Improvement on Lennard-Jones–Devonshire theory for predicting liquid–solid phase transition

Hamid Modarress, G.Ali Mansoori

ABSTRACT

In this paper the potential energy of the Lennard-Jones and Devonshire (LJD) model has been corrected to increase its PVT prediction abilities. The correction of potential energy is done in two ways (i) taking the coordination number as a function of temperature and volume to improve the second virial prediction ability and (ii) taking pair correlation effects into account to improve the phase transition prediction ability. The results of calculations indicate improvement both on PVT behavior in the above range of variation especially on the phase transition prediction ability in solid–liquid and vapor–liquid regions.

INTRODUCTION

Many equations of state have been proposed, which most of them are effective in the vapor–liquid region but only a few can be applied to the solid–liquid region. There is no known equation of state which can be used continuously in all regions.

One of the theories which can lead to derivation of an equation of state for solid–liquid and liquid–vapor phase states is Lennard-Jones and Devonshire (LJD) cell theory. This theory has a sound theoretical basis, it shows several shortcomings in application, namely, it predicts negative pressures at the vapor–liquid region and high temperatures. Also it fails to predict solid–liquid transition in its original form and needs modifications to provide with such ability.

In this paper an attempt is made to improve LJD theory by introducing a proper potential function.

The essence of the LJD theory is described as follows:

(1) The available volume of a fluid may be divided into identical cells assigning one molecule in each cell.
(2) The cells can be chosen so that their centers form a regular lattice (for example, fcc).
(3) The molecules can be regarded as moving independently in their cells.

With these assumptions, the potential energy can be expressed as

\[ U = U_s + \sum_{i=1}^{N} \left[ w(r_i) - w(0) \right], \]

where \( r_i \) is the vector representing the displacement of molecules from their cell center and \( [w(r_i) - w(0)] \) (the cell field) shows the difference between potential energy when a molecule is displayed from its cell center. The cell energy \( U_s \) in Eq. (1) is the energy when all molecules are in their cell centers.

The configurational integral in terms of potential energy can be expressed as

\[ Z = \int \cdots \int \exp(-\beta U) dr_1 \cdots dr_N \]

and then from Eq. (1) for \( U \),

\[ Z = \int \cdots \int \exp \left[ -\frac{U_s}{kT} - \frac{1}{kT} \sum_j [w(r_j) - w(0)] \right] dr_1 \cdots dr_N, \]

where \( \beta = 1/kT \) and \( k \) is the Boltzmann’s constant.

Pourgheyser et al., using the smearing approximation for the first nearest-neighbor interactions and considering the single occupancy cells expressed the potential difference \( [w(r_j) - w(0)] \) in terms of a Lennard-Jones potential function in the following form:

\[ \sum_j [w(r_j) - w(0)] = \begin{cases} \frac{4}{3} C \gamma_i^2 \left[ \frac{16.5}{V^{**}} - \frac{7.5}{V^{**}} \right] & 0 \leq \gamma_i \leq 0.5, \\ \infty & 0.5 < \gamma_i \end{cases}, \]

where \( C \) is the coordination number of the cell, \( \gamma_i (= r_i/a) \) and \( V^{**} (= V/N\sigma^3) \) are the dimensionless distance and volume, respectively. Also in this equation \( \varepsilon \) and \( \sigma \) are the parameters of a Lennard-Jones potential function.

For the fcc lattice \( U_s \) was presented as

\[ U_s = 24N\varepsilon \left[ \frac{1.01}{4V^{**}} - \frac{1.205}{2V^{**}} \right]. \]

From the above results, pressure can be calculated through the well-known statistical mechanical equation as

\[ Z = \left( \frac{V^{**}}{V} \right)^{N(\beta U_s/kT) - 1} \]

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\[ P = \left( \frac{\beta U_s}{k} \right) \left( \frac{V^{**}}{N\varepsilon} \right)^{N(\beta U_s/kT) - 1} \]

