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LATTICE MODEL THEORY OF THE EQUATION OF STATE COVERING THE GAS, LIQUID, AND SOLID PHASES

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ABSTRACT

This study aims at obtaining the three stable states of matter and the corresponding phase transitions with a single model. Patterned after Lennard-Jones and Devonshires's theory, a simple cubic lattice model containing two fcc sublattices (α and β) is adopted. The interatomic potential is taken to be the Lennard-Jones (6-12) potential. Employing the Cluster Variation Method, the Weiss and the pair approximations on the lattice gas failed to give the correct phase diagrams. Hybrid approximations are then devised to describe the lattice term in the free energy. A lattice vibration term corresponding to a free volume correction is included semi-phenomenologically. The combinations of the lattice part and the free volume part yield the three states and the proper phase diagrams. To determine the coexistence regions, the equalities of the pressure and Gibbs free energy per molecule of the coexisting phases are utilized. The ordered branch of the free energy gives rise to the solid phase while the disordered branch yields the gas and liquid phases. It is observed that the triple point and the critical point quantities, the phase diagrams and the coexistence regions plotted are in good agreement with the experimental values and graphs for Argon. It is also apparent in the investigation that the vibrational term was vital in getting the three phases.

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I. INTRODUCTION

At present, there is still a need for a unified theory that will cover all three phases of matter as well as generate the proper transformations observed among phases. This study is an attempt to meet this need by utilizing a single model to formulate the equation of state of a simple substance semiquantitatively.

The model proposed here is the rigid lattice gas model of Horiguchi and Tanaka[1] with an effective vibration of the atoms about the lattice sites to represent a free volume correction. Section II describes the model while Section III presents the results of the Weiss and the pair approximations in the Cluster Variation Method (CVM)[2] as applied to the lattice part of the model. A new set of approximations called the hybrid approximations is presented in Section IV, based on the CVM. The effective free volume correction is also formulated. Section V describes the results and compares them with the results of the expandable model calculations by Mori, et al.[3] and the experimental studies for Argon.[4]

II. THE MODEL

According to classical statistical mechanics, the Helmholtz free energy of a system of N particles is given by

$$F = - k_B T \ln Z_N = F_k + F_c \tag{1}$$

where Z_N is the canonical partition function of the system, k_B is the Boltzmann constant and T is the absolute temperature. The division of the free energy into the kinetic part

$$F_k = N k_B T \ln \lambda^3 \tag{2}$$

with $\lambda^3 = (h^2/2\pi m k_B T)^{3/2}$, and the configurational part

$$F_c = - k_B T \ln Q_N. \tag{3}$$

where Q_N is the configurational integral

$$Q_N = \frac{1}{N\,!} \int e^{-\beta U(r^N)}\, dr^N, \tag{4}$$

is the natural way of representing the total free energy. The evaluation of the integral in (4), however, is a formidable task. An alternative classification of the contributions to the free energy is offered by the lattice gas model which · avoids the difficult integrations.

The total free energy is alternatively split into two quantities

$$F = F^L + F^V$$

where F^L is the lattice part arising purely from the configurational free energy F_c and is evaluated conveniently in the Cluster Variation Method. The effective free volume F^V contains part of the configurational free energy and part of the kinetic free energy which are usually dropped in lattice model calculations.

In this work, the rigid lattice model (RLM) is adopted because in the pressure range of interest, the lattice constant of the crystalline state does not change appreciably. Figure 1 shows a simple cublic lattice with f.c.c. α and β sub-lattices. N atoms are distributed over the L lattice sites forming the above lattice structure and with a fixed lattice constant a. The number density is then defined by

$$\rho \equiv \frac{N}{L} = \frac{1}{v} \tag{6}$$

where $v = \overline{V}/Na^3$ and $\overline{V} = La^3$.

Similarly, the number densities of α sites and β sites are

$$\rho_\alpha = \frac{N_\alpha}{L_\alpha} \tag{7}$$

$$\rho_\beta = \frac{N_\beta}{L_\beta} \tag{8}$$

where L_α and L_β are the number of the α sites and β sites, respectively, while N_α and N_β are the corresponding number of atoms on the α and β sites. One has the following relations:

$$N_\alpha + N_\beta = N, \tag{9}$$

$$L_\alpha + L_\beta = L, \tag{10}$$

$$L_\alpha = L_\beta = \frac{1}{2} L. \tag{11}$$

A long range order (L.R.O.) parameter is defined by

$$R \equiv (\rho_\alpha - \rho)/(1 - \rho). \tag{12}$$

Since the completely ordered state is described by a state in which all α sites are occupied, ρ_α is equal to unity and hence $R = 1$. In the completely disordered state, both the α and β sites are equally populated, hence, $\rho_\alpha = \rho_\beta = \rho$ and consequently $R = 0$. As defined by (12), therefore, the L.R.O. parameter is properly chosen. In terms of this parameter, the number densities on the α and β sites are written as

$$\rho_\alpha = \rho + (1 - \rho) R \tag{13}$$

$$\rho_\beta = \rho - (1 - \rho) R. \tag{14}$$

It is of interest in this paper to investigate systems described by the Lennard-Jones potential

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{15}$$

with σ denoting the distance where the potential is zero and $-\epsilon$ being the minimum value of the potential. The following dimensionless (reduced) quantities are introduced for calculational convenience,

$$\tilde{T} = \frac{kT}{\epsilon}, \quad \tilde{P} = \frac{Pa^3}{\epsilon}, \quad \tilde{F} = \frac{F}{\epsilon}, \quad \tilde{g} = \frac{g}{\epsilon}. \tag{16}$$

The free volume is now introduced as an effective vibration of the atoms about the lattice sites.

The free energy of a molecule confined in a harmonic potential well is known to be

$$\tilde{f}^{V} = -\tilde{T}\,\ln q = \frac{\tilde{\omega}}{2} + \tilde{T}\,\ln(1 - e^{-\tilde{\omega}/\tilde{T}}) \tag{17}$$

where $\tilde{\omega}$ is a reduced frequency defined by $\tilde{\omega} = \hbar\omega/\epsilon$, ω being the classical frequency. The symbol q represents the canonical partition function of a simple harmonic oscillator. Assuming that all the molecules see identical confining cages (Einstein model), the vibrational free energy per lattice site may be written as

$$\tilde{f}^{V} = \frac{\tilde{F}^{V}}{L} = \frac{\rho\tilde{\omega}}{2} + \rho\tilde{T}\,\ln(1 - e^{-\tilde{\omega}/\tilde{T}}). \tag{18}$$

The quantity $\tilde{\omega}$ is an unknown function of the parameter R and/or density ρ. One knows by physical considerations that it should be an increasing function of these quantities since the stiffness of the confining potential increases with R and/or ρ. In this paper, a linear dependence on R is proposed, namely

$$\tilde{\omega} = Z_0 R + \omega_0 \tag{19}$$

where Z_0 and ω_0 are adjustable parameters. The parameter ω_0 can be interpreted as a measure of the relative stiffness of the confining potential in the disordered configuration compared to that of the ordered state. The parameter Z_0 on the other hand, can be chosen to give the correct triple point temperature. Equations (18) and (19) define the free volume term which will be added to the lattice free energy in later discussions.

III. THE WEISS AND THE PAIR APPROXIMATIONS

In this section, the consequences of the purely lattice free energy F^L are examined in the Weiss and the pair approximations of the Cluster Variation Method.

The variational function for the one-site or Weiss approximation in the CVM is given by the trial free energy per lattice site,

$$\tilde{f}^L = \frac{\tilde{F}^L}{L} = [3\tilde{U}(1) + 6\tilde{U}(2) + 4\tilde{U}(3) + 3\tilde{U}(4)]\ \rho^2$$

$$- [3\tilde{U}(1) - 6\tilde{U}(2) + 4\tilde{U}(3) - 3\tilde{U}(4)]\ (1-\rho)^2 R^2$$

$$+ \frac{1}{2}\tilde{T}\{[\rho + (1-\rho)R]\ \ell n[\rho + (1-\rho)R] + (1-\rho)(1-R)\ \ell n[(1-\rho)(1-R)]$$

$$+ [\rho - (1-\rho)R]\ \ell n[\rho - (1-\rho)R] + (1-\rho)(1+R)\ \ell n[(1-\rho)(1+R)]\} \quad (20)$$

in terms of the L.R.O. parameter R and $\tilde{U}(k) = \phi(k)/\epsilon$ which is the reduced pair interaction with the kth nearest neighbor atom. Upon specifying the temperature $\tilde{T}$ and volume v, Eq. (20) becomes a function of R alone and minimization is easily done by setting

$$\left(\frac{\partial \tilde{f}^L}{\partial R}\right)_{T,v} = 0. \quad (21)$$

The non-zero solution for R yields the ordered state of the free energy per lattice site $\tilde{f}^L_{ORD}$. The disordered state corresponding to the fluid state arises from Eq. (20) with the solution R = 0, i.e.

$$\tilde{f}^L_{DIS} = [3\tilde{U}(1) + 6\tilde{U}(2) + 4\tilde{U}(3) + 3\tilde{U}(4)]\ \rho^2 + \tilde{T}[\rho\ \ell n\ \rho + (1+\rho)\ \ell n(1-\rho)]. \quad (22)$$

The system's actual free energy is then deduced from

$$\tilde{f}^L = \mathrm{Min}\{\tilde{f}^L_{ORD}, \tilde{f}^L_{DIS}\}. \quad (23)$$

From thermodynamics, expressions for the pressure and Gibbs free energy per molecule (chemical potential) can be obtained. Specifically, for the rigid lattice model these are:

$$\tilde{P} = -\tilde{f} + \rho\left(\frac{\partial \tilde{f}}{\partial \rho}\right)_{\tilde{T}L}, \quad (24)$$

$$\tilde{g} = (\tilde{f} + \tilde{P})\ v. \quad (25)$$

The ordered pressure and chemical potential follow from (24) and (25) if the ordered free energy is substituted while the corresponding disordered quantities are obtained if the disordered free energy is used.

