A New Equation of State Based on Hole Theory : Application to Low Molecular Weight Materials[1]

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ABSTRACT

A new equation of state previously developed by equally partitioning hole volume into each segment was applied to low molecular weight materials. Application to these materials showed that the PVT surface of this EOS was unaffected by chain length, thus this EOS conforms to the principle of corresponding state theory.

This EOS described properly the pressure effects like in the case of polymer melts. It is found that the cell volume assumed by this EOS is much larger than that of SS model. This is because more free volume is given to segment at the same reduced temperature and pressure.

KEY WORDS : hole theory, cell theory, equation of state, principle of corresponding state

INTRODUCTION

It is well known that liquid state has both properties of gas and solid state. For the intermolecular distance, liquid state is similar to solid state. But like gas state, molecules in liquid state share all the volume of system with each other, and there exist some holes between molecules[1,2].

The basic approaches to describe these properties of liquid state are divided into two branches; one is derived from the ideal gas state and the other is based on crystal structure. Free volume theories are based on the crystal structure. In these theories volume is divided into N cells and the cell volume is allowed to change under the influence of pressure and temperature. There could be some holes or vacant cells(hole theory)[3-5], or none(cell theory)[6,7]. In the cell theory, volume change is explained by the change of cell volume only, while in the hole theory major change in volume is described by the number of holes and the change of cell size plays a minor role. The example of this type is the model developed by Simha and Somcynsky[3]. They introduced the concept of free length and that of liquid was obtained by linear superposition between "solid-like" term and "gas-like" term. Their equation of state(EOS) was successfully applied in describing PVT relations of polymer melts[8] and low molecular weight[9,10], but cannot account for the pressure effect properly[9].

In this paper, the EOS of our previous work[11] was applied to low molecular weight. The description of the PVT relation of low molecular weight materials which are of finite chain length is affected by the structural parameter of EOS. In this EOS the PVT relation is nearly unaffected by these parameters and this EOS shows good description of pressure effect.

THEORY - RECAPITULATION

The physical meaning of free volume is the space into which the center of mass of a given molecule can move under the influence of intermolecular potential generated by neighboring segments around the center of the cell[7].

$$v_f = \int_{cell} \exp\left(-\frac{E(r)-E(0)}{kT}\right)dr \tag{1}$$

It is nearly impossible to obtain analytical expression for free volume by applying complicated intermolecular potentials except some cases. The well-known analytical expression for the case of ideal gas and square-well potential[6]

$$v_f = \omega \tag{2}$$

$$v_f = \omega - \lambda v^* \tag{3}$$

where ω, λ, and v^* are the cell volume, geometric factor, and hard-core volume respectively. The remaining problem in the hole theory is how to express free volume obtained by inserting hole using known free volume expression. Simha and Somcynsky, and other researchers used linear superposition between "solid-like" term(Eq. 3) and "gas-like" term(Eq. 2) according to occupied site fraction.

$$\begin{aligned} v_f = l_f^3 &= \left(y\left(\omega^{1/3} - 2^{-1/6} v^{1/3*}\right) + (1-y)\omega^{1/3}\right)^3 \\ &= \left(\omega^{1/3} - 2^{-1/6} v^{*1/3} + 2^{-1/6} v^{*1/3}(1-y)\right)^3 \end{aligned} \tag{4}$$

where occupied site fraction

$$y = \frac{sN}{sN + N_h} \tag{5}$$

As shown in Eq. 4 the additional free volume generated by hole is related to the hard-core volume and is not dependent on cell volume. It is good when hole fraction is high, that is, a segment is surrounded by holes(Fig. 1(b)). But for the case that hole fraction is low, the segment that moves into the hole at the same time can collide with each other if the hard-core volume is large. In other words, the larger the hard-core volume, the smaller the space that can be obtained by introduction of hole(Fig. 1(a)).

Linear superposition assumption leads to this result. In this assumption, free volume changes linearly according to hole fraction, and proportionality constant is hard-core volume.

