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Advances in Applied Science Research, 2012, 3 (5):3053-3059

ISSN: 0976-8610
CODEN (USA): AASRFC

Thermodynamic study of liquid with solver ζ & suitable η_{max} as a pole in basic two parameter Khasare's equation of state

S. B. Khasare[1], Vrushali S. Khasare[2], Shashank S.Khasare[3]

[1]Department of Physics, Science College Congress Nagar,Nagpur, Maharashtra State, India
[2]Department of Information Technology, Indian Institute of Technology,Khargpur, West Bengal, India
[3]Department of Computer Science, College of Engineering Pune, Maharashtra State, India

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ABSTRACT

Author develops or built a simple condition for cluster formation/decay by considering the thermodynamics of molecules within an effective potential of mean force due to the cluster. Efforts are made to estimate cavity in fluid, using equation of state equation of State .The temperature dependence of structural properties and thermodynamic behavior of water clusters has been studied. Computations based on ζ as a solver predict the closeness of thermodynamic values. From the profile of the fluid the model results are discussed in terms of formation of cavity due to closed surface along with its associated energy. As per the expectation, for water it is observed that size of the cavity is rapidly decreased due to breaking of hydrogen bonds as the temperature of liquid increases. Present calculation is based upon the sample thermodynamic data such as ultrasonic wave, density, volume expansion coefficient and ratio of specific heat, and it's inter consistency with thermodynamic relations contain model parameter such as size and energy.

Key Words: Equation of State, LJ Potential, Computer Algebra, Molecular Clusters.

PACS: 51.30. +i Thermodynamic properties, equations of state
PACS: 36.40.Ei Phase transitions in clusters
PACS: 05.70.Ce thermodynamics
PACS: 68.03.Cd Surface tension and related phenomena
PACS: 61.20.Gy Theory and models of liquid structure

INTRODUCTION

In this paper, the author applies the extended scaled particle theory developed in their several papers [1-7] to study the size distribution of water clusters at equilibrium. However, the model is very simple, and there has a new equations/physical results in this paper. The main equations (1-5) have published in previous papers. The numerical results based on equations (1-5) and listed in Tables 1-3 are not merely qualitative calculations, but support or lead to physical conclusions. Author feel the progress in this paper is very little as compared with previous refs [1-7].

The size distribution of water clusters at equilibrium is studied and computational technique is being developed to obtain some results on the aggregation of molecular clustering in the liquid state. The properties of hard sphere provide the theoretical backbone of equations of state for real fluids. Extended scaled particle theory [1-3] is presently used to calculate thermodynamic measurable parameters. Since equation of state was designed to capture the packing interactions in a fluid. It would seem to be an ideal theory for calculating thermodynamic measurable parameters. The two parameters are necessary for real fluids, the radius and binding energy of molecule. Author [4-5] used equation of state for a strong repulsive potential together with a weak attractive potential.

The following set of parameters required for calculating ultrasonic wave velocity, density, and volume expansion coefficient using two parameters along with suitable ζ as a solver. It is 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 scaled particle theory containing single parameters have limited success. Different cavity is required to reproduce thermodynamic property. Because hard sphere model for real fluids is not sufficient and significant to reproduce density and velocity data simultaneously. Hence it is necessary to use equation of state which contains minimum two model parameter. Author modifies basic scaled particle theory by introducing hard sphere cavity diameter along with the concept of binding energy.

Here equation of state is tested for real liquid at different temperature. Model parameters for water are associated by solving three equations assuming suitable average real molecular weight of cluster. Naturally these model parameters for real liquid have simple correspondence with thermodynamic properties such as ultrasonic velocity, bulk density and volume expansion coefficient. Molecular weight of cluster comes out to be a real number and temperature dependant.