To avoid enormous graphical construction in determining the coexistence regions, the coexistence conditions for two phases A and B are used, namely

$$\tilde{P}(\rho_A) = \tilde{P}(\rho_B) \tag{26}$$

$$\tilde{g}(\rho_A) = \tilde{g}(\rho_B) \tag{27}$$

for a given temperature $\tilde{T}$. This pair of conditions is equivalent to Maxwell's equal-area construction in the $\tilde{P}$-v isotherm or the common tangent construction in the $\tilde{f}_m$ - v isotherm, where $\tilde{f}_m$ = fxv denotes the reduced Helmholtz free energy per molecule.

Calculations with the purely lattice term in the Weiss approximation as described above yield a couple of major difficulties:

(1) It is not possible to get the liquid state and the liquid-gas critical point in the Lennard-Jones potential due to the stiff repulsion in the first nearest neighbor. A very soft core potential is necessary to obtain a fluid loop in the disordered branch of free energy.

(2) Adopting an unrealistically soft core, a fluid loop is realized. However, the liquid appears in the wrong region of the phase diagram, namely gas, solid, liquid in that order with decreasing volume.

The Weiss approximation, one may conclude, has favorable features if one wishes to describe remelting at high pressures where the existence of the vapor pressure curve and the critical point is not of concern. In the region near the triple point, however, which is the focus of this investigation, the Weiss approximation cannot give the proper phase diagrams even with the addition of a free volume correction.

One order higher in the hierarchy of approximations in the CVM is the two-site or pair approximation. The variational free energy of the lattice in this approximation is given by

$$
\begin{aligned}
\tilde{f}^{L} = {} & 3\{\tilde{U}(1)\, X_{\alpha\beta}(1) + \tilde{T}_{\alpha\beta}[X_{\alpha\beta}(1)\, \ln X_{\alpha\beta}(1) \\
& + (\rho_\alpha - X_{\alpha\beta}(1))\, \ln(\rho_\alpha - X_{\alpha\beta}(1)) + (\rho_\beta - X_{\alpha\beta}(1))\, \ln(\rho_\beta - X_{\alpha\beta}(1)) \\
& + (1 - \rho_\alpha - \rho_\beta + X_{\alpha\beta}(1))\, \ln(1 - \rho_\alpha - \rho_\beta + X_{\alpha\beta}(1))]\} \\
& + 3\{\tilde{U}(2)\, X_{\alpha\alpha}(2) + \tilde{T}\,[X_{\alpha\alpha}(2)\, \ln X_{\alpha\alpha}(2) \\
& + 2(\rho_\alpha - X_{\alpha\alpha}(2))\, \ln(\rho_\alpha - X_{\alpha\alpha}(2)) + (1 - 2\rho_\alpha + X_{\alpha\alpha}(2))\, \ln(1 - 2\rho_\alpha + X_{\alpha\alpha}(2)]\} \\
& + 3\{U(2)\, X_{\beta\beta}(2) + \tilde{T}\,[X_{\beta\beta}(2)\, \ln X_{\beta\beta}(2) \\
& + 2(\rho_\beta - X_{\beta\beta}(2))\, \ln(\rho_\beta - X_{\beta\beta}(2)) + (1 - 2\rho_\beta + X_{\beta\beta}(2))\, \ln(1 - 2\rho_\beta + X_{\beta\beta}(2)]\} \\
& + 4\{U(3)\, X_{\alpha\beta}(3) + \tilde{T}\,[X_{\alpha\beta}(3)\, \ln X_{\alpha\beta}(3) \\
& + (\rho_\alpha - X_{\alpha\beta}(3))\, \ln(\rho_\alpha - X_{\alpha\beta}(3)) + (\rho_\beta - X_{\alpha\beta}(3))\, \ln(\rho_\beta - X_{\alpha\beta}(3)) \\
& + (1 - \rho_\alpha - \rho_\beta + X_{\alpha\beta}(3))\, \ln(1 - \rho_\alpha - \rho_\beta + X_{\alpha\beta}(3))]\} \\
& + \frac{3}{2}\,\{\tilde{U}(4)\, X_{\alpha\alpha}(4) + \tilde{T}\,[X_{\alpha\alpha}(4)\, \ln X_{\alpha\alpha}(4) \\
& + 2(\rho_\alpha - X_{\alpha\alpha}(4))\, \ln(\rho_\alpha - X_{\alpha\alpha}(4)) + (1 - 2\rho_\alpha + X_{\alpha\alpha}(4)\, \ln(1 - 2\rho_\alpha + X_{\alpha\alpha}(4))]\} \\
& + \frac{3}{2}\,\{\tilde{U}(4)\, X_{\beta\beta}(4) + \tilde{T}\,[X_{\beta\beta}(4)\, \ln X_{\beta\beta}(4) \\
& + 2(\rho_\beta - X_{\beta\beta}(4))\, \ln(\rho_\beta - X_{\beta\beta}(4)) + (1 - 2\rho_\beta + X_{\beta\beta}(4))\, \ln(1 - 2\rho_\beta + X_{\beta\beta}(4))]\} \\
& - \frac{31}{2}\,\tilde{T}\,[\rho_\alpha \ln \rho_\alpha + (1 - \rho_\alpha)\, \ln(1 - \rho_\alpha) + \rho_\beta \ln \rho_\beta + (1 - \rho_\beta)\, \ln(1 + \rho_\beta) \qquad (28)
\end{aligned}
$$

The notation $X_{\alpha\beta}$ (j) represents the pair correlation parameter between a pair of jth neighbors one of which is an α site, the other a β site. The other pair parameters are defined in the same manner. This trial free energy is minimized with respect to the six pair correlation parameters $X_{\alpha\beta}$ (1), $X_{\alpha\alpha}$ (2), $X_{\beta\beta}$ (2), $X_{\alpha\beta}$ (3), $X_{\alpha\alpha}$ (4) and $X_{\beta\beta}$ (4), and with respect to R which enters through ρ_α and ρ_β. The minimum value with R non-zero gives rise to the ordered state free energy, $\tilde{f}^{L}_{ORD}$.

In analogy with the Weiss approximation, the disordered free energy in the two-site approximation is obtained with R = 0 and the pair parameters related by $X_{ij}(k) = X_{ji}(k) = X(k)$,

$$\begin{aligned}\tilde{f}^{L}_{DIS} = {} & 3\{U(1)\,X(1) + \tilde{T}[X(1)\,\ell n X(1) + 2(\rho - X(1))\,\ell n(\rho - X(1)) \\ & + (1 - 2\rho + X(1))\,\ell n(1 - 2\rho + X(1))]\} \\ & + 6\{U(2)\,X(2) + \tilde{T}[X(2)\,\ell n\,X(2) + 2(\rho - X(2))\,\ell n(\rho - X(2)) \\ & + (1 - 2\rho + X(2))\,\ell n(1 - 2\rho + X(2))]\} \\ & + 4\{U(3)\,X(3) + \tilde{T}[X(3)\,\ell n\,X(3) + 2(\rho - X(3))\,\ell n(\rho - X(3)) \\ & + (1 - 2\rho + X(3))\,\ell n(1 - 2\rho + X(3))]\} \\ & + 3\{U(4)\,X(4) + \tilde{T}[X(4)\,\ell n\,X(4) + 2(\rho - X(4))\,\ell n(\rho - X(4)) \\ & + (1 - 2\rho + X(4))\,\ell n(1 - 2\rho + X(4))]\} \\ & - 31\,\tilde{T}[\rho\,\ell n\,\rho + (1 - \rho)\,\ell n(1 - \rho)]. \qquad (29)\end{aligned}$$

The pair parameters are determined by minimizing (29) with respect to the X(k), k = 1, 2, 3, 4. The ordered and disordered pressure and chemical potential are determined from (24) and (25) with the ordered and disordered free energies substituted, respectively.

