

## **Estimation of nano sized spherical cavity using extended scaled particle theory for Lennard-Jones fluid**

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### **ABSTRACT**

*In this paper extended scaled particle approach has used to compute thermodynamic behavior of real fluid. In order to predicts closeness of values computed for ultrasonic wave velocity, thermodynamic molar volume and volume expansion coefficient simultaneously, needs an assumptions like multiple of molecular weight along with ratio of specific heat closer to unity, in liquid state. From the profile of the individual liquids the results are discussed in terms of hard sphere cavity diameter and depth of minimum potential (binding energy) at fixed temperature (liquid state).*

**Key words:** Equation of State (EOS), LJ Potential, Hard-Sphere (HS) Potential, Computer Simulation.

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### **INTRODUCTION**

The concept of hard sphere (HS) body is useful in development of theories of liquid state. The properties of hard sphere provide the theoretical backbone of many equations of state (EOS) for real fluids. The Carnahan-Sterling<sup>1</sup> (EOS) for non attraction rigid spheres provides an accurate representation of compressibility factor ( $Z$ ) as a function of reduced density. There is considerable interest in developing more accurate hard sphere equation to improve prediction of interaction of real fluids. The accuracy of (HS-EOS) is to compare ( $Z$ ,  $\rho$ ) behavior exact (HS) data obtain from molecular simulation results given by many workers.

Alder, and Wainwright<sup>2</sup> studied the equation of state and the collision rate for systems containing different number of particles. The dependence of the results on the number of particles at various densities, in order to obtain a quantitative description of the equilibrium properties along with existence of a first order phase transition for hard spheres was discussed. They used molecular dynamics (MD) to study the behavior of a small number of elastic spheres in liquid. Alder, Hoover and Young<sup>3</sup> used (MD) and obtained high-density (EOS) and entropy for hard disks and spheres. Hoover and Ree<sup>4</sup>, have made a Monte Carlo (MC) determination of the pressure and absolute entropy of the (HS) solid to confirm the existence of a first order melting transition for a classical many body system of hard spheres and to discover the densities of the coexisting phases for liquid ( $\rho d^3 = 0.67$ ) and solid ( $\rho d^3 = 0.74$ ), satisfy the thermodynamic equilibrium conditions of equal pressure and chemical potential at constant temperature. Barker and Henderson<sup>5</sup>, used (MC) values for the Radial Distribution Function (RDF) for a system of (HS) fluid.

Adams<sup>6</sup> found that the chemical potential is considerably more dependent on the sample size than the pressure. The chemical potential was obtained in agreement with that found by integrating over pressure as a function of volume.

Their equations produced were closely related to those used in Scaled Particle Theory (SPT). Woodcock<sup>7</sup> proposed an approximate closed-form representation of the (EOS) for (HS) fluid. He uses the known virial coefficients, to reproduce the exact (numerical) (EOS) with a greater accuracy. Erpenbeck and Wood<sup>9</sup>, studied the equation of state of the hard-sphere fluid by a computer simulation method for volumes ( $1.6 < V_0 < 25$ ) with ( $108 < N < 4000$ ) particles and results are compared to the theoretical dependence for the NPT ensemble, to estimate thermodynamic limit. The (MD) results are compared with Pade approximants to the virial series and the equation of state was compared with a number of analytic expressions for the hard-sphere equation of state. The most widely used EOS Carnahan-Sterling (CS) is given below.

$$Z = \frac{[1 + \eta + \eta^2 - \eta^3]}{(1 - \eta)^3}, \quad \eta = \frac{\pi \rho d^3}{6} \quad (1)$$

Several improved hard-sphere equations have been proposed. An accurate analytic and theoretically-based equation of state for the Lennard-Jones (LJ) fluid is proposed by Kolafa and Nezbeda<sup>9</sup>. The equation of Kolafa introduces an additional term to the numerator of the (CS) equation.

$$Z = \frac{\left[1 + \eta + \eta^2 - \eta^3 - \frac{2}{3}(\eta^3 + \eta^4)\right]}{(1 - \eta)^3} \quad (2)$$

The equation is based on a perturbed virial expansion with a theoretically defined temperature-dependent reference hard sphere term. The expansion is written for the Helmholtz free energy which guarantees the thermodynamic consistency of the pressure and internal energy. The equation covers much wider range of temperatures (up to seven times the critical temperature) than existing equations and is significantly more accurate and has less parameter than the best equation available.

