Analytic Equation of State and Thermodynamic Properties of Solid FCC C$_{61}$D$_2$ Based on an Analytic Mean Field Approach

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Analytic expressions for the equation of state and internal energy of poly-exponential solids are derived based on the analytic mean field potential (AMFP) method. The formalism is applied to fcc C$_{61}$D$_2$. Two sets of potential parameters are determined by fitting the experimental compression data of C$_{61}$D$_2$ up to 1 GPa at 343 and 307 K, respectively. The difference between the two sets of parameters is small. Whereas the difference between the potential of the C$_{61}$D$_2$ molecules and that of the C$_{60}$ molecules is fairly prominent, the conclusion is different from that in the literature, and the reason is unclear at present. The thermo-physical properties including the isothermals, thermal expansion, isochoric heat capacity, Helmholtz free energy and internal energy are calculated and analyzed. The theoretical results agree well with the experimental data available for solid C$_{61}$D$_2$.

Key words: AMFP; Morse Potential; Equation of State; Fullerene; Thermodynamic Properties.

1. Introduction

Over the past years, C$_{60}$ and its derivatives have continued to attract considerable attention, due to both their elegant molecular structures and the intriguing structural, dynamic, and electronic properties of the solid phases of fullerenes. Pristine, C$_{60}$, has the form of a spherical shell, with 60 symmetrically equivalent carbon atoms [1]. At high temperature, the C$_{60}$ molecules form a face-centered cubic (fcc) structure with free molecular rotation. Below 260 K the lattice transforms into a simple cubic (sc) structure with a temperature- ($T$) [2 – 4] and pressure- ($P$) [5, 6] dependent degree of molecular orientational order, which freezes into an orientational glass below 90 K [7]. The transitions, and structures of the high- and low-temperature phases have been the objects of numerous experimental and theoretical studies.

In order to study the thermodynamic properties of C$_{60}$ better, several studies have recently been carried out on fullerenes modified by adding small side groups to decrease the symmetry of the molecule. The first step was to add only an oxygen atom to form the fullerene epoxide C$_{60}$O, the next to add instead the slightly larger CH$_2$ group to form C$_{61}$H$_2$ [7]. The effect of perturbing the icosahedral symmetry of C$_{60}$ by the addition of the O or CH$_2$ side group upon orientational order-disorder and glass transitions in solid C$_{60}$ has been studied by a combination of high-resolution capacitance dilatometry and single-crystal X-ray and powder inelastic neutron scattering. Both fullerene derivatives C$_{60}$O (epoxide) and C$_{61}$H$_2$ (6.5-annulene) are shown to undergo a sequence of transitions similar to that found in pure C$_{60}$.

Although the structure and phase behaviour of C$_{61}$H$_2$ have been studied at zero-pressure [7, 8], little is known about its properties under high pressure, especially its thermodynamic properties at high temperature and pressure. Lundin et al. [7] have therefore investigated the equation of state of C$_{61}$D$_2$ (which should have physical properties practically identical to those of C$_{61}$H$_2$) using the same equipment [9] and method as applied previously to C$_{60}$ [10, 11] and C$_{70}$ [12]. Lundin et al. [7] have fitted the Murnaghan equation to their experimental data, and have found a linear dependence of the bulk modulus on the pressure within the whole experimental pressure range. Although the scatter in the data of the bulk modulus is prominent, they concluded that the addition of a CH$_2$ side group to C$_{60}$ does not give a large effect on the bulk modulus, and the side group dwells in the intermolecular interactions remained those between C$_{60}$ “bellies” [7]. The present paper is concerned with the calculation of the thermodynamic properties of fcc C$_{61}$D$_2$. The
research on the thermo-physical properties of solid C_{61}D_{2} would be helpful for understanding the structure and phase properties of C_{60} and its derivatives. It is shown in the following sections that some conclusions deduced in the present paper are different from those of Lundin et al.