Calculations in the two-site cluster approximation showed a significant improvement in the sense that even with the Lennard-Jones potential, the fluid loop can exist in a reasonable range of temperature. This implies that if one disregards the presence of the solid phase in the diagram, a finite critical temperature is realized, making the existence of a liquid state more feasible.

A basic difficulty however is the instability of the results with variation in the order of the nearest neighbors included in the calculation. If only the nearest and second neighbor pairs are included, the free energy of the ordered branch is lower than the disordered branch of free energy. However, when third or fourth nearest neighbors are included, the disordered branch becomes lower.

It is in the spirit of these difficulties in the Weiss and pair approximations that a physically reasonable way of combining them was devised as described in the following section.

IV. THE HYBRID APPROXIMATIONS

The hybridization procedure is based on a sound physical observation that neighbors which are situated farther from the site under consideration are more blurred in their details than the nearer sites. Applying this to the lattice problem, the first nearest neighbors are treated in the two-body approximation while the farther neighbors (2nd, 3rd, 4th, etc.) are described in the Weiss approximation. Variations of this process are clearly possible.

It is convenient in the hybrid approximations to adopt the notation [2 - (m)1] to indicate that the effect of the nearest neighbor interaction is calculated in the pair approximation while the next m shells of interacting neighbors are treated in the Weiss approximation. Hybrid approximations [2-1], [2-(3)1], [2-(5)1], and [2-(7)1] are investigated. The trial free energies in these hybrid approximations are the following:

$$\begin{aligned}\tilde{f}^L[2-1] = 3\,[\tilde{U}(1)\,X_{\alpha\beta}(1) + U(2)\,(\rho_\alpha^2+\rho_\beta^2) + 3\tilde{T}\,[X_{\alpha\beta}(1)\,\ln X_{\alpha\beta}(1) + (\rho_\alpha - X_{\alpha\beta}(1))\,\ln(\rho_\alpha \\ - X_{\alpha\beta}(1)) + (\rho_\beta - X_{\alpha\beta}(1))\,\ln(\rho_\beta - X_{\alpha\beta}(1)) + (1-\rho_\alpha-\rho_\beta+X_{\alpha\beta}(1))\,\ln(1-\rho_\alpha-\rho_\beta \\ + X_{\alpha\beta}(1))] - \frac{5}{2}\tilde{T}\,[\rho_\alpha \ln\rho_\alpha + (1-\rho_\alpha)\ln(1-\rho_\alpha) + \rho_\beta\ln\rho_\beta + (1-\rho_\beta)\ln(1-\beta_\beta)]\end{aligned} \tag{30}$$

$$\tilde{f}^L[2-(3)\,1] = \tilde{f}^L[2-1] + 4\,\tilde{U}(3)\,\rho_\alpha\rho_\beta + \frac{3}{2}U(4)\,(\rho_\alpha^2+\rho_\beta^2) \tag{31}$$

$$\tilde{f}^L[2-(5)\,1] = \tilde{f}^L[2-(3)\,1] + 12\,\tilde{U}(5)\,\rho_\alpha\rho_\beta + 6\tilde{U}(6)\,(\rho_\alpha^2+\rho_\beta^2) \tag{32}$$

$$\tilde{f}^L[2-(7)\,1] = \tilde{f}^L[2-(5)\,1] + 3\tilde{U}(7)\,(\rho_\alpha^2+\rho_\beta^2) + 4\tilde{U}(8)\,\rho_\alpha\rho_\beta. \tag{33}$$

These trial free energy expressions are minimized with respect to R and the pair function $X_{\alpha\beta}(1)$ giving rise to the ordered values of the free energies in the different hybrid approximations for non-zero R, as functions of density ρ and temperature T.

In order to obtain the disordered branch of the free energy in these approximation, R is set to zero and the resulting expressions are minimized with respect to the single pair parameter X(1). One then gets the following:

$$\tilde{f}^L_{DIS}[2-1] = 3[U(1)\,X(1) + 2\tilde{U}(2)\,\rho^2] + 3\tilde{T}\,[X(1)\,\ell n\,X(1) + 2(\rho - X(1))\,\ell n(\rho - X(1)) + (1 - 2\rho + X(1))\,\ell n(1 - 2\rho + X(1)) - 5\tilde{T}\,[\rho\,\ell n\,\rho + (1-\rho)\,\ell n(1-\rho)] \tag{34}$$

$$\tilde{f}^L_{DIS}[2-(3)\,1] = \tilde{f}^L_{DIS}[2-1] + [4\tilde{U}(3) + 3\tilde{U}(4)]\,\rho^2 \tag{35}$$

$$\tilde{f}^L_{DIS}[2-(5)\,1] = \tilde{f}^L_{DIS}[2-(3)\,1] + [12\tilde{U}(5) + 12\tilde{U}(6)]\,\rho^2 \tag{36}$$

$$\tilde{f}^L_{DIS}[2-(7)\,1] = \tilde{f}^L_{DIS}[2-(5)\,1] + [6\tilde{U}(7) + 4\tilde{U}(8)]\,\rho^2. \tag{37}$$

The corresponding ordered and disordered pressure and chemical potential follow from (24) and (25).

All the above hybrid approximations on the lattice Helmholtz free energy per site displayed basically the same characteristics when plotted as functions of volume. A finite value for the critical temperature T_c is a common feature reminiscent of the pair approximation. Although the lattice part alone does not suffice to correctly describe the thermodynamic phase diagrams and the three states, all the hybrid approximations resulted into a lower ordered free energy consistently. They are therefore susceptible to a corrective treatment which essentially raises the ordered relative to the disordered free energy like the free volume correction described earlier.

There are four combinations arising from the four hybrid approximations on the lattice investigated. The trial free energies of the combined lattice and free volume parts are as follows:

$$\tilde{f}[2-1] = \tilde{f}^L[2-1] + \tilde{f}^V \tag{38}$$

$$\tilde{f}[2-(m)\,1] = \tilde{f}^L[2-(m)\,1] + \tilde{f}^V \quad m = 3,\ 5,\ 7, \tag{39}$$

where $\tilde{f}^L$ is defined by (18) and (19).

As before, the ordered state free energy $\tilde{f}_{ORD}$ in the various approximations are obtained by minimizing the above equations with respect to R and $X_{\alpha\beta}(1)$. The corresponding disordered free energy branches follow by setting R = 0 and minimizing the corresponding expressions

$$\tilde{f}_{DIS}[2-1] = \tilde{f}^{L}_{DIS}[2-1] + \tilde{f}^{V}_{DIS} \tag{40}$$

$$\tilde{f}_{DIS}[2-(m)\,1] = \tilde{f}^{L}_{DIS}[2-(m)\,1] + \tilde{f}^{V}_{DIS} \qquad m = 3,\ 5,\ 7 \tag{41}$$

with respect to X(1). Use of equations (24) and (25) enables one to get the expressions for the ordered pressure and chemical potentials

$$\tilde{P}_{ORD}[2-1] = -\tilde{f}_{ORD}[2-1] + \rho\left(\frac{\partial \tilde{f}_{ORD}[2-1]}{\partial \rho}\right)_{T,L} \tag{42}$$

$$\tilde{P}_{ORD}[2-(m)\,1] = -\tilde{f}_{ORD}[2-(m)\,1] + \rho\left(\frac{\partial \tilde{f}_{ORD}[2-(m)\,1]}{\partial \rho}\right)_{T,L} \qquad m = 3,\ 5,\ 7 \tag{43}$$

$$\tilde{g}_{ORD}[2-1] = (\tilde{f}_{ORD}[2-1] + \tilde{P}_{ORD}[2-1])\,v \tag{44}$$

$$\tilde{g}_{ORD}[2-(m)\,1] = (\tilde{f}_{ORD}[2-(m)\,1] + \tilde{P}_{ORD}[2-(m)\,1])\,v \qquad m = 3,\ 5,\ 7 \tag{45}$$

and the corresponding disordered pressure and chemical potentials.

In all approximations, the system's actual free energy is given by the lower of the two branches of free energy, namely

$$\tilde{f} = \mathrm{Min}\{\tilde{f}_{ORD},\ \tilde{f}_{DIS}\}. \tag{46}$$

The results of these approximations are presented and discussed in the next section.

