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Geometry of the vapor-liquid coexistence near the critical point

E. PIÑA*
Departamento de Ciencias Básicas
Universidad Autónoma Metropolitana-Azcapotzalco
Apartado postal 16–306, 02200 México, D.F., México

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ABSTRACT. The geometry of the thermodynamic surface of the liquid-vapor coexistence is studied in a space whose coordinates are densities of mass, energy, and entropy. Main emphasis is given to the vicinity of the critical point. Geometric assumptions made are the asymptotic behavior of thermodynamic derivatives without a priori correction to scaling hypothesis. Analysis of the results leads to the proposal that the leading correction exponent is $1 - \alpha - \beta = \gamma + \beta - 1$.

RESUMEN. Se estudia la geometría de la superficie termodinámica de la coexistencia vapor-líquido en un espacio cuyas coordenadas son las densidades de masa, energía y entropía. Se pone el mayor énfasis en la vecindad del punto crítico. Se acepta como hipótesis geométrica el comportamiento asintótico de las derivadas termodinámicas sin ninguna hipótesis *a priori* sobre las correcciones al escalamiento. El análisis de las consecuencias nos lleva a proponer que el exponente dominante de corrección es $1 - \alpha - \beta = \gamma + \beta - 1$.

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1. INTRODUCTION

The representation of thermodynamic properties by geometric surfaces has a well-known history and many first rank scientists have used geometric representations of thermodynamics for different purposes [1,2].

The use of these geometric surfaces needs no more justification than the obvious qualitative insight one obtains from graphic representation of any physical function.

The physical system considered here is an ordinary real fluid with two phases, liquid and vapor. Only stable thermodynamic equilibrium is taken into account.

The geometry used in this paper is ordinary classical differential geometry [3]. A different geometry proposed by Tisza [4] and based on the fact that rigid motions in a thermodynamic space have no physical meaning, states that affine transformations are more adaptable to thermodynamics. However, affine geometry is not as intuitive, and the matrices used by Tisza to specify his geometry are not well-defined at the critical point. Also, the ordinary graphics of thermodynamic relations can not be easily incorporated into this geometry.

An Euclidean space is adapted here using mass density, energy density, and entropy density as rectangular coordinates. This choice of coordinates is based on the increased

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*Also at Instituto Tecnológico de Monterrey, campus Estado de México.

symmetry observed near the critical point when these thermodynamic variables are used to express the observed thermodynamic relations graphically [5].

Thermodynamic equilibrium states are represented in this space by points lying on a surface. This surface expresses the thermodynamic relations between coordinates.

The geometry used in this paper to represent the physical system is closely related to Gibbs' geometry [1]. Gibbs used entropy, energy and volume as orthogonal coordinates in space. Points in thermodynamic equilibrium form a particular surface in this space, which corresponds to the particular fluid it represents. Pressure and temperature determine the orthogonal direction to the surface. Liquid and vapor coexistence in equilibrium is represented in Gibbs' space by two points with different coordinates and one plane tangent to each of the two points. For a one-component fluid, any thermodynamic variable at coexistence is a function of only one independent variable, and in this work, the temperature was chosen as the independent variable at coexistence.

As the temperature changes, the plane tangent to the two coexistence points rolls on the surface, touching two branches of the coexistence curve. This curve, formed by the two coexistence points when the temperature is varied, has two branches, liquid and vapor which are connected at the critical point. The envelope of the family of planes formed as they roll on the coexistence curve produces the thermodynamic two-phase surface. This is a developable surface formed by rulers connecting the two coexisting points on the liquid and vapor coexistence curves, respectively. All these geometric arguments have been expressed in Gibbs' paper [1]. A generalization of these same ideas for any thermodynamic system has been presented by Buckingham [6].

Working in Gibbs' space, Piña and Mata [7] studied the developable surface formed by the rulers connecting coexisting points. These rulers are tangent to the edge of regression which is present in a developable surface. Piña and Mata have expressed the equation of this particular edge of regression as a function of the vapor pressure and the chemical potential at coexistence.

In this paper, the geometric properties previously obtained in Gibbs' space are not only reproduced with little change in the different space presented here, but the geometric ideas are further elaborated, and geometric objects not previously considered in thermodynamics are explicitly calculated, with main emphasis on the critical point.

Some thermodynamic information at the critical point is necessary to attain this objective. This information is given in quantitative form, assuming the accepted exponents [8,9,10] for some thermodynamic quantities. A survey of the thermodynamic basis is presented in the next section. Griffiths and Wheeler [11] found using field variables (pressure, temperature, chemical potential) a preferred direction along the coexistence curve.

Although the coordinates used in this paper are different from those of Griffiths and Wheeler, it was found useful their suggestion for studying the preferred direction along the coexistence curve. This geometric property has an analogue in the conjugated coordinates which are the densities of the extensive variables used in our study.

Looking for physically meaningful results, the common features of the behaviour of geometric objects will be stressed as the critical point is approached.

