Mean spherical model approximation : surface tension, shear viscosity and self-diffusion coefficient of liquids

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The mean spherical model approximation (MSMA) has been successfully used by different workers to derive the structures of liquids. The square-well attractive tail in the present case combined with MSMA, results in simple closed analytical expressions for surface tension, an equilibrium property and shear viscosity and self-diffusion coefficient, the transport properties of liquids. It is gratifying to note that there is a good agreement between the calculated and experimental values with the same set of parameters for both types of properties along with the effective mass prescription.

1. Introduction

There is now considerable evidence (Gopala Rao & Murthy, 1974, 1975; Gopala Rao & Nammalvar, 1975, 1976) that a useful model to elucidate the structural properties of both metallic and non-metallic liquids is the mean spherical model approximation (MSMA). One of the key areas of the future development of this model is its application to some other properties of liquids like surface tension, an equilibrium property and also shear viscosity and self-diffusion coefficients, an equilibrium property and also shear viscosity and self-diffusion coefficients, the transport properties. It is with this interest, we propose to test the validity of the closed analytical simple expressions derived, especially for these properties, using the square well (SW) potential along with the MSMA

2. Theory

We start with the Fowler's expression for surface tension (Fowler, 1937) which is given by

$$\gamma = \frac{\pi \rho^2}{8} \int_0^\infty r^4 \frac{du}{dr} (r) g(r) dr \qquad \qquad \text{... (1)}$$

where, $g(r)$ is the radial distribution function (RDF),

$u(r)$ is the intermolecular force potential, and rest of the symbols have their usual connotations.

For SW potential we have

$$\frac{du(r)}{dr} = -\infty, \quad r = \sigma$$

$$= +\infty, \quad r = \lambda\sigma$$

$$= 0, \quad r \neq \sigma, \lambda\sigma \qquad \qquad \dots (2)$$

We write

$$\frac{du(r)}{dr} = -k_B T \, e^{\frac{u(r)}{K_B T}} . \frac{d}{dr}\left(e^{-\frac{u(r)}{K_B T}}\right) \qquad \dots (3)$$

and

$$\frac{d}{dr}\left(e^{-\frac{u(r)}{K_B T}}\right) = e^{\varepsilon/K_B T}\delta(r-\sigma), \quad 0 < r < \sigma$$

$$= (1-e^{\varepsilon/K_B T})\delta(r-\lambda\sigma), \quad \sigma < r < \lambda\sigma \qquad \dots (4)$$

Here, ε and λ are the depth and breadth of the SW potential model under consideration.

Now terminating the upper limit of the integral in eq. (1) at $\lambda\sigma$, splitting the integral into regions of 0 to σ and σ to $\lambda\sigma$ and then imposing the delta function properties we can write eq. (1) as

$$\gamma = \frac{\pi\rho^2 k_0 T\sigma^4}{8}[g(\sigma)-(1-e^{-\varepsilon/k_B T})g(\lambda\sigma)\lambda^4] \qquad \dots (5)$$

where, ε $g(\sigma)$ is the RDF evaluated at r slightly greater than σ and $g(\lambda\sigma)$ is that evaluated at r slightly less than $\lambda\sigma$.

We recall from statistical considerations (Eyring *et al.* 1967) that

$$g(\sigma) = -c(\sigma)$$

Here $c(\sigma)$ is the direct correlation function (DCF) evaluated at $r = \sigma$ in the Wertheim-Thiele solution of Percus-Yevick (PY) equation for hard spheres (Wertheim, 1963; Thiele 1963) given by

$$c(r) = -\frac{1}{(1-\eta)^4}\left[(1+2\eta)^2 - 6\eta\left(1+\frac{\eta}{2}\right)^2\left(\frac{r}{\sigma}\right) + \frac{\eta}{2}(1+2\eta)^2\left(\frac{r}{\sigma}\right)^3\right]$$

where, $\eta = \frac{\pi\rho\sigma^3}{6}$ is the packing fraction and ρ is the number density.

Thus,

$$g(\sigma) = \frac{1+\eta/2}{(1-n)^2} \qquad\qquad .. \quad (6)$$

The relation between DCF and RDF at $r = \lambda\sigma$ for the potential function under discussion is given by (Egelstaff, 1967)

$$c(\lambda\sigma) = (1 - e^{-\varepsilon/k_B T})g(\lambda\sigma) \qquad\qquad ... \quad (7)$$

and

$$c(\lambda\sigma) = \frac{\epsilon}{k_B T}, \quad r = \sigma \qquad\qquad ... \quad (8)$$

by virtue of MSMA. Substituting for $g(\sigma)$ and $g(\lambda\sigma)$ from eqs. (6), (7) and (8) and rearranging the terms eq. (5) finally assumes the form

$$\gamma = \frac{3RT\eta\sigma}{4V}\left[\frac{\epsilon\lambda^4}{k_B T} - \frac{1+\eta/2}{(1-\eta)^2}\right] \qquad\qquad ... \quad (9)$$

