

# Weeks–Chandler–Andersen Model for Solid–Liquid Equilibria in Lennard-Jones Systems

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Weeks–Chandler–Andersen (WCA) perturbation theory is used to develop a model for calculating solid–liquid equilibria in Lennard-Jones (LJ) systems. This LJ-WCA model has two components: an equation of state for LJ liquids derived in this work, and an equation of state for LJ solids derived previously.<sup>1</sup> The model is demonstrated to capture the solid–liquid equilibria for pure argon and pure krypton, including the melting and density data.

## Introduction

The equations of state are used in engineering to predict the properties of the solid, liquid, and gas states. While there are numerous equations of state capable of describing the properties of fluids, that is, both liquids and gases, there are only a few equations of state capable of describing the properties of solids. More importantly, there are no known equations of state capable of describing the properties of *both* fluids and solids. This means that, to calculate the solid–liquid equilibrium, we normally use two separate models, one to calculate the properties of the liquid phase and one to calculate the properties of the solid phase. This situation is somewhat analogous to calculating the high-pressure vapor–liquid equilibria using the vapor fugacity coefficient calculated from a vapor equation of state and the liquid activity coefficient calculated from a liquid-solution theory, instead of calculating both fugacity coefficients from an equation of state that is applicable to both phases.

For example, in our recent work,<sup>1</sup> to estimate the melting pressure data, a solid-state model is used to calculate the fugacity coefficients in the solid phase and a fluid-state model is used to calculate the fugacity coefficients in the liquid phase. The two models are derived from different theoretical concepts and approximations. The solid-state model is derived on the basis of Weeks–Chandler–Andersen (WCA) theory<sup>2,3</sup> for Lennard-Jones (LJ) molecules. The liquid-state model is derived on the basis of the statistical associating fluid theory (SAFT)<sup>4</sup> for square-well molecules<sup>5</sup> fitted to argon data. While this is a sound approach that works, it requires two different sets of parameters, one for each equation of state.

In this work, we explore a more pedagogically appealing idea of using the same theoretical concept for both liquid and solid phases at least near the solid–liquid boundaries at high densities. Toward this end, we develop a liquid equation of state (EOS) based on WCA theory and use it in place of SAFT, along with the solid EOS<sup>1</sup>, which is also based on WCA theory. We realize that this prototype is not expected to be accurate in the low-density limit in which the WCA first-order approximation is not accurate.

## WCA Liquid-State Model

In WCA theory, the LJ pair potential,  $V(r)$ , is divided into two parts, the reference potential,  $V_0(r)$ , and the perturbation,

$V_1(r)$ , by a break point of  $\lambda$  as defined by Kang et al.:<sup>2,3</sup>

$$V(r) = V_0(r) + V_1(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (1)$$

$$V_0(r) = \begin{cases} V(r) - F(r) & r \leq \lambda \\ 0 & r \geq \lambda \end{cases} \quad (2)$$

$$V_1(r) = \begin{cases} F(r) & r \leq \lambda \\ V(r) & r \geq \lambda \end{cases} \quad (3)$$

where  $r$  is the intermolecular separation,  $\epsilon$  is the potential well depth, and  $V(\sigma) = 0$ . The function  $F(r)$  is given by

$$F(r) = V(\lambda) - \left( \frac{dV}{dr} \right)_{r=\lambda} (\lambda - r) \quad (4)$$

where  $\lambda$  is set to  $2^{1/6}\sigma$  as in the original WCA perturbation theory.<sup>6</sup>

