Single partition function for three phases

(specific heat/Cv/critical properties/phase transitions)

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ABSTRACT The significant structures theory of liquids has been extended to take into account (i) translational degrees of freedom in the degeneracy term and (ii) the perturbation term which becomes important near the critical region. With these improvements, the calculated thermodynamic properties of argon agree very well with experimental results from the melting point through the critical point, along the coexistence curve as well as along the critical isochore and for the solid and the vapor.

The properties of simple liquids can be calculated from first principles (1). For complicated liquids one must resort to model calculations. A model is also useful if one is to write a single partition function that embraces all three phases, as we are undertaking to do in this study. The application of this model can be found in the book Significant Liquid Structures (2) and in the more recent literature for a wide variety of further applications (3).

The liquid state is intermediate between the solid and gaseous states and, therefore, it is to be expected that the thermodynamic properties of a liquid will be intermediate between those of its gaseous and solid states.

X-ray studies of liquids (4) indicate considerable short-range order with nearest neighbor distances only slightly different from those of solids. Therefore, for liquids one can speak of a quasi-lattice structure with the typical 12% expansion of a liquid due to the introduction of vacancies or holes into the structure.

The introduction of a molecule-sized hole requires an energy equal to the heat of vaporization. Such a molecule-sized hole will convert three vibrational degrees of freedom into three translations as it is cooperatively moved about by neighboring molecules. Because these molecule-sized holes will be distorted as they are moved about, they will be called "fluidized vacancies," or simply "vacancies" for short. Such vacancies moved about cooperatively by neighbors simulate the behavior of a gaseous molecule in having both the same energy and entropy. It is therefore to be expected that there should be as many vacancies per unit volume of liquid as there are molecules per unit volume of vapor, so that the sum of the densities of the liquid and vapor should be constant except for a linear drift toward lower mean densities with increasing temperature because of the thermal expansion of the lattice. This qualitative explanation of the experimental law of rectilinear diameters (5, 6) was first pointed out long ago (7). On the average, a vibrating molecule will be stopped by a nearest neighbor in a fraction of the oscillations Vw/V. Consequently, we take Vw/V of the degrees of freedom as solid-like and (V - Vw)/V of the normal modes as gas-like. Here, Vw and V are the molar volume of solid-like structure present in the liquid and the molar volume of the liquid, respectively.

Theory

Based on the above considerations, three structures are considered to be significant in bulk liquid (8-10): (i) molecules vibrating as they do in a solid; (ii) fluidized vacancies cooperatively propelled through the solid, converting three vibrational degrees of freedom into three translational degrees of freedom and thus simulating the behavior of a gas molecule; and (iii) degeneracies for the solid-like molecule provided by the fluidized vacancies. As the critical point is approached, every cooperative cluster has the option of being in the liquid or in the vapor state. A second degeneracy factor is required for interpreting the critical phenomena. These considerations lead to the following equation for the partition function for a mole of liquid:

\[ f_N = [f_s + f_s' n(X - 1) e^{-aE_s/R T(X - 1)} N/X (f_g)^{N(X - 1)/X}] \times (N/V - V_s)^{1/2} \left( e^{q_0/k T} + e^{-q_0/k T} \right)^{N/q} \]

where \( f_s \) and \( f_s' \) are the solid-like partition function, the partition function for the molecule occupying a vacancy, and the gas-like partition function, respectively, and \( X = V/V_s \).

For a molecule such as argon we write

\[ f_s = \frac{e^{E_s/R T}}{(1 - e^{-\theta/T})^3}, \]

\[ f_s' = \frac{e^{E_s/R T}}{(1 - e^{-\theta/T})^{2\gamma - y}} \left( \frac{2\pi m k T}{\hbar^2} \right)^{1/2} \ell^v \]

\( (y = 1, 2, 3) \)

and

\[ f_g = \frac{(2\pi m k T)^{3/2}}{\hbar^3} (V - V_s). \]

The notations used in the above expressions are: \( E_s \), the energy of sublimation; \( \theta \), Einstein characterization temperature; \( m \), mass of a molecule; \( k \), Boltzmann's constant; \( h \), Planck's constant; \( \ell \), free length; \( R \), gas constant; \( T \), temperature; \( q \), cluster size; \( N \), Avogadro's number; \( a' \), change of surface energy per molecule; and \( n \) and \( a \), dimensionless constants whose values are determined by the model.

