

Rigidity Symmetry Line for Thermodynamic Fluid Equations-of-State

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Abstract

We report progress towards a modern scientific description of thermodynamic properties of fluids following the discovery (in 2012) of a coexisting critical density hiatus and a supercritical mesophase defined by percolation transitions. The state functions density $\rho(p, T)$, and Gibbs energy $G(p, T)$, of fluids, e.g. CO₂, H₂O and argon exhibit a symmetry characterised by the rigidity, $\omega = (dp/d\rho)_T$, between gaseous and liquid states along any isotherm from critical (T_c) to Boyle (T_B) temperatures, on either side of the supercritical mesophase. Here, using experimental data for fluid argon, we investigate the low-density cluster physics description of an ideal dilute gas that obeys Dalton's partial pressure law. Cluster expansions in powers of density relate to a supercritical liquid-phase rigidity symmetry (RS) line ($\omega = \rho_{rs}(T) = RT$) to gas phase virial coefficients. We show that it is continuous in all derivatives, linear within stable fluid phase, and relates analytically to the Boyle-work line (BW) ($w = (p/\rho)_T = RT$), and to percolation lines of gas (PB) and liquid (PA) phases by: $\rho_{BW}(T) = 2\rho_{PA}(T) = 3\rho_{PB}(T) = 3\rho_{RS}(T)/2$ for $T < T_B$. These simple relationships arise, because the higher virial coefficients (b_n , $n \geq 4$) cancel due to clustering equilibria, or become negligible at all temperatures ($0 < T < T_B$) within the gas phase. The Boyle-work line $(p/\rho_{BW})_T$ is related exactly at lower densities as $T \rightarrow T_B$, and accurately for liquid densities, by $\rho_{BW}(T) = -(b_2/b_3)_T$. The RS line, $\omega(T) = RT$, defines a new liquid-density ground-state physical constant ($\rho_{RS}(0) = (2/3)\rho_{BW}(0)$ for argon). Given the gas-liquid rigidity symmetry, the entire thermodynamic state functions below T_B are obtainable from $b_2(T)$. A BW-line ground-state crystal density $\rho_{BW}(0)$ can be defined by the pair potential minimum. The Ar₂ pair potential, $\phi_{ij}(r_{ij})$ determines $b_2(T)$ analytically for all T . This report, therefore, advances the salient objective of liquid-state theory: an argon $p(\rho, T)$ Equation-of-state is obtained from $\phi_{ij}(r_{ij})$ for all fluid states, without any adjustable parameters.

Keywords

Liquid-State Theory, Cluster Physics, Percolation Lines,

1. Introduction

It is over 150 years since the birth of classical thermodynamics, whence J. W. Gibbs (**Figure 1**) published his description of thermodynamic properties and transitions between different phases as state functions on 2-dimensional, e.g., temperature (T) and pressure (p), surfaces [1]. In the same year, van der Waals PhD thesis [2] (**Figure 2**) introduced the concepts of a theoretical Equation of state $p(V, T)$ for pressures of a gas at fixed V (volume) and T , based upon his hypothesis that there exists a singularity described by the node of a cubic Equation. van der Waals' Equation-of-state defines a hypothetical critical temperature T_c , pressure p_c and singular volume V_c at the "critical point". For all $T > T_c$ and all $p > p_c$ there is no delineation between gas and liquid states in van in gas-liquid "continuity" theory.

1.1. Thermodynamic States and State Functions

In his classic treatise [1], Gibbs introduced the concept of a state function of any two state variables, for example pressure (p) as a function of temperature (T) and volume (V) as illustrated in **Figure 1** p - V - T 3D phase diagram. Given the state function heat capacity at constant pressure (C_p), Gibbs defined both enthalpy ($dU + pdV = C_p dT$) and entropy ($dS = C_p d \log_e T$), that are precise statements of the 1st- and 2nd-laws of classical thermodynamics, respectively [3].

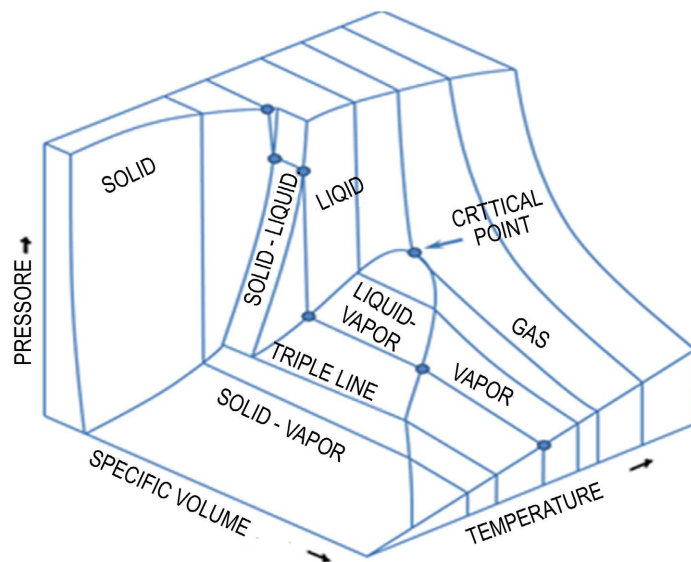


Figure 1. A Gibbs' $p(V, T)$ surface of thermodynamic equilibrium states showing $p(V, T)$ isotherms and phase boundaries as well-defined mathematical lines: the pressure surface is a function of volume (V) and temperature (T), showing some isotherms with Gibbs phases boundaries. A hypothetical van der Waals critical point is also shown.

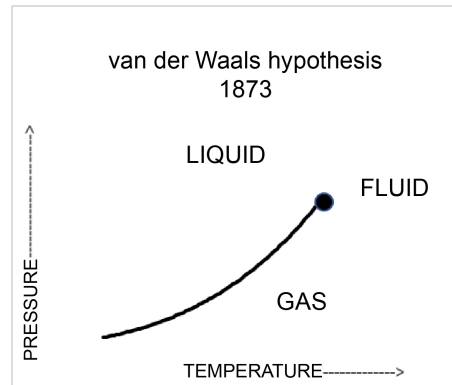


Figure 2. Phase diagram hypothesised by van der Waals on p - T surface: in his thesis of 1873: he defined a critical point when liquid and gas densities became equal with thermodynamic continuity to a supercritical fluid by both gas and liquid on the basis of his cubic Equation of state for $p(V, T)$.

