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Equation of state for pure fluids at critical temperature

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In this paper, we employ the concept of probability for creating a cavity with diameter d in fluid along with the perturbation and variation approach, and develop an equation of state (EOS) for a hard sphere (HS) and Lennard–Jones (LJ) fluids. A suitable axiomatic form for surface tension $S(r)$ is assumed for the pure fluid, with r as a variable. The function $S(r)$ has an arbitrary parameter m. $S(r) = A + B(d/r)/[1 + m(d/r)]$. We use the condition in terms of radial distribution function $G(\lambda d, \eta)$ containing the self-consistent parameter λ and the condition of continuity at $r = d/2$ to determine A and B. A different EOS can be obtained with a suitable choice of m and the EOS has a lower root-mean-square deviation than that of Barker–Henderson BH2 for LJ fluids.

Keywords: equation of state, Lenard–Jones potential, hard-sphere potential, liquid mixture

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1. Introduction

The hard sphere can serve as a basic reference system for many perturbation and variation theories.[1−3] There exists a close connection between the thermodynamic and structural properties of model fluids. With suitable approximations, the bulk and structural properties of liquids may be studied. In perturbation and variation theories it is observed that, at high temperatures, only the repulsive part of potential is prominent, while at lower temperatures the attractive part becomes appreciable.

For intermolecular potentials, all of the thermodynamic functions may be expressed in terms of the contact values of the radial distribution functions (RDF). The expressions are particularly simple for hard-core fluids, since in that case the internal energy reduces to that of an ideal gas, while in the pressure equation it is only the contact values rather than the full RDF that appears explicitly. Therefore, knowledge of the contact values $g(\sigma)$ of the RDF in hard-core fluids where σ is the separation at contact between the centers of two interacting fluid particles is sufficient to obtain the equation of state (EOS) of these systems.

In the present formulation, the EOS and expressions for the contact values of the RDF are determined. The use of a precise and well-defined probability distribution function[4−7] in a perturbation theory opens up the possibility of deriving a simple method for the determination of the thermodynamic properties of a more realistic model. We assume the surface tension as some arbitrary function $S(r)$ of cavity radius r.

This paper is organized as follows. In Section 2 the partition function approach is used to computate the probability distribution function and related work is done. Subsection 2.2 deals with the thermodynamic work done. The EOS and the expression for surface tension are derived using algebra. The necessary calculation is presented in Subsection 2.3. Section 3 is devoted to the results corresponding to different values of an arbitrary parameter m and the self-consistent parameter k_c. Lastly Section 4 contains the discussion and conclusion pertaining to the derived EOS.

2. Formulation of work done

Consider the formation in a hard sphere fluid of a cavity of radius r. Let $\rho G(r, \eta)$ be the concentration of the centers of the spheres on the surface of the cavity. Reduced number density is given by $\eta = (\pi/6)\rho d^3$. The cavity plays exactly the role of the hard sphere of diameter $(2r - d)$, since it excludes the centers of other particles from the spherical region. The function $G(r, \eta)$ may be calculated through the thermodynamic probability considerations. $\mathrm{d}p_c(r) = 4\pi r^2 \rho G(r, \eta)\mathrm{d}r$ is the conditional probability that a particle is found in the spherical shell of thickness $\mathrm{d}r$ at distance r from the center of the cavity.

For a hard sphere the probability that a cavity of radius $r < d/2$ is empty is $p(r) = 1 - (4/3)\pi r^3 \rho$, since one particle, at most, may be located there.

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The probability,[8] that a spherical shell contains the molecule may be represented as

$$-\mathrm{d}p(r) = p(r)\cdot \mathrm{d}p_{\mathrm{c}}(r) = p(r)\left[\rho G(r,\eta)4\pi r^2\,\mathrm{d}r\right].$$

Here $\mathrm{d}p_{\mathrm{c}}(r)$ is related to a small amount of reversible work done $\mathrm{d}W(r)$, and it is given by a simple relation[2]

$$\mathrm{d}p_{\mathrm{c}}(r) = \beta\,\mathrm{d}W(r).$$

2.1. Work done for $r \le d/2$

Let us consider a cavity of volume v in liquid having volume V about a specific point. The probability $p(v)$ of finding a molecule in the cavity may be expressed as

$$p(v) = v\rho, \quad \rho = N/V,$$

and the probability of the cavity being empty is $[1-p(v)]$.