The Solid Partition Function. The Einstein characterization temperature and the energy of sublimation are volume-dependent. In this study their values are taken as constant. However, for more accurate constant pressure specific heat, \( c_p \), compressibility, \( \beta \), and thermal expansion coefficient, \( \alpha \), one should use

\[ E_s = E_0(V_s) \text{ and } \theta = \theta(V_s). \]

The volume-dependence of \( E_s \) and \( \theta \) has been determined in the case of the alkali metals (11). With a proper pair potential, the solid partition function can be calculated.

The Partition Function for the Molecule Occupying a Vacancy. For a simple liquid like argon, as the temperature increases there is a certain probability that it acquires enough energy to change some of its vibrational degrees of freedom into a translational degree of freedom. In \( f_g' \), the \( y \) degrees of freedom a molecule uses in entering the vacancy are transla-
Table 1. Parameters used in the calculation and the critical properties

<table>
<thead>
<tr>
<th>In/N</th>
<th>Critical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 10.8</td>
<td>Pr = 54.8 (Obs. 48.0)</td>
</tr>
<tr>
<td>a = 0.00534</td>
<td>V_C = 81.9 (Obs. 75.3)</td>
</tr>
<tr>
<td>V_P = 24.61 ml</td>
<td>T_C = 150.84 (Obs. 150.7)</td>
</tr>
<tr>
<td>$\theta$ = 54.2</td>
<td>$E_C$ = 1860.3</td>
</tr>
<tr>
<td>$\gamma$ = 1</td>
<td></td>
</tr>
</tbody>
</table>

In $A_1$: $\alpha^* = 0.107; c = 0.1 - 0.102 (T < T_C); 0.017 (T > T_C)$.

* Observed (Obs.) data from ref. 2.

The resulting value for $\ell$ is chosen such that

$$\left(1 - e^{-\beta/T}\right)^{\frac{2\pi mkTm}{h}} \ell = 1.$$  \[5\]

The degeneracy term which governs the critical phenomena. Eq. 1 without the last term is quantitatively accurate away from the critical point. However, it neglects the fact that small clusters of $q$ molecules in the liquid can reorganize as vapor with only the expenditure of the interfacial energy and the energy of expansion and the gravitational energy arising from the change in density. Of these three energies, the surface energy will predominate near the critical point. The degeneracy factor $\left(\left[e^{\frac{\sigma q^2/kT}{|T_c - T|}} + e^{-\sigma q^2/kT}\right]/2\right)^{N/q}$ reduces to 1 at the critical point because $qa'$ becomes zero and for $|T_c - T|$ large is allowed in $A$.

We consider just how $C_V$ changes with temperature when the volume is held constant at the critical volume, $V_C$. Near the critical point, every cooperative cluster of $q$ molecules has the option of being in the liquid state with a Helmholtz free energy $qa'$ below that of the critical structure or alternatively in the vapor state with free energy $qa'$ higher. Accordingly, the Helmholtz free energy $A$ may be written as

$$A = -kT \ell n \left[ f_N \left( e^{\frac{\sigma q^2/kT}{|T_c - T|}} + e^{-\sigma q^2/kT}\right)^{N/q} \right]$$  \[8\]

which reduces to $A_0 = -kT \ell n f_N$ as it should at the critical point where $a' = 0$. If we take

$$A_1 = -kT \ell n \left[ \frac{1}{2} \left( e^{q^2/kT} + e^{-q^2/kT}\right) \right]^{N/q},$$  \[7\]

then we have

$$A = A_0 + A_1$$  \[8\]

and all properties are the sum of the properties arising from $A_0$ and $A_1$. If Eq. 7 is expanded into a series and the higher terms are neglected, we obtain

$$A_1 \approx -\frac{N}{2} \frac{a'^2}{kT}.$$  \[9\]

This approximation requires that $qa' < kT$.

Because liquid and vapor are in equilibrium, mixing is prevented by the gravitational effect on density and by the surface tension which depends on the two principal radii of an ellipsoid. The cluster size, $q$, tends to remain small to keep its surface energy at a minimum, but for clusters to be stable they must not be too small. As the temperature is raised, coalescence makes clusters combine and wipes out surface energy between clusters. The growth of cluster with $T$ is slow except in the vicinity of $T_C$. The net effect due to coalescence is a small decrease in $qa'$ by a factor proportional to $|\Delta T|^{-\alpha}$. Accordingly, we may write

$$A_1 = -c|\Delta T|^{2-\alpha}.$$  \[10\]

Here the constant $c$ may be related to the order parameter $\rho_L - \rho_g$ in a certain way. For simplicity we take it as a constant that has one value for $T < T_C$ and a different value for $T > T_C$.