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\[ P = \left( \frac{\beta U_s}{k} \right) \left( \frac{V^{**}}{N\varepsilon} \right)^{N(\beta U_s/kT) - 1} \]

\[ P = \left( \frac{\beta U_s}{k} \right) \left( \frac{V^{**}}{N\varepsilon} \right)^{N(\beta U_s/kT) - 1} \]
\[ P = kT \left( \frac{\partial \ln Z}{\partial V} \right)_{N,T}, \]  

(6)

due to using Eqs. (3), (4), and (5) in Eq. (6) and for the fcc lattice \((C = 12)\), the pressure in the dimensionless form becomes

\[ P^* = 24 \left( \frac{1.01}{V_{f}^*} - \frac{1.205}{V_{f}^*} + \frac{T^*}{V_{f}^*} \left( \frac{\partial V_{f}^*}{\partial V^*} \right)_{N,T^*} \right), \]  

(7)

where \(P^* (= \rho \sigma^3/k)\) and \(T^* (= kT/\varepsilon)\) are dimensionless pressure and temperature, respectively.

The first term in Eq. (7) is due to lattice energy \(U_i\) [see Eq. (5)]. This term appears from replacing Eq. (5) in Eq. (6). The dimensionless free volume \(V_{f}^*\) in Eq. (7) is defined as \(V_{f}^* = (V_f / \sigma^3)\) and for fcc lattice can be presented as

\[ V_{f}^* = 4\pi \nu^2 V^* \int_{0}^{0.5} y_i^2 \exp \left( \frac{-4}{\nu^2} \frac{C}{T^*} \left( \frac{16.5}{\nu^2} - \frac{7.5}{\nu^2} \right) \right) dy_i \]  

(8)

it is worth noting that \(r_i = a y_i\) where \(a\) is the lattice parameter and in fcc lattice \(a^3 = \nu^2 (V/N)\) and this is shown by \(\nu^2 V^*\) in the above equation.

The success of Pourghesyr et al.\textsuperscript{12} equation lays on its ability to predict solid–liquid and liquid–vapor phase transition continuously. However, it is unable to improve the negative pressure as obtained for low temperatures by the original LJD cell theory.\textsuperscript{10} Also it gives critical properties which are even higher than predicted values by LJD theory.

In this paper attempts are made to improve potential energy function in such a way that not only the phase behavior can be predicted in all regions continuously but from the resulting equation of state, positive pressures can be calculated.

### IMPROVING POTENTIAL ENERGY

We propose the following general form for the potential energy in the LJD model as represented by Eq. (4):

\[ \Sigma w(r_j) - w(0) = \begin{cases} 
 4 \left( \frac{C}{V_{f}^*} \right) \left( \frac{A}{V_{f}^*} - \frac{B}{V_{f}^*} \right) & 0 \leq y_i \leq 0.5 \\
 0 & y_i > 0.5 
\end{cases} \]  

(9)

where \(A\) and \(B\) are adjustable parameters, which can be calculated from critical conditions\textsuperscript{13}

\[ \frac{\partial P^*}{\partial V^*} \bigg|_{T^*} = 0, \]  

(10)

\[ \frac{\partial^2 P^*}{\partial V^*} \bigg|_{T^*} = 0, \]  

(11)

and \(T^*_c\) is dimensionless critical temperature and is expressed as

\[ T^*_c = \frac{K}{\varepsilon} T_c. \]

The values of parameters \(A\) and \(B\) in Eq. (7) have been calculated by Eqs. (7)–(11) for a fcc lattice \((C = 12)\) using

### TABLE I. The parameters of \(A\) and \(B\) of Eq. (9) for argon and xenon.

<table>
<thead>
<tr>
<th>(T^*_c)</th>
<th>(V^*_c)</th>
<th>(P^*_c)</th>
<th>(A)</th>
<th>(B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.26</td>
<td>3.16</td>
<td>1.18</td>
<td>7.248</td>
</tr>
<tr>
<td>Xe</td>
<td>1.31</td>
<td>2.90</td>
<td>0.116</td>
<td>6.856</td>
</tr>
</tbody>
</table>

The results are reported in Table I and the \(P^*-V^*\) isotherm diagrams calculated by these parameters are shown in Fig. 1.

