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Nano cavity dependent thermodynamic study of Lennard-Jones Bio- fluids using scaled particle approach.

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ABSTRACT

Efforts are made to estimate cavity size dependent, thermodynamic properties of some organic liquids, using scaled particle approach (SPA). The basic assumption applied is multiple of molecular weight with physical limitations of ratio of specific heats. Computations based on this assumption predict the closeness of values for ultrasonic wave velocity, thermodynamic molar volume and volume expansion coefficient. From the profile of the individual fluid the results are discussed in terms of cavity of nano scale and its associated energy at fixed temperature (liquid state). Further, closeness of computed thermodynamic properties is tested for different possible size of bio molecules in liquid state.

Key Words: Equation of State (EOS), LJ Potential, Hard-Sphere (HS) Potential, Computer Algebra.
PACS: Equations of state gases, 51.30. +i
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INTRODUCTION

Computational methods being developed, such as molecular dynamics, have obtained some results on the aggregation of solute molecule and molecular clustering in the solution. Thermodynamic aptness of the hard sphere potential serves as the base for Scaled particle theory developed by Reiss et al. The properties of hard sphere provide the theoretical backbone of many equations of state (EOS) for real fluids. Khasare and Deshpande [1] developed simple (EOS) for (HS) and (LJ) uid. Extended scaled particle theory (ESPT) [2- 3] 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 uids are the radius and its binding energy. Khasare [4- 5] 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(η, βε) for fluid of (LJ) molecules enclosing in a cavity diameter (d) is defined as

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

Where v is volume of cavity containing few chemical units, V is volume, P is a pressure, ρ= N/V is the density, T is temperature, ε 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 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. 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.

Mathematical model for Bio Fluid:

Khasare [5] expressed the pair potential between single molecule with remaining molecules as a sum of reference ideal repulsive potential φ0(r) and perturbing term φ1(r). This perturbing term is a sum of non-ideal repulsive potentials and attractive potentials term given by following expression.

$$\varphi(r) = \varphi_0(r) + \varphi_1(r) = \varphi_{HS}(r) + \lambda\,[\varphi_{rep}(r) + \varphi_{attra}(r)];\ 0 \leq \lambda \leq 1.0 \qquad (2)$$

Where λ is the perturbing parameter.

Hence final expression [4] for (ESPT) an (EOS) for a real fluid is expressed as

$$Z = Z_0 + Z_1 \qquad (3)$$

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

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

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

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

Now relation (4), d = ασ, $\alpha^6 = 3.0$, 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 α, d and σ are the arbitrary constants, (HS) Diameter and (LJ) parameter respectively.

The other expressions thermodynamically derivable expressions is as given below.

$$\frac{M_{eff}u^2}{\gamma RT} = \frac{\partial(Z\eta)}{\partial\eta} = y = y_0 + y_1 \qquad (4)$$

$$M_{eff} = \zeta \cdot M;\ \zeta = \left[\zeta_{\min,}, \zeta_{\max}; M = molecularweigth\right] \qquad (5)$$

For $\alpha^6 = 3.0$ we have

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

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

and

$$\frac{M_{eff}u^2\alpha T}{\gamma RT} = \frac{\partial(ZT)}{\partial T} = x = x_0 + x_1; \qquad (6)$$

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

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

R = (8.314)10^7 J/mole K; N_A = (6.02215)10^{23} mol $^{-1}$; pressure = (101.2928) kPa;

For real fluid, present EOS is tested by considering η= v/V and βε > 0. The term v/V is taken as the probability for creating a cavity in fluid, assuming presence of group of molecules in cavity.

S1 = Alanine [89.15]; S2 = Valine [117.15]; S3 = Proline [115.13];
S4 = Leucine [131.17]; S5 = Water [18.00];

RESULTS

The results are obtained by solving equations (3, 4, 6) containing two model parameters (η, βε). The thermodynamic related parameters are presented in (Table 1) to (Table 5)(see appendix).