2. Mathematical model for real Fluid:

Now hard sphere system can be considered as an ideal liquids and it is a simple for thermodynamic study. A compressibility factor Z for fluid of Lennard-Jones molecules enclosing in a cavity diameter (d) is defined as

$$Z(\eta,\beta\varepsilon)=\frac{\beta P}{\varsigma\rho}\quad,\ \beta=\frac{1}{k_B T}\ ,\beta\varepsilon=\frac{\tau}{T}\ \ ,\tau=\frac{\varepsilon}{k_B},\quad \eta=\frac{v}{V}=\frac{\pi\rho d^3}{6}\ ,0<\zeta<1 \tag{1}$$

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, ζ as solver 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.

Final expression for extended scaled particle theory an equation of state for a real fluid is expressed as

$$\frac{\beta P}{\varsigma\rho}=Z(\eta,\beta\varepsilon)=Z_0(\eta,\beta\varepsilon)+Z_1(\eta,\beta\varepsilon) \tag{2}$$

Where,

$$Z_0=\frac{\left[1+(2-m)\eta+(3-2m)\eta^2\right]}{(1-\eta)^2(1-m\eta)}\quad ;Z_1=\frac{\left(f_1\beta\varepsilon+f_2\beta^2\varepsilon^2\right)(m-4)\eta}{(1-mn)}\ ;\ m=3/4 \tag{3}$$

and

$$f_1=-3\left[\left(\frac{4}{9}\right)\alpha^{12}-\left(\frac{4}{3}\right)\alpha^{6}\right]\qquad ;\ f_2=\left(\frac{3}{2}\right)\left[\left(\frac{16}{21}\right)\alpha^{24}-\left(\frac{32}{15}\right)\alpha^{18}+\left(\frac{16}{9}\right)\alpha^{12}\right] \tag{4}$$

It is important to note that in above eq. (3) nearest pole η_{max} is 1/m or 1.Now relation (4), d = α σ, for α^6 = 3.0 and m=3/4, we have.

$$Z_0=\frac{\left[1+\left(\frac{5}{4}\right)\eta+\left(\frac{3}{2}\right)\eta^2\right]}{\left[(1-\eta)^2\left(1-\left(\frac{3}{4}\right)\eta\right)\right]};\ Z_1=\frac{-\left(\frac{3432}{35}\right)\beta^2\varepsilon^2\eta}{\left(1-\left(\frac{3}{4}\right)\eta\right)} \tag{5}$$

Here α, d and σ are arbitrary constant, hard sphere diameter and Lennard-Jones parameter respectively.

The other thermodynamically derivable expression is as given below.

$$\frac{Mu^2}{\varsigma\gamma RT} = \frac{\partial(Z\eta)}{\partial\eta} = y = y_0 + y_1 \tag{6}$$

For α^6 =3.0, and m=3/4 we have

$$y_0 = \frac{(-56\eta - 33\eta^2 + 75\eta^3 - 16)}{(-1+\eta)^3(-4+3\eta)^2} \quad ; y_1 = \frac{(13728/35)\beta^2\varepsilon^2\eta(-8+3\eta)}{(-4+3\eta)^2} \tag{7}$$

, and

$$\frac{Mu^2\alpha T}{\varsigma\gamma RT} = \frac{\partial(ZT)}{\partial T} = x = x_0 + x_1 \tag{8}$$

For α^6 =3.0, and m=3/4 we have

$$x_0 = \frac{\left[1 + \left(\frac{5}{4}\right)\eta + \left(\frac{3}{2}\right)\eta^2\right]}{\left[(1-\eta)^2\left(1 - \left(\frac{3}{4}\right)\eta\right)\right]} \quad ; x_1 = \frac{(3432/35)\beta^2\varepsilon^2\eta}{(1-(3/4)\eta)} \tag{9}$$

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

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

3.0 Generalization:

Hence we have following general set of equations containing thermodynamic reduced variable [η, τ], containing solver ζ.

$$\frac{\beta P}{\varsigma\rho} = Z(\eta, \beta\varepsilon) = \xi(\eta, \tau) \tag{10}$$

$$\frac{Mu^2}{\varsigma\gamma RT} = \frac{\partial(Z\eta)}{\partial\eta} = \psi(\eta, \tau) \tag{11}$$

$$\frac{Mu^2\alpha T}{\varsigma\gamma RT} = \frac{\partial(ZT)}{\partial T} = \omega(\eta, \tau) \tag{12}$$

We define Ordering= [1-ζ] and E-parameter = [1-ζ]R. For gas phase we have ordering tends to minimum, and entropy tends to maximum, while in liquid state ordering tends to maximum, and entropy tends to minimum.