The equation of state for pure and binary fluids of hard spheres is proposed by Malijevsky and Veverka<sup>10</sup>.

$$Z = \frac{1 + 1.506\eta + 1.6539\eta^2 + 0.3262\eta^3}{(1 - \eta)^3(1 + 0.056\eta + 0.5979\eta^2 + 0.3076\eta^3)} \quad (3)$$

This equation has the form of the Pade approximant of the rescaled virial series and uses the first seven virial coefficients. Hence the equation is superior to the Carnahan-Starling, Erpenbeck-Wood and Kolafa (EOS). It is shown that its accuracy is almost the same as the precision of recent simulation data. In contrast to the above equations, Yelash and Kraska<sup>11</sup> reported a generic (EOS) for the (HS) fluid incorporating the high density limit without a pole at  $\eta = 1$ .

$$Z = \frac{3 + 8\eta + 14\eta^2 + 14\eta^3 + \left(\frac{14}{3}\right)\eta^4}{(3 - 4\eta)} \quad (4)$$

Mehrdad Khanpour and Parsafar<sup>12</sup> present a simple method of obtaining various equations of state for hard sphere fluid. They used the first several virial coefficients of hard sphere fluid and guess the equations of state by using the asymptotic expansion method. Among the equations of state obtained in this way are Percus-Yevick, (SPT) and (CS), (EOS). They combined the (MC) results on (HS) fluid with the asymptotic expansion method and many other (EOS) for (HS) fluid. Khasare and Deshpande<sup>13</sup> developed simple (EOS) for (HS) and (LJ) fluid.

Extended scaled particle theory (ESPT)<sup>14-15</sup> is presently used to calculate thermo-dynamic measurable parameters. Since (ESPT) was designed to capture the packing interactions in a (HS) fluid. It would seem to be an ideal theory for calculating thermodynamic measurable parameters. The two input parameters are necessary for (ESPT) hard sphere fluids are the radius and its binding energy. Khasare<sup>16-17</sup> uses (ESPT) for a strong repulsive potential together

with a weak attractive potential.

The set of parameters required for calculating ultrasonic wave velocity, density, and volume expansion coefficient is not same as that of Gibbs free energy. Many workers observed that above thermodynamic properties are highly sensitive to the choice of hard sphere (cavity) radii. Real fluid can be represented by minimum of two parameters such as size of the molecule and its binding energy, hence SPT containing single parameter have limited success i.e. to reproduce density data, and suitable hard sphere diameter can be selected. Similarly, to reproduce wave velocity different size of hard sphere diameter is required. Because hard sphere model for real fluids is not sufficient and significant to reproduce density and velocity data simultaneously. Hence it is necessary to extend domain of SPT by introducing additional parameters (binding energy!). Khasare modifies basic SPT theory by introducing hard sphere cavity diameter along with the concept of binding energy.

Now (HS) system can be considered as an ideal liquids and it is a simple for thermodynamic study. A compressibility factor  $Z(\eta, \beta\varepsilon)$  for fluid of (LJ) molecules enclosing in a cavity diameter ( $d$ ) is defined as

$$Z(\eta, \beta\varepsilon) = \frac{\beta P}{\rho}, \quad \beta = \frac{1}{k_B T}, \quad \beta\varepsilon = \frac{\tau}{T}, \quad \tau = \frac{\varepsilon}{k_B}, \quad \eta = \frac{v}{V}$$

Where  $v$  is volume of cavity containing few chemical units,  $V$  is volume,  $P$  is a pressure,  $\rho = N/V$  is the density,  $T$  is temperature,  $\varepsilon$  is binding energy of cluster containing chemical units and  $k_B$  is Boltzmann constant.