In this paper, we did not stick to the notion of linear superposition between "gas-like" term and "solid-like" term because the cell model itself(with no holes) can describe the

thermodynamic properties successfully only with "solid-like" term. Instead, we divide free length into two terms : free length by cell model and additional free length generated by introduction of holes.

$$l_f = l_{f\cdot cell} + l_{f\cdot hole} \tag{6}$$

The square-well potential was used to evaluate the free length of cell model.

$$l_{f\cdot cell} = \omega^{1/3} - 2^{-1/6} v^{*1/3} \tag{7}$$

To obtain free length generated by hole all of the free length of hole was equally partitioned to each segment.

$$l_{f\cdot hole} = \frac{N_h}{N_s}\omega^{1/3} = \frac{1-y}{y}\omega^{1/3} \tag{8}$$

By inserting Eq. 7 and 8 into Eq. 6, we could obtain a new free volume expression.

$$v_f = l_f^3 = \left(\omega^{1/3} - 2^{-1/6} v^{*1/3} + \frac{1-y}{y}\omega^{1/3}\right)^3 \tag{9}$$

The concept of equi-partition of hole free length is depicted in Fig. 2. In Fig. 2 free volume added by hole is between solid and dotted lines.

EQUATION OF STATE

With the proposed free volume expression, we could obtain the new equation of state expression. In hole theories, the configurational partition function is factorized into three terms: combinatory, free volume and energy term.

$$Z = g v_f^{cN} \exp\left(-\frac{E_o}{kT}\right) \tag{10}$$

where g is combinatory factor and we used Flory's expression. E_0 is the internal energy and Prigogine's expression was used. Together with these expressions and free volume expression proposed here, EOS can be derived by following standard procedure of statistical thermodynamics. The resulting equation of state is

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\left(y\tilde{V}\right)^{1/3}}{\left(y\tilde{V}\right)^{1/3} - 2^{-1/6} y} + \frac{2y}{\tilde{T}}\left(\frac{1}{y\tilde{V}}\right)^2\left[1.011\left(\frac{1}{\left(y\tilde{V}\right)}\right)^2 - 1.2045\right] \tag{11}$$

$$\frac{s}{3c}\frac{1}{y}\left(\frac{s-1}{s}+\frac{1}{y}\ln(1-y)\right)+\frac{-\frac{2}{3y}\left(y\tilde{V}\right)^{1/3}}{\left(y\tilde{V}\right)^{1/3}-2^{-1/6}y}$$
$$=\frac{1}{6\tilde{T}}\left(\frac{1}{y\tilde{V}}\right)^{2}\left(2.409-3.033\left(\frac{1}{y\tilde{V}}\right)^{2}\right) \tag{12}$$

As shown above, Eq. 11 contains only reduced variables, while Eq. 12 contains structural parameters, $s/3c$ and $(s-1)/s$. Strictly speaking, this equation of state does not obey the principle of corresponding state because of these terms. But for a long chain molecules these terms converge limiting values, and it could be said that the principle of corresponding state could be applied to this model.

But for low molecular weight materials, the chain length is finite and the structural parameters depend on the chain length. To obey the principle of corresponding state, it is necessary that the PVT surface of EOS should not be affected by chain length.

RESULTS

The behavior of the new EOS was compared with Simha and Somcynsky model in Fig. 3. At high pressure, this EOS shows the same behavior as SS model. At low pressure, occupied site fraction in this model decreases faster than SS model. This affects free volume change with temperature(Fig. 3(b)).

For polymer melts, such behavior affects to the PVT calculation and this EOS showed good agreement with experimental data, especially at low pressure. For low molecular weight materials, chain length could affects the PVT surface of EOS via structural parameters, $s/3c$ and $(s-1)/s$. But as stated before, chain length should not affect the PVT surface to conform to the principle of corresponding state. The PVT surface of PSU175 are shown in Fig. 4. As shown in this figure, this EOS is not affected by chain length and conforms to the principle of corresponding state. In this paper the relation between chain length and external degrees of freedom is

$$3c = s+3 \tag{13}$$

This relation does not distinguish between terminal and middle segment. Furthermore, Eq. 13 is not appropriate to represent the external degrees of freedom of short chains. For this reason, we excluded those materials that have two or less segments in this paper.

In table 1, characteristic and molecular parameters are shown. These parameters were calculated from experimental PVT data. For two models, the accuracy is nearly the same. Characteristic temperature and volume of SS model is smaller than that of this model, indicating that this model is less sensitive to temperature than SS model.

From the view point of molecular parameters, this model assumes larger segment than SS model. This can be anticipated from the free volume. The free volume of this model is larger than that of SS model at the same reduced temperature and pressure. To represent real motion of segments, less holes should be introduced in this model compared with SS model. This leads to larger value of characteristic temperature in this model. Thus, the potential bowl represented by this model is deeper and wider than that of SS model

In Fig. 5, experimental data for PSU537 are plotted. At high pressure two models exhibit the same behavior, but at low pressure, SS model deviates from experimental data, which also was observed in our previous work. The materials considered here show the same behavior(Table 2).