V. RESULTS AND CONCLUSIONS

Having obtained the free energy and pressure expressions in the hybrid approximations with free volume correction, one makes use of the coexistence conditions (26) and (27) to obtain the phase transformations and the coexistence regions for melting, condensation and sublimation. Applying these conditions appropriately over a range of temperature $\tilde{T}$, the $\tilde{P}\tilde{T}$ diagrams shown in Figure 2 for a simple, classical system are generated for various hybrid approximations with free volume correction. The coexistance diagram is shown in Figure 3 for the [2 - (7)1] hybrid approximation with lattice vibration. The vibrational parameter ω_0 is taken to be .01 for all hybrid approximations while $z_0 = 1.256$ for the [2 - (3)1] and [2 - (5)1] approximations and $z_0 = 1.415$ for the [2 - (7)1] hybrid approximation.

The typical behavior of an isotherm for temperatures above the triple point is shown in Figures 5a, b, and c where an isotherm of temperature $\tilde{T} = 0.71$ is plotted in the pressure, Helmholtz free energy per molecule, and chemical potential against density diagrams in the [2 - (5)1] approximation with free volume correction.

The typical behavior of an isotherm for temperatures below the triple point temperature is shown in Figures 6a, b, and c. Plotted in the pressure, Helmholtz free energy per molecule, and chemical potential against diagrams is the $\tilde{T} = 0.68$ isotherm in the [2 - (3)1] approximation with free volume correction. There is a slight variation here since two transitions, gas to liquid and gas to solid, compete because both are possible under the criteria (26) and (27). It is the gas to solid transition which is realized, however, since it corresponds to a lower Helmholtz free energy per molecule and lower chemical potential.

In Table 1, the triple point quantities are shown. The results of the present rigid lattice calculations (Row I) are compared with the expandable lattice calculations (Row II) by Mori et al.[3] and the experimental values for Argon (Row III). Similarly, the critical point quantities are displayed in Table 2. Within the thermodynamic region of interest, it is apparent that the present rigid lattice theory is better than the expandable lattice theory. Calculations for the latent heat of transformations using the Clausius-Clapeyron equation and the phase diagrams obtained in the present theory are being done. The authors hope to present the results in the future.

To improve the present theory, it is desirable to obtain a more accurate formulation of the free volume term, ultimately avoiding the phenomenological part. Raising the order of the CVM approximation is a possible option. A better alternative way is suggested by introducing more types of lattice sites, effectively shrinking the lattice spacing. In this process, the effect of vibration is gradually and partly incorporated into the lattice term. A physical limit in the spacing might exist after which the ad hoc addition of the vibrational or free volume term becomes unnecessary.

The nature of the convergence of the results in the hierarchy of approximations in the CVM toward the correct ones is not yet clear (even for systems related to the lattice gas, e.g. magnetic systems, binary alloys, etc.). A related question is the stability of the general results with respect to the order of neighbors included. As the interaction becomes long-ranged, one must naturally include more neighbors in the calculations. The authors believe that the order of the approximation and the range of interaction are intimately connected. The hybrid approximations introduced in this paper are the simplest ways of investigating the effects of longer-ranged interactions. It is obvious that higher orders in the CVM can also be hybridized which, hopefully, may shed more light to the present querry.

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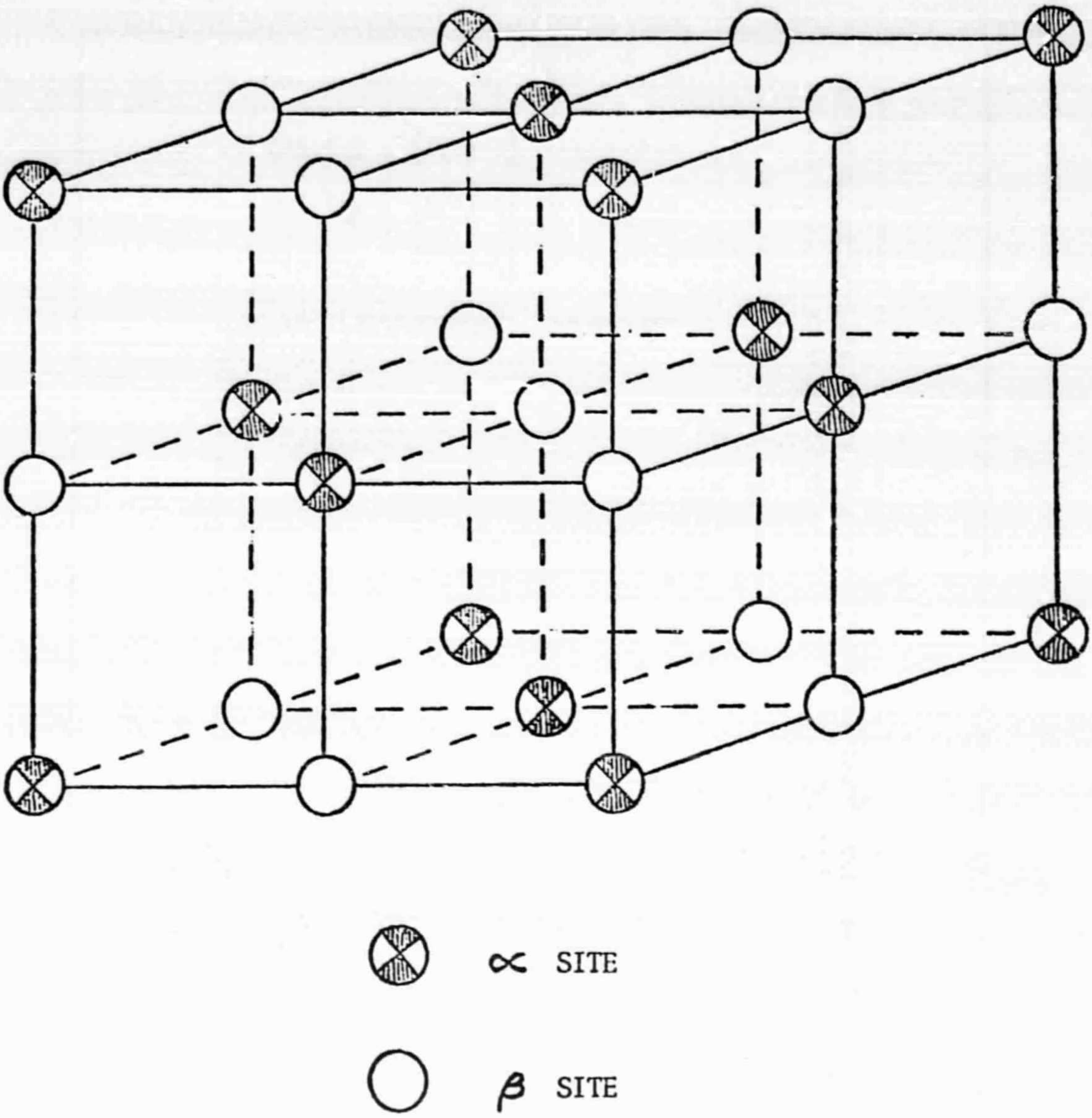

Figure 1. The simple cubic lattice formed by α and β sites. Both the α and β sublattices are face-centered cubic in structure.