2. THERMODYNAMIC PROPERTIES

The thermodynamics of a definite quantity of a pure substance is expressed here in the variables used by Ley-Koo and Green [8].

By using critical pressure, temperature and volumen (P_c, T_c and V_c), quantities can be expressed as physically dimensionless. The fundamental coordinates I use are mass density, energy density and entropy density and these are defned as functions of the volume V, the energy U, and the entropy S by the equations

$$\rho = \frac{V_c}{V}, \qquad u = \frac{U}{Vp_c}, \qquad s = \frac{ST_c}{Vp_c}. \tag{1}$$

We also have Gibbs relation

$$ds = -\tilde{T}\,du - \tilde{\mu}\,d\rho, \tag{2}$$

and Gibbs-Duhem relation

$$d\tilde{P} = \rho\,d\tilde{\mu} + u\,d\tilde{T}, \tag{3}$$

where $\tilde{P}$, $\tilde{T}$, and $\tilde{\mu}$ are the Sengers and Sengers [9] variables, which are defined by

$$\tilde{T} = -\frac{T_c}{T}, \qquad \tilde{\mu} = \frac{\mu T_c}{TP_cV_c}, \qquad \tilde{P} = \frac{PT_c}{TP_c}, \tag{4}$$

where P, T, μ are the pressure, temperature, and chemical potential, respectively.

These quantities are related by equation

$$\tilde{P} = \rho\tilde{\mu} + u\tilde{T} + s. \tag{5}$$

Asymptotic properties near the critical point are represented by critical exponents associated with the leading term of any quantity expressed as a function of temperature deviations $\Delta\tilde{T} = |1 + \tilde{T}|$,

$$\left(\frac{\partial\tilde{\mu}}{\partial\tilde{T}}\right)_\rho = q_1 \qquad \text{(finite)}, \tag{6}$$

$$\left(\frac{\partial\tilde{T}}{\partial u}\right)_\rho = \frac{1}{\rho T^2 C_V} = q_2\Delta\tilde{T}^\alpha \qquad (\alpha \doteq 0.1), \tag{7}$$

$$\left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T = \frac{1}{T\rho^2\kappa_T} = q_3\Delta\tilde{T}^\gamma \qquad (\gamma \doteq 1.2), \tag{8}$$

where q_i are coefficients, having a finite value at the limit $\Delta\tilde{T} = 0$, C_V is the heat capacity at constant volume and κ_T is the isothermal compressibility.

On the coexistence curve, the difference in liquid and vapor densities is a function of the temperature differences $\Delta\tilde{T}$ with an exponent β. This is found by taking the derivative of the density with respect to the temperature T calculated on the coexistence curve. This derivative has a divergence with an exponent $\beta - 1$:

$$\frac{d\rho(\tilde{T})}{d\tilde{T}} = q_4 \Delta\tilde{T}^{\beta-1} \quad (\beta \doteq 0.325). \tag{9}$$

Exponents and coefficients q_i may be a function of the path one follows to attain the critical point. Equations (6–9) may be exact equations, if the q_i's are not constants. The behavior of many other thermodynamic variables is determined by the previously assumed dependence of these four quantities (6–9).

For example, the other nine partial derivatives relating the variables $\rho, u, \tilde{T}, \tilde{\mu}$, become

$$\left(\frac{\partial u}{\partial \rho}\right)_T = -\left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_\rho = -q_1, \tag{10}$$

$$\left(\frac{\partial \rho}{\partial \tilde{T}}\right)_\mu = -\left(\frac{\partial \rho}{\partial \tilde{\mu}}\right)_T \left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_\rho = -\frac{q_1}{q_3}\Delta\tilde{T}^{-\gamma}, \tag{11}$$

$$\left(\frac{\partial u}{\partial \tilde{\mu}}\right)_T = \left(\frac{\partial \rho}{\partial \tilde{T}}\right)_\mu = -\frac{q_1}{q_3}\Delta\tilde{T}^{-\gamma}, \tag{12}$$

$$\begin{aligned}\left(\frac{\partial u}{\partial \tilde{T}}\right)_\mu &= \left(\frac{\partial u}{\partial \tilde{T}}\right)_\rho + \left(\frac{\partial u}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial \tilde{T}}\right)_\mu \\ &= \frac{1}{q_2}\Delta\tilde{T}^{-\alpha} + \frac{q_1^2}{q_3}\Delta\tilde{T}^{-\gamma},\end{aligned} \tag{13}$$

$$\left(\frac{\partial \tilde{T}}{\partial \rho}\right)_u = -\left(\frac{\partial \tilde{T}}{\partial u}\right)_\rho \left(\frac{\partial u}{\partial \rho}\right)_T = q_1 q_2 \Delta\tilde{T}^{\alpha}, \tag{14}$$