Every thermodynamic state point on a Gibbs surface is defined where two lines cross and characterised by the number of degrees of freedom (F) in its specification by Gibbs phase rule. For a one-component system ($C = 1$) then, for P phases in coexistence, $F = C - P + 2$. All single-phase state points when ($F = 2$) are defined when an isotherm crosses an isobar, *i.e.*, by T , p . A state point in a two-phase region ($F = 1$) is defined when either an isotherm or an isobar crosses a coexistence line. The coexistence lines are defined by the intersection of lines of chemical potential (μ), on the $\mu(p, T)$ surface. The triple point volumes (**Figure 1**) are defined by the intersection of two coexistence lines. There is no such consistent thermodynamic definition of the “critical point”, shown in **Figure 1**.

van der Waals assumed that the cubic Equation-of-state

$$p = \frac{\rho kT}{1 - b\rho} - a\rho^2 \quad (1)$$

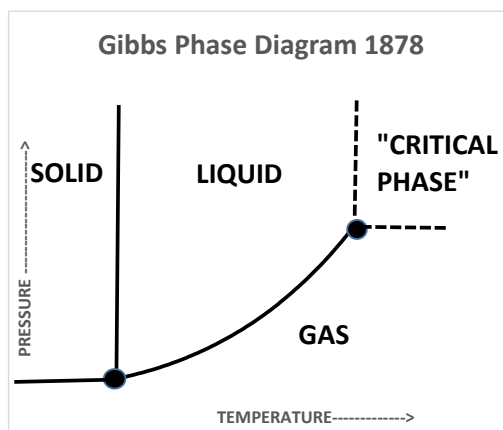
has a singularity that confirms the existence of a critical volume to be an established scientific truth. The van der Waals interpretation, also depicted as p - T phase diagram in **Figure 2**, was based upon just two near-critical isotherms with limited $p(V, T)$ data points for CO_2 reported in 1869 by Andrews. The Andrews-van der Waals hypothesis gave rise to the earliest predictions of solid-liquid-gas phase diagrams.

1.2. Historic Phase Diagrams

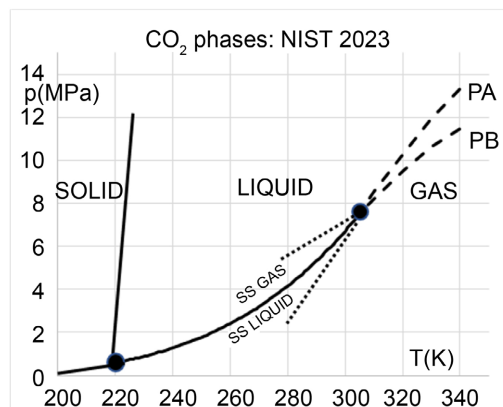
The Gibbs phase rule for all state points on the p - T surface gave rise to various conjectures of p - T diagrams showing gas, liquid, and solid regions. In the very early days, the solid-liquid transition was believed to be independent of pressure, and the gas-liquid coexistence line was reasonably known. Gibbs [4], unaware of van der Waals’ thesis at the time also interpreted Andrews’ discovery of a temperature above which a gas could not be liquified by increasing pressure. Gibbs

noted that there is also a pressure above which a gas cannot be liquified by reducing the temperature. Gibbs thought there was a second triple point and described the region as the “critical phase” as distinct from van der Waals continuous fluid hypothesis (**Figure 3(a)**). Hannay [5] also correctly observed that the Andrews experiments are indicative of a 1st-order phase transition at T_c .

Figure 3(b) for CO₂, drawn from present NIST thermophysical fluid property data [6], shows the definition and determination of the critical p_c , T_c point where the two percolation lines cross. The Gibbs-Hannay interpretation is closer to the modern description of the critical line between coexisting densities at T_c . The critical density hiatus and supercritical mesophase are now established science, confirmed by computer experiments on minimalist models [7], confirmed by review in depth from the literature experimental measurements covering 150 years since Andrew’s [8], and, recently confirmed, *inter alia*, by the debunked universality hypothesis [9].



(a)



(b)

Figure 3. (a) Gibbs [4] (1878)-Hannay [5] (1882) hypothetical phase diagram. (b) Present carbon dioxide phase diagram obtained from modern thermodynamic data compilation [(NIST 2023 [6]) showing percolation loci above T_c (dashed lines) that define the supercritical mesophase, and below T_c (dotted lines) become the metastable stability limit or “spinodal” lines [8].

Gas and liquid percolation lines, PB and PA, are defined by a change in the state function rigidity (ω) when hetero-phase bonded clusters of “liquid” in gas (density ρ_{PB}) and clusters of “gas” in liquid (density ρ_{PA}) have the same T , p and G (Gibbs chemical potential) at two different coexisting densities. This condition defines a 1st-order phase transition. At the gas-liquid critical point T_c - p_c the rigidity of both phases goes to zero, triggering a phase transition that terminates at the critical 2-phase coexistence pressure where the percolation lines intersect. **Figure 2** and **Figure 3** show that Gibbs and Hannay were closer to the scientific truth than van der Waals and the prevailing universality hypotheses of theoretical physics, and NIST employees still [6] [7] [8] [9].

1.3. State Function Rigidity

Rigidity is a defining state function that describes the distinction between gas states below the Boyle temperature and liquid or solid states. It decreases with density for a gas and increases with density for a liquid or solid. It is a reciprocal compressibility and related to Gibbs energy and hence also to density fluctuations by the following equalities of classical and statistical thermodynamics.

$$\begin{aligned}\omega &= \left(\frac{dp}{d\rho} \right)_T = -\frac{V}{K_T} = V \left(\frac{dp}{d \ln V} \right)_T = \rho \left(\frac{dG}{dp} \right)_T = \left(\frac{d\mu}{d \ln N} \right)_{V,T} \\ &= RT / \left(\langle \Delta N^2 \rangle \right)_{V,T}\end{aligned}\quad (2)$$

where K_T is the isothermal compressibility, G is Gibbs energy, μ is Gibbs chemical potential and (N/V) is number density. It is the symmetry of the rigidity, rather than the compressibility, that reveals the connection to percolation transitions that can define the distinction between gaseous states, and liquid or solid states below the Boyle temperature. Accurate rigidity data have been used, *inter alia*, to invalidate hypotheses that describe all gas-liquid critical points as being a singularity with universal scaling laws [9].

2. Rigidity Symmetry

2.1. Rigidity Symmetry of CO₂

For pure fluids, rigidities can be obtained from the heat capacity data in NIST thermophysical web book [6], given the speed of sound (c) values and the heat capacity ratio, then $\omega = c^2 C_p / C_v$. The rigidities of isotherms below T_B are shown in **Figure 4** for CO₂.

The Boyle-work (BW) line ($w = p/\rho_{BW} = RT$) [10] is seen to be perfectly linear for CO₂. A similar line can be defined by the rigidity symmetry (RS) line ($\omega = dp/d\rho)_T = RT$), defined as $\rho_{RS}(T)$, connects all state density points on the isotherms at a somewhat lower density than $\rho_{BW}(T)$ when the $\omega(\rho, T)$ state point has the same rigidity (ω) as the ideal gas at that temperature. The RS line is also linear. In the following sections we will relate the RS line to the BW line.

