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## Phase Equilibrium Calculations by Equation of State v2

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### SUMMARY

Practical methods for phase equilibrium calculations by the equation of state for a perfect solid and liquid (v2) are described using examples of worksheets. Using the Microsoft Excel worksheets, the pressure, Gibbs energy and other thermodynamic quantities of a molecular system are obtained as functions of temperature and volume. Some examples of VBA (Visual Basic for Applications) programs are given to obtain volume and other thermodynamic properties as a function of temperature under a given pressure. The thermodynamic consistency test is performed as a function of temperature at a given pressure, where the difference between the heat capacity under a constant pressure and that under a constant volume should equal to an expression consisting of the thermal expansion coefficient, temperature, volume and isothermal compressibility.

KEY WORDS: phase equilibrium, equation of state, perfect solid and liquid, thermodynamic consistency

### 1. INTRODUCTION

Solid-liquid-gas transition is observed in ordinal substances [1]. The phase transition is a result of intermolecular interactions at a finite temperature [2]. This phenomenon is calculated by the equation of state (EOS) for these phases [1, 2]. An equation of state for a perfect solid is proposed [3, 4] using a simplified model of a face-centered cubic lattice of a pure substance consisting of spherical molecules. The Lennard-Jones interaction is assumed as follows [1]:

$$u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (1)$$

The constant  $\varepsilon$  is the depth of the potential well and  $\sigma$  is the separation at which  $u(\sigma) = 0$ . Constants  $\varepsilon$  and  $\sigma$  are used as the units of energy and length, respectively.

The van der Waals EOS [1] is assumed for a liquid phase and the three phase equilibrium is derived in previous studies [5, 6]. The pressure EOS is written as follows:

$$p = \frac{NkT}{V - Nb} - a \left( \frac{N}{V} \right)^2 \quad (2)$$

The first term on the right hand side (RHS) of the equation is the repulsion effect in a 1-D hard sphere system [2]. The symbol  $N$  indicates the number of molecule in the system. The Boltzmann constant is written as  $k$ . The symbols  $p$ ,  $V$  and  $T$  are the pressure, volume and temperature, respectively. This repulsion term is modified by Carnahan-Starling for a 3-D hard sphere system [7]:

$$p(V, T) = \frac{kT}{v} \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{a}{v^2}, \quad (3)$$

$$v \equiv \frac{V}{N}, \quad \eta \equiv \frac{\pi \sigma_{HS}^3}{6v},$$

where  $a$  is the van der Waals coefficient and  $\eta$  is the packing fraction.

The internal energy of the van der Waals EOS is expressed as follows [2, 8]:

$$U(V, T) = \frac{3}{2} NkT - \frac{aN^2}{V}. \quad (4)$$

## 2. MAIN CHARACTER OF EQUATION OF STATE FOR A PERFECT SOLID

Pressure  $p$  and internal energies  $U$  of each phase, i.e., solid and liquid, are written as functions of temperature and volume [9].

The internal energy of the EOS for a perfect solid is the sum of the averaged kinetic energy and the potential energy [9]:

$$U(V, T) = \frac{3}{2}NkT + E_{p,ext}(V, 0K), \quad (5)$$

The pressure EOS for a perfect solid is given as [9]:

$$p(V, T) = \frac{NkT}{V} - \left( \frac{\partial E_{p,ext}(V, 0K)}{\partial V} \right)_T + \frac{6\sigma^3 NkT}{V^2}. \quad (6)$$

The entropy  $S$  is expressed as a function of volume and temperature by the standard thermodynamic procedure [1, 3, 5, 9].

The most important characteristic of the present EOS is that it is composed of the perfect gas term, 0 K term and an additional term proportional to the temperature  $T$ . The last term is not included in the internal energy in the present paper.

$$p(V, T) = p(\text{perfect gas}) + p(0K) + p(T > 0K) \quad (7)$$

## 3. CRITICAL POINT

The solid-gas critical point is obtained from a plot of pressure  $p$  vs. volume  $V$  as shown in Fig. 1. This calculation is shown with an example of VBA programs [10]. To run the program, “macros” is chosen in Microsoft Excel as described in Figs. 2 and 3. Another program for calculating the critical point in the liquid phase is attached [11]. A plot of  $p$  vs.  $v$  in the liquid phase is obtained by running this program as shown in Fig. 4.

