Gas-solid coexistence of the Lennard-Jones system

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LETTERS TO THE EDITOR

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NOTES

Gas–solid coexistence of the Lennard-Jones system

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In a recent paper,¹ Barroso and Ferreira reported on free energy calculations of the Lennard-Jones (LJ) system at solid–liquid and solid–gas coexistence, from Monte Carlo simulations. In that paper, they compared the absolute values of the free energy along the melting line with those calculated from an equation of state for the solid phase, developed by the present author.² In this note we want to make the same comparison for the sublimation line, on which no data was reported in Ref. 2. The present data is—to our knowledge—the most accurate available in literature on gas–solid phase coexistence of the LJ system. In the following, we will consider all values in reduced (LJ) units.

In Ref. 2, we proposed a simple explicit expression for the free energy of the face-centered cubic (fcc) LJ crystal, obtained by fitting the energy and pressure data from molecular dynamics simulations for a large number of state points. The only “empirical” input required in the final expression for the free energy is the triple-point temperature T_{trip} . In Ref. 2, we choose the value $T_{\text{trip}}=0.687$ (reduced units) reported by Agrawal and Kofke.³ However, for the present comparison with the data of Ref. 1, we rather use the estimate $T_{\text{trip}}=0.692$ from Ref. 1. The gas–solid coexistence line (sublimation line) is subsequently evaluated from the condition of equal chemical potential and pressure for both phases, where the thermodynamic properties for the gas phase are calculated from the equation of state by Johnson *et al.*⁴ (hereafter called the Johnson EoS), as was done in Ref. 1. It should be noted, however, that strictly speaking the Johnson EoS is only valid for temperatures larger than 0.7; we have therefore also calculated the coexistence properties from the virial equation of state (up to the third virial coefficient) for the gas phase, however, the difference with the results from the Johnson EoS was negligible. In Fig. 1 we compare our results for the pressure (solid line) and density (dashed line) at coexistence with the results from Barroso and Ferreira¹ (filled symbols) and Agrawal and Kofke³ (open symbols). We find excellent agreement. In Fig. 2, we show the excess free-energy per particle as a function of temperature along the sublimation line. Again, the solid line is obtained from our equation of state, the filled symbols are the

results from Barroso and Ferreira.¹ The two results agree within 0.3%.

The advantage of evaluating the sublimation line from an equation of state (EoS), rather than from direct simulations as was done in Ref. 1, is that one can obtain an arbitrary number of points on the line, which allows for an accurate fit of the thermodynamic data. By contrast, in Ref. 1 only eight points on the line were listed. Moreover, from the equation of state, the sublimation line can be evaluated for arbitrarily low temperatures. Since the pressure (and thus the gas density) decreases by some 7 orders of magnitude if the temperature is lowered from $T=0.692$ to $T=0.3$ (the lowest temperature considered in this work), the most accurate fit is obtained by considering the deviation from the low temperature limit. In the limit $T \rightarrow 0$, the leading terms in the pressure p and chemical potential μ of the solid phase are²

$$\lim_{T \rightarrow 0} p(\rho, T) = \rho^2 \frac{\partial u^{\text{stat}}(\rho)}{\partial \rho},$$

FIG. 1. Pressure (solid line and circles) and density of the solid phase (dashed line and squares) as function of temperature, along the gas–solid coexistence line. The lines are evaluated from the equation of state in Ref. 2; the filled and open symbols are the results from Ref. 1 and Ref. 3, respectively.

FIG. 2. As Fig. 1, but for the excess free energy per particle.

$$\lim_{T \rightarrow 0} \mu(\rho, T) = u^{\text{stat}}(\rho) + \rho \frac{\partial u^{\text{stat}}(\rho)}{\partial \rho},$$

with u_{stat} the static energy per particle in the crystal, which can be expressed as $u_{\text{stat}} = d_2 \rho^2 + d_4 \rho^4$, with the coefficients d_2 and d_4 given in Table I. For the gas-phase properties in the limit $T \rightarrow 0$ we may use $p \rightarrow 0$ and $\mu = T \ln \rho$. At coexistence, the gas-phase density ρ_g and solid-phase density ρ_s in the limit $T \rightarrow 0$ are then given by the set of equations,

$$\left. \begin{aligned} 0 &= 2d_2\rho_s^3 + 4d_4\rho_s^5 \\ T \ln \rho_g &= 3d_2\rho_s^2 + 5d_4\rho_s^4 \end{aligned} \right\} \Rightarrow \left\{ \begin{aligned} \rho_s &= \left(\frac{-d_2}{2d_4} \right)^{1/2} \\ \ln \rho_g &= -\frac{d_2^2}{4d_4} \frac{1}{T} \end{aligned} \right.$$

TABLE I. Values for the parameters in Eqs. (1)–(3).

n	a_n	b_n	c_n	d_n
0	10.486 31	10.491 07	...	...
1	−16.817 71	−16.838 18	−0.134 343	...
2	35.100 31	34.957 54	−0.095 079 5	−14.453 920 93
3	−48.764 87	−47.664 12	0.137 215	...
4	36.391 36	33.908 21	−0.161 890	6.065 940 096
5	−10.907 88	−9.011 857	...	...

Hence, we have fitted the data at finite temperature for the pressure P_{coex} , the gas-phase density ρ_g and solid-phase density ρ_s at coexistence to the expressions,

$$\ln \left(\frac{P_{\text{coex}}}{T} \right) = -\frac{d_2^2}{4d_4} \frac{1}{T} + \sum_{n=0}^5 a_n T^n, \quad (1)$$

$$\ln \rho_g = -\frac{d_2^2}{4d_4} \frac{1}{T} + \sum_{n=0}^5 b_n T^n, \quad (2)$$

$$\rho_s = \left(\frac{-d_2}{2d_4} \right)^{1/2} + \sum_{n=1}^4 c_n T^n. \quad (3)$$

The results for the parameters a_n , b_n , and c_n from a least-square fit of 3921 points on the sublimation line from $T = 0.3$ to $T = 0.692$, are listed in Table I. The largest deviation of the fit from the actual data is 0.01%. Again, we remind that we used the estimate $T_{\text{trip}} = 0.962$ for the triple point temperature, rather than the value $T_{\text{trip}} = 0.687$ from Agrawal and Kofke.³ The effect of this number on P_{coex} is small however; the pressure calculated from the fit (1), multiplied by 1.0123, is within 0.02% of the data at coexistence calculated with the use of $T_{\text{trip}} = 0.687$, i.e., the difference is about 1%. The same multiplication factor on ρ_g from Eq. (2) is within 0.04% of the data from $T_{\text{trip}} = 0.687$; the effect of T_{trip} on ρ_s is negligible.

In conclusion, the sublimation line as calculated from the equation of state in Ref. 2 is in excellent agreement with the data of Barroso and Ferreira.¹ This result provides further support for the accuracy of both the method of calculation in Ref. 1, and the equation of state in Ref. 2.

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¹M. A. Barroso and A. L. Ferreira, J. Chem. Phys. **116**, 7145 (2002).

²M. A. van der Hoef, J. Chem. Phys. **113**, 8142 (2000).

³R. Agrawal and D. A. Kofke, Mol. Phys. **85**, 43 (1995).

⁴J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, Mol. Phys. **78**, 591 (1993).