An inspection of the $\omega(T)$ isotherms in **Figure 4** shows a symmetry that is consistent with the existence of a supercritical mesophase within which it

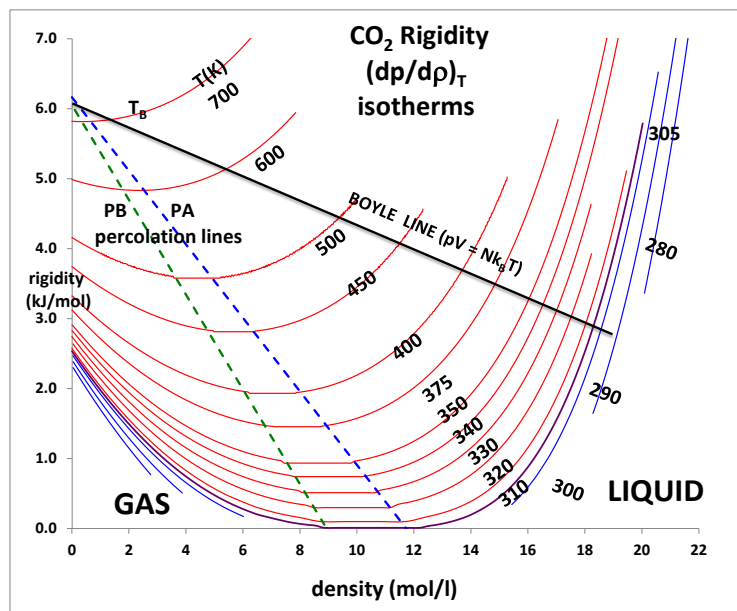


Figure 4. Isotherms of carbon dioxide showing the percolation loci that define the supercritical mesophase taken from the NIST thermophysical property databank [6]; the Boyle line [10]: (also referred to by others as the zero line) is also shown (solid black line) from the Boyle temperature of the dilute gas to a triple point isotherm: the green and blue dashed lines are the gas and liquid phase percolation transition densities referred to in Figure 3 and previously in reference [7].

remains constant along any isotherm and decreases from RT at the Boyle temperature (T_B , defined as in Figure 4 as isotherm above which there is no minimum in $p(\rho)_T$), to zero within the critical divide for all fluids [7] [8].

The percolation transition lines shown in Figure 4 are manifested as third- and higher-order discontinuities in the Gibbs energy p - T derivatives that depend upon density fluctuations. As the coexisting densities of liquid and gas densities become closer with $T < T_c$, the fluctuations increasingly reflect a symmetric hetero-phase presence in both phases. The experimental evidence for heterophase fluctuations is reproducible and well documented: see e.g., the review of Yukalov [11]. The role of heterophase fluctuations in gas-liquid criticality by percolation of the phase volume has been established. This implies changes of state in composition of the system, but still in-keeping with Gibbs definition of a “phase”, *i.e.*, with two degrees of freedom, T and p as originally observed by Gibbs for “critical phases” [4]. The symmetry seen for CO_2 appears to be a characteristic property of all pure atomic and molecular liquids regardless of the Hamiltonian complexity, even for water.

2.2. Rigidity Symmetry of Water

The observations regarding CO_2 also apply to complex liquids, and in particular the critical coexistence properties for steam and water [12]. Notwithstanding the known complexities of the steam-water molecule, and the quantum effects of the H-bonds in cluster and solid structures, the thermodynamic Equation-of-state

for water reveals a near perfect steam-water rigidity symmetry, and hence also a linear $\rho_{RS}(T)$ line. The data, illustrated in **Figure 5**, can be obtained from NIST tabulations [6] which has been calculated from the Wagner-Pruss Equation-of-state [13]. For water, the NIST Equation-of-state [6] [13] contains upwards of 100 arbitrary adjustable parameters to represent the experimental thermophysical fluid data to within an accuracy that it has been measured.

Given the correct scientific description of the phase transitions, the percolation lines PB and PA, and the BW and RS lines, this number of adjustable parameters can be reduced to zero, without loss of precision, provided we can deduce the correct science to determine the necessary physical constants. We illustrate this plausible objective briefly here, with just one supercritical isotherm (673 K or 400°C), and a point on the RS line (**Figure 5**) *i.e.* density $\rho_{rs} = 35.5$ mol/l corresponding to the rigidity $\omega = 5.65$ kJ/mol of the ideal gas steam limit $\rho \rightarrow 0$.

From **Figure 5** we infer the following:

- 1) The thermodynamic state functions, e.g. $p(\rho, T)$, of steam along any isotherm below T_B for all densities below the percolation transition density $\rho_{PB}(T)$, will be continuous in all derivatives, and represented by a virial expansion in powers of density.
- 2) Given the rigidity symmetry seen in **Figure 5**, $p(\rho, T)$ for water can be obtained from the same expansion coefficients used to describe steam isotherms at the higher densities above $\rho_{PA}(T)$ and for densities below the RS line on any isotherm in an expansion in powers of the density difference $\Delta\rho_{RS} = (\rho - \rho_{RS})_T$.
- 3) The function $p(\rho)_T$ and $p(\Delta\rho_{RS})_T$ are empirically quadratic. If that is the

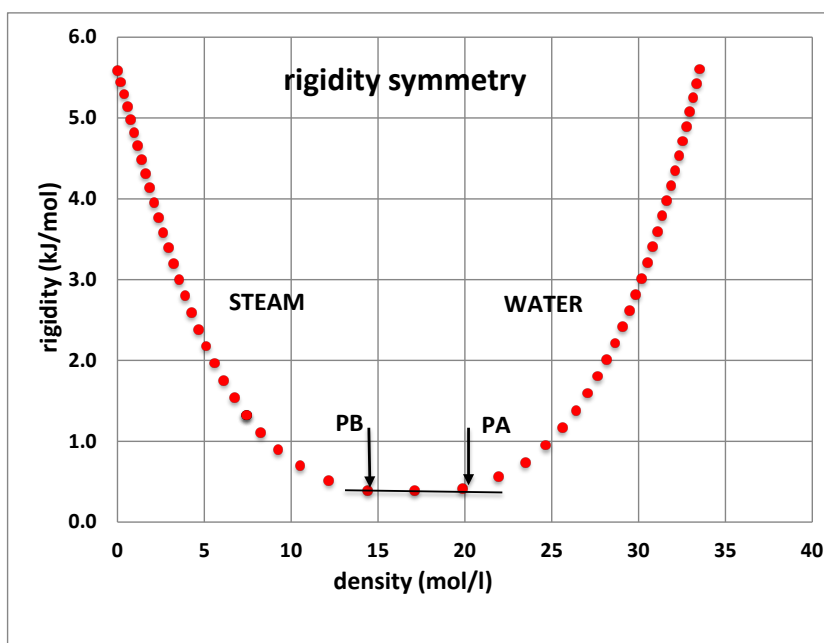


Figure 5. Rigidity, $(dp/d\rho)_T$, of a supercritical isotherm of steam and water at 400°C (673 K: $T/T_c = 1.04$) taken from the NIST thermophysical property databank [6]: at a density of 32.5 mol/l, supercritical water has the same rigidity as its corresponding state ideal dilute gas, *i.e.*, steam, at 673 K and 155 MPa.

general case, the same two virial coefficients that describe the gas phase for densities below the PB line can be used to represent the $p(\rho, T)$ data for the supercritical liquid region between T_c and T_B for densities between the PA and RS lines at, and above the PA line, *i.e.* $\rho_{PA}(T)$.

4) The RS line shown has a pressure of 155 MPa at 673 K. The whole isotherm, experimentally, extends to higher temperatures, up to T_B (= 1250 K) for steam, and pressures to 1000 MPa [13]. This region is amenable to an expansion around the BW line $\rho_{BW}(T)$ along the same isotherm.

5) The steam section, including the mesophase, requires only the first 2 or 3 coefficients in an expansion in powers of density, the two physical constant densities ρ_{PB} and ρ_{PA} , and the Boyle temperature T_B , for accurate representation of $\omega(T = 673)$, over the whole measured pressure range up to 1000 MPa of its existence for densities below and above ρ_{PB} and ρ_{PA} respectively.

