Thermodynamics of Three-Phase Equilibrium in Argon Based on a Perfect Solid and a Perfect Liquid (v4)

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Equations of state (EOS) are proposed for a system consisting of a perfect solid and a perfect liquid made up of single spherical molecules. The Lennard–Jones interaction is assumed for this system. Molecular dynamics simulations are performed to determine the temperature and density dependences of the internal energy and pressure. The internal energy term in the EOS is the sum of the average kinetic and potential energies at 0 K and the temperature-dependent potential energy. The temperature-dependent term of the average potential energy is assumed to be a linear function of the temperature and its coefficient is expressed as a polynomial of the number density. The pressure is expressed in a similar way, where the pressure satisfies the thermodynamic EOS. The equilibrium condition is solved numerically for the phase equilibrium of argon. The Gibbs energy gives a reasonable transition pressure for three-phase equilibrium in argon. The thermodynamic properties at low pressures have significant temperature dependences.

Keywords: Equation of state, Phase diagram, Triple point, Critical constants, Gibbs energy

1 Introduction

Many studies have obtained the equation of state (EOS) for the fluid phase of a Lennard–Jones system [1,2]. Such studies are based on molecular dynamics (MD) and Monte Carlo (MC) simulations in the equilibrium state [3]. The EOS obtained was used to investigate the gas–liquid equilibrium. Phase equilibria have been studied by both equilibrium and non-equilibrium molecular simulation techniques [4–11], which give good accuracies.

In contrast, we propose a simplified EOS for simplifying the understanding and the treatment of free energy calculations for the three-phase equilibrium in an argon system. The internal energy \( U \) of this simplified model for a perfect solid is composed of the average kinetic energy and the average potential energy \( U_e \) at 0 K of a face-centered cubic (FCC) lattice [12]:

\[
U(V,T) = \frac{3}{2} NkT + U_e(V,0 \text{ K})
\]  

(1)

The pressure \( p \) is given by [12]:

\[
p(V,T) = \frac{NkT}{V} - \frac{\left( \frac{\partial U_e(V,0 \text{ K})}{\partial V} \right)_T}{V}
\]  

(2)

The temperature-dependent virial term is included in an extended model [12]:

\[
p = \frac{NkT}{V} - \frac{\left( \frac{\partial U_e(V,0 \text{ K})}{\partial V} \right)_T}{V} + \frac{6N\sigma^2kT}{V^2}
\]  

(3)

This EOS for a solid and the van der Waals equation can explain the three-phase equilibrium in an argon system [13,14].

A previous study (v3) proposed a new EOS for the liquid phase based on MD simulations [15]. It includes the temperature dependence of the average potential energy:

\[
U(V,T) = \frac{3}{2} NkT + U_e(V,0 \text{ K}) + g(V)NkT
\]  

(4)

Here, \( g(V) \) is a function of the volume of the molecular system [15]. This function is a simple linear function of the number density in v3 [15].

In this study, the function \( g(V) \) is a polynomial of the number density.
density to express the complex density dependence of the average potential energy. It is thus a modified version of the EOS given in our previous study. It is expected to give improved agreement between calculated and observed thermodynamic quantities.

2 Analysis of MD simulations

MD simulations [3] are performed to obtain the temperature and density dependences of the internal energy and pressure. The molecular interactions of the present spherical molecules are assumed to have the Lennard–Jones form [16]. The Lennard–Jones potential, \( u(r) \) is expressed as a function of the interatomic distance \( r \):

\[
  u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right].
\]

(5)

where \( \varepsilon \) is the depth of the potential well and \( \sigma \) is the separation at which \( u(r) = 0 \). The constants \( \varepsilon \) and \( \sigma \) are used as units of energy and length, respectively (Table 1).