We state general the expression[9] of probability $p(d)$ for the cavity being empty as

$$p(d) = \frac{\displaystyle\int_0^R \mathrm{e}^{-\beta u(r)}4\pi r^2\,\mathrm{d}r}{\displaystyle\int_0^R 4\pi r^2\,\mathrm{d}r},\ r \le d;$$
$$R = \left[\frac{3V}{4\pi}\right]^{1/3},\ \beta = \frac{1}{k_{\mathrm{B}}T}. \tag{1}$$

In the above equation, the interaction pair-potential $u(r)$ can be treated as hard sphere potential u_{HS} if $r < d$, and $u(r)$ is treated as the u_{LJ} potential for $r \ge d$. Therefore we have the interaction pair-potential,

$$u(r) = u_{\mathrm{HS}},\ r < d;$$
$$u(r) = u_1(r) = 4\epsilon\Big[\Big(\frac{\sigma}{r}\Big)^{12} - \Big(\frac{\sigma}{r}\Big)^{6}\Big],$$
$$\sigma = \alpha d,\ r \ge d, \tag{2}$$

where ϵ is the depth of the LJ potential, α relates the HS parameter d to the corresponding LJ parameter σ. With the help of the hard sphere potential, we define the following Heaviside function

$$\exp[-\beta u_{\mathrm{HS}}] = \mathrm{Heaviside}(r-d), \tag{3}$$

where $\mathrm{Heaviside}(r-d) = 0$ for $r < d$ and $\mathrm{Heaviside}(r-d) = 1$ for $r \ge d$.

We now evaluate $p(d)$ by removing higher order terms $O(d^6)$. The expression for probability $p(d)$ is stated as sum of two parts, $p_0(d)$ namely for hard sphere potential and $[p_1(d)$ and $p_2(d)]$ are grouped together as the LJ potential

$$p(d) = p_0(d) + [p_1(d) + p_2(d)] = 1 - \frac{d^3N}{R^3}f(\beta\epsilon),$$

where $p_0(d)$ is related to hard sphere parameter d, and $[p_1(d), p_2(d)]$ are related to the variable ϵ and d

$$p_0(d) = \left[1 - \frac{d^3N}{R^3}\right],\ p_1(d) = \left[\frac{F_1 d^3N}{R^3}\right],$$
$$p_2(d) = \left[\frac{F_2 d^3N}{R^3}\right],$$
$$F_1(\alpha) = \frac{4(\alpha^6-3)\beta\epsilon\alpha^6}{3},$$
$$F_2(\alpha) = -\frac{8\beta^2\epsilon^2\alpha^{12}(15\alpha^{12}-42\alpha^6+35)}{105},$$
$$f(\beta\epsilon) = 1 - F_1(\alpha) - F_2(\alpha).$$

Proposal 1 For a hard sphere, $p_0(r)$ is the probability[3] that a cavity is empty. A general expression for probability $p(r)$ can be given as

$$p(r) = p_0(r) + [p_1(r) + p_2(r)]$$
$$= 1 - \frac{r^3N}{R^3}f(\beta\epsilon), \quad r \le d/2. \tag{4}$$

And the probability that a spherical shell contains the molecule may be represented as

$$-\mathrm{d}p(r) = p(r)\cdot \mathrm{d}p_{\mathrm{c}}(r) = p(r)\big[\rho G(r,\eta)4\pi r^2\,\mathrm{d}r\big],$$

where

$$p_0(r) = \Big[1 - \frac{r^3N}{R^3}\Big] = \Big[1 - \frac{(4\pi r^3/3)N}{V}\Big],$$
$$p_1(r) = \Big[\frac{F_1(\alpha)r^3N}{R^3}\Big],\ p_2(r) = \Big[\frac{F_2(\alpha)r^3N}{R^3}\Big].$$

In terms of reduced number density $\eta = (\pi/6)\rho d^3$ and number density $\rho = N/V$ (N is the Avogadro number), the above equation can be expressed as

$$p(r) = p_0(r) + [p_1(r) + p_2(r)] = 1 - \frac{8\eta r^3}{d^3}f(\beta\epsilon), \tag{5}$$

where

$$p_0(r) = \Big[1 - \frac{8\eta r^3}{d^3}\Big], \quad p_1(r) = \Big[\frac{8\eta F_1(\alpha)r^3}{d^3}\Big],$$
$$p_2(r) = \Big[\frac{8\eta F_2(\alpha)r^3}{d^3}\Big].$$