It is observed that [(672 < ζ < 1117) and (2.79nm < radius < 3.30nm)], [(5063 < ζ

< 8397) and (6.07nm < radius < 7.19nm)], [(75785 < ζ < 124893) and (14.99nm < radius < 17.7nm)], [(4493 < ζ < 7452) and (6.07nm < radius < 7.18nm)], [(4493 < ζ < 7452) and (6.07nm < radius < 7.18nm)], [(145.9 < ζ < 110064.4) and (0.96nm < radius < 9.14nm)], corresponding to L-alanine, L-valane, L-proline, L-Leucine and Water respectively. For all liquid [ζ/γ] comes out to be fairly constants. If 0 < α < 0.1 size of cavity shifted to nano meter

DISCUSSION

Bio-molecule history:
1) *Alanine (2-Aminopropanoic acid), Molecular formula ($C_3H_7NO_2$):*
The -carbon atom of alanine is bound with a methyl group (-CH_3), making it one of the simplest -amino acids with respect to molecular structure and also resulting in alanine's being classified as an aliphatic amino acid. The methyl group of alanine is non-reactive and is thus almost never directly involved in protein function. Alanine is a nonessential amino acid, meaning it can be manufactured by the human body, and does not need to be obtained directly through the diet. Alanine is found in a wide variety of foods, but is particularly concentrated in meats. Alanine plays a key role in glucose-alanine cycle between tissues and liver. In muscle and other tissues that degrade amino acids for fuel, amino groups are collected in the form of glutamate by transamination

.***2)*** *Valine (2-amino-3-methylbutanoic acid) Molecular formula ($C_5H_{11}NO_2$):*
Valine is an essential amino acid; hence it must be ingested, usually as a component of proteins. It is synthesized in plants via several steps starting from pyruvic acid. The initial part of the pathway also leads to leucine. The intermediate α-ketoisovalerate undergoes reductive amination with glutamate. Along with leucine and isoleucine, valine is a branched-chain amino acid. It is named after the plant valerian. In sickle-cell disease, valine substitutes for the hydrophilic amino acid glutamic acid in hemoglobin. Because valine is hydrophobic, the hemoglobin does not fold correctly

3) *Proline (Pyrrolidine-2-carboxylic acid) Molecular formula ($C_5H_9NO_2$):*
Proline acts as a structural disruptor in the middle of regular secondary structure elements such as alpha helices and beta sheets; however, proline is commonly found as the first residue of an alpha helix and also in the edge strands of beta sheets. Proline is also commonly found in turns, which may account for the curious fact that proline is usually solvent-exposed, despite having a completely aliphatic side chain. Because proline lacks hydrogen on the amide group, it cannot act as a hydrogen bond donor, only as a hydrogen bond acceptor. The hydroxylation of proline is a critical biochemical process for maintaining the connective tissue of higher organisms. Severe diseases such as scurvy can result from defects in this hydroxylation, e.g., mutations in the enzyme proly hydroxylase or lack of the necessary ascorbate (vitamin C) cofactor

4) *Leucine (2-Amino-4-methylpentanoic acid), Molecular formula ($C_6H_{13}NO_2$):*
Leucine is classified as a hydrophobic amino acid due to its aliphatic isobutyl side chain. Leucine is an essential amino acid. As an essential amino acid, leucine is unable to be synthesized by animals. Consequently, it must be ingested, usually as a component of proteins. In plants and microorganisms, leucine is synthesized from pyruvic acid by a series of enzymes. Leucine is the only dietary amino acid that has the capacity to stimulate muscle protein synthesis. Leucine has since earned more attention on its own as a catalyst for muscle growth and muscular insurance. Leucine is a branched-chain amino acid (BCAA) since it possesses an aliphatic side-chain that is non-linear.

In order to obtain unique choice in terms of [η, βε], model input parameters [ζ ,Cp/Cv] are chosen. Hence it is necessary to accept the choice of [ζ ≥ 1.0]. It is observed that basic model parameters (η) and (βε) are depends upon the choice of [ζ, γ = Cp/Cv] thermodynamic variables. Present type of calculations is useful for above bio-fluids where molecular weight (thermodynamic inertia!) and [Cp, Cv] are not well defined in pure liquid or liquid mixture.

