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## Numerical Calculations in Phase Equilibrium by Equation of State v3

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### SUMMARY

A practical method for phase equilibrium calculations using the equation of state for a perfect solid and a perfect liquid is shown along with examples of Excel worksheets. The molecular systems of a perfect solid and a perfect liquid are assumed to be composed of single-type spherical molecules. The molecular interaction is expressed by a Lennard-Jones potential function. The pressure and internal energy of the system are expressed as functions of temperature and volume. Other thermodynamic functions such as entropy are also given as functions of temperature and volume. A thermodynamic constancy test is performed.

KEY WORDS: phase equilibrium, equations of state for a perfect solid and a perfect liquid, thermodynamic constancy test

### 1. INTRODUCTION

The new equation of state (EOS) of a liquid is derived [1] from molecular dynamics simulations of a Lennard-Jones system. This paper provides some details on phase equilibrium calculations using the equation of state v3.

The internal energy  $U(V, T)$  is expressed as functions of volume  $V$  and temperature  $T$ :

$$U(V, T) = \frac{3}{2} NkT + U_e(V, 0 \text{ K}) + g(V)NkT, \quad (1)$$

where  $N$  is the number of molecules in the system and  $k$  is the Boltzmann constant. The first term is the average kinetic energy and the second term is the volume-dependent average potential energy at 0 K. The third term represents the temperature-dependent average potential energy, which may also be dependent on the volume as a function of  $g(V)$ . These functions are assumed separately for a perfect solid and a perfect liquid.

The pressure EOSs are expressed as follows to satisfy the thermodynamic EOS [2]:

$$p(V, T) = \frac{NkT}{V} - \frac{dU_e(V, 0 \text{ K})}{dV} + f(V)NkT + \left( \frac{dg(V)}{dV} \right) NkT \ln(kT) \quad (2)$$

The first term is the contribution of average kinetic energy for a perfect gas. The second term corresponds to the average potential energy at 0 K. The third term represents the temperature-dependent virial term [3-8]. The last term is related to the last term of Eq. (1) and is added to satisfy the thermodynamic EOS [2].

### 2. EQUATION OF STATE

The EOS functions shown in Eqs. (1) and (2) are assumed in the derivation of the equation of state. The volume per molecule is used in the following expressions:

$$v = \frac{V}{N} \quad (3)$$

The following functions are adapted for simplicity [1]:

$$\frac{U_{e,s}(v, 0 \text{ K})}{N\varepsilon} = 6\left(1 + \frac{1}{128}\right)\frac{\sigma^{12}}{v^4} - 12\left(1 + \frac{1}{5}\right)\frac{\sigma^6}{v^2} \quad (\text{Solid}) \quad (4)$$

$$\frac{U_{e,f}(v, 0 \text{ K})}{N\varepsilon} = 1.0692052 \times \left(1.5\frac{\sigma^{18}}{v^6} - 8.2\frac{\sigma^3}{v}\right) \quad (\text{Liquid}) \quad (5)$$

The terms containing the high powers  $v^{-4}$  and  $v^{-6}$  in Eqs (4) and (5), respectively, represent the short range force effects. The other terms represent the long range force effects.

The coefficient functions  $g(v)$  and  $f(v)$  are assumed as below [1]:

$$g_s(v) = 1.35\frac{\sigma^3}{v}, f_s(v) = 6\frac{\sigma^3}{v^2}, F_s(v) = \int 6\frac{\sigma^3}{v^2} dv = -6\frac{\sigma^3}{v} \quad (\text{Solid}) \quad (6)$$

$$g_f(v) = \frac{\sigma^3}{v}, f_f(v) = 4.9\frac{\sigma^3}{v^2}, F_f(v) = -4.9\frac{\sigma^3}{v} \quad (\text{Liquid}) \quad (7)$$

Using the definition of  $F_f(v)$ , the entropy change is written as follows [1]:

$$\Delta S = S(V_f, T_f) - S_0 = g(V_f)Nk + Nk \ln\left(\frac{V_f}{N\sigma^3}\right) + F(V_f)Nk + \left(\frac{3}{2}Nk + g(V_f)Nk\right) \ln\left(\frac{kT_f}{\varepsilon}\right) \quad (8)$$

$$S_0 = Nk \ln\left(\frac{Nv_{\max}}{N\sigma^3}\right) \quad (9)$$

Hereafter, the entropy change is expressed as a function of entropy  $S$ .