CONCLUSION

In this paper, a new free volume and a new equation of state were applied to low molecular weight materials. This EOS conforms to the principle of corresponding state although chain length is finite. Larger segment is assumed in this model compared with SS model because free volume is larger than that of SS model at the same reduced temperature and pressure.

The new EOS derived in our previous work could reproduce PVT data of low molecular weight materials well. In particular, this new EOS shows good results at low pressure compared with SS model.

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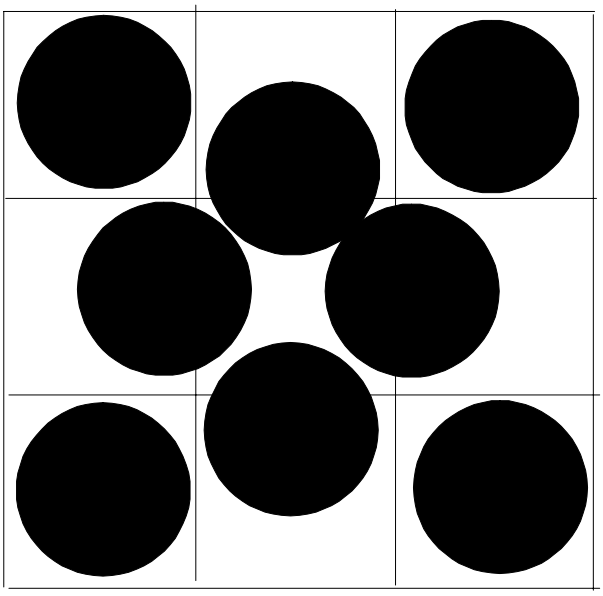

Fig. 1(a)

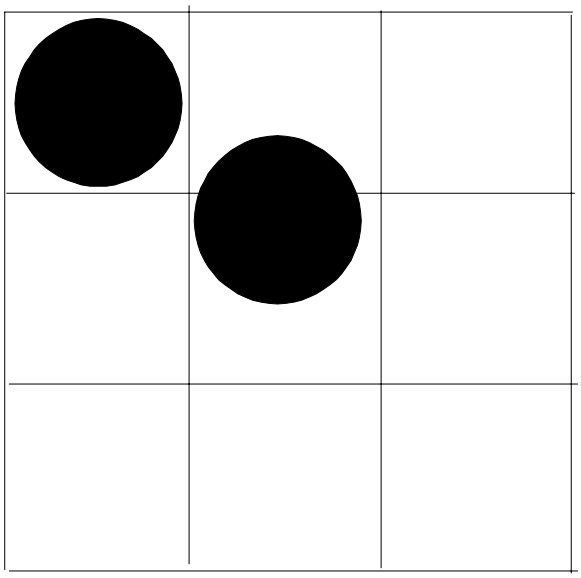

Fig. 1(b)

Fig. 1 Hole Model in the Limiting Cases((a) : Solid Region, (b) : Ideal Gas Region)