The relation[2] gives the reversible work $W(r)$,

$$\beta W(r) = -\ln[p(r)],\ r \le d/2, \tag{6}$$

necessary to create a cavity of radius r in the real fluid. $p(r)$, W, and G depend exclusively upon (r,η,ϵ). It is necessary that $W(r)$ is to be obtained by removing higher order terms $O(\eta^2)$, and splitting into two parts as follows:

$$\beta W = \beta W_0 + [\beta W_1 + \beta W_2],\ r \le d/2, \tag{7}$$

with

$$\beta W_0 = -\ln\Big[1 - \frac{8\eta r^3}{d^3}\Big],\ \beta W_1 = \Big[\frac{8\eta F_1(\alpha)r^3}{d^3}\Big],$$
$$\beta W_2 = \Big[\frac{8\eta F_2(\alpha)r^3}{d^3}\Big].$$

W_0 corresponds to the hard sphere interac-

tion potential, while $[W_1, W_2]$ relates to the the perturbing LJ potential part. Expression for $[(\mathrm{d}W_0/\mathrm{d}r), (\mathrm{d}W_1/\mathrm{d}r), (\mathrm{d}W_2/\mathrm{d}r)]$ can be written as

$$\beta\frac{\mathrm{d}W_0}{\mathrm{d}r} = \frac{24\eta r^2}{d^3[1-8\eta r^3/d^3]},$$
$$\beta\frac{\mathrm{d}W_1}{\mathrm{d}r} = \Big[\frac{24\eta F_1(\alpha) r^2}{d^3}\Big],$$
$$\beta\frac{\mathrm{d}W_2}{\mathrm{d}r} = \Big[\frac{24\eta F_2(\alpha) r^2}{d^3}\Big].$$

Normally $W(r)$ is related to the thermodynamic work done against external force (pressure) and internal force (surface tension). Combining Eqs. (4) and (6) we have

$$\frac{\mathrm{d}p}{p} = -\beta\mathrm{d}W = -4\pi\rho G(r,\eta) r^2\mathrm{d}r,\ r \le d/2. \quad (8)$$

Now we can express $G(r,\eta)$ as

$$G(r,\eta) = \frac{\beta}{\rho}\Big[\frac{\mathrm{d}W}{\mathrm{d}V}\Big] = \frac{1}{[1-8\eta r^3/d^3]} - F_1(\alpha) - F_2(\alpha),\ r \le d/2. \quad (9)$$

2.2. Work done for $r \ge d/2$

Work done is stated as

$$\mathrm{d}W(r) = P\mathrm{d}V - S\mathrm{d}A = k_\mathrm{B}T\rho G(r,\eta)\mathrm{d}V. \quad (10)$$

Here $\mathrm{d}A$ and $\mathrm{d}V$ are the increase in surface area and volume, respectively. For real fluid, hard sphere potential along with perturbing potential (LJ) contributes an effective net positive value for surface tension. The net positive value is for the surface tension S for LJ. Therefore, from the above equation we have the following expression for $G(r,\eta)$

$$G(r,\eta) = \frac{[P - 2S/r]}{\rho k_\mathrm{B}T}. \quad (11)$$

However, an EOS for a fluid in terms of hard sphere diameter d and binding energy ϵ is expressed[3] as

$$\frac{\beta P}{\rho} = [1 + 4\eta\ g(d)]. \quad (12)$$

Proposal 2 In order to improve the EOS we write the second proposal in terms of a modified condition as

$$g(d) = G(\lambda d, \eta);$$
$$\lambda = \exp\{-k_\mathrm{c}[F_1(\alpha) + F_2(\alpha)]\eta\}. \quad (13)$$

Because an empty sphere of radius d affects the remainder of the fluid precisely like another molecule, and λ is a self-consistent function. If $k_\mathrm{c} = 0$ then we have the old condition $g(d) = G(d,\eta)$. Thus equation (12) can be written as

$$\frac{\beta P}{\rho} = [1 + 4\eta\ G(\lambda d, \eta)]. \quad (14)$$

To proceed further, we need to know the dependence of r on surface tension $S(r)$. For surface tension, r is not too small but finite.

We assume[5] the following expression

$$S(r) = S_0\Big[1 + 2\delta\Big(\frac{d}{r}\Big)^m\Big],\ r \ge d/2, \quad (15)$$

where A and B are constants to be determined. The surface tension,[3] suggested by Kirkwood and Buff[6] can be obtained for $m = 1$ as

$$S(r) = S_0\Big[1 + 2\delta\Big(\frac{d}{r}\Big)\Big],\ r \ge d/2. \quad (16)$$

Both the expressions are normally satisfied by the following physical requirement! which seem to be not necessary

$$\lim_{r\to\infty} S(r) = S_0 = \text{constant}. \quad (17)$$

Here efforts are taken to obtain the EOS by using the algebraic method. As a starting point, we now assume different functional forms, which satisfy the above Eq. (17)

$$S(r) = A + \frac{B(d/r)}{[1 + m(d/r)]},\ r \ge d/2, \quad (18)$$

by substitution of $S(r)$, we obtain the corresponding $G(r)$ as given below

$$G(r,\eta) = \frac{\beta P}{\rho} - \frac{d}{r}A - \frac{(d/r)^2 B}{[1 + m(d/r)]},\ r \ge d/2.$$