### 3. THERMODYNAMIC QUANTITIES

Averages of the potential energy, pressure and other thermodynamic quantities are obtained using worksheets [9]. The most basic quantity is the average potential energy at 0 K and its contribution to pressure is shown in Fig. 1. At the minimum potential energy,  $p = 0$ . The pressure  $p$  and its derivative with respect to volume are plotted as a function of number density in Fig. 2. The components of pressure are shown in Fig. 3. The short range and long range forces are the most important contributors and the virial term at  $T > 0$  is also large. In Fig. 4, the components of the internal energy are plotted as a function of number density. The temperature-dependent term is not significantly large in this case. Figure 5 gives the components of the entropy as a function of number density. The ideal gas term and the virial term at  $T > 0$  ( $F(V)Nk$ ) are large.

The phase transition points are obtained from the  $G/N$  vs.  $p$  plot in Fig. 6. The cross points are the phase transition points as indicated by the arrows in Fig. 6.

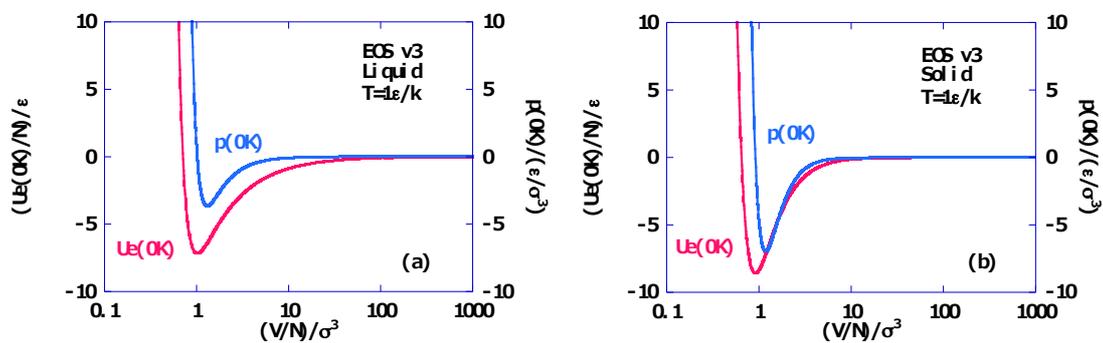


Fig. 1 Average potential energy at 0 K and its contribution to pressure vs. volume plots.

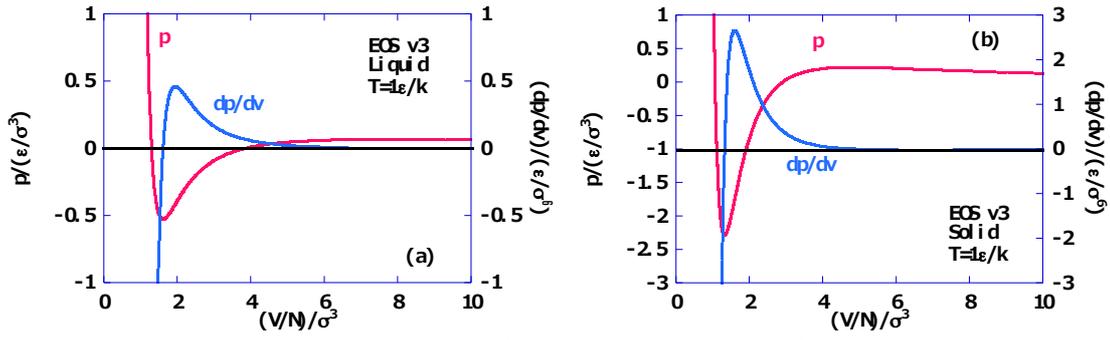


Fig. 2 Pressure  $p$  and its derivative vs. volume plots.

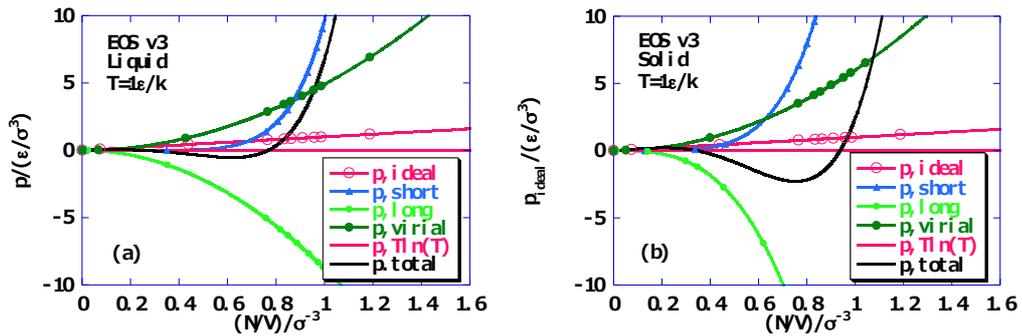


Fig. 3 Components of pressure vs. number density plot.