$$\left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_u = \left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_\rho + \left(\frac{\partial \tilde{\mu}}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial \tilde{T}}\right)_u = q_1 + \frac{q_3}{q_1 q_2}\Delta\tilde{T}^{\gamma-\alpha}, \tag{15}$$

$$\left(\frac{\partial \tilde{\mu}}{\partial \rho}\right)_u = \left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_u \left(\frac{\partial \tilde{T}}{\partial \rho}\right)_u = q_1^2 q_2 \Delta\tilde{T}^{\alpha} + q_3 \Delta\tilde{T}^{\gamma}, \tag{16}$$

$$\left(\frac{\partial u}{\partial \rho}\right)_\mu = -\left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_u, \tag{17}$$

$$\left(\frac{\partial \tilde{\mu}}{\partial u}\right)_\rho = \left(\frac{\partial \tilde{T}}{\partial \rho}\right)_u. \tag{18}$$

Divergencies with exponent $-\alpha$ are associated with the derivatives of ρ or u with respect to $\tilde{T}$ or $\tilde{\mu}$, keeping constant the other ρ or u variable. Divergencies with exponent $-\gamma$ are associated with the derivatives of ρ or u with respect to $\tilde{T}$ or $\tilde{\mu}$, keeping constant the other $\tilde{T}$ or $\tilde{\mu}$ variable. Finite quantities are derivatives of $\tilde{T}$ with respect to $\tilde{\mu}$, or ρ with respect to u, or the corresponding inverse derivatives.

Some derivatives show correcting exponents like

$$\left(\frac{\partial u}{\partial \tilde{T}}\right)_{\mu} = \frac{q_1^2}{q_3}\Delta\tilde{T}^{-\gamma}\left(1 + \frac{q_3}{q_1^2 q_2}\Delta\tilde{T}^{\gamma-\alpha}\right) \tag{19}$$

or

$$\left(\frac{\partial u}{\partial \rho}\right)_{\mu} = \left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_{u} = q_1\left(1 + \frac{q_3}{q_1^2 q_2}\Delta\tilde{T}^{\gamma-\alpha}\right). \tag{20}$$

These have the correcting exponent $\gamma - \alpha$ and the correcting coefficient $q_3/q_1^2 q_2$ repeated.

This observation is not trivial because it may be related to corrections to scaling [9]. However, the exponent $\gamma - \alpha$ is not *a fortiori* the first correcting exponent. A lower correcting exponent could be included in the q_i quantities to account for deviations from the finite limit. If that is the case, it is interesting to note that this implies that the coefficient for exponents lower than $\gamma - \alpha$ must be the same for the derivatives $\left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_{\rho}$ and $\left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_{u}$ since the difference has only a $\gamma - \alpha$ exponent. Furthermore this is not the only example to be found.

Corrections-to-scaling with lower exponents seem necessary if we consider thermodynamic variables on any branch of the coexistence curve.

By chain rule the derivative of the chemical potential at coexistence becomes

$$\frac{d\tilde{\mu}(\tilde{T})}{d\tilde{T}} = \left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_{\rho} + \left(\frac{\partial \tilde{\mu}}{\partial \rho}\right)_{T}\frac{d\rho(\tilde{T})}{d\tilde{T}}. \tag{21}$$

Substitution of (6–9) gives

$$\frac{d\tilde{\mu}(\tilde{T})}{d\tilde{T}} = q_1 + q_3 q_4 \Delta\tilde{T}^{\gamma+\beta-1}. \tag{22}$$

A second derivative implies

$$\frac{d^2\tilde{\mu}(\tilde{T})}{d\tilde{T}^2} = \frac{dq_1}{d\tilde{T}} + \frac{dq_3q_4}{d\tilde{T}}\Delta\tilde{T}^{\gamma+\beta-1} + q_3q_4(\gamma+\beta-1)\Delta\tilde{T}^{\gamma+\beta-2}. \tag{23}$$

This derivative is assumed finite at the critical point [8,9,10] and $\Delta\tilde{T}^{\gamma+\beta-2}$ becomes divergent. Thus we are forced to introduce a correction-to-scaling coefficient of $\gamma + \beta - 1$ in q_1 to avoid that divergence. On the other hand it is a nice property, according to the

Essam-Fisher conjecture [12], the exponent $\gamma+\beta-1$ is half the exponent $\gamma-\alpha$ previously considered in the partial derivatives:

$$\gamma+\beta-1=1-\alpha-\beta=(\gamma-\alpha)/2. \tag{24}$$

This is assumed to be true in this paper.

Using only asymptotic behavior and the condition that $\tilde{\mu}''$ should be finite at the critical point, leads one to suggest that the correction exponent might be (24). This same suggestion was also made in a different way by Green, Cooper, and Sengers [10], who assumed extended scaling and the existence of the preferred direction introduced by Griffiths and Wheeler [11].