Let  $\lambda = \lambda_0$  represent a simple system with known properties and  $\lambda = \lambda_1$  can be a system under consideration. This leads to a perturbation theories, which requires only information of reference system.

Here (ESPT) is tested for different types of real liquids at fixed temperature and to begin with, model parameters for pure liquid are evaluated by assuming ratio of specific heat equal to unity and suitable average real molecular weight of cluster. Molecular weight of cluster comes out to be a real number. Hence its next closest higher integer is first assumed and correspondingly ratio of specific heat is assumed. Next using subsequent theoretical domain, model parameters for real liquid have been established to estimate thermodynamic properties such as ultrasonic velocity, bulk density and volume expansion coefficient.

## 2. ESPT for Real Fluid :

Khasare<sup>15-17</sup> expressed the pair potential between single molecule with remaining molecules as a sum of reference ideal repulsive potential  $\phi_0(r)$  And perturbing term  $\phi_1(r)$ . This perturbing term is a sum of non-ideal repulsive potentials and attractive potentials term given by following expression.

$$\phi(r) = \phi_0(r) + \phi_1(r) = \phi_{HS}(r) + \lambda [\phi_{rep}(r) + \phi_{attra}(r)]; \quad 0 \leq \lambda \leq 1.0 \quad (6)$$

Where  $\lambda$  is the perturbing parameter.

Hence final expression<sup>20</sup> for (ESPT) an (EOS) for a real fluid is expressed as

$$Z = Z_0 + Z_1 \quad (7)$$

$$Z_0 = \frac{[1 + (2 - m)\eta + (3 - 2m)\eta^2]}{(1 - \eta)^2(1 - m\eta)}; \quad m = 3/4$$

$$Z_1 = \frac{(f_1\beta\varepsilon + f_2\beta^2\varepsilon^2)(m - 4)\eta}{(1 - m\eta)}$$

$$f_1 = -3 \left[ \left( \frac{4}{9} \right) \alpha^{12} - \left( \frac{4}{3} \right) \alpha^6 \right]$$

$$f_2 = \left(\frac{3}{2}\right) \left[ \left(\frac{16}{21}\right) \alpha^{24} - \left(\frac{32}{15}\right) \alpha^{18} + \left(\frac{16}{9}\right) \alpha^{12} \right]$$

Now relation <sup>17</sup>,  $d = \alpha\sigma$ ,  $\alpha^6 = 3.0$ , we have

$$Z_0 = \frac{\left[ 1 + \left(\frac{5}{4}\right)\eta + \left(\frac{3}{2}\right)\eta^2 \right]}{\left[ (1-\eta)^2 \left( 1 - \left(\frac{3}{4}\right)\eta \right) \right]}$$

$$Z_1 = \frac{-\left(\frac{3432}{35}\right)\beta^2 \varepsilon^2 \eta}{\left( 1 - \left(\frac{3}{4}\right)\eta \right)}$$

Where  $\alpha$ ,  $d$  and  $\sigma$  are the arbitrary constants, (HS) Diameter and (LJ) parameter respectively.

The other expressions thermodynamically derivable expressions is as given below.

$$\frac{M_{eff} u^2}{\gamma RT} = \frac{\partial(Z\eta)}{\partial\eta} = y = y_0 + y_1 \quad (8)$$

$$M_{eff} = \zeta \cdot M; \zeta = [\zeta_{min}, \zeta_{max}; M = \text{molecular weight}]$$

For  $\alpha^6 = 3.0$  we have

$$y_0 = \frac{(-56\eta - 33\eta^2 + 75\eta^3 - 16)}{(-1 + \eta)^3 (-4 + 3\eta)^2}$$

$$y_1 = \frac{(13728/35)\beta^2 \varepsilon^2 \eta (-8 + 3\eta)}{(-4 + 3\eta)^2}$$

and

$$\frac{M_{eff} u^2 \alpha T}{\gamma RT} = \frac{\partial(ZT)}{\partial T} = x = x_0 + x_1; \quad (9)$$