**Table 1. Lennard–Jones parameters [16]**

<table>
<thead>
<tr>
<th>(( \varepsilon/k ))/kJ</th>
<th>( \varepsilon/10^{-21} ) J</th>
<th>( \sigma/10^{-10} ) m</th>
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<tr>
<td>111.84</td>
<td>1.54</td>
<td>3.623</td>
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<table>
<thead>
<tr>
<th>(( \varepsilon/\sigma^3 ))/MPa</th>
<th>(( \varepsilon/\sigma^3 ))/atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.5</td>
<td>320</td>
</tr>
</tbody>
</table>

\( NTV \) ensemble [3] simulations are performed at many fixed number densities \( (N/V) \) for a system with \( N = 256 \) and a sufficiently long cut-off distance. Figures 1 and 2 show examples of the simulation results [15]. The average potential energy \( U_e \) and the pressure \( p \) of each phase are fitted by linear functions of

\[
  U_e = U_e(0 \text{ K}) + a(U_e)NkT
\]

(6)

\[
  p = p(0 \text{ K}) + a(p)NkT
\]

(7)

The coefficients \( a(U_e) \) and \( a(p) \) are shown in Figures 1 and 2. They are expressed by the function \( h(v) \):

\[
  h(v) = \frac{\sigma^3}{v} - \frac{1}{10} \left(\frac{\sigma^3}{v}\right)^3 + \frac{1}{60} \left(\frac{\sigma^3}{v}\right)^5.
\]

(8)

Here, \( v \) is the volume per molecule:

\[
  v = \frac{V}{N}.
\]

3 Equation of state

The present EOS has the following form [15]:

\[
  U(V,T) = \frac{3}{2}NkT + U_e(V,0 \text{ K}) + g(v)NkT,
\]

(10)

\[
  p(V,T) = \frac{NkT}{V} - \frac{dU_e(V,0 \text{ K})}{dV} + f(v)NkT + \left(\frac{dg(v)}{dv}\right)NkT\ln(kT).
\]

(11)
Figure 3. Gibbs energy per molecule $G/N$ vs. pressure at $T_3=0.7491\;\varepsilon/k$. Arrow indicates the triple point.

$$\frac{U_v(v,0\;K)}{N\varepsilon} = 0.94215515 \times \left[ 6 \left( 1 + \frac{1}{128} \frac{\sigma_v^3}{v^3} \right) - 12 \left( 1 + \frac{1}{5} \frac{\sigma_v^3}{v^3} \right) \right]. \text{ (Solid)}$$ (12)

$$\frac{U_v(v,0\;K)}{N\varepsilon} = \left( 1.5 \frac{\sigma_v^8}{v^8} - 8.2 \frac{\sigma_v^4}{v^4} \right). \text{ (Liquid)}$$ (13)

$$g_v(v) = 1.4h(v),\quad f_v(v) = 6\frac{h(v)}{v}. \text{ (Solid)}$$ (14)

$$g_v(v) = 1.1h(v),\quad f_v(v) = 5\frac{h(v)}{v}. \text{ (Liquid)}$$ (15)

In this study, the potential energy of the solid at 0 K includes an adjustable parameter that is chosen as in Eq. (12) to reproduce the triple point. These EOS are called EOS for a perfect solid and liquid.

The last term in Eq. (11) is included to ensure that Eqs. (10) and (11) satisfy the thermodynamic EOS [16].

The entropy $S$ is written as [15]:

$$S(Nv,T) = \frac{3}{2} Nk \ln \left( \frac{kT}{\varepsilon} \right) + Nk \ln \left( \frac{\nu}{\sigma_v^3} \right)$$

$$+ F(v)Nk + g(v)Nk \ln \left( \frac{kT}{\varepsilon} \right) + g(v)Nk, \quad \text{and} \quad F(v) = \int f(v)dv$$ (16)

### 4 Phase equilibrium in $T$–$p$ space

The condition of the phase equilibrium between phases 1 and 2 in $T$–$p$ space is expressed by:

$$p_1(V_1, T) = p_2(V_2, T),$$

$$\frac{G_1(V_1, T)}{N_1} = \frac{G_2(V_2, T)}{N_2}$$ (17)

Since the EOSs are known to be functions of volume and temperature, this equation can be solved numerically [12,13]. An example is shown in Figure 3 at the triple point. The adjustable parameter in the average potential energy of solid at 0 K is chosen to reproduce the observed triple point of argon [16]. The thermodynamic properties are compared for the experimental and simulation results given in Table 2. The calculated properties are reasonable.