Several years ago, Wang et al. proposed the analytic mean field potential (AMFP) method [13–16], and they applied it to many materials. Bhatt et al. [17, 18] further applied the AMFP method to lead and alkali metals, and concluded that in comparison with other theoretical models the AMFP method is computationally simple, physically transparent and reliable in the study of thermodynamic properties at high pressures and high temperatures. Recently, Sun et al. proved that the AMFP method is an analytic approximation of the free energy from experiments at high pressure, whereas the Morse potential is too hard and gives compression curves prominently deviating from experiments [26, 27]. Here we also mention the intermolecular contributions to the CUST of Zubov et al. [24, 25].

The present paper is organized as follows. In Section 2 we derive an analytic equation of state based on the AMFP approach. In Section 3 the parameters of the double-exponential potential are determined by fitting experimental data of solid C_{61}D_{2}, and the numerical results are compared with experiments. In Section 4 the conclusion is presented.

2. Analytic Equation of State

In the poly-exponential potential

\[
\epsilon(s) = \epsilon_0 \sum_{j=14}^{m} C_j \exp[\lambda_j(1 - r/r_0)]
\]

\(r_0\) is the equilibrium distance and \(\epsilon_0\) the well depth. For the double-exponential potential we have \(m = 2\), and

\[C_1 = \lambda_2/(\lambda_1 - \lambda_2), \quad C_2 = -\lambda_1/(\lambda_1 - \lambda_2).
\]

The two parameters \(\lambda_1\) and \(\lambda_2\) describe the decay of the potential versus the radial coordinate \(r\).

In terms of the FVT, the free energy can be expressed as [19, 23, 29, 30]

\[
\frac{F}{NkT} = \frac{3}{2} \ln(2\pi\mu kT/h^2) + \frac{u(0)}{2kT} - \ln v_f,
\]

where \(\mu\) is the mass of the C_{61}D_{2} molecule. \(u(0)\) is the potential energy of a molecule, as the lattice is static, and \(v_f\) is the free volume:

\[
u_f = 4\pi \int_0^{R_m} \exp[-g(r,V)/kT]r^2 dr,
\]

where \(R_i = \delta_i a\) is the distance of molecules in the \(i\)-th shell with the centre molecule at \(i = 0\), \(a\) is the nearest-neighbour distance. \(z_i\) and \(\delta_i\) are structural constants (the values for the fcc structure have been given in [32]), \(g(r,V)\) is the potential energy of a molecule as it roams from the centre to a distance \(r\). In terms of the AMFP approach [13–19], \(g(r,V)\) can be expressed by the static energy \(E_s(a)\) of a molecule:

\[
g(r,V) = \frac{1}{2} \left[ \left(1 + \frac{r}{a}\right) E_s(a + r) + \left(1 - \frac{r}{a}\right) E_s(a - r) - 2E_s(a) \right],
\]

\(g(r,V)\) can be expressed by the static energy \(E_s(a)\) of a molecule:

\[
g(r,V) = \frac{1}{2} \left[ \left(1 + \frac{r}{a}\right) E_s(a + r)
\]

\[+ \left(1 - \frac{r}{a}\right) E_s(a - r) - 2E_s(a) \right],
\]

\(E_s(a)\) can be expressed by the static energy \(E_s(a)\) of a molecule:

\[
g(r,V) = \frac{1}{2} \left[ \left(1 + \frac{r}{a}\right) E_s(a + r)
\]

\[+ \left(1 - \frac{r}{a}\right) E_s(a - r) - 2E_s(a) \right],
\]
to temperature and reduced volume can be expressed as:

\[ E_c(a) = \frac{1}{2} u(0) = \frac{1}{2} \sum_{\mathbf{r} \neq \mathbf{0}} z(x, y). \]  

(7)

\[ r_m = (3a^3/4\pi \gamma)^{1/3} \approx a/2 \] is the Wigner-Seitz radius, which can be approximated by the largest displacement of the center molecule. \( \gamma \) is the structure constant; for the fcc structure it is \( \sqrt{2} \).