$$x_0 = \frac{\left[ 1 + \left(\frac{5}{4}\right)\eta + \left(\frac{3}{2}\right)\eta^2 \right]}{\left[ (1-\eta)^2 \left( 1 - \left(\frac{3}{4}\right)\eta \right) \right]}$$

$$x_1 = \frac{(3432/35)\beta^2 \varepsilon^2 \eta}{(1 - (3/4)\eta)}$$

The present (EOS) is tested by extending the domain of theory such as the definition  $\eta = v/V$  and  $0 < \beta\varepsilon < 2.0$  for real fluid. Here one has to accept the term  $v/V$  as the probability for creating a cavity in fluid and in this cavity, group of molecule are assumed to be present. In gas phase one chemical unit is sufficient while in liquid state group

of chemical units are required to obtain thermodynamic properties, which is natural and logical. In the present work ten samples of real fluids are considered at fixed temperature.

$S_1 = \text{benzotrill}[103.1]$ ;  $S_2 = \text{tetrahydrofuran}[72.11]$ ;  $S_3 = \text{O- cresol}[108.1]$ ;

$S_4 = 2 \text{ methylpropanol}[74.12]$ ;  $S_5 = \text{ethylmethylketone}[72.11]$ ;  $S_6 = \text{benzene}[78.11]$ ;

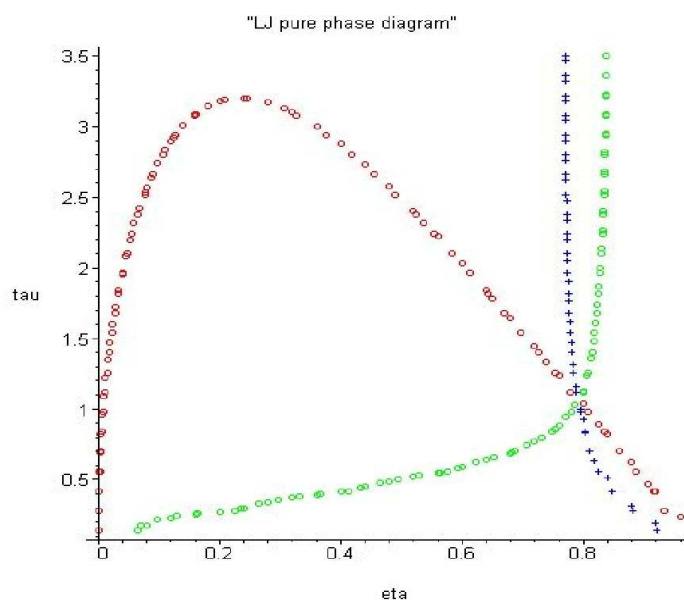
$S_7 = \text{acetophenon}[120.1]$ ;  $S_8 = \text{clorobenzene}[112.6]$ ;  $S_9 = \text{toulene}[92.14]$ ;

$S_{10} = \text{bromobenzene}[157.1]$ .

## RESULTS AND DISCUSSION

The results are obtained by solving equations (7, 8, 9) containing two model parameters ( $\eta$ ,  $\beta\epsilon$ ). The thermodynamic related parameters are presented in (Table 1) and two model parameters ( $\eta$ ) and ( $\beta\epsilon$ ) are presented in (Table 2).

In the following figure different pairs of  $[\tau]$  corresponding to equation (7), equation (8) and equation (9) are plotted in red circle, in blue cross and in green circle respectively.



**Figure (1):  $(\eta)_{\text{liq}} = 0.7715822166$ ;  $(\beta\epsilon)_{\text{liq}} = 0.8506314831$ ;  $T = 303.15\text{K}$**

In order to obtain unique choice in terms of  $[\eta, \beta\epsilon]$ , i.e. common intersection point in  $[\tau = 1 = ()]$  plot along with necessary condition in terms of model input parameters  $[\zeta, C_p/C_v]$  are accepted. If one is not ready to accept the above choice the common intersection is loosed and have to accept three solutions corresponding to three-intersection point in  $[\eta, \tau]$  plots. This happen only when one select  $[\zeta = 1]$ . Hence it is necessary to accept the choice of  $[\zeta \geq 1.0]$ . It is observed that basic model parameters ( $\eta$ ) and ( $\beta\epsilon$ ) are depends upon the choice of  $[\zeta, \gamma = C_p/C_v]$  thermodynamic variables.