6) The same coefficients that describe the steam density expansion could also describe an expansion about density point ρ_{RS} on the water phase in powers of the density difference $\Delta\rho = (\rho_{RS} - \rho)_{\text{water}}$ along the same isotherm, and below T_c by the difference $\Delta\rho = (\rho_{BW} - \rho)_{\text{water}}$ to the triple point.

All other high-density liquid-side thermodynamic properties could be obtained from the rigidity isotherms, via the equalities in Equation (2) for all temperatures, including Gibbs energies and two-phase regions and coexistence lines. Other thermodynamic state functions, *e.g.* Gibbs energies that determine phase coexistence boundaries thermodynamic properties can likewise be prescribed in terms of the various physical constants for water at temperatures up to T_B and 1000 MPa. In the following sections of this report, however, we will focus on the rigidity symmetry of argon, as the exemplary simple liquid, and its relationship to the percolation lines PA and PB, and the Boyle line.

2.3. Gas-Liquid Symmetry of Argon

All phase transition lines, and 2-phase coexistence regions, on a Gibbs p - T surface, for example, are determined by the Gibbs energy state function; two distinct states of different density (or molar volume) have the same T , p and molar Gibbs energy (chemical potential). Van der Waals critical point hypothesis can be tested simply by comparing theory, *i.e.*, van der Waals Equation Gibbs energy, with experimental, *i.e.* Gibbs energy along the critical isotherm (151 K) for argon from NIST thermophysical property web book that uses TSW Equation-of-state [6] [14] (Figure 4). The van der Waals Gibbs energy from Equations (1) and (2)

$$G^* = RT \left[\frac{b}{b-V} - \ln \left(1 - \frac{b}{V} \right) - \frac{2a}{V} \right] \quad (3)$$

in which G^* is the excess Gibbs energy relative to the ideal gas at the same T , p .

$\Delta G/RT$ for the critical isotherm of argon, referenced to the critical line constant value G_c , is shown in Figure 6, between the maximum coexisting gas density and minimum coexisting liquid densities at T_c for the NIST [6] critical isotherm (151 K). This accurate experimental description of the critical isotherm

can be compared with van der Waals singularity prediction in the most favourable comparison, *i.e.* when the two constants a and b are exactly fitted to correctly predict the critical state point $T_c - P_c$. Then we obtain the van der Waals V_c for argon that corresponds to a singular critical density ρ_c of 11.0 mol/l, *i.e.* slightly below the maximum coexisting gas density

The van der Waals hypothesis completely misses the essential physics of critical point ($T - p$) thermodynamics [7] [8]. The hard-sphere reference model implicitly determines the structure in mean-field and perturbation theories. Since the original van der Waals' hypothesis, countless generic variations have also failed. All such theories of simple liquids neglect an essential symmetry between gas and liquid states, arising from the cluster physics description, especially in the vicinity of the critical point T_c, p_c .

Near-critical coexistence properties involve hetero-phase fluctuations and the supercritical mesophase, determined by clustering effects and manifested as percolation transitions with discontinuities in density fluctuations or rigidity as given by Equation (2). Mean-field and first-order perturbation theories are only quantitatively successful nearer to the triple point where hetero-phase fluctuations are minimal. Sedunov [15] has investigated the importance of molecular clustering equilibria in atomic (argon), and molecular (CO_2 and H_2O) gases, and reported that these effects play an important part of the description of thermodynamic properties of all real gases, and hence also gas-liquid phase transitions. Gibbs energy differences are the driving force for all first-order phase transitions. **Figure 6** shows that van der Waals Equation (1) gets the science of critical coexistence completely wrong.

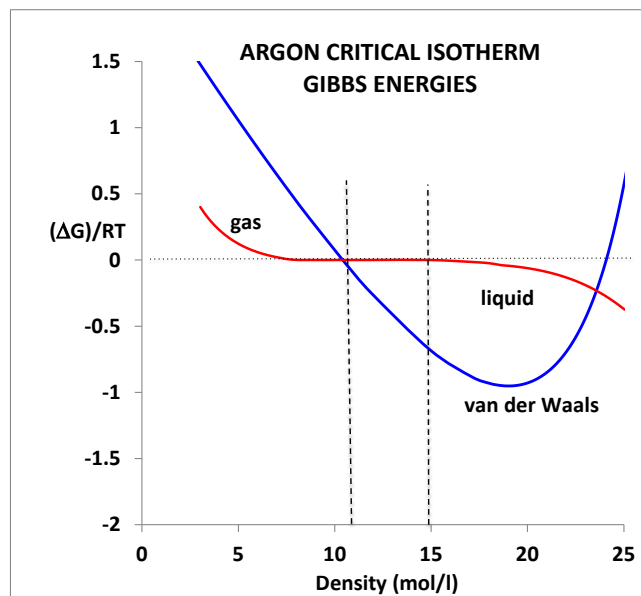


Figure 6. The experimental Gibbs energy of argon along the critical isotherm (151 K), referenced to the value at the critical T, p , compared to the prediction of van der Waals Equation in its most favorable interpretation when the two parameters a and b are fitted to the critical point T_c and p_c , respectively.

A more significant observation from the experimental Gibbs energy critical isotherm in **Figure 6**, is that the symmetry between states below the maximum coexisting gas density, and states above the minimum coexisting liquid density applies to Gibbs energies. Between these two physical constant state points, determined by the intersection of percolation lines, T_c , p_c and G_c (Gibbs chemical potential) are all constant. At the critical line, the rigidity is zero as the density fluctuations in Equation (2) diverge. We can see from Equation (2) that this symmetry in $G(p, T)$ relates to the state function rigidity (ω) and to the same density fluctuations in both gas and liquid phases at T_c .

Rigidity symmetry has its origins in the statistical cluster physics of real gases that is mirrored by the cluster physics of voids or vacancies, *i.e.* available volume, in liquids. The van der Waals mean-field approximation in Equation (1) and all similar mean-field theories of liquids, and perturbation theories of hard sphere fluid reference state [16] all neglect this essential physics that determines the thermodynamic state functions and Equation-of-state of both gases and liquids [9]. Real gases are composed of clusters of atoms or molecules, even at very low finite densities, to some extent, for all temperatures below T_B .

3. Cluster Physics of the Gas Phase

3.1. Equilibrium Constants

Any real gas below T_B is a multicomponent mixture of monomers, dimers, trimers etc. [15]. Each species obeys the ideal gas law of partial pressures at a sufficient low density. The equilibrium constants k_n for multiple molecular clusters, e.g., $(\text{H}_2\text{O})_n$ or $(\text{CO}_2)_n$ or atomic clusters, e.g., argon $(\text{Ar})_m$ denoted generally by A_m can be expressed as sequence of gas phase chemical reactions according to the equilibria: $nA \leftrightarrow A_n$. The equilibrium constants can be expressed as a series in which $[A_1]$ is the monomer density fraction and $[A_n]$ fraction of cluster size n .