The calculated values of surface tension from eq. (9) have been given along with experimental values in table 2. The necessary potential parameters taken from second virial coefficients have been listed in table 1 (Hirschfelder *et al* 1954). The

Table 1. Potential parameters from second virial coefficient

Sl. No.	Liquids	Dia. σ_o Å	ϵ/K_β 7°K	λ
1.	Argon	3.162	69.4	1.85
2.	Neon	2.382	19.5	1.87
3.	Krypton	3.362	98.3	1.85
4.	Xenon	3.760	127.7	1.85
5.	Nitrogen	3.299	53.7	1.87
6.	*Bromine	4.258	523.34	1.56
7.	Carbon dioxide	3.917	119.0	1.83
8.	Methane	3.40	88.8	1.85
9.	Etnane	3.535	244.0	1.652
10.	Propane	4.418	347.0	1.464
11.	Butane	4.812	387.0	1.476
12.	Ethylene	3.347	222.0	1.677
13.	*Pentane	5.422	386.2	1.52
14.	*Benzene	5.17	840.1	1.37
15.	toam	2.61	1290.0	1.20

*Parameters are obtained from compressibility sum rule.

molar volumes have been obtained from densities available elsewhere (International Critical tables, 1928).

Table 2. Surface tension of liquids

Sl No.	Liquids	Temp. °K	Mol. Vol. c.c	λ dyne/cm. Cal.	λ dyne/cm. Obs.
1.	Argon	86.0	28.00	14.06	13.20
2.	Neon	25.0	16.26	4.40	5.50
3.	Krypton	119.8	34.73	16.88	16.10
4.	Xenon	165.0	42.95	20.26	19.30
5.	Nitrogen	74.0	34.00	9.20	9.39
6.	Bromine	293.0	50.50	43.68	41.50
7	Carbon dioxide	248.0	45.74	9.64	9.13
8.	Methane	111.7	37.83	13.60	16.00
9.	Ethane	173.0	53.46	15.41	—
10.	Propane	193.0	70.30	14.66	—
11.	Butane	293.0	96.50	10.92	—
12.	Ethylene	252.0	68.29	7.05	—
13.	Pentane	293.0	112.0	11.84	13.72
14.	Benzene	293.0	89.0	27.37	28.60
15.	Water	363.0	18.65	47.50	60.75

The procedure depicted above can also be adopted to get an expression for the shear viscosity of liquids. Using Born-Green's equation (Johnson *et al* 1964) the shear viscosity is given by

$$\mu = \frac{2\pi}{15}\left(\frac{m}{k_B T}\right)^{\frac{1}{2}} \int_0^\infty n_2(r)\frac{du}{dr}(r)\, r^4 dr \qquad \ldots (10)$$

where, $n_2(r) = \rho^2 g(r)$

Making use of the delta function property eq. (10) becomes

$$\mu = -\frac{2\pi}{15}\left(\frac{m}{k_B T}\right)^{\frac{1}{2}} \rho^2 k_B T \sigma^4 [g(\sigma)-g(\lambda\sigma)(1-e^{-\varepsilon/k_B T})\lambda^4]. \qquad \ldots (11)$$

which ultimately with MSMA results

$$\mu = \frac{0.8\sigma\eta}{V}(MRT)^{\frac{1}{2}}\chi \qquad \ldots (12)$$

where,

$$\chi = \frac{\varepsilon\lambda^4}{k_B T}\frac{1+\eta/2}{(1-\eta)2}$$

Eq. (12) does not give encouraging results as, at this stage, one has to take into account the concept of effective mass due to *caging effect* as has already been done by several workers (Egelstaff 1967; Gopala Rao 1975; Gopala Rao *et al*, unpublished). The effective mass of the molecule can be calculated by assuming it to be a sphere of diameter 1* and is given by

$$m \eta g(\sigma) \left(\frac{l^*}{\sigma} \right)^3 \qquad (13)$$

Here l^* is the correlation length and is taken to be equal to the lattice constants from X-ray data as is generally done (Gopala Rao 1975; Gopala Rao *et al*, unpublished).

Taking this effective mass into consideration eq. (12) can be finally written as

$$u = 0.8 \left\{ \frac{Mg(\sigma)(l^*\eta)^3 RT}{\sigma V^2} \right\}^{1/2} \chi \qquad \dots (14)$$

The eq. (14) has been used to calculate the shear viscosities of some typical liquids and have been given in table 3.