In the present model calculations, it is easy to study the size of cluster molecules at fixed temperatures. [ζ_{min}, ζ_{max}] are scaling integers corresponding to [γmin, γ_{max}];

Table 1: Assumed two-thermodynamic model parameter [M. W. = 89.09; velocity = 155100cm=sec; density = 1.01296gm=cc; = 0.07701K 1; temp = 303.15K] for L-alanine bio fluid

S.No	ζ	γ	ζ/γ	η	βε	radius (nm)
1	672.4	1.00	672.3	0.9281953547	2.710970088	2.791767284
2	739.3	1.10	672.1	0.9281869673	2.710506281	2.881519918
3	806.2	1.20	671.9	0.9281785782	2.710042537	2.965942020
4	873.1	1.30	671.6	0.9281701894	2.709578937	3.045754382
5	939.9	1.40	671.4	0.9281618039	2.709115598	3.121533407
6	1117.8	1.66	670.7	0.9281394349	2.707880374	3.307205768

Table 2: Assumed two-thermodynamic model parameter [M. W. = 117.15; velocity = 156450cm/sec; density = 1.00968gm/cc; = 0.03636K $^{-1}$; temp = 303.15K] for L-valane bio fluid

S.No	ζ	γ	ζ/γ	η	βε	radius (nm)
1	5063.2	1.00	5063.2	0.9647647853	5.531747853	6.079324312
2	5565.5	1.10	5059.5	0.9647564852	5.529820551	6.274024992
3	6067.0	1.20	5055.8	0.9647481851	5.527894377	6.457074935
4	6567.8	1.30	5052.2	0.9647398769	5.525968043	6.630045479
5	7067.9	1.40	5048.5	0.9647315782	5.524044329	6.794197976
6	8397.8	1.66	5038.7	0.9647094323	5.518917340	7.196051121

Table 3: Assumed two-thermodynamic model parameter [M. W. = 115.13; velocity = 156105cm/sec; density = 1.00981gm/cc; = 0.015015K $^{-1}$; temp = 303.15K] for L-proline bio fluid

S.No	ζ	γ	ζ/γ	η	βε	radius (nm)
1	75784.9	1.00	75784.9	0.9851106119	13.08559152	14.99887774
2	83222.4	1.10	75656.7	0.9851023150	13.07473264	15.47426675
3	90634.6	1.20	75528.8	0.9850940170	13.06388792	15.92062539
4	98021.8	1.30	75401.4	0.9850857282	13.05306605	16.34187014
5	105383.8	1.40	75274.2	0.9850774380	13.04225799	16.74111354
6	124893.4	1.66	74936.0	0.9850553111	13.01349210	17.71616025

Table 4: Assumed two-thermodynamic model parameter [M. W. = 131.17; velocity = 156960cm/sec; density = 1.00935gm/cc; = 0.03636K $^{-1}$; temp = 303.15K] for L-Leucine bio-fluid

S.No	ζ	γ	ζ/γ	η	βγ	radius (nm)
1	4492.9	1.00	4492.9	0.9647652995	5.531867080	6.066901716
2	4938.6	1.10	4489.7	0.9647570543	5.529952175	6.261214706
3	5383.7	1.20	4486.4	0.9647487975	5.528036557	6.443899085
4	5828.1	1.30	4483.2	0.9647405419	5.526122240	6.616526959
5	6271.9	1.40	4479.9	0.9647322851	5.524208828	6.780353058
6	7452.1	1.66	4471.3	0.9647102833	5.519114361	7.181417856

Table: 5 -Thermodynamic property for water, cluster size and assumed two-thermodynamic model parameters for water

S.No		Vel.	Den.	Temp.	αx10-4	γ	ζ	η	βε	radius (nm)
1		144800	0.99973	283.15	0.89	1.0041	110064.4	0.97528	7.88515	9.1504
2		148300	0.99823	293.15	2.08	1.0065	7289.0	0.94228	3.37393	3.6617
3		151000	0.99568	303.15	3.04	1.0157	2042.3	0.91526	2.29592	2.3750
4		153000	0.99225	313.15	3.90	1.0254	864.2	0.89073	1.77920	1.7690
5		154400	0.98807	323.15	4.65	1.0399	465.8	0.86893	1.48238	1.4298
6		155200	0.98324	333.15	5.22	1.0547	306.2	0.85147	1.30773	1.2368
7		155500	0.97781	343.15	5.86	1.0694	203.1	0.83231	1.15815	1.0725
8		155500	0.97183	353.15	6.43	1.0861	145.9	0.81488	1.04904	0.9558

5.0 Future insights from model and thermodynamic data

In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its thermodynamic properties. Particles are classified according to size. Here in terms of ultrafine cavity diameter, present bio particles cover a range between [2.8 nm, 17.7 nm] and for water (bio-fluid!) [0.96 nm, 9.15 nm]. Water has nano clusters in one dimension between 1 and 10 nano meters. 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 bio liquid state.

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