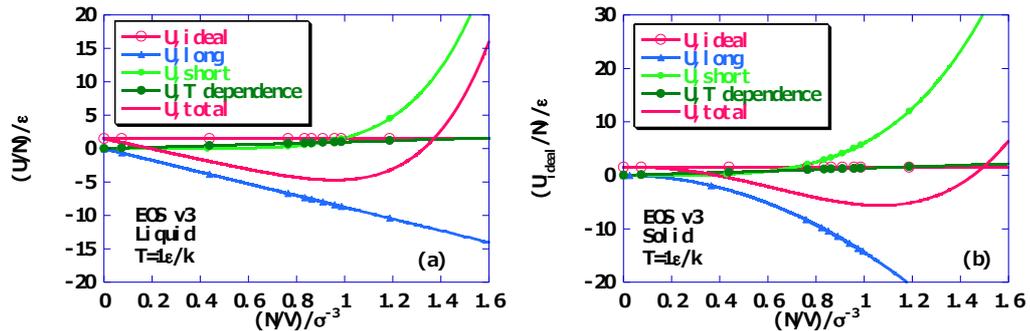


Fig. 4 Components of the internal energy vs. number density plots.

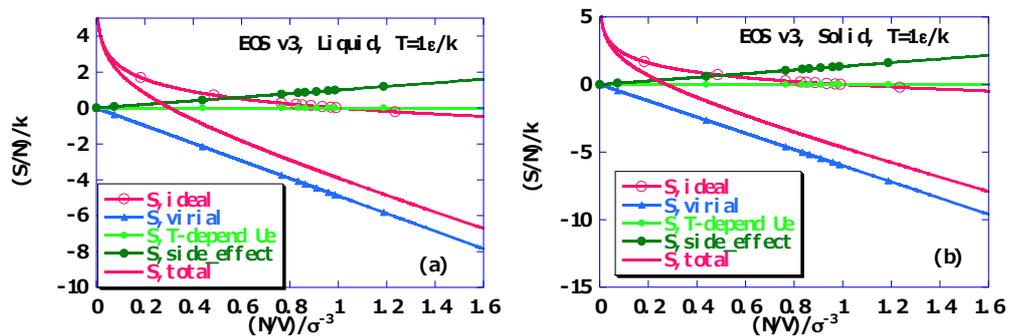


Fig. 5 Components of the entropy vs. number density plots.

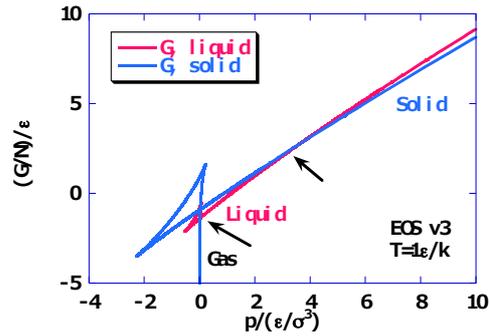


Fig. 6 Gibbs energy per molecule vs. pressure plot.

#### 4. THERMODYNAMIC CONSISTENCIES

Thermodynamic consistencies are tested using the following equation [2]:

$$C_p - C_v = \frac{\alpha^2 TV}{\kappa_T} \quad (10)$$

The heat capacity under a constant pressure  $C_p$ , the heat capacity under a constant volume  $C_v$ , the expansion coefficient  $\alpha$  and the isothermal compressibility  $\kappa_T$  are typical notations used in thermodynamics [2].

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad (11)$$

$$C_v = \left( \frac{\partial U}{\partial T} \right)_V \quad (12)$$

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad (13)$$

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \quad (14)$$

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

$$p(V, T) = p_0 \quad (15)$$

This is solved using the Goal Seek feature in Microsoft Excel [10].

The heat capacities at  $p = 0.01 \epsilon/\sigma^3$  are given in Fig. 7. Figure 8 shows the expansion coefficient. The isothermal compressibility is shown in Fig. 9.