The total potential energy calculated from Eq. (9) for the values of parameters \(A\) and \(B\) are shown in Fig. 2. As it is seen from this figure applying the critical conditions causes the dominant effect of the repulsion forces appear near the cell walls. This is what we expect from a real potential function. But in the case of the potential function proposed by Pourghesyr et al.\textsuperscript{12} it is seen that near the cell wall the attractive forces are dominant which is contrast to the expected variation of a real potential function.

### IMPROVEMENT OF PRESSURE PREDICTION

The results presented in the preceding section indicate that although the potential energy was improved for its behavior near the cell wall, the isotherms, in Fig. 1, show the negative pressures at low temperature. Therefore we use the following approaches to make the improvement for pressure.

(i) Taking coordination number as a function of \(T\) and \(V\).

(ii) Considering the pair correlation effects by introducing a perturbation term \((\gamma)\) in the potential function.

(i) The coordination number: It is reasonable to assume that for a matter the coordination number has a specific value which corresponds to the shape of its lattice in high densities (solid state) and then decreases with decreasing density (from liquid to vapor states). The basis for this assumption can be explained as follows: In solid the coordination number has its largest value, but as it goes to the liquid and then to the vapor the lattice structure is destroyed and the disorder occurs in the system. Therefore on average, a smaller num-

![FIG. 1. Effect of improved \(A\) and \(B\) parameters on the \(P^*-V^*\) isotherm curves.](image-url)
number of neighboring particles are found around a central particle. In other words the coordination number is dependent on the disorder of a system and can be considered as a decreasing function of volume and temperature.

From the other aspects, LJD theory is unable to predict proper values for the second virial coefficient \( B_2 \). We believe this is due to the improper assumption that the coordination number is considered as a constant in this theory. To elucidate this point further we consider the virial expansion equation

\[
Z = 1 + \frac{B_2}{V} + \frac{B_3}{V^2} + \cdots,
\]

where

\[
\lim_{V \to \infty} (Z - 1)V = B_2,
\]

and for a constant coordination number \( C \), we derive \( B_2 \) by rearranging Eq. (7) and comparing its terms with the virial expansion equation to obtain \( B_2 \) in the following form:

\[
B_2 = \left[ \frac{2C}{T^*} - \frac{1.01}{V^{*3}} - \frac{1.205}{V^*} \right] + \left[ \frac{4C}{3T^*} - \frac{2B}{V^{*2}} \right] \frac{G_1}{G} = 0,
\]

where

\[
V^* \to \infty,
\]

\[
G_1 = \int_0^{0.5} \frac{y^4}{\lambda^4} \left[ \frac{C_1 y_i^2}{T^* - \frac{16.5}{V^{*2}} - \frac{7.5}{V^*}} \right] dy_i,
\]

\[
G = \int_0^{0.5} \frac{y^2}{\lambda^2} \left[ \frac{C_1 y_i^2}{T^* - \frac{16.5}{V^{*2}} - \frac{7.5}{V^*}} \right] dy_i.
\]

As it is seen from Eq. (12), taking \( C \) as a constant gives an incorrect limit for the second virial coefficient, i.e., \( B_2 = 0 \). Therefore we take \( C \) a function of \( T \) and \( V \). A possible form for the functionality for \( C \) which has the proper condition, that is, giving a finite value for \( B_2 \) as \( V \) goes to infinity can be presented in the following exponential form:

\[
C = x_1 \exp \left( -\frac{x_2 V^* + x_3}{V^*} \right) T^*,
\]

which can be approximated as

\[
C = x_1 \exp \left( -\frac{x_2 V^* + x_3}{V^*} \right).
\]

Therefore for functionality of \( C \) presented by Eq. (16) we derive Eq. (7) as

\[
P^* = \frac{2.02C}{V^{*5}} - \frac{2.41C}{V^{*4}} - \frac{\partial C}{\partial V^*} \frac{2.02}{V^{*4}} - \frac{2.41}{V^{*2}} \left( \frac{T^*}{V^*} - \frac{4}{3} \frac{\partial C}{\partial V^*} \right) \frac{A}{V^{*4}} \frac{B}{V^{*2}} \frac{G_1}{G} + \frac{4C}{3} \frac{4A}{V^{*5}} - \frac{2B}{V^{*3}} \frac{G_1}{G}.
\]

Parameters \( A \) and \( B \) of Eq. (9) have been improved so that Eq. (17) can predict pressures closer to experimental values for liquid–solid equilibrium pressure of argon and xenon. Figure 3 shows the effect of this correction on the isotherms calculated by Eq. (17). The value of parameters \( x_1, x_2, \) and \( x_3 \) in Eq. (16) have been calculated from Eqs. (10), (11), and (17) for argon and xenon. The results are shown in Table II.