RESULTS

The results are obtained by solving equations (2, 6, 8) containing two model parameters [η, β ε], with solver ζ. The thermodynamic related parameters are presented in (table- 1).

From table-2 it is observed that for m=3/4, with nearest pole η_{max}=1.0, as temperature increases [283.15 < T< 353.15], solver changes [0.9085593156e-5 < ζ < 0.6852510501e-2] corresponding to reduced density [0.9752855602> η> 0.8148808797] and cavity [1.909386296 > radius (AU) > 1.815426708], for water.

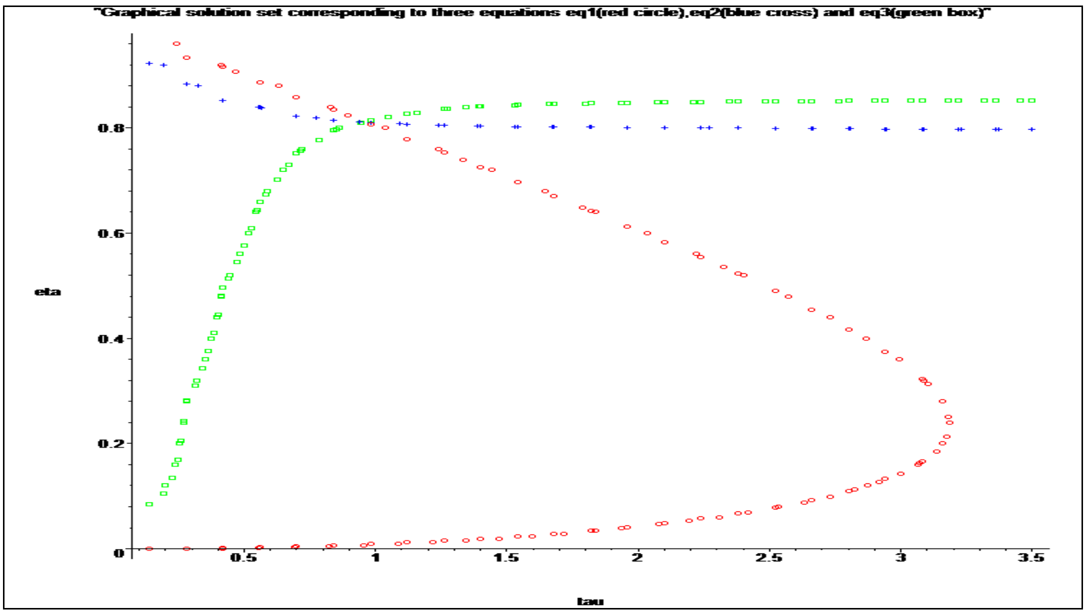
From table-3 it is observed that for m = 4/3, with nearest pole η_{max}=0.75, as temperature increases [283.15 < T< 353.15], cavity parameters remains fairly constant [0.3903103521e-6 < ζ < 0.7203254343e-5] corresponding to reduced density [0.7499608766> η> 0.7499059873], and [1.749293729 < radius (AU) < 1.765832957], for water.