The leading term of the density diameter divergence [8,9] also suggests the same correction exponent $1-\alpha-\beta$ for the expression (9) in the form

$$\begin{aligned} q_4 &= N+F\Delta\tilde{T}^{1-\alpha-\beta}+\cdots, \\ \frac{d\rho(\tilde{T})}{d\tilde{T}} &= N\Delta\tilde{T}^{\beta-1}+F\Delta\tilde{T}^{-\alpha}+\cdots \end{aligned} \tag{25}$$

The derivative of the energy density at coexistence, also obtained from chain rule, is

$$\begin{aligned} \frac{du(\tilde{T})}{d\tilde{T}} &= \left(\frac{\partial u}{\partial\tilde{T}}\right)_\rho+\left(\frac{\partial u}{\partial\rho}\right)_T\frac{d\rho(\tilde{T})}{d\tilde{T}} \\ &= \frac{1}{q_2}\Delta\tilde{T}^{-\alpha}-q_1q_4\Delta\tilde{T}^{\beta-1}. \end{aligned} \tag{26}$$

Once again the correcting exponent $1-\alpha-\beta$ appears and a parallel formal expansion on the R.H.S. of Eqs. (25), (26) is found.

We will see that these exponents appear in connection with any geometric object, a fact that will be stressed at the conclusion.

3. THE GEOMETRY OF THE ONE PHASE REGION

We choose an Euclidian space of orthogonal coordinates ρ, u, and s. The position vector in this space is $\mathbf{r}$:

$$\mathbf{r}=(\rho,u,s) \tag{27}$$

Equilibrium thermodynamic states are represented in this space by a surface representing the relation between the mass, energy, and entropy densities of any pure substance

$$s=s(\rho,u). \tag{28}$$

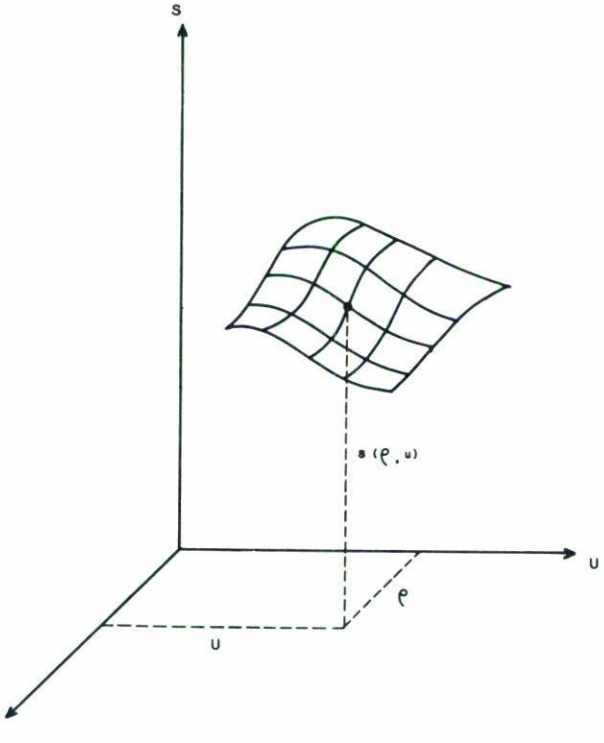

FIGURE 1. Thermodynamic surface representing the functional relation among the densities of entropy, mass, and energy.

This surface will be described using the language and methods of classical differential geometry as found in standard treatises on this subject [3]. (See Fig. 1).

The thermodynamic surface is parametrized with mass density ρ and energy density u as coordinates in the form

$$\mathbf{r} = (\rho, u, s(\rho, u)). \tag{29}$$

Derivatives of the function $s(\rho, u)$ have physical meaning according to the Gibbs relation (2):

$$\tilde{T} = -\left(\frac{\partial s}{\partial u}\right)_{\rho}, \qquad \tilde{\mu} = -\left(\frac{\partial s}{\partial \rho}\right)_{u}. \tag{30}$$

Tangent vectors to the surface along the coordinate curves ρ and u are obtained by (29) differentiating the position vector with respect to the ρ and u variables:

$$\mathbf{e}_{\rho} = \left(\frac{\partial \mathbf{r}}{\partial \rho}\right)_{u} = (1, 0, -\tilde{\mu})$$

and

$$\mathbf{e}_u = \left(\frac{\partial \mathbf{r}}{\partial u}\right)_\rho = (0, 1, -\tilde{T}). \tag{31}$$

The cross product between these vectors is a vector perpendicular to the surface

$$\mathbf{e}_\rho \times \mathbf{e}_u = (\tilde{\mu}, \tilde{T}, 1) \tag{32}$$

and the chemical potential and the temperature give the orientation of the plane tangent to the surface.

