Significant Liquid Structure Theory: Liquid-Vapour Transition

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Received 1 August 1977; accepted 22 October 1977

A reduced equation of state for real fluids has been obtained from Henderson's version of significant structure theory. Calculated critical constants are in fair agreement with the observed values.

On the basis of the cell model Henderson suggested an important modification of significant liquid structure theory. It consists of replacing the Einsteinian oscillator representing solid-like degree of freedom by the cell-model postulates of Lennard-Jones and Davonshire. Calculation of thermodynamic properties with the resulting partition function (Eq. 1) were made only for an idealized potential function, namely rigid sphere approximation

\[ Z = (f_0)^{N(V-V_s)/V} (f_1)^{N(V_s)/V} \left( 1 + n_h \exp \left( - \frac{\xi}{kT} \right) \right)^{N(V_s)/V} \]  

where

\[ f_0 = \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \left( \frac{eV}{N} \right) \]

\[ f_1 = \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \psi \exp \left( - \frac{\Psi(0)}{2kT} \right) \]

\[ \Psi(0) = \epsilon \left( \frac{V_s}{V} \right)^2 - 2.4 \left( \frac{V_s}{V} \right)^4 \]

and \( \psi = \frac{2\pi\sqrt{2}}{N} Vg \)

Properties of real fluids may, however, be evaluated in a straightforward manner by using Eq. (1). The calculated compressibility factor for argon was found to be in good agreement with the experimental values in the high pressure region.

Calculations

In the present study, we have employed Henderson's partition function to obtain a reduced equation of state for a real fluid. Our aim is to see how far this equation of state reproduces the liquid-vapour transition. By following the standard techniques, we have

\[ PV = \frac{N \epsilon}{kT} \left[ 1 - \ln \left( \frac{8 \xi}{kT} \right) + \frac{2Z \xi}{kT} \left( \frac{V_s}{V} \right) \right] \]

where

\[ B = \exp \left( \frac{\xi}{kT} \right) + n \left( \frac{V}{V_s} - 1 \right) \]  

In Eq. (2), \( \xi \) is the hole-molecule exchange energy, \( g, g_1 \), and \( g_2 \) are complicated integrals whose values are tabulated as a function of \( V/V* \) and \( kT/\epsilon \). \( V* = N\sigma^3 \), where \( \sigma \) is the hard sphere diameter and \( N \) is the Avogadro number.

For computational purposes it is necessary to know the hole-molecule exchange energy, \( \xi \). Previous workers had assumed that it is proportional to \( E_s \), the energy of sublimation of a solid at 0K, and inversely proportional to the number of holes, \( n_h \),

\[ \xi = \frac{aE_s}{V-V_s} \]

Here \( V \) is the liquid molar volume, \( V_s \) the molar volume of the solid at the melting point and \( a \) is a proportionality constant. The value of \( a \) is estimated in a semi-empirical way or, more often, it is treated as a parameter along with \( E_s \).

We may imagine that the molecules in a liquid are to be pushed away from their equilibrium positions so as to make a hole or a vacancy. In the displaced position, a molecule is not in a very stable condition; because of proximity with the neighbouring molecules, the displaced molecule will experience a repulsive force and its potential energy will be raised. It is, therefore, reasonable to make an approximation that holes are created predominantly against the repulsive part of the potential.

\[ \xi = \epsilon \left( \frac{V_s}{V} \right)^4 \]

where \( \epsilon \) is the Lennard-Jones potential depth.

Results and Discussion

Actual calculation of close-packed volume, \( V_0 = \frac{N\sigma^3}{\sqrt{2}} \), for argon, neon, krypton and xenon have been made from known collision diameters and it is found that the ratio \( V_s/V_0 \) for these substances is around 1.46 while the computer calculations of Alder and Wainwright indicate a phase-transition at \( V_s = 1.5 V_0 \) for rigid sphere systems. So \( V_s \) is approximately taken equal to \( V* \) in our calculations.

Finally we have taken \( n = 12 \), i.e. equal to the...
In order to locate the transition accurately, we have also computed the values of $g$, $g_L$ and $g_M$ at several values of $V/V^*$ and $T^*$ which have not been covered in the above mentioned literature source. We have obtained these by numerical integration using Gauss quadrature method and these are given in Table 2.