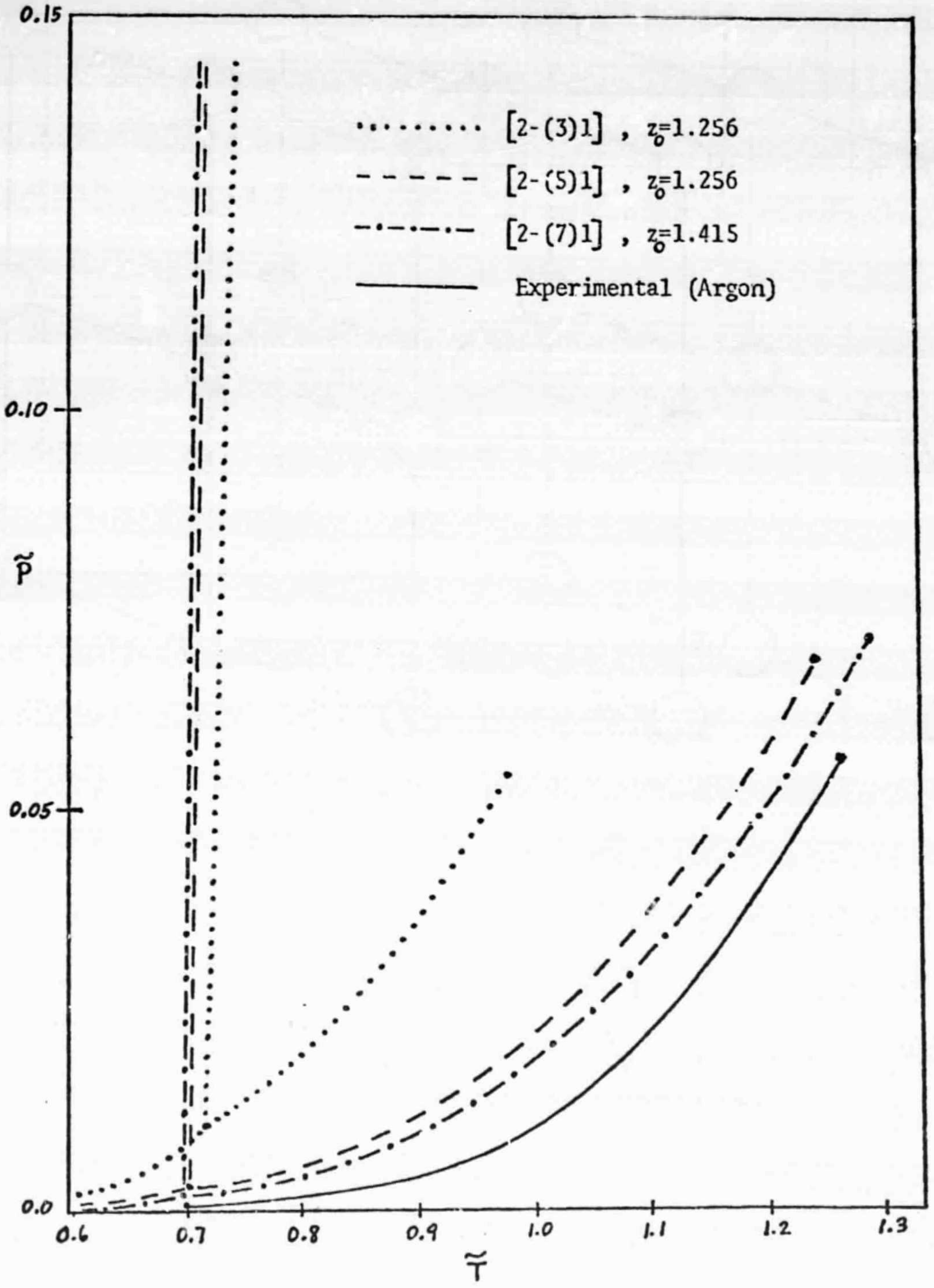

Figure 2. The pressure vs. temperature ($\tilde{P}\tilde{T}$) diagrams in the hybrid approximations with free volume correction (ω_0 = .01).

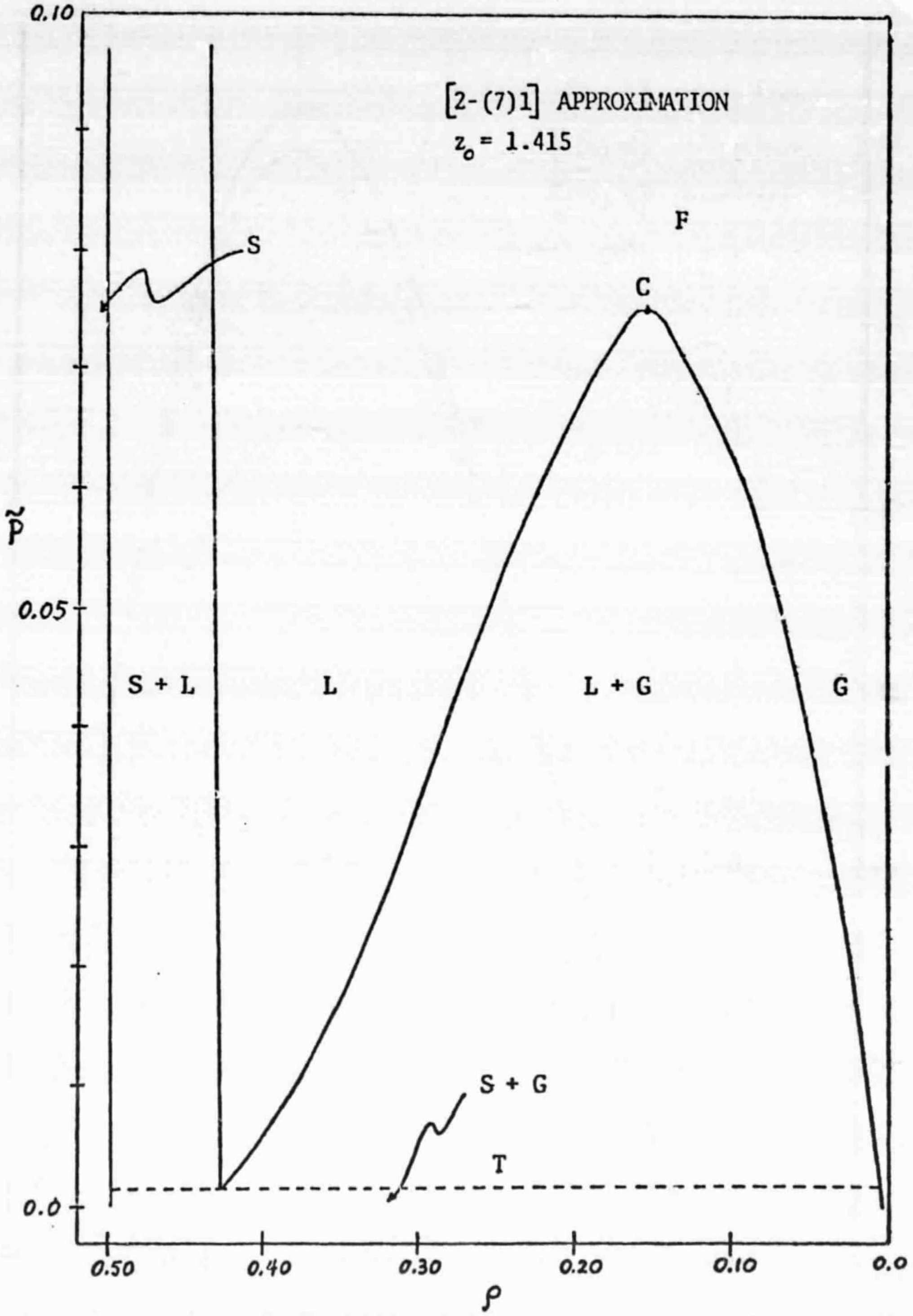

Figure 3. The coexistence diagram in the pressure vs. density ($\tilde{P}$ - ρ) plot and in the [2-(7)1] approximation with free volume correction (ω_0 = .01).