(ii) Potential energy function: In the original LJD theory the pair correlation effects between molecules \( i \) and \( j \) which are represented by \( \alpha_{ij} \) have been ignored and then the potential function \( u_{ij}(r_i, r_j) \) which is the potential of molecules \( i \) and \( j \) when displaced from their cell centers by the vector displacement \( r_i \) and \( r_j \) is approximated as

\[
u_{ij}(r_i, r_j) = w_{ij}(r_i) + w_{ij}(r_j),
\]

where \( w_{ij}(r_i) \) is also approximated as

\[
w_{ij}(r_i) = \frac{1}{2} u_{ij}(0, 0) + [u_{ij}(r_i, 0) - u_{ij}(0, 0)].
\]

In the above equation \( u_{ij}(0, 0) \) is the potential function when molecules \( i \) and \( j \) are both in their cell center and \( u_{ij}(r_i, 0) \) is the potential energy when molecule is displaced from the cell center by the vector \( (r_i) \). A similar equation can be written for \( w_{ij}(r_j) \).

Using Eq. (19) the potential of the next-nearest-neighbor molecule on the molecule \( i \) can be presented as

$u_i(r_j) = \sum_j w_{ij}(r_j)
= \sum_j \frac{1}{r_i} u_{ij}(0,0) + \sum_j [u_{ij}(r_i,0) - u_{ij}(0,0)]. \quad (20)$

Therefore, the total potential function $U$ will be

$$U = \sum_{i=1}^{N} u_i(r_i) \quad (21)$$

and substituting from Eq. (20) into Eq. (21) we have

$$U = \sum_{i} \sum_{j} \frac{1}{2} u_{ij}(0,0) + \sum_{i} \sum_{j} \{[u_{ij}(r_i,0) - u_{ij}(0,0)] + \gamma\}. \quad (22)$$

In the above equation the pair correlation effects which can be expressed by $\sum_{i} \sum_{j} \alpha_{ij}(r_i, r_j)$ have been ignored. To increase the accuracy in the calculation of configurational integral $Z$ in Eq. (2), inclusion of the $\frac{1}{2} \sum_{i} \sum_{j} \alpha_{ij}(r_i, r_j)$ term is a necessity. However, its evaluation in Eq. (2) through integration is difficult but not impossible. Therefore to account for the pair correlation effect we introduce a perturbation term $\gamma$ in the total potential function [Eq. (22)] to obtain

$$U = \sum_{i} \sum_{j} \frac{1}{2} u_{ij}(0,0) + \sum_{i} \sum_{j} \{[u_{ij}(r_i,0) - u_{ij}(0,0)] + \gamma\}. \quad (23)$$

Introducing $\gamma$ which can be considered a function of temperature and pressure does not change, the proper functionality of the configurational integral. Therefore substituting for $U$ from Eq. (24) into Eq. (2) we have

$$Z = \left[ \int_{V_i} \exp\left[-\beta \sum_{j} \frac{1}{2} u_{ij}(0,0)\right] \times \exp\left[-\beta \sum_{j} \{[u_{ij}(r_i,0) - u_{ij}(0,0)] + \gamma\}\right] \, dr_i \right]^{N}. \quad (24)$$