The slowly varying factor $q^1/3T$ occurring in Eq. 9 is partly responsible for the volume of $a$ in Eq. 10.

Because the $A$-versus-$V$ curve passes through a region of mechanical instability, $A_Q(T,V_C)$ cannot be calculated directly from the partition function $f_N(T,V_C)$. Instead, the following method was used. First, the Helmholtz free energies for the liquid, $A_L$, and the gas, $A_g$, were calculated from $f_N(T,V)$. Then, we assume

$$A_Q(T,V_C) = \chi A_L(T,V_L) + (1 - \chi)A_g(T,V_g)$$  \[11\]

in which $\chi$ and $(1 - \chi)$ are the fractional amounts of the liquid and gas phases, respectively. The value of $\chi$ can be obtained from the coexistence curve

$$\chi = \frac{\rho_L - \rho_g}{\rho_L - \rho_g} = \frac{b_1}{b_2} |\Delta T|^{\beta} = constant.$$  \[12\]

Table 2. Liquid volume, pressure, thermal expansion coefficients, and compressibility of liquid argon

<table>
<thead>
<tr>
<th>T, K</th>
<th>V_L, ml</th>
<th>P, atm</th>
<th>$a \times 10^3$ deg$^{-1}$</th>
<th>$b \times 10^4$ atm$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>83.85</td>
<td>28.36</td>
<td>28.20</td>
<td>0.652</td>
<td>0.680</td>
</tr>
<tr>
<td>87.29</td>
<td>28.82</td>
<td>28.66</td>
<td>0.979</td>
<td>1.000</td>
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<tr>
<td>90.0</td>
<td>29.19</td>
<td>29.03</td>
<td>1.310</td>
<td>1.319</td>
</tr>
<tr>
<td>100.0</td>
<td>30.74</td>
<td>30.38</td>
<td>3.333</td>
<td>3.20</td>
</tr>
<tr>
<td>110.0</td>
<td>32.73</td>
<td>32.05</td>
<td>7.08</td>
<td>6.58</td>
</tr>
<tr>
<td>120.0</td>
<td>35.44</td>
<td>34.15</td>
<td>13.26</td>
<td>11.98</td>
</tr>
<tr>
<td>130.0</td>
<td>39.46</td>
<td>37.31</td>
<td>22.5</td>
<td>20.0</td>
</tr>
<tr>
<td>140.0</td>
<td>46.34</td>
<td>45.7</td>
<td>35.7</td>
<td>31.26</td>
</tr>
<tr>
<td>143.0</td>
<td>49.66</td>
<td>---</td>
<td>40.56</td>
<td>---</td>
</tr>
<tr>
<td>145.0</td>
<td>52.67</td>
<td>---</td>
<td>43.82</td>
<td>---</td>
</tr>
<tr>
<td>T_C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Observed (Obs.) data are from ref. 12. More recently observed data (13) only differ slightly from these data.
Table 3. $C_V$ along the critical isochore ($\rho = \rho_c$)

<table>
<thead>
<tr>
<th>$T$, K</th>
<th>$C_V$</th>
<th>$C_V$</th>
<th>$C_V$</th>
<th>$C_V$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0.1)</td>
<td>(0.102)</td>
<td>(0.102)</td>
<td>obs.</td>
</tr>
<tr>
<td>132.7</td>
<td>3.57</td>
<td>15.15</td>
<td>15.46</td>
<td>17.52</td>
</tr>
<tr>
<td>140.0</td>
<td>3.58</td>
<td>17.05</td>
<td>17.39</td>
<td>20.0</td>
</tr>
<tr>
<td>145</td>
<td>3.58</td>
<td>19.08</td>
<td>19.46</td>
<td>22.18</td>
</tr>
<tr>
<td>147</td>
<td>3.58</td>
<td>20.38</td>
<td>20.79</td>
<td>25.48</td>
</tr>
<tr>
<td>149</td>
<td>3.58</td>
<td>22.65</td>
<td>23.1</td>
<td>27.90</td>
</tr>
<tr>
<td>150.84</td>
<td>3.58</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
<tr>
<td>150.96</td>
<td>3.58</td>
<td>5.49</td>
<td>$\infty$</td>
<td>10.47</td>
</tr>
<tr>
<td>151.0</td>
<td>3.58</td>
<td>5.30</td>
<td>$\infty$</td>
<td>9.7</td>
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<tr>
<td>151.53</td>
<td>3.58</td>
<td>4.43</td>
<td>$\infty$</td>
<td>8.32</td>
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<tr>
<td>152.43</td>
<td>3.58</td>
<td>4.01</td>
<td>$\infty$</td>
<td>7.53</td>
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<td>153.13</td>
<td>3.58</td>
<td>3.85</td>
<td>$\infty$</td>
<td>7.43</td>
</tr>
<tr>
<td>153.84</td>
<td>3.58</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