The residual Helmholtz free energy,  $A^{\text{res}}$ , can then be expanded, up to the first order, as follows:

$$\frac{A^{\text{res}}}{Nk_{\text{B}}T} = \frac{A_0^{\text{res}}}{Nk_{\text{B}}T} + \frac{A^{\text{pert}}}{Nk_{\text{B}}T} \quad (5)$$

where  $N$  is the number of molecules,  $k_{\text{B}}$  is the Boltzmann constant,  $T$  is the absolute temperature,  $A_0^{\text{res}}$  is the reference residual Helmholtz free energy, and  $A^{\text{pert}}$  is the first perturbation of the Helmholtz free energy. The reference system is approximated using an equivalent hard-sphere system of diameter  $d$ . We follow Verlet and Weis<sup>7,8</sup> procedure to obtain  $d$ :

$$d = d_{\text{B}} \left( 1 + \frac{\sigma_1}{2\sigma_0} \delta \right) \quad (6)$$

where

$$d_{\text{B}} = \int_0^\lambda \left\{ 1 - \exp \left( - \frac{V_0(r)}{k_{\text{B}}T} \right) \right\} dr \quad (7)$$

$$\delta = \int_0^\lambda \left\{ \left( \frac{r}{d_{\text{B}}} - 1 \right)^2 \frac{d \left\{ \exp \left( - \frac{V_0(r)}{k_{\text{B}}T} \right) \right\}}{dr} \right\} dr \quad (8)$$

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**TABLE 1: Coefficients  $D_{ij}$** 

$D_{11} = -1.024\ 028$	$D_{12} = -0.598\ 918$
$D_{21} = 0.363\ 988$	$D_{22} = -1.277\ 853$
$D_{31} = -0.570\ 022$	$D_{32} = 2.125\ 006$
$D_{41} = 0.532\ 256$	$D_{42} = -2.020\ 867$
$D_{51} = -0.259\ 057$	$D_{52} = 0.991\ 370$
$D_{61} = 0.050\ 531$	$D_{62} = -0.194\ 186$

$$\sigma_0(\eta) = \frac{Z^{\text{hs}} - 1}{4\eta} \quad (9)$$

$$\sigma_1(\eta) = 2\sigma_0 + \frac{\partial g^{\text{hs}}(x, \eta)}{\partial x} \Big|_{x=1} \quad (10)$$

In this Verlet–Weis procedure,  $x = r/d$ ,  $g^{\text{hs}}$  is the hard-sphere radial distribution function (rdf), and  $\eta$  is the hard-sphere packing fraction related to the number density,  $\rho_n$ , by

$$\eta = \frac{\pi}{6} \rho_n d^3 \quad (11)$$

We apply the Carnahan–Starling expression<sup>9</sup> for the  $Z^{\text{hs}}$  in eq 9:

$$Z^{\text{hs}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (12)$$

Once a value of  $d$  is obtained for a particular  $\rho_n$  and  $T$ ,  $A_0^{\text{res}}$  in eq 5 is taken to be that of a hard-sphere system with diameter  $d$  and density  $\rho_n$ , which is given by the Carnahan–Starling expression:<sup>9</sup>

$$\frac{A^{\text{res,hs}}}{Nk_B T} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \quad (13)$$

and  $A^{\text{pert}}$  is given by

$$\frac{A^{\text{pert}}}{Nk_B T} = \frac{2\pi}{k_B T} \rho_n \int_d^\infty g^{\text{hs}}(x, \eta) V_1(r) r^2 dr \quad (14)$$

For the hard-sphere rdf,  $g^{\text{hs}}$ , in eqs 10 and 14, one of the analytical forms available is that of Percus–Yevick (PY) approximation, up to the third shell, by Chang and Sandler.<sup>10</sup> We correct this PY rdf using Verlet–Weis<sup>7</sup> adjustment to an almost perfect fit with the exact hard-sphere rdf. In eq 14, the values of rdf in the outer shells are approximated to be unity.