Then

$$k_2 = [A_2]/[A_1]^2; \quad k_3 = [A_3]/[A_1]^3; \quad k_n = [A_n]/[A_1]^n \quad (4)$$

At low density, the partial pressures of $[A_n]$ from Dalton's law can be summed as a series for the cluster density species (ρ_p) at total pressure (p), then

$$p = \rho_p RT = [A_1] + k_2 [A_1]^2 + \dots + k_n [A_1]^n + \dots \quad (5)$$

$$\rho RT = [A_1] + 2k_2 [A_1]^2 + \dots + nk_n [A_1]^n + \dots \quad (6)$$

substituting from Equation (6) in Mayer expansion for pressure in terms of the atom density powers, $\rho^{(n-1)}$ that define the virial coefficients b_n [16]

$$p = \rho RT (1 + b_2 \rho + b_3 \rho^2 + \dots + b_n \rho^n + \dots) \quad (7)$$

by combining terms, we obtain the relationships between coefficients b_n and K_n

$$b_2 = -k_2 \quad (8)$$

$$b_3 = 4k_2^2 - k_3 \quad (9)$$

$$b_4 = 18k_2k_3 - 20k_2^3 - 3k_4 \quad (10)$$

These relationships hold for all the $b_n(T)$ and $k_n(T)$ for all $T < T_B$. Since all the $k_n(T)$ are everywhere positive, there must be a significant cancellation, to some unknown extent, of the higher virial terms in the Mayer cluster expansion Equation (7). Only $b_2(T)$ and $b_3(T)$, of argon for example, are required to represent accurate gas pressures in the range from $T_B > T > 0$ at densities below the percolation line ρ_{PB} and for all isotherms below T_c for all densities below the gas-liquid and gas-solid coexistence lines down to zero K. The cancellation of b_4 is already evident for all $T > T_c$ (151 K) as seen in **Figure 7**.

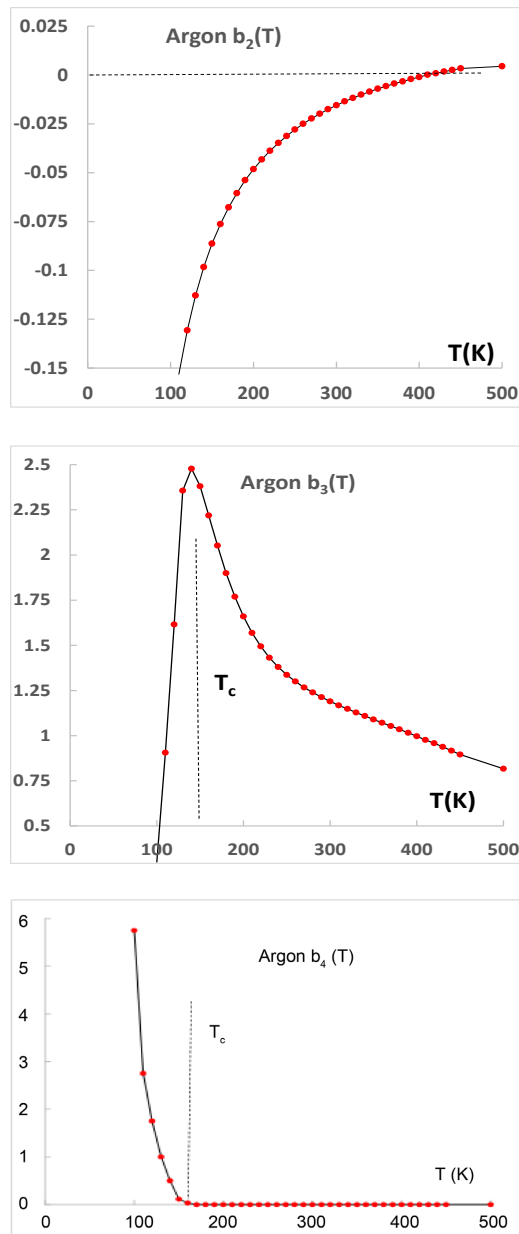


Figure 7. Argon virial coefficients b_2 , b_3 and b_4 in units of $(\text{l/mol})^n/10^{3(n-1)}$.

3.2. Virial Coefficients

Accurate experimental values of $b_2(T)$ and $b_3(T)$ (**Figure 7**) have recently been reported for argon from sound velocity (c) measurements in the temperature range 100 to 500 K [17]. Using known b_2 and b_3 values, we can obtain $b_4(T)$ in the same T -range given also the NIST experimental heat capacity and sound velocity data for argon. By plotting $[\omega/(RT) - (1 + 2b_2\rho + 3b_3\rho^2)]$ versus ρ^3 we obtain the $b_4(T)$ values also shown in **Figure 7**.

The Mayer virial series [16], Equation (7), is a Taylor expansion for pressure derivatives in powers about zero density, whence ‘bond’ lengths within clusters that determine k_n become negligible compared to divergent correlation lengths between clusters that determine the density in Equation (5). Hence, the concept of rigidity symmetry [18] means that the liquid properties can all be determined from the corresponding-state gas phase given only the lower virial coefficients. We can now proceed to specify the thermodynamic state functions, notably, the Boyle and critical and triple point temperatures, BW and/or RS lines, and the coexisting percolation densities at T_c .

We note that $b_3(T)$ and $b_2(T)$ appear to be linearly related for $T > T_c$ and contain information on T_c . $b_3(T)$ shows a maximum at T_c whereas b_4 goes to zero for all $T > T_c$. All the higher virial coefficients $n > 4$ either cancel similarly or will become negligible at the low densities below the ρ_{PB} line. Hence, we can determine physical constants and thermodynamic Equations-of-state from only the lower virial coefficients b_2 and b_3 for the gas phase.

Both the BW and RS lines extend to hypothetical amorphous and crystalline solid states, *i.e.* insofar as they would obey classical statistical mechanics at the lower temperatures. The neglect to a large extent of the higher terms $b_n \geq b_4$ in the virial expansion can be justified by an analysis of the expansion of the gas pressure in terms of equilibrium constants defined in the low-density limit obedience to Dalton’s law of partial pressures for argon. We do not yet know whether this is also the case for more complex molecular liquids CO_2 or water, probably not.

3.3. Coexisting Gas and Liquid Densities at T_c

The percolation pressures, of bound clusters in the gas, and of gaseous voids in the liquid, with decreasing T , intersect to trigger a critical point coexistence line at T_c and a supercritical mesophase with linear hybrid properties (**Figure 3(b)**). The percolation transitions are higher-order phase transitions that delineate the gas phase below the Boyle temperature when the clusters of ‘liquid-in-gas’ diverge to percolate the phase volume. There are no phase transitions for all gas densities below the PB-line density of gaseous bonded clusters ρ_{PB} . The gas phase Equation-of-state is given by the Mayer virial expansion, for given T and for $\rho < \rho_{PB}$ we have the following, formally exact up to the first thermodynamic discontinuity, Mayer cluster expansions [16]

Work

$$w = \left(\frac{p}{\rho} \right)_T = RT \left(1 + b_2 \rho + b_3 \rho^2 + \dots + b_n \rho^{n-1} \right) \quad (11)$$

Rigidity

$$\omega = \left(\frac{dp}{d\rho} \right)_T = RT \left(1 + 2b_2 \rho + 3b_3 \rho^2 + \dots + n b_n \rho^{n-1} \right) \quad (12)$$

Solidity

$$\sigma = \left(\frac{d^2 p}{d\rho^2} \right)_T = RT \left(2b_2 + 6b_3 \rho + \dots + n(n-1)b_n \rho^{n-2} \right) \quad (13)$$

The Boyle work ratio for the critical isotherm (151 K) of argon is plotted in **Figure 8**. Both work (w) and rigidity (ω) decrease with increasing density for a gas and mesophase densities below PA; both increase with density for the liquid phase above a minimum very slightly greater than $\rho_{PA}(T_c)$. The rigidity, $\omega = RT$, however, is more convenient reference point in describing Equations-of-state and Gibbs energies for phase transitions. Its derivative, solidity σ , Equation (13) is -ve for a gas, zero in the mesophase, and +ve for liquid phase. We can use these Equations to show that there must exist a maximum coexisting gas-phase density along the percolation line PB, at state point whereupon both ω and σ go to zero at T_c [7] [8].