The liquid–gas critical point is determined by numerically solving the following Eq [15,17]:

$$\left( \frac{\partial p}{\partial V} \right)_T = \left( \frac{\partial^2 p}{\partial V^2} \right)_T = 0$$ (18)

Table 3 compares the obtained critical point with the experimental result [16] and that determined by molecular simulation [8]. The calculated critical temperature agrees well with the experimental [16] and simulation results [8]. In addition, the EOS critical pressure is higher than that observed experimentally. The critical molar volume is close to the experimental results [16]. The comparison is satisfactory with respect to the critical constants.

The transition pressure is plotted as a function of temperature in Figure 4 and compared with the experimental [18–22] and simulation [2, 4–11] results for argon. The pressure is plotted on a logarithmic scale due to its very wide range. The overall transition pressure for argon is well reproduced as a function of temperature.

Figure 5 shows the transition temperature–number density relation for argon and compares the calculated results with the simulation results [2, 4–11]. The phase boundaries of the liquid and solid branches obtained from EOS calculations deviate

<table>
<thead>
<tr>
<th>$T_3$ / K</th>
<th>$p_3$ / atm</th>
<th>$\rho_L$ / (g/cm$^3$)</th>
<th>$\Delta_{SL}H$ / (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOS v1</td>
<td>69</td>
<td>1.75</td>
<td>1.129</td>
</tr>
<tr>
<td>EOS v2</td>
<td>84</td>
<td>0.30</td>
<td>1.134</td>
</tr>
<tr>
<td>EOS v3</td>
<td>77</td>
<td>0.31</td>
<td>1.181</td>
</tr>
<tr>
<td>EOS v4</td>
<td>84</td>
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<td>1.158</td>
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<tr>
<td>Exp</td>
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<td>0.68</td>
<td>1.417</td>
</tr>
<tr>
<td>MC</td>
<td>77</td>
<td>0.32</td>
<td>1.396</td>
</tr>
</tbody>
</table>

Table 2. Comparison of EOS and experimental [18] and MC [10] triple points. The mass density of the liquid $\rho_L$ and the change of enthalpy in the solid–liquid transition $\Delta_{SL}H$ are also given.
slightly from the simulation results at high temperatures. Some differences in the gas–liquid transition region found in our previous study [15] are reduced in the present study.

Figure 6 compares the calculated configurational entropy per molecule $S_c/N$ with the simulation results [10]. The configurational entropy $S_c$ has the following form in the perfect solid and liquid model:

$$S_c(V', T) = Nk \ln \left( \frac{V}{N\sigma^3} \right) + F(v)Nk + g(v)Nk + Nk$$

The main feature of the phase equilibrium line in the solid–liquid transition is that the configurational entropies are almost constant as a function of temperature. This feature is reasonably well reproduced; therefore, the overall features of the configurational entropy by the EOS are in agreement with the simulation results [10]. We intend to improve the differences in the liquid phase below the critical point in a future study.

Figure 7 shows the average potential energies per molecule $U_e/N$ at the phase boundaries:

$$U_e(V, T) = U_e(V, 0 \text{ K}) + g(v)NkT, \text{ (solid)}$$

$$U_e(V', T) = U_e(V', 0 \text{ K}) + g(v)NkT, \text{ (liquid)}$$

These results are also compared with the simulation results [2,10,11]. The average potential energies of the solid, liquid, and gas generally correspond well with the simulation results. However, the average potential energies at liquid–solid equilibrium differ slightly from the observed results [10,11]; we intend to investigate this in a future study.