We propose the following double summation to approximate eq 14 for practical use:

$$\frac{A^{\text{pert}}}{Nk_B T} = 12 \sum_{i=1}^6 \sum_{j=1}^4 D_{ij} \left( \frac{\epsilon}{k_B T} \right)^i (\eta_{\text{LJ}})^j \quad (15)$$

The coefficients,  $D_{ij}$ , are listed in Table 1. The summation representation is accurate to an absolute average deviation (AAD) of 0.007% relative to the original integral form in the range of  $0.1 \leq \eta_{\text{LJ}} \leq 0.5$  and  $0.2 \leq \epsilon/(k_B T) \leq 1.5$ . The LJ reduced density,  $\eta_{\text{LJ}}$ , is defined as

$$\eta_{\text{LJ}} = \frac{\pi}{6} \rho_n \sigma^3 \quad (16)$$

The equation of state therefore can be presented as a pressure equation as follows:

$$\frac{P}{\rho_n k_B T} = 1 + \eta_{\text{LJ}} \frac{\partial}{\partial \eta_{\text{LJ}}} \left( \frac{A^{\text{res}}}{Nk_B T} \right) \quad (17)$$

**TABLE 2: Parameters for Argon and Krypton**

	$T$ range (K)	$\sigma$ (Å)	$\epsilon/k_B$ (K)	AAD $P$ (%)	AAD $V$ (%)	data source
argon	85–107	3.4094	119.111	1.17	0.17	12
krypton	118–144	3.6372	164.445	0.98	0.03	12

Substituting eqs 5, 13, and 15 into eq 17 gives

$$\frac{P}{\rho_n k_B T} = 1 + \frac{Z^{\text{hs}} - 1}{1 - q} + 12 \sum_{i=1}^6 \sum_{j=1}^4 D_{ij} \left( \frac{\epsilon}{k_B T} \right)^i (\eta_{\text{LJ}})^j \quad (18)$$

The “correction”  $1 - q$  on the reference term is present due to the use of the equivalent hard-sphere diameter  $d$  and, consequently, the equivalent hard-sphere packing fraction  $\eta$  in  $Z^{\text{hs}}$  (eq 12).

$$q = \frac{3\eta d_B \delta}{2d \sigma_0} \left[ \frac{\partial}{\partial \eta} \left( \frac{\partial g^{\text{hs}}}{\partial x} \right) \Big|_{x=1} - \frac{5 - 2\eta}{(1 - \eta)(2 - \eta)} \left( \frac{\partial g^{\text{hs}}}{\partial x} \right) \Big|_{x=1} \right] \quad (19)$$

where  $d$ ,  $d_B$ ,  $\delta$ , and  $\sigma_0$  are defined in eqs 6–9.

### Application to LJ-Like Real Systems

The state of equilibrium is calculated by equating the chemical potential:

$$\mu^{\text{S}} = \mu^{\text{L}} \quad (20)$$

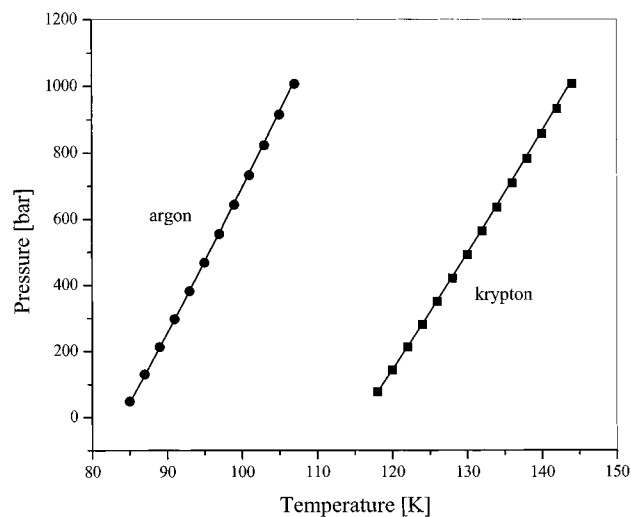
where  $\mu$  is the chemical potential. The chemical potential can be obtained from