The volume of a fcc solid is \( V = Na^3/\gamma \). For simplicity, we introduce the dimensionless reduced free volume \( \tilde{v}_f \), the reduced volume \( y \), and the reduced radial coordinate \( x \) as follows:

\[ v = 4\pi x^3 \tilde{v} = 4\pi \gamma V \tilde{v}_f, \]  

(8)

\[ y = a/r_0 = (V/V_0)^{1/3}, \]  

(9)

\[ V_0 = N(r_0)^3/\gamma, \]  

(10)

\[ x = r/a, \quad x_m = \frac{r_m}{a} \approx \frac{1}{2}. \]  

(11)

The reduced free volume \( \tilde{v}_f \) and its derivatives with respect to temperature and reduced volume can be expressed as:

\[ \tilde{v}_f = \int_0^{x_m} \exp[-g(x, y)/kT] x^2 \, dx, \]  

(12)

\[ \tilde{v}_{fa} = T \frac{\partial}{\partial T} \tilde{v}_f \]  

\[ = \frac{1}{kT} \int_0^{x_m} \exp[-g(x, y)/kT] g(x, y)x^2 \, dx, \]  

(13)

\[ \tilde{v}_{fb} = -\frac{\partial}{\partial y} \tilde{v}_f \]  

\[ = \frac{1}{kT} \int_0^{x_m} \exp[-g(x, y)/kT] \frac{\partial}{\partial y} g(x, y)x^2 \, dx. \]  

(14)

Here \( g(x, y) \equiv g(r, V) \). Combining (5), (8) and (11), we have:

\[ g(x, y) \equiv g(r, V) \approx \frac{1}{4} \sum_{i \neq \mathbf{0}} z_i \left[ (1 + x) \epsilon(\delta_y + \delta_y x) 
+ (1 - x) \epsilon(\delta_y - \delta_y x) - 2 \epsilon(\delta_x y) \right], \]  

(15)

\[ \frac{\partial}{\partial y} g(x, y) \approx \frac{1}{4} \sum_{i \neq \mathbf{0}} z_i \delta_i \left[ (1 + x)^2 \epsilon'(\delta_y + \delta_y x) 
+ (1 - x)^2 \epsilon'(\delta_y - \delta_y x) - 2 \epsilon'(\delta_y) \right]. \]  

(16)

The compressibility factor and internal energy can be derived as:

\[ Z = \frac{PV}{NkT} = -\gamma \frac{\partial}{\partial y} \frac{u(0)}{NkT} = \frac{P}{NkT} + \frac{P}{NkT}, \]  

(18)

\[ P \frac{\partial V}{\partial T} = -\gamma \frac{\partial}{\partial y} \frac{u(0)}{NkT} = 1 + \frac{\gamma}{3} \frac{\partial}{\partial T} - \frac{u(0)}{NkT} \]  

(19)

\[ \frac{\partial}{\partial y} u(0) = \sum_{i \neq \mathbf{0}} z_i \delta \epsilon'(\delta_y), \]  

(20)

\[ \frac{P}{NkT} = 1 + \frac{\gamma}{3} \frac{\partial}{\partial T} \tilde{v}_f - \frac{u(0)}{NkT} \]  

(21)

\[ \frac{U}{NkT} = -T \left. \frac{\partial}{\partial T} F \right| = \frac{3}{2} + \frac{u(0)}{2kT} + \frac{T}{\tilde{v}_f} \frac{\partial}{\partial T} \tilde{v}_f \]  

(22)

where \( P_c \) is the critical pressure and \( P_1 \) the thermal pressure deduced from the free volume.

By using the above equations, all other thermodynamic quantities can be analytically derived. The derivations are straightforward. However, the expressions for the thermal expansion coefficient, compressibility coefficient and isochoric heat capacity are redundant; we would calculate these quantities by using numerical differentiation instead of the analytic expressions. The compressibility factor can be seen as a function of the variables \( y \) and \( T \), \( Z = Z(y, T) \). In terms of the function, the formulas for the thermal expansion coefficient, compressibility coefficient and isochoric heat capacity can be reduced to the following form:

\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{3}{V} \left( \frac{\partial y}{\partial T} \right)_p \]  

(23)

\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{3}{V} \left( \frac{\partial P}{\partial T} \right)_y \]  

(24)

\[ C_v = \frac{1}{Nk} \left( \frac{\partial U}{\partial T} \right)_v = \frac{u}{NkT} + T \frac{\partial}{\partial T} \left( \frac{U}{NkT} \right)_y. \]  

(25)
In our calculations it is found that following the steps of the numerical differentiations in (23) – (25) can reach stable numerical results, \( \Delta T = 0.00001 \cdot T \) and \( \Delta y = 0.00001y \).