Figure 8 shows the configurational Helmholtz energy $A_c$ as a function of the temperature on the solid–liquid phase boundaries. The calculated $A_c$ corresponds to that of the MC simula-

<table>
<thead>
<tr>
<th>$T_c$ / K</th>
<th>$\rho_c$ / atm</th>
<th>$V_c$ / (cm$^3$/mol)</th>
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<tbody>
<tr>
<td>EOS v1</td>
<td>133</td>
<td>47</td>
</tr>
<tr>
<td>EOS v2</td>
<td>166</td>
<td>40</td>
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<td>EOS v3</td>
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<td>81</td>
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<td>75</td>
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<tr>
<td>Exp</td>
<td>151</td>
<td>48</td>
</tr>
<tr>
<td>MD</td>
<td>148</td>
<td>41</td>
</tr>
</tbody>
</table>
tion result [10] at low and intermediate temperatures. However, some improvement is necessary for \( A_c \) at high temperatures \((T > 2.5 \varepsilon/k)\), which we also intend to address in a future study.

Finally, Figure 9 compares \( A_c \) at the solid–gas-phase boundary with that from the MC simulation [10]. The EOS (v4) gives \( A_c \) values on the solid–gas-phase boundary that are comparable with those of the MC simulation [10].

5 Thermodynamic properties at a constant pressure

This section considers thermodynamic quantities at low pressures by comparing the EOS and simulation results.

The Gibbs energy is plotted in Figure 10 as a function of temperature at \( P = 2 \text{ atm} = 6.25 \times 10^{-3} \varepsilon/\sigma^3 \). This is compared with the Kolafa–Nezbeda (KN)-EOS determined from many simulation results for the Lennard–Jones system [2]. As Figure 10 is enlarged near the transition points, the comparison is generally satisfactory. The entropies of the liquid and solid are negative for the present choice of the entropy origin. Consequently, the Gibbs energy plot differs from the usual plot [16]. The melting point \( T_m \) and the boiling point \( T_b \) are fixed in Figure 10:

\[
T_m = 83.9 \text{ K} = 0.750 \frac{\varepsilon}{k},
\]

\[
T_b = 88.0 \text{ K} = 0.787 \frac{\varepsilon}{k},
\]

\[
P = 2 \text{ atm} = 0.625 \times 10^{-3} \varepsilon / \sigma^3
\]

(21)

Considering that the calculated pressure at the triple point is higher than the experimental one (Table 2), the above temperatures are reasonable.

Figure 7. Average potential energy per molecule \( U_e/N \) vs. temperature in phase equilibrium of argon. Comparison of EOS and simulation results [10].

Figure 8. Configurational Helmholtz energy per molecule \( A_c/N \) vs. temperature in solid–liquid equilibrium of argon. Comparison of EOS and simulation results [10].

Figure 9. Configurational Helmholtz energy per molecule \( A_c/N \) vs. temperature in the solid–gas equilibrium of argon. Comparison of EOS and simulation results [10].

Figure 11 shows the volume per molecule as a function of temperature at \( P = 2 \text{ atm} \). This is compared with the present MD results and the KN-EOS [2]. The MD simulation is performed on an 864-particle system using a standard NTP ensemble [3]. This comparison demonstrates that the present simple EOS is useful.

The internal energy is plotted as a function of temperature at \( P = 2 \text{ atm} \) in Figure 12. The comparison on the internal energy is satisfactory, as was the case for the volume.

Figure 13 shows the enthalpy per molecule as a function of temperature at \( P = 2 \text{ atm} \). The calculated enthalpy is in agreement with the simulation results for the Lennard–Jones system. The KN-EOS is better than the present EOS in the liquid phase [2].
The Helmholtz energy per molecule is shown in Figure 14 and the entropy per molecule is depicted in Figure 15. The overall features of the Helmholtz energy are satisfactory in comparison with the KN-EOS [2]. The value of the entropy for the liquid obtained by the EOS is close to that obtained by the simulations [2]. The entropies of the liquid and the solid are negative based on the present choice of the entropy origin.

Figure 16 compares the expansion coefficient $\alpha$ calculated using the EOS with that obtained by simulations. Although $\alpha$ for the liquid and solid differ slightly from that obtained by the simulations, the overall features show good similarity. The KN-EOS [2] gives a better expansion coefficient in the liquid phase than the present EOS.