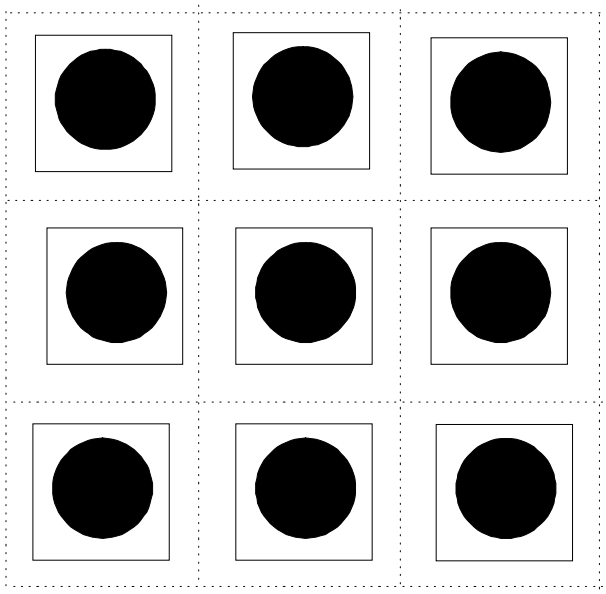

Fig. 2 Representation of Free Volume Obtained by Hole

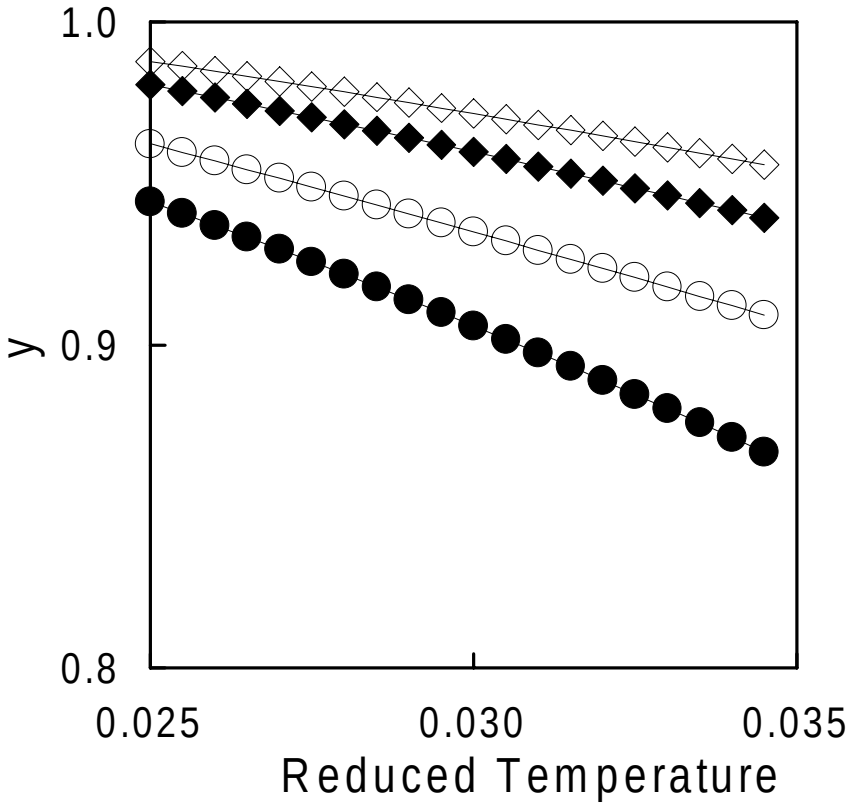

Fig. 3(a)

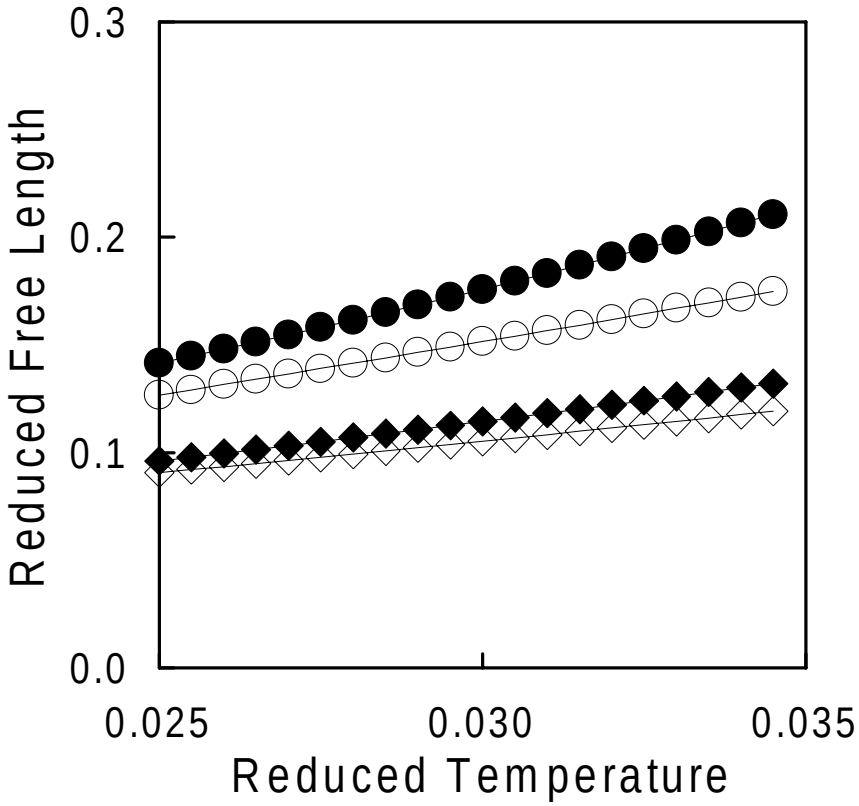

Fig. 3(b)