Important objects are the metric matrix or first fundamental form introduced with ordinary scalar products

$$\mathbf{A} = \begin{pmatrix} \mathbf{e}_\rho \cdot \mathbf{e}_\rho & \mathbf{e}_\rho \cdot \mathbf{e}_u \\ \mathbf{e}_\rho \cdot \mathbf{e}_u & \mathbf{e}_u \cdot \mathbf{e}_u \end{pmatrix} = \begin{pmatrix} 1 + \tilde{\mu}^2 & \tilde{\mu}\tilde{T} \\ \tilde{\mu}\tilde{T} & 1 + \tilde{T}^2 \end{pmatrix} \tag{33}$$

and the unitary vector $\mathbf{g}$ in the direction orthogonal to the surface (32)

$$\mathbf{g} = \frac{(\tilde{\mu}, \tilde{T}, 1)}{(1 + \tilde{\mu}^2 + \tilde{T}^2)^{1/2}}. \tag{34}$$

Derivatives of the vectors (31) with respect to the coordinates, are projected onto the $\mathbf{g}$ direction to give the symmetric matrix called the second fundamental form of the surface

$$\begin{aligned} \mathbf{B} &= \begin{pmatrix} \mathbf{g} \cdot \frac{\partial \mathbf{e}_\rho}{\partial \rho} & \mathbf{g} \cdot \frac{\partial \mathbf{e}_\rho}{\partial u} \\ \mathbf{g} \cdot \frac{\partial \mathbf{e}_u}{\partial \rho} & \mathbf{g} \cdot \frac{\partial \mathbf{e}_u}{\partial u} \end{pmatrix} \\ &= \frac{1}{(1 + \tilde{\mu}^2 + \tilde{T}^2)^{1/2}} \begin{pmatrix} -\left(\frac{\partial \tilde{\mu}}{\partial \rho}\right)_u & -\left(\frac{\partial \tilde{\mu}}{\partial u}\right)_\rho \\ -\left(\frac{\partial \tilde{T}}{\partial \rho}\right)_u & -\left(\frac{\partial \tilde{T}}{\partial u}\right)_\rho \end{pmatrix}. \end{aligned} \tag{35}$$

This is proportional to the stiffness form introduced by Tisza [4]. The second fundamental form (35) is a symmetric matrix as the result of a well-known Maxwell relation. At the critical point, any component of this matrix goes to zero with an exponent α.

Any tangent direction $\mathbf{n}$ to the surface may be written as a linear combination of the vectors (31):

$$\mathbf{n} = n_\rho \mathbf{e}_\rho + n_u \mathbf{e}_u = (n_\rho, n_u), \tag{36}$$

where (n_ρ, n_u) are the contravariant components of vector $\mathbf{n}$. Normal surface curvature in the $\mathbf{n}$ direction is defined by the quotient

$$\lambda = \frac{\mathbf{n}\mathbf{B}\tilde{\mathbf{n}}}{\mathbf{n}\mathbf{A}\tilde{\mathbf{n}}}, \tag{37}$$

where the tilde denotes the transpose vector

$$\tilde{\mathbf{n}} = \begin{pmatrix} n_\rho \\ n_u \end{pmatrix}. \tag{38}$$

Extremal values of the curvature (37) are the principal curvatures λ_1 and λ_2 and the corresponding directions $\mathbf{n}_1$ and $\mathbf{n}_2$ are the principal directions. These are solutions to the characteristic equation

$$\mathbf{n}_i\mathbf{B} = \lambda_i \mathbf{n}_i \mathbf{A} \qquad (i = 1, 2), \tag{39}$$

and the principal directions $\mathbf{n}_1$ and $\mathbf{n}_2$ are orthogonal with respect to the metric $\mathbf{A}$,

$$\mathbf{n}_1 \mathbf{A} \tilde{\mathbf{n}}_2 = 0. \tag{40}$$

Although Gaussian curvature could be defined only in terms of matrix $\mathbf{A}$, it is here introduced dividing the determinant of matrix $\mathbf{B}$ by the determinant of matrix $\mathbf{A}$. This is also the product of the two principal curvatures λ_1 and λ_2:

$$\lambda_1\lambda_2 = \frac{1}{(1+\tilde{\mu}^2+\tilde{T}^2)^2}\left(\frac{\partial \tilde{T}}{\partial u}\right)_\rho \left(\frac{\partial \tilde{\mu}}{\partial \rho}\right)_T. \tag{41}$$

This quantity is positive almost everywhere in thermodynamics. In the one-phase region, it becomes zero only at the critical point with an exponent $\alpha+\gamma$ determined by the exponents of the partial derivatives in the numerator of this equation. Positiveness of that Gaussian curvature shows that both principal curvatures have the same sign and that the surface is of the elliptic class having both curvatures on the same side of the surface. This property is related to the stability of the system as discussed in any textbook on thermodynamics. Gaussian curvature in the two-phase region is considered in next section. The coexistence curve is the boundary between the one-phase region and the two-phase surface. It belongs to both surfaces and the normal curvature has two different values according to which surface is considered, the one-phase or two-phase, respectively.