The above equation can be rearranged to give

$$Z = \exp\left[-\beta N \sum_{j} \frac{1}{2} u_{ij}(0,0)\right] \exp(-\beta N \gamma) \times \left[ \int_{V_i} \exp\left[-\beta \sum_{j} [u_{ij}(r_i,0) - u_{ij}(0,0)]\right] \, dr_i \right]^{N}, \quad (25)$$

and this equation can be expressed in terms of the previously introduced terms $U_s$ and $V_f$ as

$$Z = \exp(-\beta U_s) \exp(-\beta \gamma N) V_f^{N}, \quad (26)$$

where

$$U_s = \sum_{i} \sum_{j} \frac{1}{2} u_{ij}(0,0) \quad (27)$$

and $V_f$ is defined as

<table>
<thead>
<tr>
<th></th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>2.394</td>
<td>0.104</td>
<td>0.325</td>
</tr>
<tr>
<td>Xe</td>
<td>2.085</td>
<td>0.025</td>
<td>0.182</td>
</tr>
</tbody>
</table>

TABLE II. The parameters of $x_1$, $x_2$, and $x_3$ of Eq. (10) for argon and xenon.
TABLE III. The $a$, $b$, $c$, and $d$ parameters of Eq. (32) for argon, xenon, and krypton.

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>4.2159</td>
<td>-3.9586</td>
<td>-3.8411</td>
<td>4.1611</td>
</tr>
<tr>
<td>Xe</td>
<td>0.0182</td>
<td>-2.1661</td>
<td>-0.0182</td>
<td>1.1767</td>
</tr>
<tr>
<td>Kr</td>
<td>-0.0628</td>
<td>-1.3657</td>
<td>0.0569</td>
<td>0.4249</td>
</tr>
</tbody>
</table>

\[ V_f = \int_{V_i} \exp\left[ -\beta \sum_j \left( u_{ij}(r_j,0) - u_{ij}(0,0) \right) \right] \, dr_j. \] (28)

Using $Z$ from Eq. (27) in Eq. (6) the following dimensionless equation for pressure can be obtained:

\[ P^* = -\left( \frac{\partial u^*}{\partial V^*} \right)_s + T^* \left( \frac{\partial \ln V^*}{\partial s^*} \right)_t - \left( C \frac{\partial V^*}{\partial V^*} \right)_s, \] (29)

where $V^*_f$ can be presented as

\[ V^*_f = \frac{V_f}{\sigma^3} = \frac{1}{\sigma^3} \int_{V_i} \exp\left[ -\beta \sum_j \left( u_{ij}(r_j,0) - u_{ij}(0,0) \right) \right] \, dr_j. \] (30)

The first and the second term in Eq. (30) are similar to the terms of Eq. (7) and can be named as $P^*_{LJD}$, that is the pressure obtained from the original potential function of LJD theory. Therefore Eq. (30) can be rewritten as

\[ \frac{\partial V^*}{\partial V^*} = \frac{P^*_{LJD} - P^*}{C}. \] (31)

As the reduced pressure $P^*$ has been corrected for the pair correlation effects its value should approach the experimental value. Taking this into consideration $(\partial V^*/\partial V^*)$ was calculated for the fcc lattice cell ($C = 12$).

Intensive investigation indicated that the calculated values of $(\partial V^*/\partial V^*)$ can give the best fit to an equation of the form

\[ \frac{\partial V^*}{\partial V^*} = \frac{a + c V^*}{1 + b V^* + d V^*^2}, \] (32)

where the calculated values of parameters $a$, $b$, and $c$ in this equation for Ar, Xe, and Kr are reported in Table III.

Now the obtained functionality of $(\partial V^*/\partial V^*)$ as presented by Eq. (33) makes the $(P^*V^*T^*)$ calculations possible through application of Eq. (30). The results are reported as $V^*$ versus $T^*$ in Figs. 4 and 5 and Tables IV and V.

RESULTS AND DISCUSSION

In Fig. 1 the isotherms obtained from improved $A$ and $B$ parameters of Eq. (9) are shown. As shown in these figures, when the constraint of satisfying critical conditions have been imposed on the model the pressure–volume curves have been shifted to the positive region of liquid–vapor phase diagrams. Also the predicted critical temperature ($T^*_c$) by the model [Eqs. (7) and (9)], using improved parameters ($T^*_c \sim 2$), is close to the experimental value ($T^*_c \sim 1.2$) where as the original model predicts a much higher value ($T^*_c \sim 10$).