Fig. 3 Behaviors of EOS Derived in this paper

(● : this model at low pressure, ○ : SS model at low pressure,

◆ : this model at high pressure,◇ : SS model at high pressure)

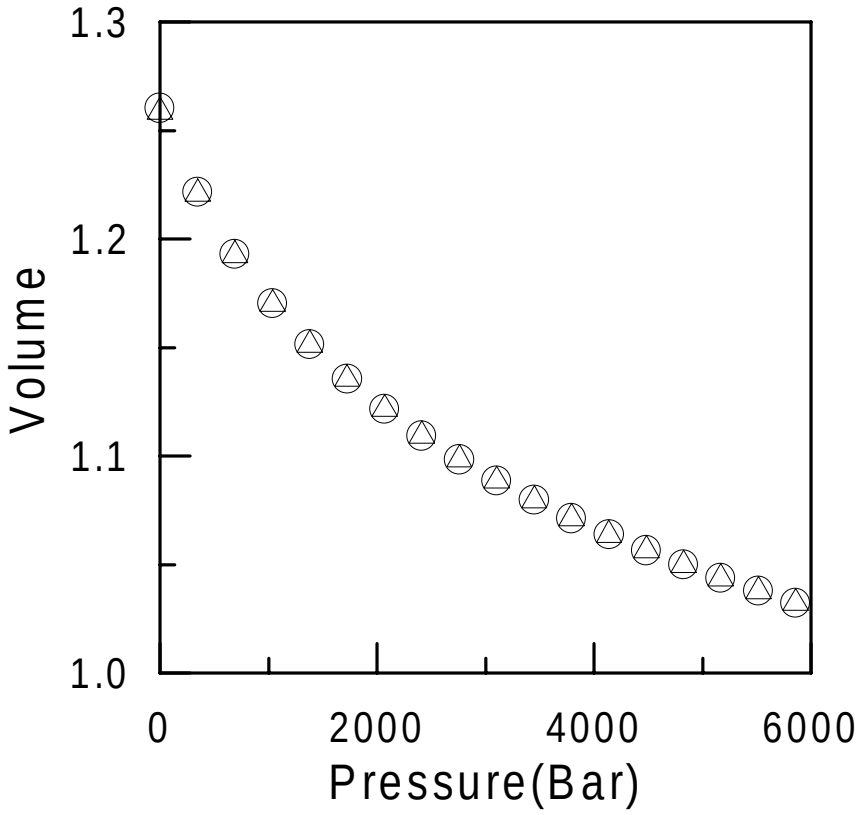

Fig. 4

Fig. 4 The Effect of Chain Length(△ : s=6, ○ : s = infinitive)

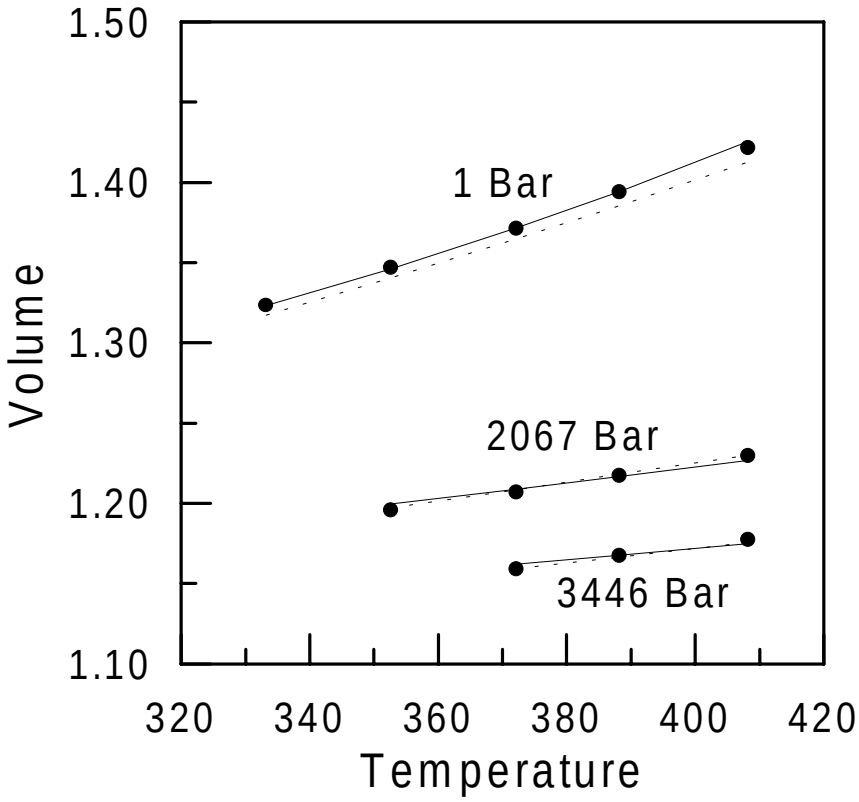
1.50
1.40
1.30
1.20
1.10
Volume
1 Bar
2067 Bar
3446 Bar
320
340
360
380
400
420
Temperature