The mean curvature H is defined as half the sum of the principal curvatures, and also half the trace of the product between matrix $\mathbf{B}$ and inverse matrix $\mathbf{A}^{-1}$:

$$2H = \lambda_1 + \lambda_2 = -\frac{1}{(1+\tilde{\mu}^2+\tilde{T}^2)^{3/2}}\left(\frac{\partial \tilde{T}}{\partial u}\right)_\rho \times \left\{1+\tilde{\mu}^2 - 2\tilde{\mu}\tilde{T}\left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_\rho + (1+\tilde{T}^2)\left[\left(\frac{\partial \tilde{\mu}}{\partial \tilde{T}}\right)_\rho^2 + \left(\frac{\partial \tilde{\mu}}{\partial \rho}\right)_T \left(\frac{\partial u}{\partial \tilde{T}}\right)_\rho\right]\right\}. \tag{42}$$

This mean curvature has a zero limit at the critical point with an exponent α. The fact that the product of the principal curvatures (41) has an exponent $\alpha+\gamma$ and the sum has an exponent α, shows that one principal curvature has a zero limit with the large exponent

γ and the other with a smaller exponent α. This is a scalar property independent of the direction by which the critical point is reached.

The principal curvatures may be written as series in the correcting exponent $\gamma - \alpha$, the difference between the principal curvature exponents.

To the lowest order in $\Delta\tilde{T}^{\gamma-\alpha}$, the principal curvatures are

$$\lambda_1 = -\frac{1}{R^2(1+\tilde{T}^2+\tilde{\mu}^2)^{1/2}}\left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T \sim \Delta\tilde{T}^{\gamma} \tag{43}$$

and

$$\lambda_2 = -\frac{R^2}{(1+\tilde{T}^2+\tilde{\mu}^2)^{3/2}}\left(\frac{\partial\tilde{T}}{\partial u}\right)_\rho \sim \Delta\tilde{T}^{\alpha}, \tag{44}$$

where

$$R^2 = 1 + \tilde{\mu}^2 - 2\tilde{\mu}\tilde{T}\left(\frac{\partial\tilde{\mu}}{\partial\tilde{T}}\right)_\rho + (1+\tilde{T}^2)\left(\frac{\partial\tilde{\mu}}{\partial\tilde{T}}\right)_\rho^2; \tag{45}$$

and the corresponding principal directions to zero order in $\Delta\tilde{T}^{\gamma-\alpha}$ are

$$\mathbf{n}_1 = (1+\tilde{T}^2+\tilde{\mu}^2)^{1/2}\left(1, -\left(\frac{\partial\tilde{\mu}}{\partial\tilde{T}}\right)_\rho\right)$$

and

$$\mathbf{n}_2 = \left(-\tilde{\mu}\tilde{T} + (1+\tilde{T}^2)\left(\frac{\partial\tilde{\mu}}{\partial\tilde{T}}\right)_\rho, 1 + \tilde{\mu}^2 - \tilde{\mu}\tilde{T}\left(\frac{\partial\tilde{\mu}}{\partial\tilde{T}}\right)_\rho\right). \tag{46}$$

The principal direction vectors have been selected with the same magnitude:

$$\mathbf{n}_1\mathbf{A}\tilde{\mathbf{n}}_1 = \mathbf{n}_2\mathbf{A}\tilde{\mathbf{n}}_2 \tag{47}$$

Corrections to the principal curvatures or the principal directions near the critical point may be calculated to any power of $\Delta\tilde{T}^{\gamma-\alpha}$. An exact solution may also be obtained but this does not seem to offer any useful information.

Normal curvature (37) for any direction $\mathbf{n}$ is expressed as a function of the principal curvatures by the Euler equation [3]:

$$\lambda = \lambda_1\cos^2\phi + \lambda_2\sin^2\phi = \lambda_1 + (\lambda_2 - \lambda_1)\sin^2\phi, \tag{48}$$

where ϕ is the angle between the particular direction $\mathbf{n}$ and the principal direction $\mathbf{n}_1$. Note that curvature λ_1 reaches zero faster than the curvature λ_2 as the critical point is approached. Therefore, as long as ϕ is a finite angle, λ goes to zero with the exponent

α corresponding to the principal curvature λ_2. Only when the directon $\mathbf{n}$ is parallel to the principal direction $\mathbf{n}_1$ and the angle ϕ is zero, does the normal curvature λ have a different exponent γ.

A similar conclusion was reached for a fluid in a temperature, pressure and chemical potential-space, and generalized to any thermodynamic system by Griffiths and Wheeler [11] who predicted the existence of a direction singled out by the nature of the phase transition. According to Griffiths and Wheeler, this direction is the tangent to the coexistence curve. In Sect. 5 of this paper where the coexistence curve is studied, we found that the principal direction $\mathbf{n}_1$ and the tangent to the coexistence curve become parallel at the critical point in accord with this geometric hypothesis.