All points on the gas-phase percolation line PB, including the maximum coexisting gas density at T_c , occur when the solidity (σ) is set to zero in Equation (13) and all terms $n > 3$ neglected, then we have

$$3\rho_{PB}(T_c) = -(b_2/b_3)_{T_c} \quad (14)$$

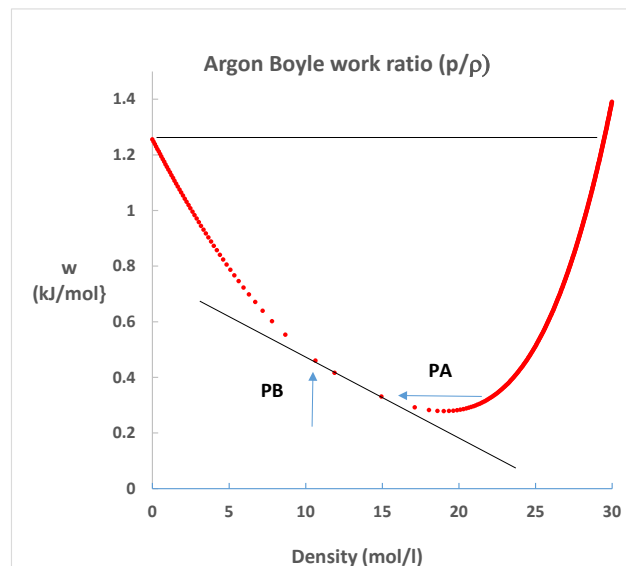


Figure 8. The experimental Boyle work ratio along the critical isotherm ($T_c = 151$ K): data from reference [6]: the percolation transition PB (gas clusters) and PA (liquid voids) correspond to the maximum coexisting gas density (ρ_{PB}) and minimum coexisting liquid density (ρ_{PA}), respectively, as indicated by the arrows.

i.e. a very simple Equation for the maximum coexisting gas density at T_c that can be shown to be very close to experimental reality. The ratio $-(b_2/b_3)_T$ (**Figure 9**) is plotted from the data of Estrada-Alexanders *et al.* (shown in **Figure 4** above) and seen to be linear in a 200 K temperature range beyond which it passes through zero at T_B and goes negative. Over this temperature range, it can be represented by a single ground-state density constant that determines $-(b_2/b_3)_T$ in using the $T \rightarrow 0$ ground-state constant from the linear region that $T \rightarrow T_B$ as illustrated in **Figure 9**. If the value at T_c is used, a slightly higher ground-state density is obtained.

Thus, if the terms $b_n > 3$ in Equations (13) and (14) are negligible for the gas phase below the PB line, the result can be used to confirm the experimental observation that the ω goes to a constant and that the solidity goes to zero at $-(b_2/3b_3)_T$. The ratio is obtained from **Figure 9** at the zero-density intercept $-(b_2/b_3)_0 = -0.1162T + 47.34$ mol/l with regression (R^2) for the range 300 - 403 K = 0.9979. This result corresponds to a maximum coexisting gas density at T_c of 10.1. This is slightly lower, but of the same order as the maximum reported experimental coexisting gas density 11.4 mol/l by Michels *et al.* [19] or 11.8 mol/l by Gilgen *et al.* [20].

Likewise, Equation (11) for the BW line can be used to obtain the minimum coexisting liquid density, again, from **Figure 8**, Boyle work $w(\rho)_T$ goes to a minimum at the density $\rho_{PA}(T_c)$. Then, $b_2 + 2b_3\rho_{PA} = 0$ at T_c , resulting in the simple equality again that the minimum coexisting liquid density at T_c is given by $\rho_{PA}(T_c) = -\frac{1}{2}(b_2/b_3)_{T_c}$. Using the ground-state constant 47.34 mol/l to define the T_B asymptotic slope of $-(b_2/b_3)_T$ data in **Figure 9**, we obtain a value $\rho_{PA}(T_c) = 14.7$ mol/l. This result is reassuringly close to the value obtained from NIST [6]

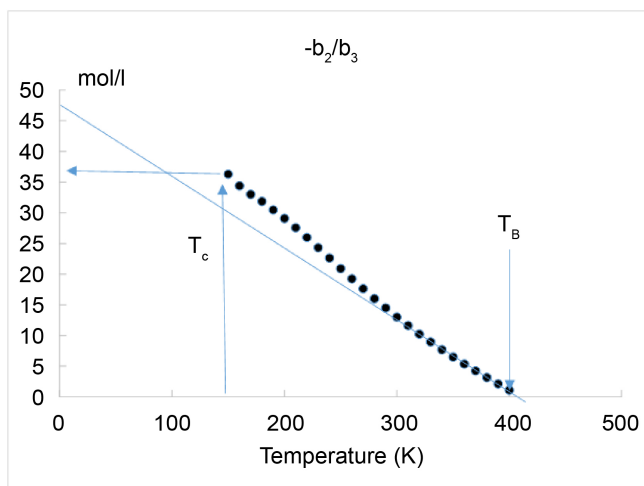


Figure 9. The ratio $-(b_2/b_3)_T$ from the data shown in **Figure 5** (reference [16]) it goes to zero at the Boyle temperature (403 K): the density corresponding to the critical temperature (151) as indicated is around 35 *i.e.* 3 times the experimental maximum coexisting gas density as indicated in **Figure 4** and **Figure 6**, and is consistent with Equation (14).

(Figure 4) ~ 14.9 mol/l and near to the minimum recorded coexisting liquid densities of Michels *et al.* (15.35 mol/l) [19] and Gilgen *et al.* (15.07 mol/l) [20].

4. Equations-of-State

4.1. Relationship between BW and RS Lines

The condition $p/\rho_B = RT$ defines the BW line that connects all these state points of both the super- and sub-critical liquid along any isotherm below T_B . If we denote the density of the Boyle-work line $\rho_{BW}(T)$, the linearity can be explained by considering the form of a rigidity symmetry line, which we will denote by $\rho_{RS}(T)$. Now, we have a relationship between these two lines that turns out to be quite simple for argon.