The isothermal compressibility $\kappa_T$ obtained by the EOS is plotted in Figure 17. Comparison of $\kappa_T$ calculated by the EOS with the MD simulation results indicates that the present EOS satisfactorily explains this quantity in the three phases.

Figure 18 shows the heat capacity under a constant pressure $C_p$. The heat capacity in the gas-phase is in reasonable agreement with the results obtained by MD simulations. For $C_p$ in the liquid phase, the calculated values are lower than those obtained by the MD simulation and the KN-EOS [2], which is a problem we intend to consider in a future study.

6 Thermodynamic consistencies

The thermodynamic consistencies were examined using the following thermodynamic Eq [16]:

![Figure 10. Gibbs energy per molecule vs. temperature at $p = 2$ atm. Comparison of EOS and simulation results [2]. The melting point is $0.750 \varepsilon/k$ and the boiling point is $0.787 \varepsilon/k$.](image1)

![Figure 11. Volume per molecule vs. temperature at $p = 2$ atm. Comparison of EOS and simulation results [2], including MD simulation of this study.](image2)

![Figure 12. Internal energy per molecule vs. temperature at $p = 2$ atm. Comparison of EOS and simulation results [2], including MD simulation of this study.](image3)

![Figure 13. Enthalpy per molecule vs. temperature at $p = 2$ atm. Comparison of EOS and simulation results [2], including MD simulation of this study.](image4)
The LHS and RHS of Eq. (22) are shown in Figure 19 for the three phases at $P = 2$ atm. No specific problems were encountered with the thermodynamic consistency.

7 Numerical calculations

Several worksheets were prepared to perform the numerical calculations, as shown in Table 4. To obtain plots (such as that shown in Figure 3), thermodynamic quantities were calculated as functions of $v = V/N$ and $T$ using worksheet functions. The equation $p \ (v; T_0) = p_0$ was solved with respect to the volume $v$ for a given temperature $T_0$ and pressure $p_0$ using Goal Seek in Microsoft Excel in the second worksheet. These worksheets are available upon request to the author (YK). They are given in the appendix. Practical methods for performing numerical calculations and the related files will be published elsewhere [23].

8 Conclusions

The phase transitions in the three phases of argon are well reproduced by EOSs for a perfect solid and liquid v4. EOS v4 for a perfect solid and liquid is given by Eqs. (8)–(15). The potential energy for argon can be expressed by the Lennard–Jones pair potential. For this reason, the Lennard–Jones potential parameters, $\epsilon$ and $\sigma$, are not adjustable. Only the coefficients in the functions of the EOS are adjustable parameters in the present

\[ (C_p - C_v) \frac{1}{N} = \frac{\alpha^2 TV}{\kappa_i N} \]  

(22)

The LHS and RHS of Eq. (22) are shown in Figure 19 for the three phases at $P = 2$ atm. No specific problems were encountered with the thermodynamic consistency.
EOS v4. Optimization of these parameters is expected to give better results that are closer to the experimentally observed results. The EOSs for a perfect solid and liquid have a simple analytic form. The set of these EOSs is expected to be employed for teaching thermodynamics in physical chemistry courses.

The authors would like to thank the Research Center for Computing and Multimedia Studies of Hosei University for the use of computer resources.

References

[23] Y. Kataoka, Y. Yamada, to be published.

Table 4. Worksheets employed for phase transition calculations.

<table>
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<th>File name</th>
<th>Purpose</th>
<th>Example of Figures</th>
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<td>G/N vs. p plot</td>
<td>Figures 3–9</td>
</tr>
<tr>
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<td>Figures 10–19</td>
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<td>EOSv4_ (P = 2atm). xls</td>
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<td>Figures 10–19</td>
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</table>

Figure 18. Heat capacity at a constant pressure per molecule \((C_p/N)\) vs. temperature at \(p = 2\) atm. Comparison of EOS and simulation results [2], including MD simulation of this study.

Figure 19. Thermodynamic consistency test (Eq. (22)).