In Fig. 2 the total potential energy calculated from improved $A$ and $B$ parameters have been compared with that of the original LJD. The shape of curves for the total potential energy indicates that improved parameters $A$ and $B$ especially on higher volume causes an increase in repulsion potential close to the cell wall. This means that near the cell walls as expected the repulsive forces are dominant and the particles can move more freely which characterize the behavior of vapor phase in a more rational manner.

In Figs. 3(a), 3(b), and 3(c) the $P^* - V^*$ isotherms obtained for the variable coordination number [Eqs. (16) and (17)] are shown. It is shown that the proposed functionality for coordination number can improve the prediction ability of ($V^*$) for liquid and vapor phases. Also it is shown in this figure that the pressure has shifted from negative to the more realistic positive values.

Figures 4 and 5 show the variation of $V^*$ versus $T^*$ of coexisting liquid and solid for argon and xenon, respectively. It is shown in this figure that the calculated values of $V^*$ are very close to the experimental values and this indicates how the correction on the LJD model for pair correlation effects provided the model with a higher prediction ability. It is also worth noting that from the original LJD model it is impossible to predict coexisting liquid and solid values of $V^*$, while the corrected model has done so with good accuracy.
Figure 6 shows the $P^* - V^*$ isotherms for xenon. It is shown in this figure that solid–liquid transition has been well predicted by the expected S shape curve at lower values of $V^*$. At higher values of $V^*$ and lower $T^*$, the isotherm curves in this figure indicate that the liquid–vapor transition has been well predicted. Therefore corrections on the LJD model have given it higher prediction ability over the original LJD model which is incapable of such predictions.

In Tables IV and V the molar volumes of solid ($V_s$, cm$^3$ mol$^{-1}$) and liquid ($V_l$, cm$^3$ mol$^{-1}$) for Ar and Xe have been calculated from Eq. (29) along with their experimental values are reported. In these tables, also, the percentage error of the calculated values compared with the experimental values are reported. As shown in Tables IV and V the percentage error is in the acceptable range, since, application of the Pourgheysar et al.$^{12}$ model results in a much higher error and the original Lennard-Jones model is incapable of predicting the solid–liquid transition.

**CONCLUSION**

Correcting the parameters of potential energy by using the coordination number as a variable improves the prediction ability of the LJD model for the liquid–vapor region.

Also correcting the potential energy for the pair correlation effects causes an improvement on predicting solid–liquid phase transition of the LJD model. Therefore, as shown in this paper considering both the coordination number as a variable and correcting the potential energy for the pair correlation effects make an improvement on the predicting ability of the LJD model over the whole solid–liquid vapor phase region.

**TABLE IV.** Calculated and experimental coexisting molar volumes of solid ($V_s$) and liquid ($V_l$) expressed in cm$^3$/mole for argon and their respective percentage errors.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Calculated $V_s$</th>
<th>Experimental $^a$ $V_s$</th>
<th>Error % $V_s$</th>
<th>Calculated $V_l$</th>
<th>Experimental $^a$ $V_l$</th>
<th>Error % $V_l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>13.88</td>
<td>15.70</td>
<td>2.09</td>
<td>16.05</td>
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<tr>
<td>92</td>
<td>13.89</td>
<td>15.67</td>
<td>1.83</td>
<td>15.96</td>
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<tr>
<td>94</td>
<td>13.89</td>
<td>15.67</td>
<td>1.50</td>
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<tr>
<td>95</td>
<td>13.90</td>
<td>15.66</td>
<td>1.41</td>
<td>15.83</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>97</td>
<td>13.90</td>
<td>15.65</td>
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<td>15.75</td>
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<tr>
<td>98</td>
<td>13.91</td>
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<td>15.71</td>
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<tr>
<td>99</td>
<td>13.91</td>
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<td>0.75</td>
<td>15.67</td>
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<td>100</td>
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<td>15.61</td>
<td>0.66</td>
<td>15.63</td>
<td>0.12</td>
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</tr>
</tbody>
</table>

$^a$Experimental values are obtained from Ref. 16.