The RS line, defined by the equality [18]

$$(dp/d\rho)_T = RT \quad (15)$$

has its origins in the symmetry of gas and liquid density fluctuations which are equivalent to ideal gas density variance along this line (Equation (2)). Again, from the rigidity virial expansion Equation (6) we see a simple prediction. If the isotherm were to be perfectly symmetric, then the virial expansion that defines the rigidity for the gas below PB-line can be applied for liquid-state densities between the PA-percolation line and the rigidity symmetry line $\rho_{RS}(T)$. Then, the rigidity for

$$\rho_{PA} < \rho < \rho_{RS}$$

$$\omega = RT \left(1 + 2b_2 \Delta\rho + 3b_3 \Delta\rho^2 + \dots + nb_n \Delta\rho^{n-1} \right) \quad (16)$$

where $\Delta\rho = (\rho_{RS} - \rho)_T$. The RS line $\rho_{RS}(T)$, when $\Delta\rho = \text{zero}$, decreases linearly with T . Along any isotherm the symmetry can be shown to extend to the BW line density $\rho_{BW}(T)$. Since for all densities beyond $\rho_{PA}(T)$ there are no phase transitions of any order, both the Boyle work ratio $w(T)$ and rigidity $\omega(T)$ are continuous in all their density derivatives along the respective lines to the first-order phase transitions on condensation. If all the higher terms $n \geq 4$ in the Equations (11)-(13) are negligible by cancellation for densities below ρ_{PB} , then, for the BW line

$$w = RT \left(1 + b_2 \Delta\rho + b_3 \Delta\rho^2 \right) \quad (17)$$

when $\Delta\rho = (\rho_{BW} - \rho)_T$. Then from (16) and (17), neglecting all b_n terms $n > 3$,

$$\rho_{RS}(T) = 2\rho_{BW}(T)/3 \quad (18)$$

It follows from Equation (18) that the BW line ($p/\rho_B = RT$) will relate to the RS line, $dp/d\rho_{RS} = RT$, for all supercritical liquid-side states essentially exactly for lower densities above T_c . In the following sections, we establish empirically that the relationship is accurate over the whole T -range for argon from T_B to the hypothetical ground-states of BW and RS lines at $T \rightarrow 0$.

4.2. Ground-State Densities

A selection of $\omega(T)$ isotherms for argon from NIST web book [6] is shown in Figure 10 for the temperature range T_c to T_B . The densities corresponding to $\omega(T)$ and $w(T)$ can be obtained very accurately at the points $\rho_{RS}(T)$ and $\rho_{BW}(T)$

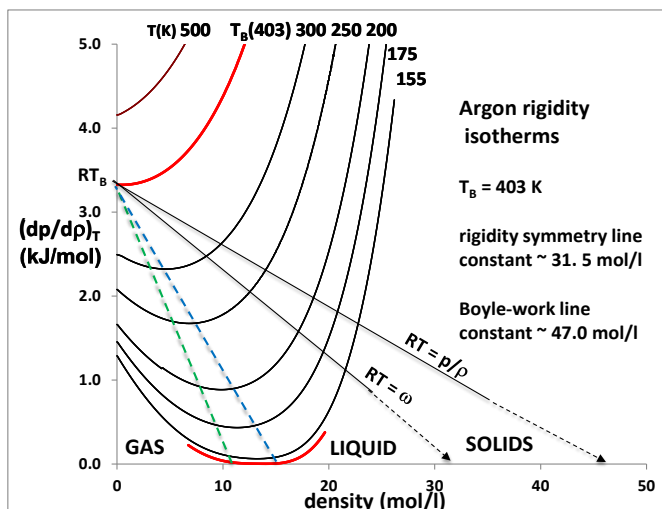


Figure 10. Rigidity isotherms for argon: the Boyle-work and rigidity symmetry lines for argon showing an extrapolation beyond intermediate hypothetical unstable states that define ground state solid density physical constants; the Boyle temperature and critical isotherms are shown as red lines; the green and blue dashed lines are the percolation loci PB and PA respectively, that bound the supercritical mesophase as shown.

and are seen to be linear. The Boyle line is perfectly linear over the entire range with a slope that is consistent with the result in Equation (14). The BW $\rho_{BW}(T)$ is essentially the same as $-b_2/b_3(T)$ in **Figure 9**, with the same constant ground-state of 47.0 ± 0.5 mol/l. This is a remarkable equality: $\rho_{BW}(T) = -(b_2/b_3)_T$ relating the BW line to only the lower virial coefficients for $T_c < T < T_B$.

The BW line $\rho_B(T)$ is empirically found to be near perfectly linear for argon from NIST data [6]. When an EXCEL trendline is fitted to the intersections whence $p/\rho_B = RT$ below T_B , as shown in **Figure 10**, we obtain the linear trendline

$$T = 8.5881\rho + 403.26K \quad (\text{regression } \langle R^2 \rangle = 0.9996)$$

to estimate the Boyle temperature (403.3 ± 0.5 K) and ground-state “crystal” constant (46.96 ± 0.05 mol/l).

The Boyle line describes a line of states for which all the virial coefficients in Equation (4) cancel. Since a straight line is continuous with all its higher derivatives zero, it is not surprising that although the BW line describes unstable states (within 2-phase regions) below about 91 K when it hits the liquid-to-FCC freezing transition, it terminates at a perfect classical close-packed crystal ground state characteristic density determined by the pair-potential Hamiltonian.

The intercept of the rigidity symmetry line at $T=0$ (32.5 mol/l) is closer to a frozen liquid state of amorphous packing of argon atoms in the liquid density range. Random close packed (RCP) density $2/\pi$ (0.6366) would correspond to a hard-sphere bond diameter of the argon dimer 0.3915 nm. The ρ_{RS} ground-state density constant for argon, however, is closer to triple-point liquid random loose packing, with a packing fraction around 50%, calculated from the experimental

Ar₂ dimer bond length, and 1/3 of maximum crystal packing (74%).

An analytical theory of simple liquids, without adjustable parameters, seems now within reach: *i.e.* to relate the Ar₂ pair-potential Hamilton to the $p(\rho, T)$ Equations-of-state in the regions of the phase diagram delineated by the lines PB, PA, RS and BW all of which are now defined by $b_2(T)$ and the linear ratio $-b_2/b_3(T)$, obtainable from BW-line, of the phase diagram, over the whole density-temperature range.

4.3. Argon Dimer Pair Potential

The fundamental objective of the theory of simple liquids [16] is to relate the intermolecular or interatomic forces that define the Hamiltonian of the system, to the $p(\rho, T)$ Equation-of-state. The pair potential for argon has been extensively studied, probably more so than any other exemplary fluid, and is known quite accurately both from original experiment [19] [20] [21] and more recently, *ab initio* quantum theory [22]. It is characterized, often only by 2 parameters e.g., Lennard-Jones, *i.e.* by the range of the minimum energy at the distance r_0 of zero force. The experimental value is $r_0(\text{Ar}_2) = 0.3704 \pm 0.005$ nm, based upon the more accurate functional representative of Boyes [21].

Assuming that the argon BW-line ground state is a perfect FCC or HCP close-packed lattice of spheres in the BW-crystal structure, we can calculate the $\rho_{BW}(T \rightarrow 0)$ constant from the reduced maximum packing density of spheres $\rho^* = Nr_0^3/V = 2^{1/2}$. Substituting the argon dimer bond length, we obtain a prediction of the $\rho_{BW}(T \rightarrow 0) = 46.21$ mol/l.

It appears that the cluster analysis in section 2 above contains information on the maximum packing of argon atoms. This is understandable from the cluster physics analysis in section 2. If all the equilibrium constants k_n were to be known, they would reveal this limiting, hypothetical, close-packed crystal density constant. The virial expansion, evidently, has its first pole at the maximum packing density of minimum energy.