The left hand side (LHS) and the right hand side (RHS) of Eq. (15) are compared in Fig. 10. This equation is satisfied within the numerical errors allowed as shown in Figs. 10 and 11. Figure 11 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.

$$\left( \frac{\partial V}{\partial T} \right)_p \approx \left( \frac{\Delta V}{\Delta T} \right)_p \quad (16)$$

The increment of pressure  $\Delta p$  is  $0.01 \epsilon/\sigma^3$  in the solid and liquid phases for the calculation of the isothermal compressibility.

$$\left( \frac{\partial V}{\partial p} \right)_T \approx \left( \frac{\Delta V}{\Delta p} \right)_T \quad (17)$$

In the case of the gas phase, the increment of pressure  $\Delta p$  is  $1 \times 10^{-4} \epsilon/\sigma^3$ . 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 observed in Figs. 10 and 11.

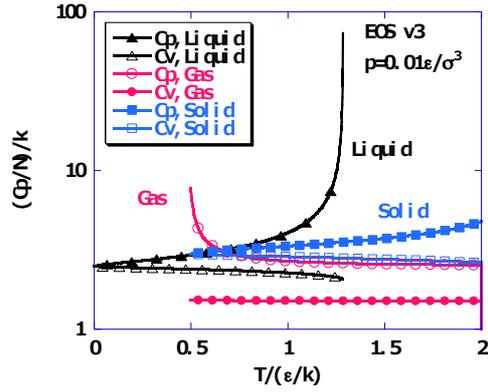


Fig. 7 Heat capacities  $C_p$  and  $C_v$  vs. temperature plot.

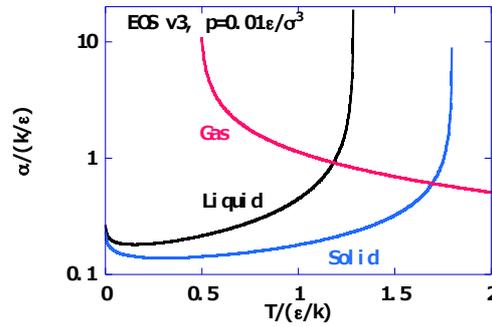


Fig. 8 Expansion coefficient vs. temperature plot.

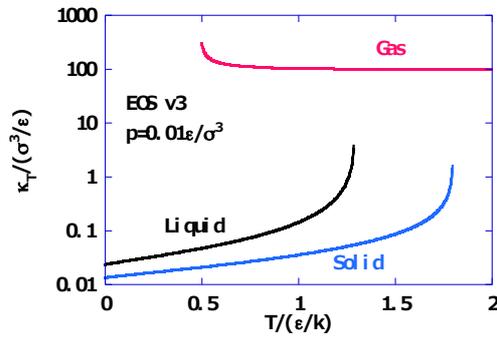


Fig. 9 Isothermal compressibility vs. temperature plot.

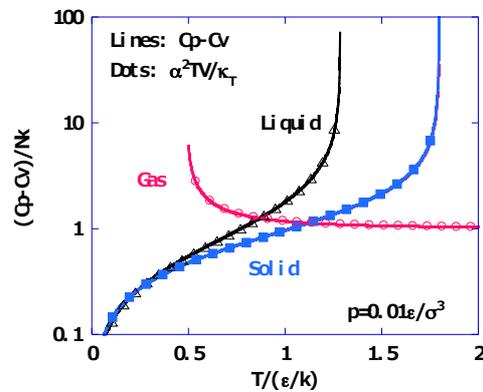


Fig. 10 Thermodynamic consistency test.

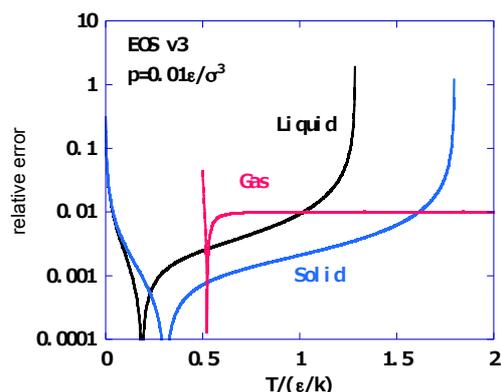


Fig. 11 Relative error  $\left| (C_p - C_v) - \frac{\alpha^2 TV}{\kappa_T} \right| / (C_p - C_v)$  vs. temperature plot.

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