In Table 3 are included the excess entropy and energy values at the meeting point for argon.

![Graph](image-url)

**Fig. 1** — Plot of $pV^*/NkT$ against $V/V^*$ for different values of $T^*$

### Table 1 — Calculated and Observed Values of Critical Constants

<table>
<thead>
<tr>
<th>$T^*_c$</th>
<th>$v_i^* = V_i/V^*$</th>
<th>$p_i^<em>c/v_i^</em>$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed mean value for Ne, Ar, N₂</td>
<td>1·28</td>
<td>3·15</td>
</tr>
<tr>
<td>Present work</td>
<td>1·25</td>
<td>3·15</td>
</tr>
<tr>
<td>Henderson</td>
<td>1·41</td>
<td>3·39</td>
</tr>
<tr>
<td>LJD</td>
<td>1·30</td>
<td>1·77</td>
</tr>
</tbody>
</table>

†From ref. 8.

<table>
<thead>
<tr>
<th>$V/V^*$</th>
<th>$g$</th>
<th>$g_L$</th>
<th>$g_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^*_c = 1·20$</td>
<td>3·1500</td>
<td>0·1212</td>
<td>1·840</td>
</tr>
<tr>
<td></td>
<td>3·2526</td>
<td>0·1286</td>
<td>2·157</td>
</tr>
<tr>
<td></td>
<td>3·8809</td>
<td>0·1255</td>
<td>2·131</td>
</tr>
<tr>
<td></td>
<td>4·9494</td>
<td>0·1679</td>
<td>4·899</td>
</tr>
<tr>
<td></td>
<td>5·6568</td>
<td>0·1184</td>
<td>1·819</td>
</tr>
</tbody>
</table>

| $T^*_c = 1·25$ | 3·1500 | 0·1184 | 2·079 | 0·1341 |
| | 3·2526 | 0·1227 | 2·110 | 0·1382 |
| | 3·8809 | 0·1597 | 4·770 | 0·2351 |
| | 4·9494 | 0·1986 | 6·920 | 0·2987 |
| | 5·6568 | 0·2036 | 11·61 | 0·4049 |

| $T^*_c = 1·30$ | 3·1500 | 0·1159 | 1·803 | 0·1240 |
| | 3·2526 | 0·1286 | 2·157 | 0·1433 |
| | 3·8809 | 0·1679 | 4·899 | 0·2454 |
| | 4·9494 | 0·2036 | 11·61 | 0·4049 |

| $T^*_c = 1·40$ | 3·1500 | 0·1184 | 2·079 | 0·1341 |
| | 3·2526 | 0·1901 | 10·97 | 0·3784 |
| | 5·6568 | 0·1968 | 13·87 | 0·4304 |

| $T^*_c = 0·70$ | 1·780 | 0·8884 | 0·2707 | 0·5672 |
| | 1·0350 | 0·3351 | 0·5440 | 0·1215 |

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coordination number. This is in conformity with the solid-like environment, which is a necessary requirement to maintain, in the formulation of the partition function.

From Eqs. (2) and (3), the equation of state in a reduced form can be obtained as follows:

$$\frac{PV^*}{NkT} = \frac{V^*}{V} \left(\frac{V^*}{V}\right)^2 \ln \frac{2me^{\frac{1}{2}}}{\epsilon} g \frac{B}{kT} \left(1 + \frac{5}{4} \frac{\xi}{kT} \right)$$

$$\times \left(\frac{12V}{V^*} - \frac{4}{kT} \frac{\xi}{kT} \right) \left(\frac{\xi}{kT} + 2\frac{g_L}{g} \frac{\xi}{kT} \right) \left(\frac{V^*}{V}\right)^2 \left(1 - 2\frac{g_L}{g} \frac{\xi}{kT} \right) \left(\frac{V^*}{V}\right)^2 \left(1 - 2\frac{g_L}{g} \frac{\xi}{kT} \right)$$

$$\times \left(\frac{12V}{V^*} - \frac{4}{kT} \frac{\xi}{kT} \right) \left(\frac{\xi}{kT} + 2\frac{g_L}{g} \frac{\xi}{kT} \right) \left(\frac{V^*}{V}\right)^2 \left(1 - 2\frac{g_L}{g} \frac{\xi}{kT} \right) \left(\frac{V^*}{V}\right)^2 \left(1 - 2\frac{g_L}{g} \frac{\xi}{kT} \right)$$