DISCUSSION

Extensive ab-initio calculations have been performed in past [6] for several possible structures of water clusters [$(H_2O)_n$; 8 < n < 20]. Infrared molecular beam depletion and fragment spectroscopy has also been employed [7] to study the absorption behavior of small water clusters [$(H_2O)_{n;}$ 2 < n < 5]. In order to obtain unique choice in terms of [η, $\beta\,\varepsilon$] model input parameters solver ζ is chosen. In the present work it is necessary to accept the choice of 0 < ζ < 1.0. It is observed that basic model parameters [η, $\beta\,\varepsilon$] are depends upon the solver ζ and thermodynamic variables. Present type of calculations is useful for above fluid where molecular weight (thermodynamic inertia!) can be easily [10, 11] estimated. In the present model calculations, it is easy to imagine the size of cavity at different temperatures.

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. It is possible to conclude that minimum size of molecular cavity can be easily estimated at a given temperature using computer algebra so that at least three thermodynamic properties could be reproducing with deeper insight in liquid state. Present study show that water molecules can fill even small cavities at equilibrium and thermodynamic conditions in terms of eq-2, eq-6 and eq-8. The stable water cluster is similar to earlier reported [8-9]. All of the stable structures found in the spherical cavities have at least one hydrogen bond per water molecule. Water-cluster distribution with respect to temperature in the liquid phase gives idea of breaking of cluster. In this paper, the author [4-7] attempted to apply previously extended scaled particle approach to the Lennard-Jones fluid. Model contains two adjustable parameters [10, 12] except for the parameters in the Lennard-Jones potential.

Graph-1(a): Graphical solution set corresponding to three equations eq2 (red circle),eq6 (blue cross) and eq8 (green box), for m=3/4, with nearest pole η_{max}=1.0, $Y_{axis} = \eta$, $X_{axis} = \tau$, temp =353.15



Graph-1(b): Graphical solution set corresponding to three equations eq2 (red line), eq6 (blue line) and eq8 (green line), for m=3/4, with nearest pole η_{max}=1.0, $Y_{axis} = \eta$, $X_{axis} = \tau$, temp =353.15

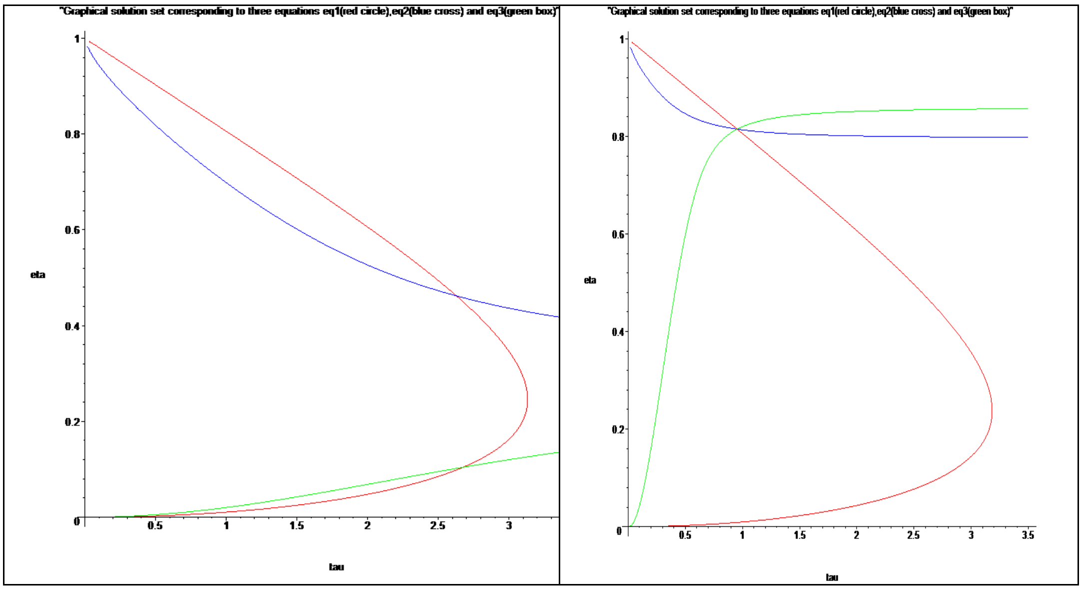


Table: 1 –Measured thermodynamic property for water

S. No	Vel.	Den.	Temp.	αx10-4	γ
1	144800	0.99973	283.15	0.89	1.0041
2	148300	0.99823	293.15	2.08	1.0065
3	151000	0.99568	303.15	3.04	1.0157
4	153000	0.99225	313.15	3.90	1.0254
5	154400	0.98807	323.15	4.65	1.0399
6	155200	0.98324	333.15	5.22	1.0547
7	155500	0.97781	343.15	5.86	1.0694
8	155500	0.97183	353.15	6.43	1.0861