$$\mu = \frac{A}{N} + \frac{P}{\rho_n} \quad (21)$$

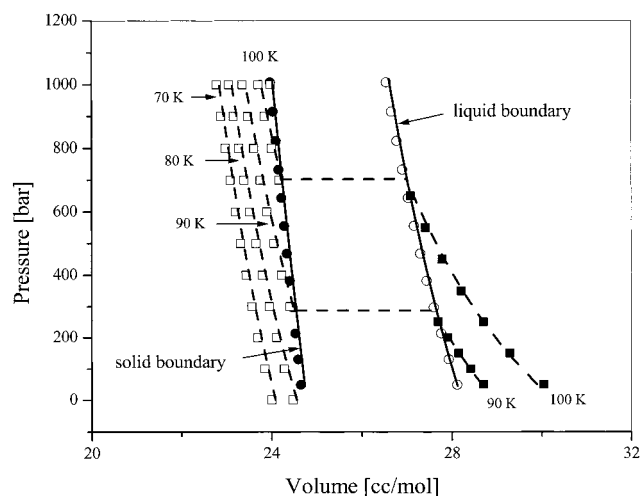
where the LJ-liquid EOS described in the previous section is used to determine the chemical potential of the liquid phase and the LJ-solid EOS<sup>1</sup> is used to determine the chemical potential of the solid phase. Because the LJ-solid EOS<sup>1</sup> is rooted in the same WCA theory, the LJ parameters obtained by regressing the solid–liquid equilibrium data (pressure and liquid molar volume) are expected to be applicable to both liquid and solid equations of state.

Argon and krypton are selected as the real systems that are well-approximated by the LJ potential and for which we have reliable melting data. The parameters obtained, their absolute average deviations (AAD), and the temperature range in which the parameters are fitted are given in Table 2. These universal parameters are found to be consistent with the LJ parameters obtained empirically from the gas-viscosity data,<sup>11</sup> which are  $\sigma = 3.453$  Å and  $\epsilon/k_B = 119.8$  K for argon and  $\sigma = 3.696$  Å and  $\epsilon/k_B = 166.1$  K for krypton.

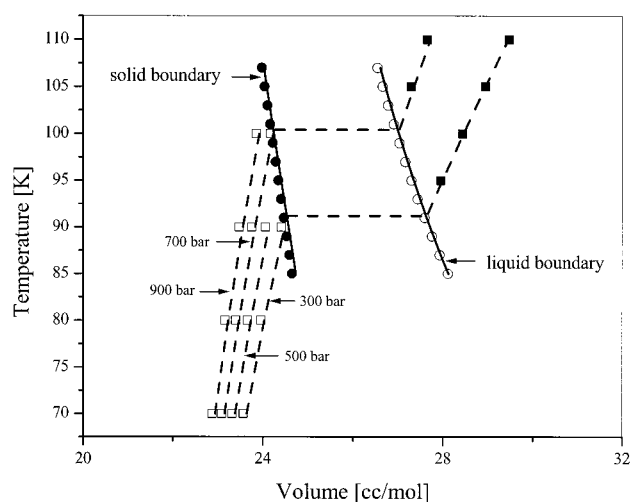
Figure 1 illustrates the melting points correlated using this approach for argon and krypton in a pressure–temperature (PT) diagram. The corresponding pressure–volume (PV) and temperature–volume (TV) diagrams are shown in Figures 2 and 3 for argon and in Figures 4 and 5 for krypton. The solid volumes at melting and the isotherms for both the solid and liquid phases