For $r/d = \lambda$ we have the following result

$$G(\lambda d, \eta) = \frac{\beta P}{\rho} - \frac{A}{\lambda} - \frac{B}{\lambda^2(1 + m/\lambda)},\ r \ge d/2.$$

2.3. Evaluation of parameters A and B

We use the continuity condition [$G(r,\eta)$ and $\mathrm{d}G(r,\eta)/\mathrm{d}r$] for the evaluation of A and B at $r = d/2$ (contact point). We have the expression for $G(r)$

$$G(r,\eta) = \frac{1}{[1-8\eta r^3/d^3]} + F_1(\alpha) + F_2(\alpha),\ r \le d/2.$$

We also have the following expressions for $G(r)$

$$G(r,\eta) = -\frac{1}{(-1+4\eta)} + \Big[\frac{4\eta}{(\lambda+m)(-1+4\eta)} + \frac{4\eta m}{\lambda(\lambda+m)(-1+4\eta)} - \frac{d}{r}\Big]A + \Big[\frac{4\eta}{\lambda(\lambda+m)(-1+4\eta)} - \frac{(d/r)^2}{[1+m(d/r)]}\Big]B,\quad r \ge d/2.$$

The values for A and B are worked out for $(\alpha)^6 = 3/2$ as follows:

$$A = A\,\mathrm{sol}(0)_m + A\,\mathrm{sol}(1)_m,$$
$$B = B\,\mathrm{sol}(0)_m + B\,\mathrm{sol}(1)_m \quad (19)$$

with

$$A\,\mathrm{sol}(0)_m = \frac{-(3/2)[-4\eta m^2 + 6\lambda\eta m^2 + \lambda m + 6\lambda^2\eta m + 2\lambda\eta m - 4\eta m + \lambda^2 + 2\eta\lambda^2 - \eta]\eta}{(\eta-1)^2(4\eta\lambda^2 + \eta - 4\eta\lambda - \lambda^2 - \lambda m)},$$

$$A\,\mathrm{sol}(1)_m = \frac{-(1+m)(\lambda+m)(-1+4\eta)F_1(\alpha)\lambda}{(4\eta\lambda^2 + \eta - 4\eta\lambda - \lambda^2 - \lambda m)},$$

$$B\,\mathrm{sol}(0)_m = \frac{(3/4)(1+2m)^2(\lambda+m)(3\lambda-2)\eta^2}{(\eta-1)^2(4\eta\lambda^2 + \eta - 4\eta\lambda - \lambda^2 - \lambda m)},$$

$$B\,\mathrm{sol}(1)_m = \frac{(1/4)(1+2m)^2(\lambda+m)(-1+4\eta)F_1(\alpha)\lambda}{(4\eta\lambda^2 + \eta - 4\eta\lambda - \lambda^2 - \lambda m)},$$

the zero represents the reference potential and one is used for the perturbing LJ potential. The EOS for model fluid can now be stated as

$$\frac{\beta P}{\rho} = Z(\mathrm{SBK}) = [\,\mathrm{eq}(0)_m + \mathrm{eq}(1)_m]. \tag{20}$$

In the above equation if the perturbing LJ potential is absent then the equation is obtained for hard sphere liquid. On the other hand, if we introduce a perturbing LJ potential, the equation represents LJ liquid only, and the hard sphere reference potential does not have any role to play

$$\mathrm{eq}(0)_m := \frac{-\lambda^2 - \lambda m + [1 + (-4-2m)\lambda + 2\lambda^2]\eta + [6m + 2 + (-2-9m)\lambda - \lambda^2]\eta^2}{[(4\lambda^2 + 1 - 4\lambda)\eta - \lambda^2 - \lambda m](1-\eta)^2},$$

$$\mathrm{eq}(1)_m = \frac{-(-1 + 4\lambda m + 4\lambda)\eta[F_1(\alpha) + F_2(\alpha)]}{[(4\lambda^2 + 1 - 4\lambda)\eta - \lambda^2 - \lambda m]}.$$

3. Results

In this section we have carried out a comparative study of compressibility factor Z for different EOSs. Results are presented in tabular form for hard spheres (Table 1) as well as for Lennard–Jones liquid (Table 2). In Table 1 $Z1 = Z(\mathrm{SBK})_{m=1/3}$, $Z2 = Z(\mathrm{CS})$ denote different EOSs. And $Z1 = Z(\mathrm{SBK})_{m=0.16}$, $Z2 = Z(\mathrm{BH2})$ denote different EOSs in Table 2 only.