Table 3. Shear viscosity of liquids

Sl. No.	Liquids	Temp. °K	Mol. Vol. c.c.	l^* Å	mpoise Cal	mpoise Obs.
1.	Argon	86.0	28.00	5.43	2.56	2 70
2.	Neon	25.0	16.26	4.52	0.90	-
3.	Krypton	119.8	34.73	5.59	3.50	3.78
4.	Xenon	165.0	42.95	6.18	5.03	5.50
5.	Nitrogen	74.0	34.00	5.66	1.75	2.00
6.	Bromine	293.0	50.50	6.67	11.06	10 00
7.	Carbon dioxide	293.0	57.14	5.575	0.574	0.71
8.	Methane	111.7	37.83	5.89	1.27	1.30
9.	Ethane	185.0	54.9	8.19	1.719	1.62
10.	Ethylene	172.0	50.0	6.46	1.18	1.50
11.	Pentane	293.0	112.0	10.3	2.368	2.40
12.	Benzene	293.0	89.0	9.76	6.836	6.50
13.	Water	363.0	18.65	4.535	2.37	3.17

Following Chapman-Enskog procedure for SW fluids (Reed and Gubbins 1973; Longuet-Higgins and Valleau 1956) we write the frictional coefficient Γ as

$$\Gamma = \frac{8}{3} \left(\frac{\pi k_B T}{m} \right)^{\frac{1}{2}} \rho\sigma^2 \left[g(\sigma) + \lambda^2 g(\lambda\sigma) \left\{ e^{\epsilon/k_B T} - \frac{\epsilon}{2k_B T} - 2\Sigma \right\} \right] \quad \dots \quad (15)$$

$$\Sigma = \int_0^\infty x^2 (x^2 + \epsilon/k_B T)^{\frac{1}{2}} e^{-x^2} dx$$

The function Σ has been calculated numerically for various values of reduced temperature by Luks et al (1966). The self-diffusion coefficient D is then given by

$$D = \frac{k_B T}{m\Gamma} \quad \dots \quad (16)$$

With the concept of effective mass and using eqs. (7) and (8) for $g(\lambda\sigma)$ eq. (6) can be written as

$$D = \frac{\dfrac{0.153\sigma}{\eta} \left\{ \dfrac{k_B T V}{M g(\sigma) l^{*3}} \right\}^3}{g(\sigma) + \dfrac{\lambda^2\epsilon}{k_B T(e^{\epsilon/k_B T} - 1)} \left\{ e^{\epsilon/k_B T} - \dfrac{\epsilon}{2k_B T} - 2\Sigma \right\}} \quad \dots \quad (17)$$

Eq. (17) has been employed to calculate the self-diffusion coefficients some liquids and have been listed in table 4 along with the experimental values.

Table 4. Self-diffusion coefficients of liquids

Sl. No.	Liquids	Temp. °K	Mol. Vol c.c.	D cm²/sec. Cal.	D cm²/sec. Obs.
1.	Argon	86.0	28.00	1.45	1.60
2.	Neon	25.0	16.26	1.361	—
3.	Krypton	119.8	34.73	1.30	1.70
4.	Xenon	165.0	42.95	0.93	1.30
5.	Nitrogen	74.0	34.00	1.665	—
6.	Bromine	293.0	50.50	1.45	2.037*
7.	Methane	111.7	37.83	3.09	3.70
8.	Pentane	293.0	112.00	1.86	5.18
9.	Benzene	293.0	89.00	1.56	1.91
10.	Water	298.0	18.15	2.94	2.44

*Compared with calculated value of Longuet-Higgins & Poppies, J. Chem. Phys.. 25, (1956) 884.

DISCUSSION

Exemplifying the model presented in this paper the three properties viz. surface tension, shear viscosity and self-diffusion coefficients of several liquids have been calculated. It is gratifying to note that there is good agreement between the theory and the experiment. Especially considering the fact that surface tension, a macroscopic property is now related to the potential parameters, the values obtained are of considerable interest. Wherever the scond virial coefficient data are not available a different method to evaluate the potential parameters had been sought for. This involves the usage of compressibility sum rule which is related to the isothermal compressibility, a quantity that can be measured accurately from an experiment. The parameters thus obtained yield reasonably good result.

Like equilibrium property, the transport properties are also very important in determining the correctness of the molecular model one considers. The agreements in the cases of viscosity and self-diffusion coefficient calculations are generally very good except in few cases. The concept of effective mass utilised presents a true picture and is a better description than multiplying the calculated values by some correction factor as has been done earlier by several workers (Vadovic & Colver, 1971). Because of the well supported features we conclude that the MSMA is a good description for nonmetallic liquids. This view is also supported by the equation of state we derived sometimes back with MSMA and in its successful applications in evaluating various thermodynamic properties (Gopala Rao & Joarder, unpublished).

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