**Figure 1.** PT diagram of argon and krypton, experimental<sup>12</sup> (points) and calculated (curves) data.



**Figure 2.** PV diagram of argon, experimental<sup>12</sup> (points) and calculated (curves) data.

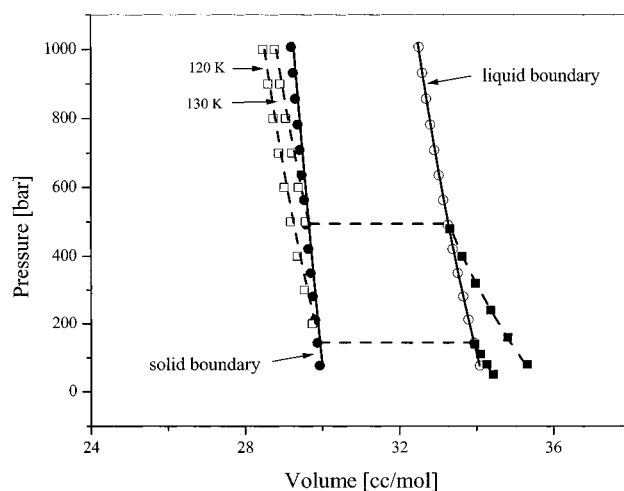


**Figure 3.** TV diagram of argon, experimental<sup>12</sup> (points) and calculated (curves) data.

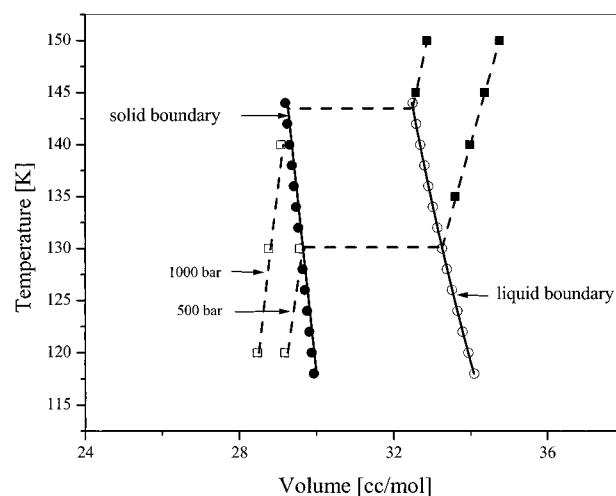
are predicted without further readjustment. These properties are found to agree with the experimental data.

### Conclusion

Weeks–Chandler–Andersen (WCA) perturbation theory is used to develop a model for calculating solid–liquid equilibria



**Figure 4.** PV diagram of krypton, experimental<sup>12</sup> (points) and calculated (curves) data.



**Figure 5.** TV diagram of krypton, experimental<sup>12</sup> (points) and calculated (curves) data.

in Lennard-Jones (LJ) systems. This LJ-WCA model has two components: an equation of state for LJ liquids derived in this work and an equation of state for LJ solids derived previously. The model is demonstrated to capture the solid–liquid equilibria for pure argon and pure krypton, including the melting and density data.

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### Notation

$A^{\text{pert}}$ : the first perturbation of the residual Helmholtz free energy.

$A^{\text{res}}$ : residual Helmholtz free energy.

$A^{\text{res,hs}}$ : hard-sphere residual Helmholtz free energy.

$A_0^{\text{res}}$ : the reference residual Helmholtz free energy.

$d$ : the equivalent hard-sphere diameter.

$d_B$ : factor in Verlet and Weis procedure.

$D_{ij}$ : coefficients of double summation representing the integral form of  $A^{\text{pert}}$ .

$F$ : potential function in WCA theory.

$g^{\text{hs}}$ : hard-sphere radial distribution function.

$k_B$ : Boltzmann constant.

$N$ : the number of molecules.

$P$ : pressure.

$q$ : correction expression in the pressure equation.  
 $r$ : intermolecular separation distance.  
 $T$ : absolute temperature.  
 $V$ : LJ pair potential function.  
 $V_0, V_1$ : reference and perturbation of LJ potential in WCA theory.  
 $x$ : dimensionless intermolecular separation distance.  
 $Z^{\text{hs}}$ : hard-sphere compressibility factor.

Greek

$\delta$ : factor in Verlet and Weis procedure.  
 $\epsilon$ : the LJ potential well depth.  
 $\eta$ : equivalent hard-sphere packing fraction.  
 $\eta_{\text{LJ}}$ : LJ packing fraction.  
 $\lambda$ : breaking point in WCA theory.  
 $\rho_{\text{n}}$ : number density.  
 $\sigma$ : the intermolecular separation distance where LJ potential is equal to zero.

$\sigma_0, \sigma_1$ : factors in Verlet and Weis procedure.

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