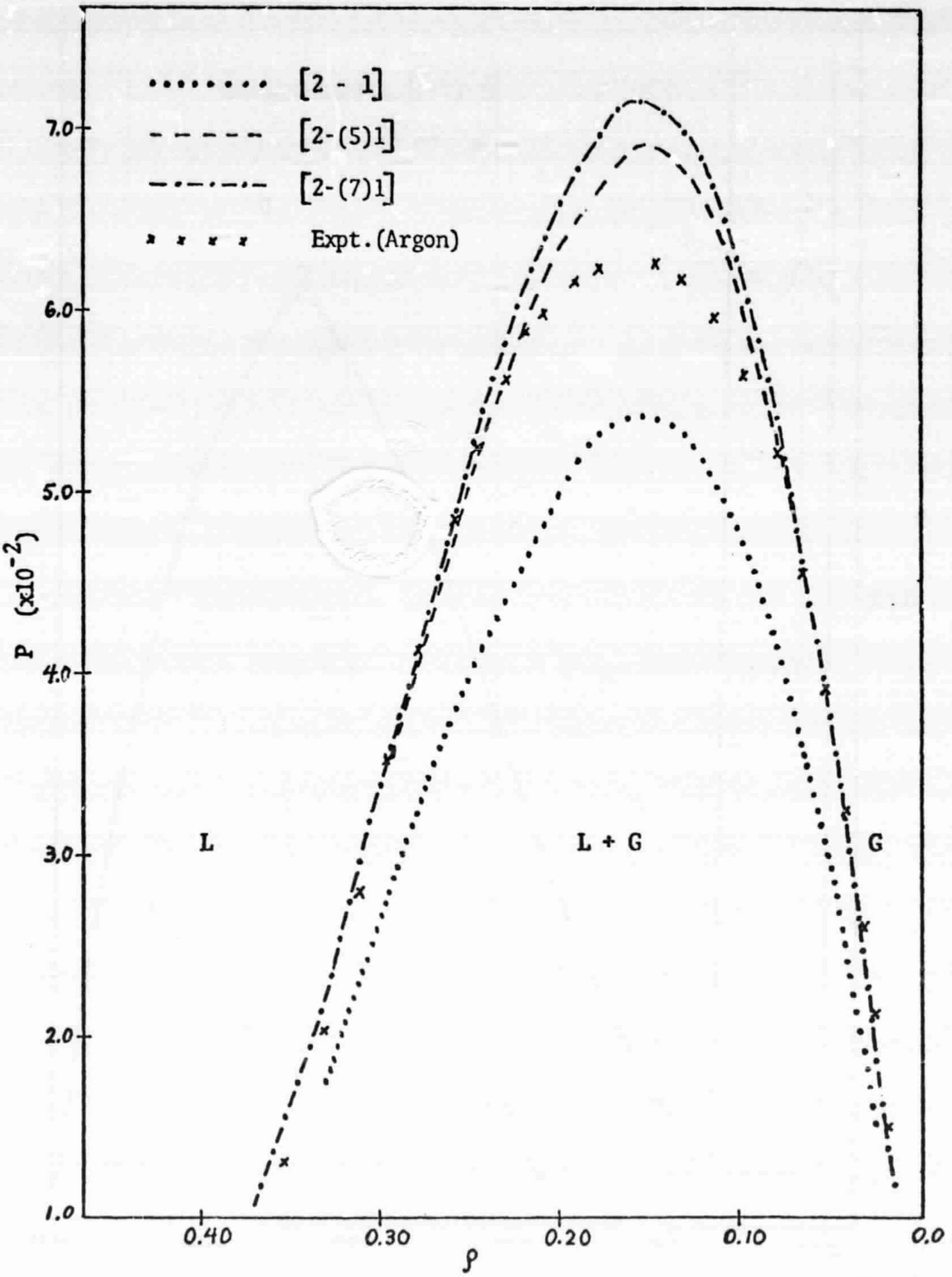

Figure 4. The liquid-gas coexistence curves. Shown here are the [2-1], [2-(5)1], and [2-(7)1] approximations, and the experimental data points for Argon. Since the liquid and the gaseous phases are both derived from the disordered branch of free energy, the vibrational parameters are unimportant in this diagram.

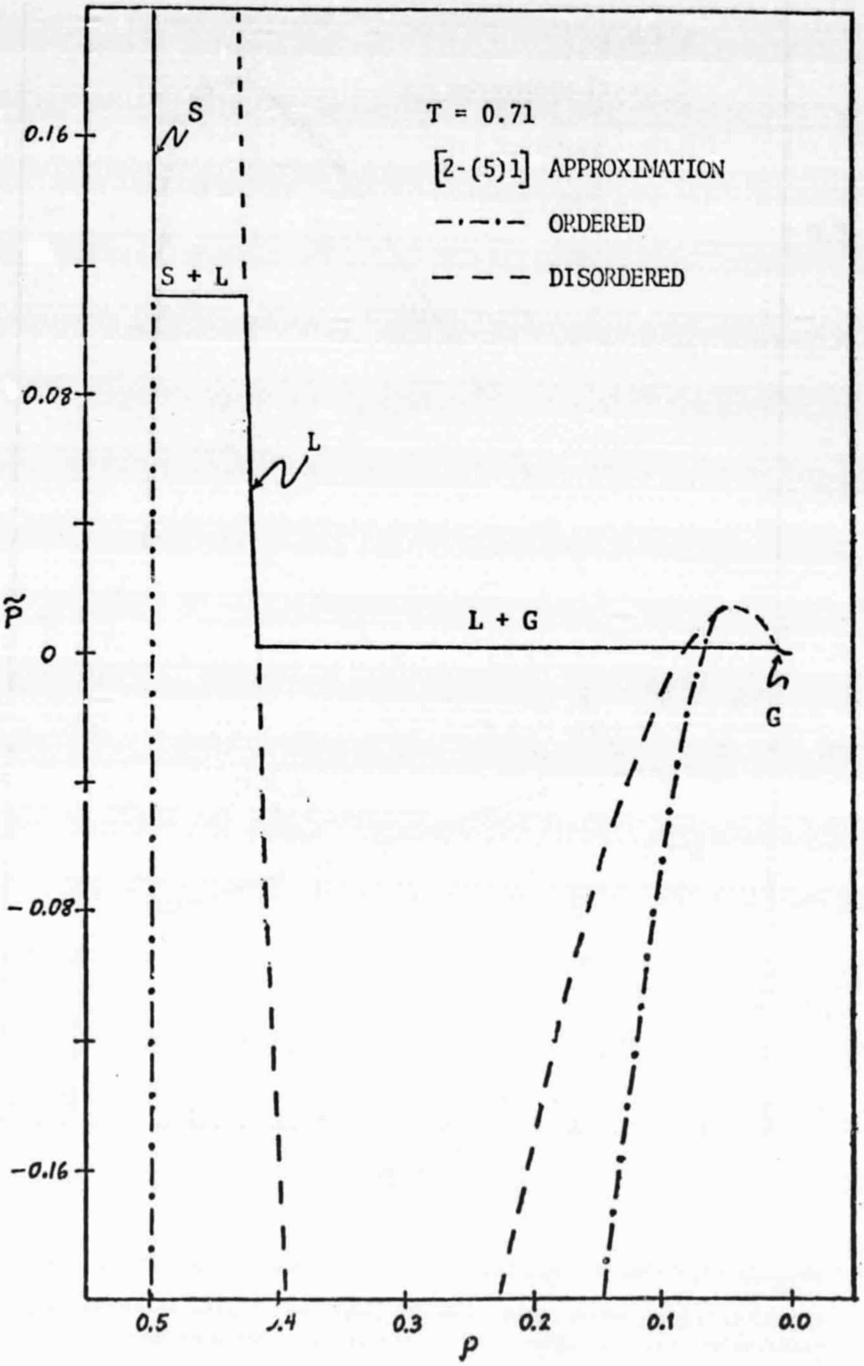

Figure 5a. The isotherm $\widetilde{T} = 0.71$ in the [2 - (5)1] approximation with free volume correction ($\omega_0 = .01$, $z_0 = 1.256$); pressure vs. density ($\widetilde{P} - \rho$) diagram.

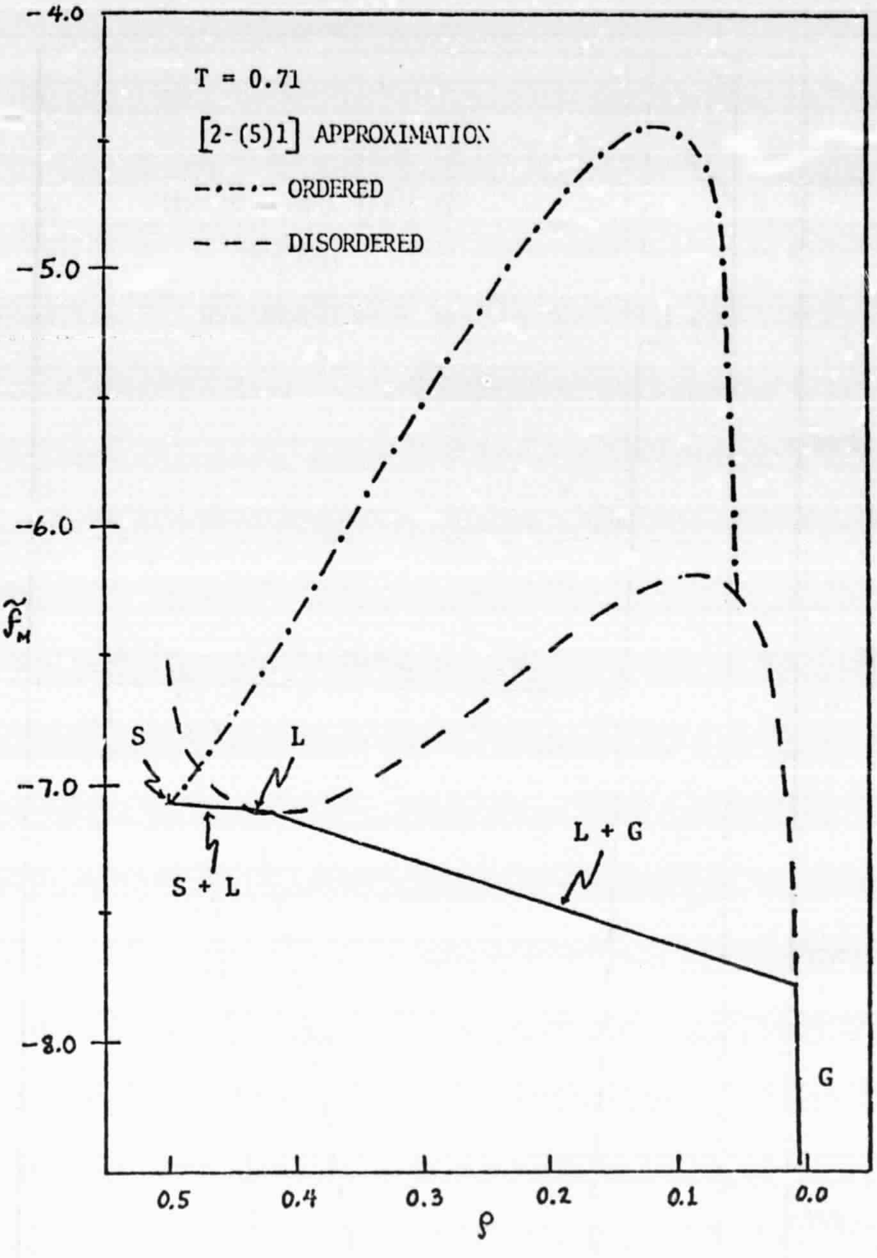

Figure 5b. The isotherm $\tilde{T} = 0.71$ in the [2 - (5)1] approximation with free volume correction (ω_0 = .01, z_0 = 1.256); Helmholtz free energy per molecule vs. density ($\tilde{f}_m - \rho$) diagram.