...(3a)

where

$$B = \exp\left(\frac{\xi}{kT}\right) + 12 \left(\frac{\xi}{kT} - 1\right)$$

and

$$\frac{\xi}{kT} = \left(\frac{V^*}{V}\right)^2$$

Fig. 1 shows a plot of $pV^*/NkT$ against $V/V^*$ for four values of $T^*$ (1·20, 1·25, 1·30 and 1·40) calculated in accordance with Eq. (3a). It is seen that Eq. (3a) correctly reproduces liquid-vapour transition; the calculated critical constants agree reasonably well with the observed values as shown in Table 1.

The values of $g$, $g_L$ and $g_M$ required for the evaluation of $pV^*/NkT$ were taken from literature.
### Table 3 — Calculated and Observed Excess Entropy and Excess Energy Values for Liquid and Solid Argon

<table>
<thead>
<tr>
<th></th>
<th>Liquid argon</th>
<th>Solid argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced melting temp. ((T^*))</td>
<td>0.701</td>
<td>0.701</td>
</tr>
<tr>
<td>Reduced volume ((V/V^*))</td>
<td>1.178</td>
<td>1.035</td>
</tr>
<tr>
<td>Reduced excess entropy ((SE/Na))</td>
<td>-3.12(-3.64)†</td>
<td>-5.72(-5.96)†</td>
</tr>
<tr>
<td>Reduced excess energy ((UE/Ne))</td>
<td>-5.72(-5.96)†</td>
<td>-7.83(-7.14)†</td>
</tr>
</tbody>
</table>

†Values in parentheses are the observed values taken from ref. 2.

which were calculated using Eqs. (4) and (5).

\[
\frac{SE}{Na} = \frac{V^*}{V} \left[ \ln \frac{2\pi\sqrt{2}}{\epsilon} gB \frac{\xi}{kT} \exp \left( \frac{\xi}{kT} \right) + \frac{12}{T^*} \right]
\]

\[
\frac{UE}{Ne} = \frac{V^*}{V} \left[ 12 \left( \frac{0.5 + \xi}{g} \right) \left( \frac{V^*}{V} \right)^4 \frac{2gM}{g} \left( \frac{V^*}{V} \right)^2 \right] \times \left( \frac{V^*}{V} \right) - \frac{T^*\xi}{kT} \exp \left( \frac{\xi}{kT} \right) \right] \quad \ldots(5)
\]

It appears that the Eyring-Ree-Henderson theory takes into account, in an adequate manner, the effect of holes, without having to assume an explicit relationship between \(\psi_f\) and the number of holes.

### Acknowledgement

The authors are grateful to the Centre of Computer Science, University of Calcutta, for computer facility. They are also thankful to Shri C. Neogy, Department of Physics, Kalyani University, for help in computer programming in an initial stage.

### Symbols used

\(Z\) = partition function
\(m\) = mass of a molecule
\(k\) = Boltzmann constant
\(T\) = temperature in Kelvin
\(h\) = planck constant
\(\epsilon\) = base of natural logarithm
\(V\) = liquid molar volume
\(N\) = Avogadro number
\(\psi_f\) = molecular free volume
\(\phi(\sigma)\) = average potential energy at the centre of the cell
\(V/V^*, V/Na^*\) = reduced volume
\(T^*, kT/\epsilon\) = reduced temperature
\(V_s\) = solid molar volume at 0°K
\(g\) = Lennard-Jones potential depth
\(\sigma\) = hard sphere diameter
\(n\) = an adjustable parameter in significant structure theory, value close to 12

\(SE\) = excess entropy per mole
\(UE\) = excess internal energy per mole

\(g, g_L, g_M\) = auxiliary functions in the Lennard-Jones and Devonshire free volume theory of liquids

\(f_s, f_e\) = molecular partition function of solid-like and gas-like molecules

### References