* Observed (Obs.) data from ref. 16

Upon differentiating Eq. 10 twice, we obtain

$$(C_V)_1(T,V_c) = c(2 - \alpha)(1 - \alpha)T^2 \Delta T^{-\alpha}$$ [13]

Next, we consider the specific heat along the coexistence curve ($\rho = \rho_L$). At a given temperature the volume along the coexistence curve, $V_L$, differs from that along the critical isochore, $V_c$. To bring a molecule from the first state to the second state isothermally requires an energy that is proportional to $P(V - V_c)$. Therefore, we take

$$A_1 = -c \sqrt{\Delta T^2 e^{-\alpha} e^{-\alpha V_c V}}$$

and

$$A(T,V) = A_0(T,V) + A_1(T,V).$$ [14]

The specific heat then takes the form

$$(C_V)_1(T,V) = C(2 - \alpha)(1 - \alpha)T^2 \Delta T^{-\alpha} e^{-\alpha V_c V}.$$ [15]

Thermodynamic properties

Once the expression for the Helmholtz free energy is written explicitly, well-known thermodynamic relationships can be used to calculate all other thermodynamic properties.

The Translational Degree of Freedom in the Degeneracy Term. For argon we found, as was to be expected, that the best results can be obtained by assuming that only the one degree of freedom a molecule uses in entering the vacancy is translational—i.e., $\gamma = 1$. The free volume $V_f$ calculated is 0.254 Å$^3$ whereas the free length $\ell = V_f^{1/3} = 0.634$ Å which is approximately 0.00% of the diameter of an argon molecule, as we expected.

Along the Coexistence Curve. Properties along the coexistence curve were calculated by using Eq. 14 with $\alpha = \frac{1}{2}$ and are given in Table 2 and Figs. 1–3. Agreement between calculated and observed values is good.
Along the Critical Isochore. Constant-volume specific heats, \( C_V \), along the critical isochore were calculated by using Eq. 13 for \( T < T_c \) as well as for \( T > T_c \). The results are given in Table 3. We notice that Eq. 15 reduces to Eq. 13 when \( \rho = \rho_c \). For \( T < T_c \), we therefore used the same value for \( c \) (0.1) in both cases (\( C_V \) values for \( c = 0.102 \) are also given for \( \rho = \rho_o \)). However, for \( T > T_c \), a much smaller \( c \) is to be expected because the liquid and vapor structures have merged.

The Critical Properties. The critical properties of argon given in Table 1 were calculated by using the conditions \( \partial p / \partial V = \partial^2 p / \partial V^2 = 0 \). The critical pressure would be slightly lower if the dimer term were included in our gas-like partition function (17). It is known that \( \rho_L - \rho_g \sim |\Delta T|^\beta \). Experimentally (18), \( \beta \sim 0.5 \). With \( A_1 \sim |\Delta T|^\alpha \), we obtain \( P_1 \sim (\rho_L - \rho_g)^{3\alpha} \). If \( \alpha = 0.5 \) and \( \beta = 0.5 \), then \( \delta = 5 - 3\alpha = 2\). These values agree with the scaling law (19, 20)

\[ \alpha + \beta (\delta + 1) = 2. \]  \[ (16) \]

Frankel (21) proposed a theory for three-dimensional cooperative phenomena using a ferromagnet and superfluid helium as examples. He used the following free energy expression:

\[ -F \sim F_0 + \left( \frac{T_c + T}{T_c} \right)^{6\delta}. \]

The second term of this is similar to our Eq. 10. \( F_0 \) is a constant in the critical region whereas our \( A_0(T, V) \) is temperature-dependent. Hubbard and Schofield (22) applied Wilson's theory of renormalization groups (23) to a liquid–vapor critical point. However, their theory only holds for sufficiently small values of \( \epsilon (4 - d) \); their application to the case \( d = 3, \epsilon = 1 \) is questionable.

In this report, we have not discussed explicitly how \( \alpha' \) is affected by the change in the cluster size that results from the uniting of small clusters. This change, however, accounts qualitatively for the sign and the small value of \( \alpha \).

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