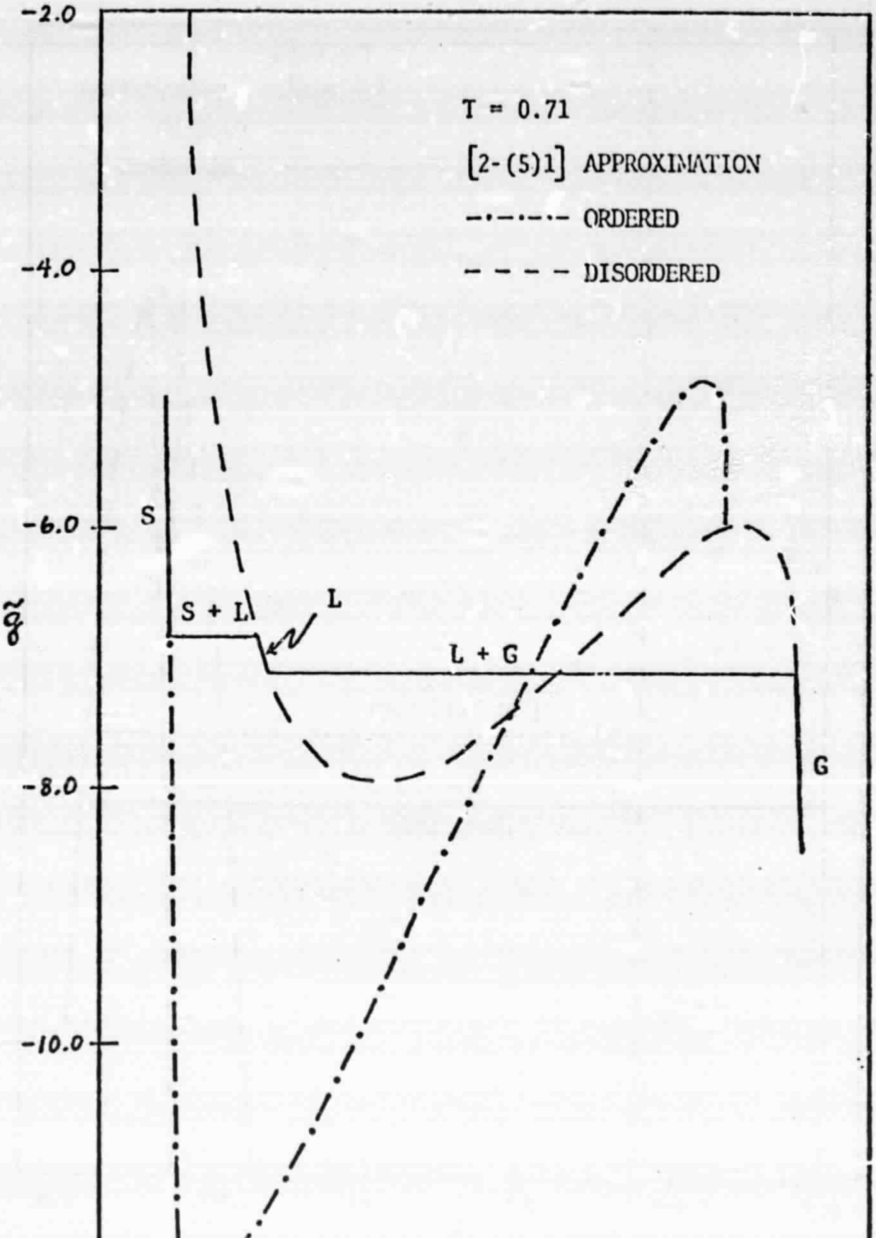

Figure 5c. The isotherm $\tilde{T} = 0.71$ in the [2 - (5)1] approximation with free volume correction ($\omega_0 = .01$, $z_0 = 1.256$); chemical potential vs. density $(\tilde{g} - g)$ diagram.

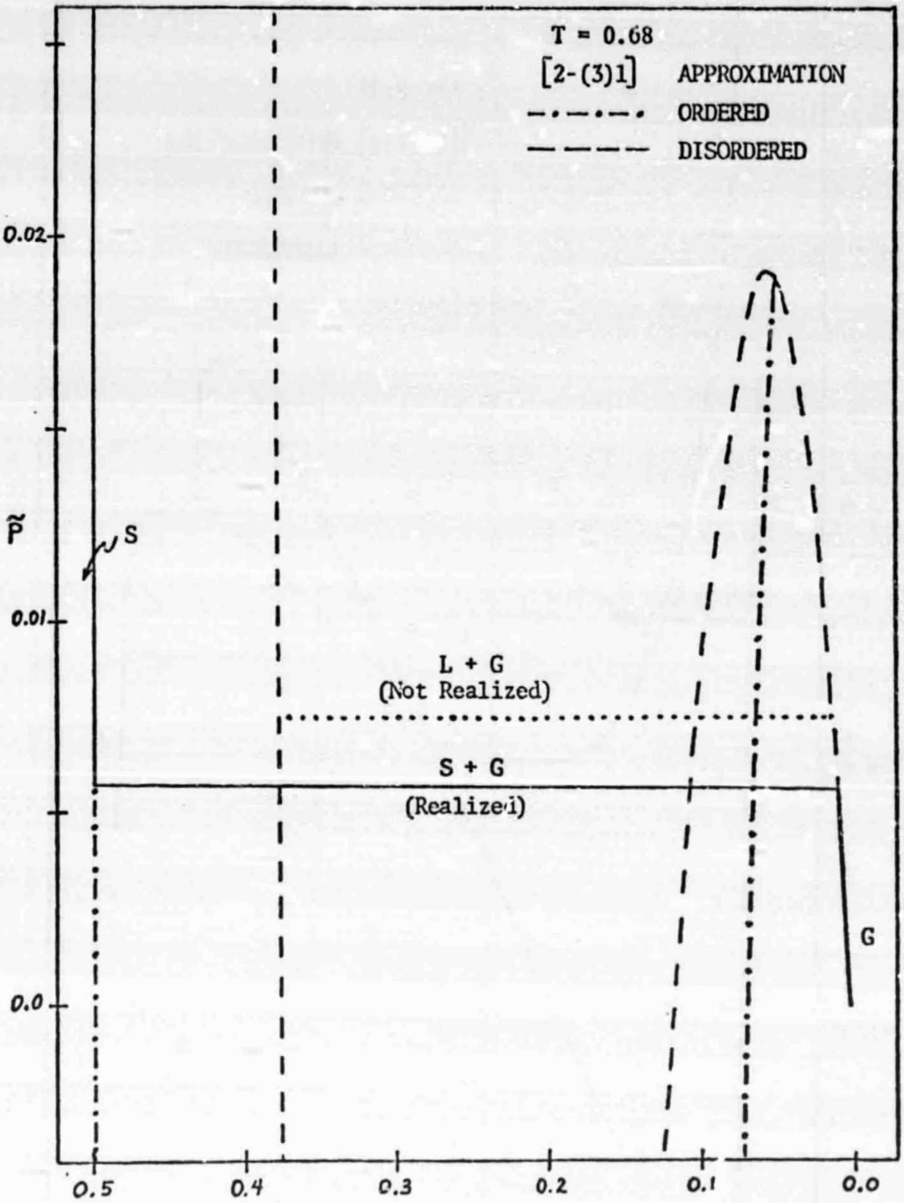

Figure 6a. The isotherm $\widetilde{T} = 0.68$ in the [2 - (3)1] approximation with free volume correction ($\omega_0 = .01$, $z_0 = 1.256$) plotted in the pressure vs. density ($\widetilde{P} - \rho$) diagram.

