_1 a_1 + x_2 a_2)}{(a_1^2 + a_2^2)} \quad (20)$$

where

$$q^{\text{PY}}(\sigma) = \frac{(1 + \eta/2)}{(1 - \eta)^2}$$

Now, we turn to calculate thermodynamic properties of liquid alkali metals using our equation of state. In such calculations, we have to select the value of packing fraction  $\eta$ . In our earlier work<sup>12</sup>, the value of  $\eta$  is obtained by fitting the first peak of the structure factor at different temperatures, this essentially means an adjustment of the hard sphere diameter  $\sigma$ . At higher temperatures, we have maintained the uniqueness of the screening parameters while the hard sphere diameters are supposed to be density dependent. We prefer to select  $\eta$  by structural property<sup>12</sup> rather than selecting  $\eta$  by fitting with an experimental value of a thermodynamic property or by a variational approach, to correlate the structural and thermodynamical properties. Firstly, we calculate the value of  $\rho Q(\rho)$  (Eq. 20) for liquid alkali metals. Table 2 reveals that  $\rho Q(\rho)$  increases with increase of the packing fraction and its value decreases with the increase of temperature.

The entropy of dense fluid is of great interest in understanding several properties of liquid metals, we can obtain excess entropy, relative to the ideal gas at the same density, quite forwardly once the equation of state is known.

$$\begin{aligned} \frac{S^{\text{ex}}}{NK} &= [S(\rho) - S^{\text{ideal}}(\rho)]/Nk \\ &= \int_0^\eta \left( \beta \frac{P}{\rho} - 1 \right) \frac{d\eta}{\eta} \end{aligned} \quad (21)$$

Solving Eq. (21) for our equation of state i.e. Eq. (14), we obtain

$$\begin{aligned} \frac{S^{\text{ex}}}{NK} &= -\frac{3a}{2} \frac{1}{(1 - \eta)^2} + a \ln(1 - \eta) + \frac{3a}{2} + \frac{12b(1 + d)}{d^2} \eta \\ &\quad + \frac{12\eta(x_1 a_1 + x_2 a_2)}{(a_1^2 + a_2^2)} \end{aligned} \quad (22)$$

The calculated values of excess entropies of liquid alkali metals at the melting temperature are found closer to those obtained by using high temperature approximation of the optimised random phase approximation (ORPA)<sup>15</sup> (See Table 4 of reference 15). Recently, Regnaut<sup>15</sup> compared the variational approach (VA) with the

**Table 2** Calculated values of  $\rho Q(\rho)$ , excess entropy and diffusion coefficient of liquid alkali metals at different temperatures.

Metal	T (K)	$\eta$	$-\rho Q(\rho)$	$-S_{ex}/K_B$	$g(\sigma)$	$D(\text{cm}^2 \text{sec}^{-1} \times 10^5)$				Eq. (25)	Expt.	
						Ours	Virial	Zhou and Stell	Ours			Virial
Li	463	0.493	1.04	4.04	5.378	5.190	5.553	5.633	5.837	5.455	4.33	6.1
	523	0.470	0.74	3.66	4.787	4.729	4.969	7.283	7.373	7.016	6.86	—
	725	0.441	0.49	3.27	4.187	4.211	4.348	10.903	10.841	10.500	12.01	—
Na	378	0.465	0.62	3.22	4.639	4.635	4.854	4.386	4.390	4.193	4.24	4.3
				(3.45)								
K	473	0.4395	0.42	3.18	4.123	4.186	4.318	6.065	5.974	5.791	6.66	8.1
	573	0.427	0.37	3.05	3.910	3.984	4.086	7.385	7.249	7.069	8.46	—
	723	0.386	0.18	2.56	3.279	3.396	3.434	11.706	11.304	11.179	14.13	—
	823	0.371	0.14	2.41	3.089	3.207	3.230	14.162	13.643	13.544	17.06	—
	343	0.451	0.38	3.21	4.278	4.382	4.549	4.573	4.464	4.300	4.71	3.7
				(3.45)								
Rb	378	0.432	0.25	2.96	3.916	4.063	4.177	5.633	5.429	5.282	6.23	6.5
												(408K)
	623	0.397	0.18	2.64	3.408	3.543	3.593	9.567	9.203	9.074	11.41	—
Cs	723	0.363	0.07	2.28	2.963	3.111	3.129	13.761	13.107	13.033	16.33	—
	313	0.470	0.65	3.57	4.743	4.730	4.969	2.643	2.930	2.523	2.47	—
				(3.52)								
Cs	373	0.448	0.48	3.29								—
	473	0.441	0.26	2.83								—
	303	0.458	0.59	3.46								—
				(3.50)								
Cs	373	0.440	0.47	3.24								—
	473	0.400	0.25	2.74								—



ORPA (perturbation expansion) in case of simple metals, by examining the essential difference for various thermodynamic quantities. In the alkalis, the difference between the VA and the ORPA comes from the estimation of the soft ranged repulsive forces and long range oscillations. Since in our equation of state both the softness of the core and the oscillations are considered, it seems to confirm the findings of Regnaut's work. Bracketted values are the experimental values of excess entropy at the melting temperature.

We also know that the equation of state is directly related with  $g(\sigma)$ , pair correlation function at hard sphere contact, it can be used to calculate diffusion coefficient as<sup>16</sup>

$$D = \frac{D_0}{g(\sigma)} \quad \text{where } D_0 = \frac{3}{8\rho\sigma^2} \left( \frac{kT}{m} \right)^{1/2} \quad (23)$$

The Eq. (23) does not include the term due to back scattering. There is no simple way of computing back-scattering term for hard sphere fluid. However, we can follow the results of computer experiments for hard sphere system by introducing a factor<sup>17</sup> ( $=0.33/\eta$ ) in Eq. (23) as

$$D = \left( \frac{0.33}{\eta} \right) \left( \frac{D_0}{g(\sigma)} \right) \quad (24)$$

The values of  $g(\sigma)$  and hence diffusion coefficients are calculated using our equation of state (Eq. 14) for liquid alkali metals at different temperatures, and the results are tabulated in Table 2. We have also compared the value of  $g(\sigma)$  for virial series considering first six terms at the same packing fractions. We find exactly same values of  $g(\sigma)$  as those obtained by our equation of state. It means that six terms are sufficient to calculate the properties of liquid metals particularly for soft reference system. For higher densities, we can include more terms to obtain correct  $g(\sigma)$ . Considering nine terms in  $g(\sigma)$  (Eq. 4), the values become closer to C.S. results. The values of the diffusion coefficient obtained from Eqs. (4), (14) and (17) are almost same and close to the experimental results. It is interesting to compare our results for the Yukawa fluid with those obtained for hard sphere molecular dynamic results. Speedy<sup>18</sup> proposed an equation for hard sphere obtained from computer simulation as

$$D_{\text{HS}} = \left( \frac{D_0}{n} \right) \left( 1 - \frac{n}{1.09} \right) (1 + n^2(0.4 - 0.83n^2)) \quad (25)$$

where  $n = \rho\sigma^3$  and  $D_0 = (\frac{3}{8})\sigma(kT/\pi m)^{1/2}$ ,  $\sigma$  is the hard sphere diameter. We find that the values of the diffusion constant for Yukawa fluid are smaller than these from hard sphere fluid which showed that the cohesive part of the intermolecular potential plays a significant role in reducing diffusion. Similar trends are observed in the recent work of Rey *et al.*<sup>19</sup>.

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