4. THE GEOMETRY OF THE TWO PHASE REGION

Liquid and vapor phases coexist in stable equilibrium at the same chemical potential $\tilde{\mu}$ and temperature $\tilde{T}$ with different values of density, energy and entropy. A coexistence state of phase equilibrium is represented in ρ, u, s space by two different points on the thermodynamic surface, one corresponding to the liquid with the large density and the other to the vapor with the smaller density:

$$(\rho_{\mathrm{L}}, u_{\mathrm{L}}, s_{\mathrm{L}}) \qquad \text{(liquid)} \tag{49}$$

and

$$(\rho_{\mathrm{G}}, u_{\mathrm{G}}, s_{\mathrm{G}}) \qquad \text{(vapor).} \tag{50}$$

Both points have the same temperature and chemical potential and therefore the tangent planes, as determined by the direction $\mathbf{g}$ at these two points, are parallel or coincident.

In addition, phase equilibrium requires that both phases have the same value of pressure $\tilde{P}$ at coexistence. Then Eq. (5) implies

$$\tilde{P} = \rho_{\mathrm{L}}\tilde{\mu} + u_{\mathrm{L}}\tilde{T} + s_{\mathrm{L}} = \rho_{\mathrm{G}} + u_{\mathrm{G}}\tilde{T} + s_{\mathrm{G}}. \tag{51}$$

According to vector notation this equation shows

$$\Delta\mathbf{r} = (\rho_{\mathrm{L}} - \rho_{\mathrm{G}}, u_{\mathrm{L}} - u_{\mathrm{G}}, s_{\mathrm{L}} - s_{\mathrm{G}}) \tag{52}$$

is orthogonal to the vector perpendicular to the surface

$$\Delta\mathbf{r} \cdot \mathbf{g} = 0. \tag{53}$$

It follows that at coexistence, the plane tangent touches the surface at the two points which represent the coexisting phases and the plane contains the straight line joining the two points.

A point on this line between the two coexistence points represents the two-phase state with a proportion of liquid and vapor determined by the ratio of the lengths of the segments into which the point divides $\Delta\mathbf{r}$.

The six components (49) and (50) and the three quantities $\tilde{T}, \tilde{\mu}, \tilde{P}$ are functions of only one independent variable, according to Gibbs' phase rule. The temperature $\tilde{T}$ is here chosen as the independent variable at coexistence: the vapor pressure $\tilde{P}\ (\tilde{T})$ and the vapor chemical potential $\tilde{\mu}(\tilde{T})$. The two positions (49) and (50) are functions of the temperature and when the temperature changes, each triad represents a branch of a curve called the coexistence curve. Liquid and vapor branches of the coexistence curve meet at the critical point where discontinuity of the coordinate ceases to exist.

As temperature changes, the tangent plane rolls on the two points (49) and (50) on the coexistence curve. The straightlines connecting the two coexisting points form a ruled surface. This surface is the envelope of the one parameter family of planes obtained when rolling on the coexisting curve. Such a surface is a developable or parabolic surface with zero Gaussian curvature [3].

Changing our coordinates does not alter in any way the geometric properties obtained a century ago by Gibbs [1] in the volume, energy, entropy space.

A developable surface is tangent to a twisted curve called the edge of regression. This curve is determined by the parameter family of planes tangent to the surface at coexistence curve and is given as a function of temperature in the form

$$\tilde{P}(\tilde{T}) = \rho\tilde{\mu}(\tilde{T}) + u\tilde{T} + s. \tag{54}$$

An edge of regression in Gibbs' space was obtained by E. Piña and O. Mata [7]. The orthogonal coordinates of this curve in our (ρ, u, s) space are

$$\left(\frac{\tilde{P}''(\tilde{T})}{\tilde{\mu}''(\tilde{T})},\ -\tilde{\mu}'(\tilde{T})\frac{\tilde{P}''(\tilde{T})}{\tilde{\mu}''(\tilde{T})} + \tilde{P}'(\tilde{T}),\ \left[\tilde{T}\tilde{\mu}'(\tilde{T}) - \tilde{\mu}(\tilde{T})\right]\frac{\tilde{P}''(\tilde{T})}{\tilde{\mu}''(\tilde{T})} + \tilde{P}(\tilde{T}) - \tilde{T}\tilde{P}'(\tilde{T})\right), \tag{55}$$

where a prime denotes a derivative with respect to temperature $\tilde{T}$.

When the edge of regression becomes a point or the point at infinity, the developable surface is a cone or a cylinder, respectively. These particular cases are not considered here because a real fluid could not have this simple surface filling the two-phase region. A cone or a cylinder imply physically linear combinations of temperature, chemical potential and sometimes pressure. From this property it can be shown that the experimental evidence does not support these particular cases.

The tangent to the edge of regression touches the thermodynamic surface at the coexisting points. This tangent has the direction

$$(1,\ -\tilde{\mu}'(\tilde{T}),\ \tilde{T}\tilde{\mu}'(\tilde{T}) - \tilde{\mu}(\tilde{T})), \tag{56}$$

which should be parallel to the vector $\Delta\mathbf{r}$ (52). This result is equivalent to the Clausius-Clapeyron equation.