Present type of calculations are useful for bio fluids or polymer liquids where molecular weight and  $[C_p, C_v]$  are not available. In the present calculations, it is easy to study the size of cluster molecules at various temperatures required in medical sciences.

$$MW_{\text{eff}} = \zeta (MW); \zeta = [\zeta_1, \zeta_2]$$

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**Table 1: Thermodynamic parameters and assumed model two-thermodynamic parameter  $[\eta, \beta\epsilon]$  for real fluid**

S.No	(MW)	density	velocity	$\alpha$	$\zeta_1$	$\gamma_1$	$\zeta_2$	$\gamma_2$
1	103.1	0.9950	140250	0.20175	35.637	1.00	36.0	1.01020
2	72.11	0.8828	125000	0.32100	15.541	1.00	66.0	1.02955
3	108.1	1.0487	152500	0.2787	10.673	1.00	11.0	1.03065
4	74.12	0.7753	110200	0.2040	77.425	1.00	78.0	1.00750
5	72.11	0.7947	117350	0.2605	33.147	1.00	34.0	1.02582
6	78.11	0.8685	127110	0.3758	8.6875	1.00	9.00	1.03603
7	120.1	1.0179	145700	0.1313	109.55	1.00	110.	1.02220
8	112.6	1.0955	124500	0.2975	12.620	1.00	13.0	1.03015
9	92.14	0.8756	129200	0.3233	11.145	1.00	12.0	1.07685
10	157.1	1.4815	114600	0.2754	13.485	1.00	14.0	1.03823

$\zeta_1$ =scaling real number;  $\zeta_2$ =scaling integer; (MW)=molecular weight.  
 $\alpha = (3)^{1/6}$ ;  $m = (3/4)$ ;  $R = (8:314)10^7$ ;  $N_A = (6:02215)10^{23}$ ; pressure =  $(1:012928)10^6$ ;

**Table 2: Model two-parameters  $[\eta, \beta\epsilon]$  for real fluids**

S.No	$\eta_1$	$\beta\epsilon_1$	radius1	$\eta_2$	$\beta\epsilon_2$	radius2
1	0.8313918988	1.151765872	10.67662805	0.8318463312	1.154881354	10.71470800
2	0.7583087738	0.804199584	7.253361909	0.7583074733	0.804189855	7.324074835
3	0.7826341655	0.893725733	6.989619397	0.7826307304	0.893707584	7.060164760
4	0.8302034102	1.143387241	13.45541388	0.8301999856	1.143359646	13.48862228
5	0.7935687066	0.940718809	9.817335313	0.7935638513	0.940688115	9.900815520
6	0.7294798161	0.719383040	6.090714566	0.7294756514	0.719367141	6.162874417
7	0.8840796209	1.676756560	16.54628478	0.8834916098	1.668255197	16.56523542
8	0.7715873593	0.850656284	7.347258674	0.7715848622	0.850641895	7.420266915
9	0.7570487058	0.800073022	7.060498952	0.7570402708	0.800032294	7.236593386
10	0.7845861814	0.901757773	7.633235384	0.7845837473	0.901741105	7.729188529

Kalidoss and Srinivasamoorthy<sup>18-19</sup> have studied the earlier<sup>14</sup> (EOS) and applied it to binary and ternary liquid mixtures using the concept of concentration dependent cavity. Deshpande<sup>20</sup> applied earlier<sup>14</sup> (EOS) to different real fluid mixture. Bhandakkar<sup>21</sup> discusses an accurate representation of molecular clusters in liquid mixtures using Khasare's equation of state.

## CONCLUSION

It is possible to conclude that minimum size of molecular cluster can be easily simulated at a given temperature using computer algebra so that at least three thermodynamic properties could be reproducing with deeper insight in liquid state.

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