3.1. Case A: hard sphere potential

A comparative study (shown in Table 1) suggests that the presented EOSs give values of $Z(\mathrm{SBK})_{m=1/3}$ and agree well with $Z(\mathrm{MD})$.

Table 1. Equation of state (EOS) for hard-sphere potential [$m = 1/3$, $k_c = 0$].

Series number	η	Z(MD)	$Z1$(SBK)	$Z2$(CS)
1	0.052	1.24	1.24	1.24
2	0.105	1.55	1.55	1.55
3	0.157	1.96	1.97	1.97
4	0.209	2.52	2.52	2.52
5	0.262	3.27	3.27	3.26
6	0.314	4.29	4.29	4.28
7	0.367	5.71	5.70	5.71
8	0.419	7.73	7.71	7.75
9	0.471	10.70	10.63	10.75
10	0.524	15.00	14.99	15.30

3.2. Case B: Lennard–Jones potential

Table 2 shows the comparison of the closeness of values of Z with molecular dynamics Z(MD) results.

For $m = 0.16$, $\alpha = (3/2)^{(1/6)}$, and $k_c = 0.59$, we have the following results for the EOS

$$\frac{\beta P}{\rho} = Z(\mathrm{SBK}) = \mathrm{eq}(0)_{0.16} + \mathrm{eq}(1)_{0.16}, \tag{21}$$

and

$$\lambda = \exp[k_c(F_1(\alpha) + F_2(\alpha))\eta] = \exp\Big[-k_c\Big(-3\beta\epsilon - \frac{69}{70}\beta^2\epsilon^2\Big)\eta\Big]$$

with critical constants $\eta_c = 0.16003719349$, $(\beta\epsilon)_c = 0.751758102119$. It is observed that the rms-deviation(SBK) = 0.0378686854701 while the rms-deviation(BH) = 0.041593.

Table 2. Self-consistent EOS for LJ fluid at critical temperature [$m = \eta_c = 0.16004$, $k_c = 0.59$].

Series number	η	Z(MD)	$Z1$(SBK)	$Z2$(BH)
1	0.052	0.72	0.76	0.74
2	0.105	0.50	0.55	0.52
3	0.157	0.35	0.38	0.36
4	0.209	0.27	0.30	0.26
5	0.262	0.30	0.35	0.27
6	0.288	0.41	0.45	0.35
7	0.340	0.80	0.86	0.74
8	0.393	1.73	1.71	1.64
9	0.445	3.37	3.34	3.36
10	0.497	6.32	6.34	6.32

Table 3 shows a good closeness in comparison with $Z2$(BH) in terms of rms deviation.

Table 3. Comparison of the parameters for the EOS for Lennard–Jones fluid.

Series number	m	k_{c1}	η_c	ϵ_c	rms deviation
1	0.1600	−0.0588	0.16004*	0.75179	0.03780
2	0.1667	−0.0588	0.15983	0.75149	0.03763
3	0.1667	−0.0588	0.15984	0.75144	0.03761
4	0.1748	−0.0588	0.15958	0.75120	0.03755
5	0.1600	−0.0590	0.16004*	0.75176	0.03787

4. Conclusion

It is thus seen that we have obtained the same mathematical result, for a physical property such as compressibility factor $(\beta P/\rho) = Z$(SBK), which corresponds to the present axiomatic form. With [$m = 0.33$, $k_c = 0$] and [$m = 0.16$, $k_c = 0.59$] for Z(HS), Z(LJ) respectively in the above formulation, for entire density region there is close agreement with Z(MD) results. It is also possible to obtain exactly the same EOS with a different arbitrary approximation in terms of the surface tension expression $S(r)$ for the contact values of the $G(\lambda d, \eta)$. It is very difficult to assume or prove that arbitrary real number m plays the role of a pole, which is related to a maximum packing fraction or a self-consistent parameter as seen from Table 3 with $*$ marked entries. If we select $k_c =$ arbitrary, $m = \eta_c$ then one may say that the present formulation is self-consistent in nature. The induction of λ opens up a density and temperature-dependent view at the contact point of molecules in fluid state, though they are interacting through the same pair potential.

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