There are four real roots for m=3/4, with nearest pole η_{max}=1.0, temp =353.15;

η=0.8148808803,τ=0.9532552778	η = 1.452014437, τ = 2.205741731
η =0.8148808803,τ =-0.9532552778	η = 1.452014437, τ =-2.205741731

, and four complex roots are

η = 1.033689879+.2426270542*I, τ = 0.1975742552+1.241860765*I	η = 1.033689879-.2426270542*I, τ = 0.1975742552-1.241860765*I
η = 1.033689879+.2426270542*I, τ = -0.1975742552-1.241860765*I	η = 1.033689879-.2426270542*I, τ = -0.1975742552+1.241860765*I

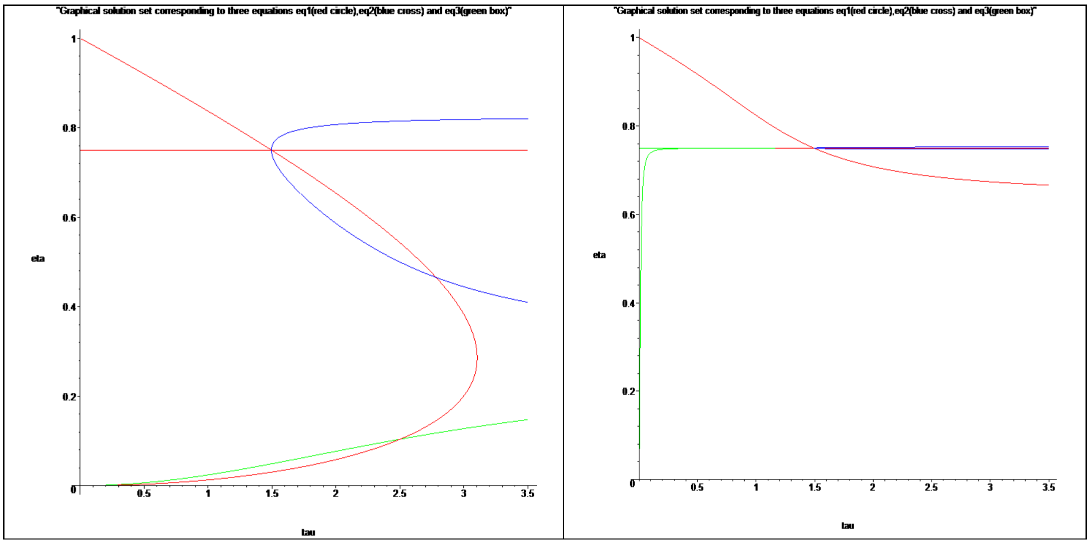
Above roots are belong to fallowing set of equations.

$$\frac{\beta P}{\varsigma\rho} = Z(\eta, \beta\varepsilon) = 0.09324849783;$$

$$\frac{Mu^2}{\varsigma\gamma RT} = \frac{\partial(Z\eta)}{\partial\eta} = 1991.794563;$$

$$\frac{Mu^2\alpha T}{\varsigma\gamma RT} = \frac{\partial(ZT)}{\partial T} = 452.2876467$$

Graph-1(b): Graphical solution set corresponding to three equations eq2 (red line), eq6 (blue line) and eq8 (green line), for m=4/3, with nearest pole η_{max}=0.75, $Y_{axis} = \eta$, $X_{axis} = \tau$, temp =353.15



There are four real roots for m=4/3, with nearest pole η_{max}=0.75, temp =353.15; .