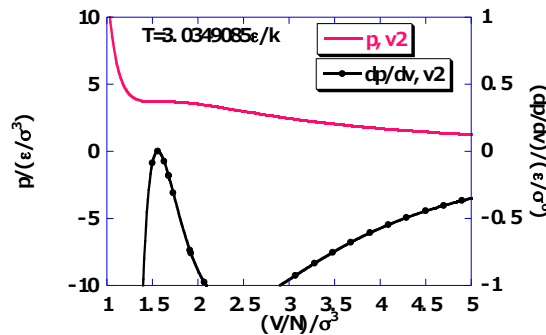


Fig. 1 Plots of  $p$  and its derivative vs.  $V$  in the solid phase at  $T = 3.0349085 \text{ } \epsilon/k$ .

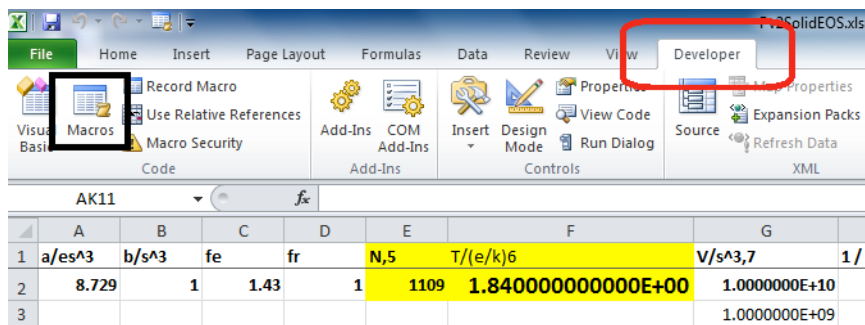


Fig. 2 Developer - Macros

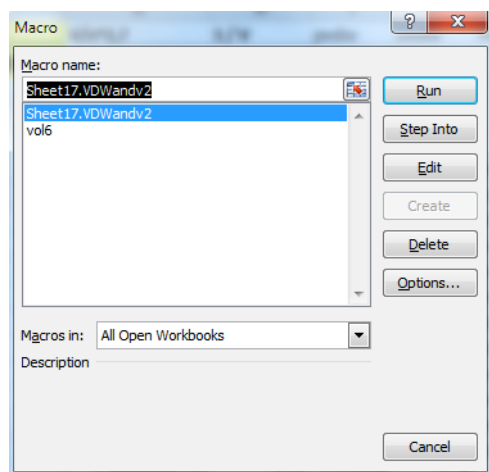
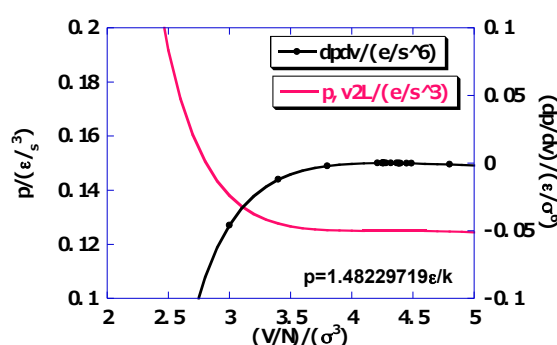


Fig. 3 Macro name – Run

Fig. 4 Plots of  $p$  and its derivative vs.  $V$  in the liquid phase at  $T = 1.48229719 \epsilon/k$ .

## 5. CALCULATION OF PHASE TRANSITION POINT

The pressure  $p$  and Gibbs energy per molecule  $G/N$  are tabulated as a function of volume  $V$  at a given temperature  $T$  as in Table 1. An example of the worksheets for this purpose is given in ref. [12]. The  $G/N$  vs.  $p$  plot is shown in Fig. 5 for the solid phase. Fig. 6 shows the  $G/N$  vs.  $p$  plot for the liquid phase. An overlapped figure of both plots (Fig. 7) is obtained by the copy and paste function in Microsoft Excel. If the calculated points are sparse as in Fig. 7, more points are necessary to fix the phase transition point precisely.

The melting temperature, vapor pressure and sublimation vapor pressure are calculated and compared with experimental and simulation results in a previous paper [9].

Table 1 Example of a table for the phase transition point calculation.