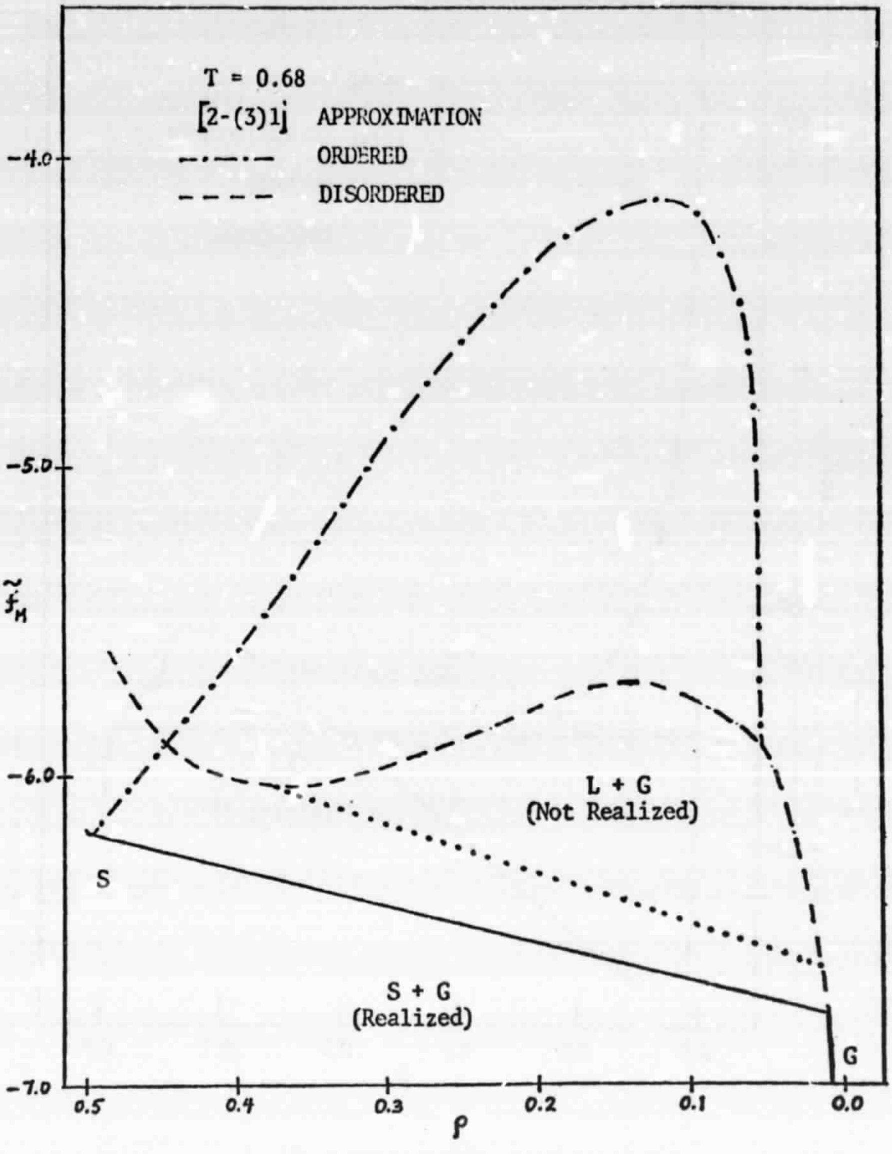

Figure 6b. The isotherm $\widetilde{T} = 0.68$ in the [2 - (3)1] approximation with free volume correction ($\omega_0 = .01$, $z_0 = 1.256$) plotted in the Helmholtz free energy per molecule vs. density ($\widetilde{f}_m - \rho$) diagram.

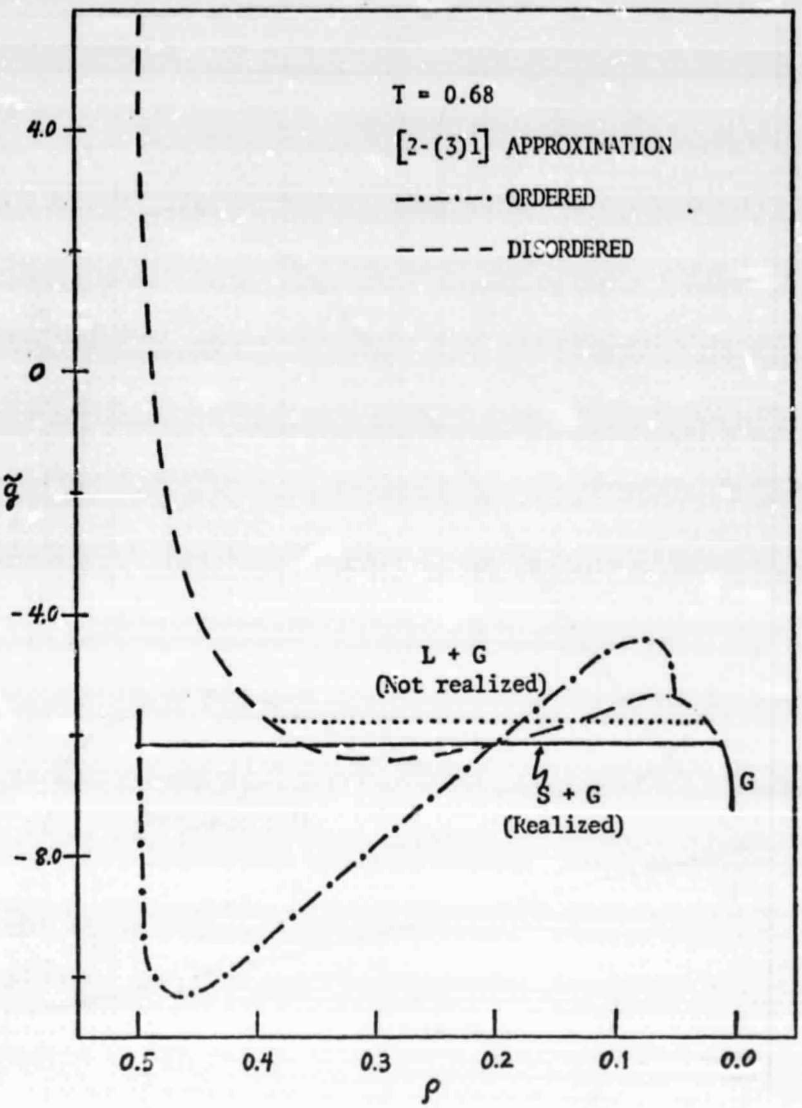

Figure 6c. The isotherm $\tilde{T} = 0.68$ in the [2 - (3)1] approximation with free volume correction ($\omega_0 = .01$, $z_0 = 1.256$) plotted in the chemical potential vs. density ($\tilde{g} - \rho$) diagram.

Table 1
The Triple Point

Model and Approximation		T_t	$P_t^* = 2P_t$	$v_t^* = v_{t/2}$	$P_t v_t / T_t$	R (LRO)
I. Rigid						
(a) [2 - (3)1]	(G)	0.713	0.0198	30.12	0.8364	0
z_0 = 1.256	(L)			1.382	0.0384	0
ω_0 = .01	(S)			1.0010	0.0278	0.9981
(b) [2 - (5)1]	(G)	0.700	0.0042	159.52	0.9571	0
z_0 = 1.256	(L)			1.187	0.00712	0
ω_0 = .01	(S)			1.00024	0.00600	0.99960
(c) [2 - (7)1]	(G)	0.698	0.0032	212.5	0.9742	0
z_0 = 1.415	(L)			1.170	0.00536	0
ω_0 = .01	(S)			1.00020	0.00458	0.99964
II. Expandable						
(a) Without	(G)	1.487	0.055	20.7	0.7686	0
Free Vol.	(L)			1.820	0.0676	0
MC2(1)	(S)			1.248	0.0463	0.9997
(b) With Free Volume ME4 (1_1, 1_2)						
(2,10)	(G)	0.7789	0.00550	130.3	0.9206	0
	(L)			1.431	0.0101	0
	(S)			1.114	0.0079	1
(3,12)	(G)	0.8509	0.02344	26.57	0.7320	0
	(L)			1.654	0.0456	0
	(S)			1.170	0.0323	1
III. Experiment	(L)	0.700	0.00151	1.186	0.00256	
(Argon)	(S)			1.035	0.00223	

Table 2
The Critical Point

Model and Approximation	T_c	$P^*_c = 2P_c$	$v^*_c = v_{c/2}$	$P_c v_c/T_c$	T_c/T_t
I. Rigid Lattice					
(a) [2-1]	0.670	0.074	3.20	0.353	
(b) [2-(3)1]	0.975	0.1080	3.16	0.350	1.367
(c) [2-(5)1]	1.237	0.1382	3.25	0.363	1.767
(d) [2-(7)1]	1.282	0.1431	3.26	0.364	1.837
II. Expandable					
(a) Without Free Free Volume					
MC2(1)	2.049	0.2001	3.682	0.3596	1.378
MC2(α)	1.751	0.1271	4.023	0.2921	
(b) With Free Volume					
ME4					
$\ell_1 = 0$	2.2974	0.3025	2.665	0.3509	
$\ell_1 = 2$	1.5331	0.2238	3.394	0.4956	1.968
$\ell_1 = 3$	1.2025	0.1999	2.920	0.4852	1.413
III. Experiment (Argon) ϵ/k = 119.8° K σ = 3.405 A	1.26	0.116	3.16	0.291	1.80