3. Numerical Results and Discussion

In this section we apply the above formalism to fcc C\(_{61}\)D\(_2\). We notice that one nonphysical phenomenon exists in the original experimental data of Lundin et al. [7]. In terms of the thermodynamic laws, the pressure should be an increasing function of the temperature. However, the experimental data of Lundin et al. [7] showed the contrary tendency, i.e. the pressure decreases as the temperature increases, as shown in Figure 1. They [7] have not explained the abnormal phenomena. Lundin et al. [7] gave three sets of experimental data at 175, 307 and 343 K. Their analysis exhibited that the solid C\(_{61}\)D\(_2\) can exist in an sc and fcc phase at low- and high-temperature regions, and the sc-to-fcc transformation temperature is about 290 K. In terms of these results, we propose a possible explanation for the abnormal phenomena. At 175 K solid C\(_{61}\)D\(_2\) exists in the sc phase; it has a low density. At 343 K solid C\(_{61}\)D\(_2\) exists in the fcc phase; it has a high density. As the two phases have compressed to the same high density, the sc phase must have a higher compression ratio \( V/V_0 \) than the fcc phase; thus the sc phase (at low temperature) has a higher pressure than the fcc phase (at high temperature). At 307 K solid C\(_{61}\)D\(_2\) may exist as a mixture of sc and fcc phases. The corresponding compression curve locates between the two curves at 175 and 343 K. Because our work mainly aimed to fit the experimental data by using the AMFP method approach and predict other thermodynamic properties of C\(_{61}\)D\(_2\), we feel it is difficult to give a sound explanation for the abnormal phenomena within the AMFP method theoretical framework of this paper. However, we think the present work may provide some issues for solving the problem.

Considering the three isothermals measured by Lundin et al. [7] at three temperatures (175, 307 and 343 K) and that the sc-to-fcc phase transition temperature of C\(_{61}\)H\(_2\) is about 290 K, we do not use the experimental data at 175 K, since at this temperature C\(_{61}\)D\(_2\) may freeze into an orientational glass. Although we have tried to fit the data at 307 and 343 K at same time, the fitting precision was not satisfactory. We thus determined two sets of parameters for the double-exponential potential by fitting the data at 307 and 343 K, respectively. The experimental data and smoothed fitting curves are plotted in Figure 1. The figure shows that the fitting precision is satisfactory. The determined values of the parameters are as follows:

\[
\begin{align*}
\lambda_1 &= 2.84, \quad \lambda_2 = 46.2, \\
r_0 &= 1.0092 \text{ nm}, \quad \varepsilon_0 = 1660 \text{ K (343 K)}, \\
\lambda_1 &= 2.70, \quad \lambda_2 = 54.0, \\
r_0 &= 1.0094 \text{ nm}, \quad \varepsilon_0 = 1710 \text{ K (307 K)}.
\end{align*}
\] (26) (27)

Equations (26) and (27) show that the difference between the two sets of parameters is small except for \( \lambda_2 \) the difference of which is about 20%.

Lundin et al. [7] have used the Murnaghan EOS to analyze their experimental data, and found that the bulk modulus at zero-pressure and 307 K is 6.4 GPa, which was in agreement with the value 6.8 GPa of solid C\(_{60}\) measured by themselves. Combining the lattice constant 1.419 nm of C\(_{61}\)H\(_2\) at ambient temperature is in accordance with that of solid C\(_{60}\), they concluded that the side groups dwell in intermolecular voids in the lattice and the main intermolecular interactions remain those between C\(_{60}\) “bellies”. However, in Fig. 2 we plot the potentials for C\(_{61}\)D\(_2\) molecules and C\(_{60}\) molecules. The figure shows that the well depth of C\(_{60}\) molecules is about 3200 K, deduced from both the Girifalco potential and the double-Yukawa potential [26, 30], far larger than 1660 and 1710 K given...
Table 1. Thermo-physical properties of the fcc phase of C_{61}D_{2} at zero-pressure calculated by using the parameters determined from the experimental data at 343 K: the lattice constant $a$ in nm, the linear thermal expansion coefficient $\alpha$ in $10^{-5}$ K$^{-1}$, the bulk modulus $B_T$ in kbar, the heat capacity $C_V$ in kJ mol$^{-1}$ K$^{-1}$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$a$ (nm)</th>
<th>$\alpha$ ($10^{-5}$ K$^{-1}$)</th>
<th>$B_T$ (kbar)</th>
<th>$C_V$ (kJ mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
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<td>54.081</td>
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<td>0.0229</td>
<td>14.235</td>
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</table>