$T/(\epsilon/k)$	$s^3/V$	$V/s^3$	$p, v2soidext/ended$	$G, v2soidext/ended$	$p, v2L liquid/ended$	$G, v2L liquid/ended$
0.75005	1.00E-03	1.00E+03	7.46E-04	-2.99E+00	7.43E-04	-3.00E+00
	1.00E-02	1.00E+02	7.09E-03	-1.34E+00	6.80E-03	-1.40E+00
	1.00E-01	1.00E+01	4.51E-02	-1.80E-01	6.95E-03	-9.03E-01
	2.00E-01	5.00E+00	4.09E-02	-1.85E-01	-1.10E-01	-1.67E+00
	3.00E-01	3.33E+00	-6.99E-02	-6.13E-01	-3.23E-01	-2.52E+00
	4.00E-01	2.50E+00	-4.01E-01	-1.55E+00	-5.93E-01	-3.29E+00
	5.00E-01	2.00E+00	-1.05E+00	-2.97E+00	-8.55E-01	-3.88E+00
	6.00E-01	1.67E+00	-1.97E+00	-4.65E+00	-1.01E+00	-4.16E+00
	7.00E-01	1.43E+00	-2.87E+00	-6.05E+00	-8.70E-01	-3.96E+00
	8.00E-01	1.25E+00	-3.01E+00	-6.25E+00	-1.50E-01	-3.01E+00
	9.00E-01	1.11E+00	-1.00E+00	-3.92E+00	1.70E+00	-8.47E-01
	1.00E+00	1.00E+00	5.40E+00	2.77E+00	5.73E+00	3.37E+00
	1.10E+00	9.09E-01	1.96E+01	1.62E+01	1.41E+01	1.13E+01

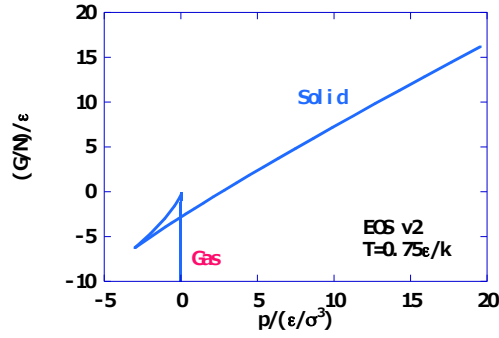


Fig. 5  $G/N$  vs.  $p$  in the solid phase at  $T = 0.75 \epsilon/k$ .

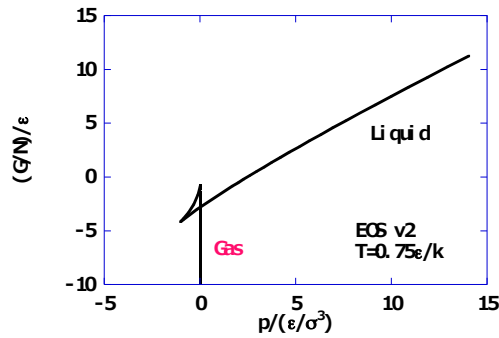


Fig. 6  $G/N$  vs.  $p$  in the liquid phase at  $T = 0.75 \epsilon/k$ .

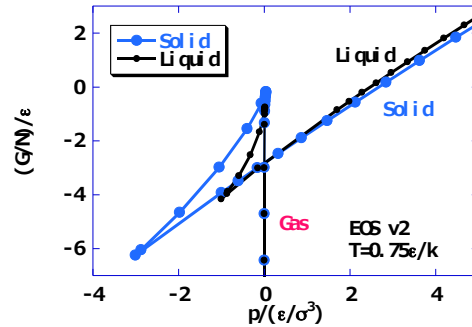


Fig. 7 Overlapped figure of  $G/N$  vs.  $p$  plots in the solid and liquid phases at  $T = 0.75 \epsilon/k$ .

## 6. THERMODYNAMIC QUANTITIES AT A GIVEN PRESSURE

The equation for a given pressure  $p_0$  must be solved to discuss the thermodynamic properties under a constant pressure  $p_0$ .

$$p(V, T) = p_0 \tag{8}$$

This is solved by Goal Seek in Microsoft Excel [13].

In practice, a reasonable trial volume should be given for each phase. The typical volume is shown below:

$$\begin{aligned} v &\approx 200\sigma^3 \text{ (gas),} \\ v &\approx 1.2\sigma^3 \text{ (liquid),} \\ v &\approx 1.1\sigma^3 \text{ (solid)} \end{aligned} \tag{9}$$

The obtained results for volume are given in Fig. 8 for  $p_0 = 0.005 \epsilon/\sigma^3$ . The entropy per molecule  $S/N$  is plotted against temperature  $T$  in Fig. 9.  $G/N$  vs.  $T$  is plotted in Fig. 10.

Some VBA programs are attached for calculations of volume and other thermodynamic quantities at a given pressure [14, 15].

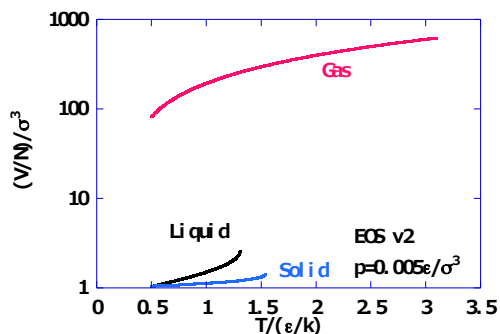


Fig. 8 Volume per molecule vs.  $T$  at  $p = 0.005 \epsilon/\sigma^3$ .