This density obtained from the pair potential agrees well with the constant obtained from **Figure 9**, $-(b_2/b_3)_T$ ratio, and with the interpolation in **Figure 10** of the BW line to $T \rightarrow 0$ ($\rho_B = 46.96$ mol/l). It is still, however, somewhat greater than the experimental HCP-argon crystal value 44.43 mol/l [23]. A small difference between the Boyle line hypothetical ground state physical constant could arise zero-point energy quantum effects in real crystal states. Argon undergoes an equilibrium FCC to HCP phase transition at a temperature around 35 K along its equilibrium experimental $(p/\rho_B)_T$ BW line [23].

4.4. Fluid Phase Diagram

Using the experimental co-existence envelope data from NIST, for the present, we can construct an accurate phase diagram that enables the bounds of the $p(\rho, T)$ Equations-of-state to be quantified. There are no arbitrary parameters other than the virial coefficients $b_2(T)$ and $b_3(T)$ and the physical constants that they

determine. The Boyle temperature T_B is determined by $b_2(T)$: when it changes sign from $-ve$ to $+ve$. The BW line ground state density is then equivalent to the $(-b_2/b_3)_T$ line, linear from $T = T_B$. The value obtained in **Figure 5** for the scaling ground-state constant is 47.34 mol/l. This compares favorably with the Kihara pair-potential value for the minimum energy of the FCC or HCP crystal 46.21 mol/l. The experimental constant obtained from BW-line isotherms is 46.96 mol/l (**Figure 10**).

This ground-state constant, determined also from the virial coefficients, can be used to sketch an accurate phase diagram (**Figure 11**) using the various simple equalities derived above. The ratio $-(b_2/b_3)_T$, below T_B , determines the BW line ground-state constant for argon. Given the simple relationships between PA, PB, RS, and BW(T), we can determine the critical temperature T_c (whence $\omega(T) \rightarrow$ zero at $\rho_{PA}(T)$ or $\rho_{PB}(T)$), and then fill in the isotherms of $p(T)$, $w(T)$, or $\omega(T)$ over the temperature range from the triple point to the BW line and beyond, to the state points above the BW line below T_B .

The second observation from the argon phase diagram is that the equilibrium regions of the BW and RS lines completely exist only within a single Gibbs supercritical “liquid” phase with $P = 1$. Whereas the percolation transitions delineate the supercritical gas and liquid regions by higher-order phase transitions, the BW and RS lines have no phase transitions and are therefore continuous in all their derivatives. Thus, both lines are defined by their ground state physical constant hypothetical densities obtained in linear interpolation limit that $T \rightarrow 0$.

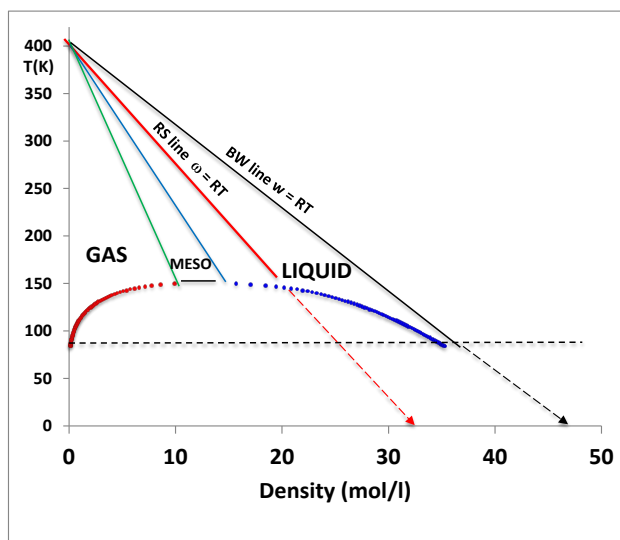


Figure 11. Temperature-density phase diagram of fluid argon states: the equilibrium mesophase defined by the percolation loci PB and PA, $\rho_{PB}(T)$ and $\rho_{PA}(T)$, are shown as green and blue solid lines respectively; both Boyle-work $\rho_{BW}(T)$ and rigidity symmetry $\rho_{RS}(T)$ are linear in the stable one-phase supercritical region in accord with Equations (16)-(18); the dashed arrows show the RS and BW ground-state constants.

5. Conclusions

A line of thermodynamic symmetry between gaseous and condensed (liquid or solid) state densities on the Gibbs T - ρ surface is perfectly well-defined by the phenomenological equality between the rigidity $(\omega - dp/d\rho)_T$ of liquid states and the properties of the low-density ideal gas, $\omega(\rho \rightarrow 0) = RT$, the RS line $\rho_{RS}(T)$. Because of the cancellation of the higher virial coefficients for simple liquids like argon, the RS line is seen to be linearly related to the BW line by $(\rho_{RS}/\rho_{BW})_T = 2/3$ along any isotherm in the whole range of its equilibrium existence.

Knowledge of the RS line for simple and more complex molecular liquids can lead to accurate physical constant Equations-of-state for all fluid states below the Boyle temperature in the spirit of van der Waals. Such progress requires the correct phase-transition science, without resort to any arbitrary or adjustable parameters, given the temperature-dependent lower virial coefficients and some physical constants that can define percolation lines and coexistence lines on the phase diagram. For regions of the extended liquid phase, and for all densities below the rigidity symmetry line, the thermodynamic properties can be accurately predicted from the properties of the gas phase below T_B given the 2nd virial coefficient b_2 and either the ratio $-(b_2/b_3)_T$ for the range $T_c < T < T_B$, or equivalently just the BW line ground state constant $\rho_{BW}(0)$.

Finally, there is a discrepancy between our result for the BW ground-state solid density constant in this analysis ($\rho_{BW}(0) = 46.96$ mol/l) whereas the experimental close-packed HCP (same density as FCC) at minimum energy $T \rightarrow 0$ K for argon: 44.20 mol/l [23]. One expects a small difference from the quantum zero-point energy of the real crystal, but not of the order 10%. Our symmetry analysis, however, assumes that the relationship between the virial coefficients b_n and equilibrium constants k_n (Equations 8-10) are analytic. This result may only apply exactly to pairwise additive Hamiltonians. If a “true” Ar₂ Kihara pair potential [24] obtained only from the second virial coefficient is used, the maximum ground-state density (46.21 mol/l), corresponding to minimum energy, is closer to our $\rho_{BW}(0)$ than to the experimental value of crystalline argon.

In conclusion, there are non-negligible non-pairwise additive terms in the real argon Hamiltonian. The contribution of 3-body triple-dipole potential dispersion force depends upon the size and shape of the r_{ij} , r_{ik} , r_{jk} triangle. The energy is positive for all acute triangles, and those up to 117°, and negative for all other obtuse triangles. The net effect of 3-body terms in dense fluid media has been known since 1970 [25] (quote: “...it is found that the effect of three-body forces is to expand the liquid by approximately 8%”). This explains the ground-state discrepancy: $\rho_{BW}(0)/1.08 \simeq \rho(A_{r\text{-expt.}})(0)$. Non-additivity does not, however, vitiate the “holy grail” of “Theory of Simple Liquids” [16], *i.e.* deriving a $p(\rho, T)$ Equation-of-state, without any fitted parameters, from a pairwise Hamiltonian.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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