Fig. 5(a)

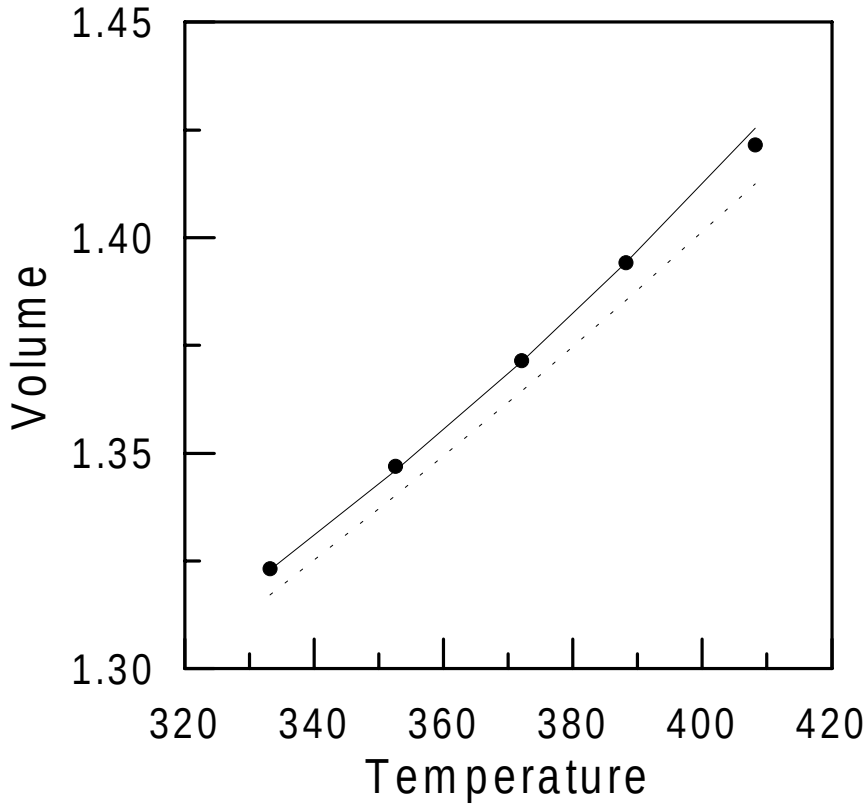

Fig. 5(b)

Fig. 5 Volume versus temperature for PSU537(a) whole pressure range (b) at zero pressure (● : experimental data, solid line : this model, dotted line : SS model)

Table 1. Characteristic and Molecular Parameters of two Models

	$T^*(K)$	$P^*(Bar)$	$V^*(cm^3/g)$	$\varepsilon^*(J)\times10^{-21}$	$v^*(cm^3)\times10^{-22}$	Error(%)
This Model						
psu175	11280	7539	1.1505	7.99		0.075
psu532	9793	6471	1.2674	7.99	1.307	0.158
psu537	10211	6398	1.2561	7.68	1.258	0.122
SS Model						
psu175	8835	8605	1.1125	5.12	0.606	0.084
psu532	7417	7822	1.2087	4.79	0.632	0.155
psu537	7755	7771	1.199	4.78	0.631	0.128

psu175 : 1-alpha-Decalylpentadecane, psu532 : n-Pentadecane

psu537 : n-Octadecane[12]

Table 2. Deviation of densities at atmospheric pressure

	This model	SS model
psu175	0.0144	0.2910
psu532	0.1200	0.5395
psu537	0.0678	0.5421