η=0.7499059873,τ=1.495790436	η = 1.018271852,τ = 0.1159330719
η=0.7499059873,τ=−1.495790436	η = 1.018271852,τ =-0.1159330719

, and four complex roots are

η =0.9908935895+ 0.1623462081e-1*I, τ =0.5825164227e-1-0.1026501152*I	η =0.9908935895- 0.1623462081e-1*I, τ =0.5825164227e-1+0.1026501152*I
η =0.9908935895+ 0.1623462081e-1*I, τ =-0.5825164227e-1+0.1026501152*I	η =0.9908935895- 0.1623462081e-1*I, τ =-0.5825164227e-1-0.1026501152*I

Above roots are belong to fallowing set of equations.

$$\frac{\beta P}{\varsigma\rho} = Z(\eta,\beta\varepsilon) = 88.70800238\,;$$

$$\frac{Mu^2}{\varsigma\gamma RT} = \frac{\partial(Z\eta)}{\partial\eta} = 0.1894809256*10^7\,;$$

$$\frac{Mu^2\alpha T}{\varsigma\gamma RT} = \frac{\partial(ZT)}{\partial T} = 430264.6645$$

Table: 2 –Output parameter for water with assumed two-thermodynamic model parameters Lennard-Jones for water with parameter m=3/4 corresponds to η_{max}< 1.0

S.No	Temp	ζ	η	τ	radius	Ordering	E
1	283.15	0.9085593156e-5	0.9752855602	0.1268205727	1.909386296	0.9999909144	83139244.62
2	293.15	0.1371934774e-3	0.9422784045	0.2963904830	1.888543466	0.9998628065	83128593.73
3	303.15	0.4896385736e-3	0.9152580963	0.4355561104	1.871911777	0.9995103614	83099291.45
4	313.15	0.1157128212e-2	0.8907326420	0.5620488295	1.857175155	0.9988428718	83043796.36
5	323.15	0.2146678127e-2	0.8689250164	0.6745891967	1.844487178	0.9978533219	82961525.18
6	333.15	0.3266355700e-2	0.8514656959	0.7646834357	1.835044712	0.9967336443	82868435.19
7	343.15	0.4923478163e-2	0.8323146005	0.8634484462	1.824547291	0.9950765218	82730662.02
8	353.15	0.6852510501e-2	0.8148808797	0.9532552805	1.815426708	0.9931474895	82570282.28

Table: 3 - Output parameter for water with assumed Lennard-Jones two-thermodynamic model parameters for water with parameter m=4/3 corresponds to η_{max}< 3/4

S.No.	Temp.	ζ	η	τ	radius	Ordering	E
1	283.15	0.3903103521e-6	0.7499608766	1.498056385	1.749293729	0.9999996097	83139967.55
2	293.15	0.1019627368e-5	0.7499581127	1.496333775	1.750167338	0.9999989804	83139915.23
3	303.15	0.1665562244e-5	0.7499544077	1.495950930	1.751657277	0.9999983344	83139861.52
4	313.15	0.2411021996e-5	0.7499494023	1.495790748	1.753669425	0.9999975890	83139799.55
5	323.15	0.3269331657e-5	0.7499426911	1.495725214	1.756133655	0.9999967307	83139728.19
6	333.15	0.4150398939e-5	0.7499349441	1.495710713	1.758998472	0.9999958496	83139654.94
7	343.15	0.5474122275e-5	0.7499228030	1.495730328	1.762238993	0.9999945259	83139544.88
8	353.15	0.7203254343e-5	0.7499059873	1.495790436	1.765832957	0.9999927967	83139401.12

CONCLUSION

There are numerous results in literature, including simulations and theoretical models, but the author has obtained qualitative results, and hence cannot be compared with experiments and other models in literature. More important is that, it is an easy way to imagine thermodynamic cavity in terms of solver ζ and eq-10, eq-11 and eq-12.

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