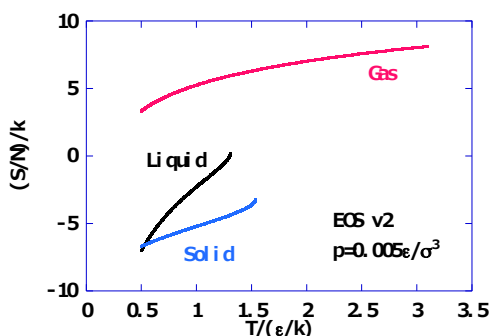


Fig. 9  $S/N$  vs.  $T$  at  $p = 0.005 \epsilon/\sigma^3$ .

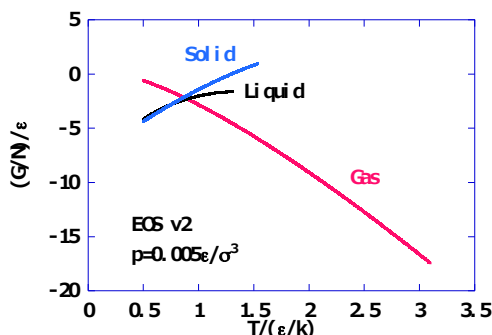


Fig. 10  $G/N$  vs.  $T$  at  $p = 0.005 \epsilon/\sigma^3$ .

Finally, an example of thermodynamic consistency tests is shown. The following equation must be satisfied in thermodynamics:

$$C_p - C_v = \frac{\alpha^2 TV}{\kappa_T} \quad (9)$$

The heat capacity under a constant pressure  $C_p$ , heat capacity under a constant volume  $C_v$ , expansion coefficient  $\alpha$  and isothermal compressibility  $\kappa_T$  are the typical notations used in thermodynamics. This equation is satisfied within numerical errors as shown in Figs. 11 and 12. Fig. 12 shows the absolute value of the difference between the LHS and the RHS of the equation normalized by the LHS. The increment of temperature  $\Delta T$  is  $0.001 \epsilon/k$  in the numerical differentiation by temperature for the calculation of the expansion coefficient.

$$\left(\frac{\partial V}{\partial T}\right)_p \approx \left(\frac{\Delta V}{\Delta T}\right)_p \quad (10)$$

The increment of pressure  $\Delta p$  is  $0.001 \epsilon/\sigma^3$  in the solid and liquid phases for the calculation of isothermal compressibility.

$$\left(\frac{\partial V}{\partial p}\right)_T \approx \left(\frac{\Delta V}{\Delta p}\right)_T \quad (11)$$

In the case of the gas phase, the increment of pressure  $\Delta p$  is  $5 \times 10^{-6} \epsilon/\sigma^3$ . The numerical error is large only for the region where the expansion coefficient, isothermal compressibility and heat capacity under a constant pressure have very large values as seen in Figs. 11 and 12.

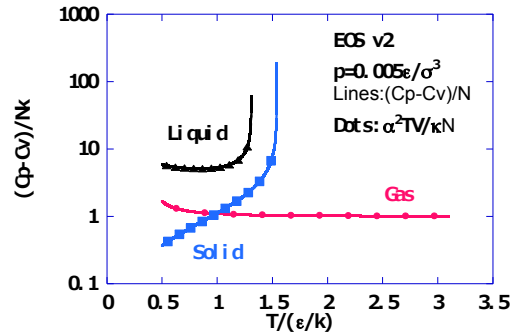


Fig. 11 Thermodynamics quantity  $(C_p - C_v)/N$  and  $\frac{\alpha^2 TV}{\kappa_T N}$  vs.  $T$  at  $p = 0.005 \epsilon/\sigma^3$ .

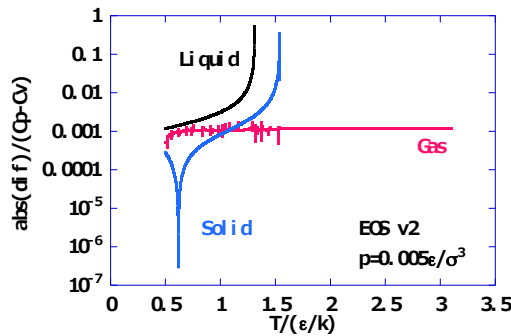


Fig. 12 Relative error  $\left| \left( C_p - C_v \right) / N - \frac{\alpha^2 TV}{\kappa_T N} \right| / \left[ \left( C_p - C_v \right) / N \right]$  vs.  $T$  at  $p = 0.005 \epsilon/\sigma^3$ .

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