Table 2. The same as for Table 1, but the parameters are determined from the experimental data at 307 K.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$a$ (nm)</th>
<th>$\alpha$ ($10^{-5}$ K$^{-1}$)</th>
<th>$B_T$ (kbar)</th>
<th>$C_V$ (kJ mol$^{-1}$ K$^{-1}$)</th>
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Fig. 2. Comparison of the double-Yukawa potential of the C_{60} molecules [30] with that of the C_{61}D_{2} molecules by using the parameters of (26) and (27), respectively.

by (26) and (27) of C_{61}D_{2} molecules. The result is different from the conclusion of Lundin et al. [7], and shows that the intermolecular interaction between the C_{61}D_{2} molecules deduced from the experimental data available at present is weaker than that between the C_{60} molecules.

In Tables 1 and 2, the calculated thermodynamic properties at zero-pressure and different temperatures by using the parameters (26) and (27) are listed, respectively. The spinodal point $T_s$ is the temperature satisfying the condition $B_T(T_s) = 0$. The system is instable for temperatures above $T_s$. From the two tables we know that $T_s$ is 1768 K and 1877 K for the parameters (26) and (27), respectively. The two tables show that the thermal expansion coefficient is an increasing function of the temperature, whereas the bulk modulus and the isochoric heat capacity are decreasing functions of the temperature. The thermal expansion coefficient becomes divergent and the bulk modulus tends to zero near the spinodal temperatures.

In Figs. 3 – 8, the results of thermodynamic properties of solid fcc C_{61}D_{2} calculated by using the double-exponential potential are plotted. The isother-
Fig. 4. Variations of the bulk modulus $B_T$ versus the pressure $P$ at the same temperatures as in Figure 3. The circles ($\circ$) are experimental data.

Fig. 5. Variation of the thermal expansion coefficient $\alpha$ versus the pressure $P$ calculated by using the parameters of (26) and (27), respectively.

Fig. 6. Variation of the isochoric heat capacity $C_V$ versus the pressure $P$ calculated in this work.

Fig. 7. Variation of the free energy $F$ versus the density $\rho$ at 343 K (a) [or 307 K (b)], 500 K, 800 K, 1200 K calculated by using the parameters of (26) and (27), respectively.

The bulk modulus versus pressure at the same temperatures are plotted in Figure 4. In the two figures, the experimental data available are also plotted for compar-
Fig. 8. The same as for Fig. 7, but for the internal energy $U$.

Figure 6 shows that $C_v$ is an increasing function of pressure, and the variation is fast at low pressure and slow at high pressure. Figures 7 and 8 plot the variation of the free energy $F$ and internal energy $U$ versus density $\rho$ at four temperatures. The two figures show that $F$ and $U$ are increasing functions of density for all temperatures, and the variation at low temperatures is faster than that at high temperatures. However, $F$ and $U$ are increasing functions of temperature at low-density condition. And the situation changes as the density increases; $F$ and $U$ become decreasing functions of temperature at high density.

4. Conclusion

In summary, expressions on the equation of state and internal energy for a poly-exponential solid have been derived, based on the AMFP method. The formalism was applied to solid fcc $C_{61}D_2$. Two sets of potential parameters were determined through fitting the experimental compression data of $C_{61}D_2$ up to 1 GPa and at 343 and 307 K, respectively. The difference between the two sets of parameters was small, whereas the difference between the potential for the $C_{61}D_2$ molecules and that for the $C_{60}$ molecules was fairly prominent. The reason is unclear at present. The calculated results agree well with the experimental data available for solid $C_{61}D_2$. We think it is very necessary to make more investigations on solid $C_{61}D_2$.

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