Note that the tangent direction (56) has, with respect to the base (31), the components

$$(1,\ -\tilde{\mu}'(\tilde{T})), \tag{57}$$

which will be used in the next section.

The normal vector to the edge of regression has the direction

$$(-[1+\tilde{T}^2]\tilde{\mu}'(\tilde{T})+\tilde{T}\tilde{\mu}(\tilde{T}),\ -[1+\tilde{\mu}^2(\tilde{T})]+\tilde{T}\tilde{\mu}(\tilde{T})\tilde{\mu}'(\tilde{T}),\ \tilde{T}+\tilde{\mu}(\tilde{T})\tilde{\mu}'(\tilde{T})), \qquad (58)$$

and the binormal vector coincides with the **g** vector, orthogonal to the surface [3].

The curvature κ and torsion τ of the edge or regression have been calculated by the Frenet equations [3]:

$$\kappa = \frac{\tilde{\mu}''(\tilde{T})[1+\tilde{T}^2+\tilde{\mu}(\tilde{T})]^{1/2}}{R^3 \frac{d}{d\tilde{T}}\frac{\tilde{P}''(\tilde{T})}{\tilde{\mu}''(\tilde{T})}} \qquad (59)$$

and

$$\tau = \frac{1}{[1+\tilde{T}^2+\tilde{\mu}^2(\tilde{T})]\frac{d}{d\tilde{T}}\frac{\tilde{P}''(\tilde{T})}{\tilde{\mu}''(\tilde{T})}}, \qquad (60)$$

where R in (59) is the magnitude of the vector (56) with the same behavior as that of quantity (45):

$$R = \left[1+\tilde{\mu}^2-2\tilde{T}\tilde{\mu}\tilde{\mu}'+(\tilde{\mu}')^2(1+\tilde{T}^2)\right]^{1/2}. \qquad (61)$$

According to present knowledge of critical behaviour the second derivative $\tilde{\mu}''(\tilde{T})$ of the chemical potential is assumed to be finite at the critical point. In such a case $\tilde{P}''(\tilde{T})$ should be divergent with an exponent $-\alpha$.

This follows from the Gibbs-Duhem relation (3)

$$\tilde{P}'(\tilde{T}) = \rho_{\mathrm{A}}\tilde{\mu}'(\tilde{T}) + u_{\mathrm{A}} \qquad (\mathrm{A}=\mathrm{L},\mathrm{G}). \qquad (62)$$

Taking the second derivative of this equation one obtains

$$\tilde{P}''(\tilde{T}) - \rho_{\mathrm{A}}\tilde{\mu}''(\tilde{T}) = \rho_{\mathrm{A}}'\tilde{\mu}'(\tilde{T}) + u_{\mathrm{A}}'. \qquad (63)$$

The values of the derivatives $\tilde{\mu}'$ and u' on the right hand side of Eq. (63) were expressed by chain rule in Eqs. (21) and (26).

Substitution in (63) gives

$$\tilde{P}''(\tilde{T}) - \rho_{\mathrm{A}}\tilde{\mu}''(\tilde{T}) = \left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T [\rho_{\mathrm{A}}'(\tilde{T})]^2 + \rho_{\mathrm{A}}'(\tilde{T})\left[\left(\frac{\partial\tilde{\mu}}{\partial\tilde{T}}\right)_\rho + \left(\frac{\partial u}{\partial\rho}\right)_T\right] + \left(\frac{\partial u}{\partial\tilde{T}}\right)_\rho. \qquad (64)$$

The most divergent terms, the middle terms on the right hand side, are exactly zero by a Maxwell relation and (64) becomes

$$\tilde{P}''(\tilde{T}) - \rho_{\mathrm{A}}\tilde{\mu}''(\tilde{T}) = \left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T [\rho_{\mathrm{A}}'(\tilde{T})]^2 + \left(\frac{\partial u}{\partial\tilde{T}}\right)_\rho. \qquad (65)$$

Each term on the right hand side of this equation has the critical exponent $-\alpha$ and this is the exponent of the term $\tilde{P}''(\tilde{T})$ on the left if $\tilde{\mu}''(\tilde{T})$ is finite. In this calculation partial derivatives are evaluated on a particular branch of the coexistence curve, taking the partial derivatives from the one-phase side of the coexistence curve.

Assuming these properties, components of the edge of regression grow without limit in the tangent direction (56) as the critical temperature is approached. This is a weak divergence with an exponent $-\alpha$.

Using the same argument, the curvature and the torsion go to zero as $\Delta\tilde{T}^{1+\alpha}$.

Since the developable, two-phase region is a parabolic surface [3], it follows that one of its principal curvatures is zero. The non-zero principal curvature is determined by the curvature and torsion of its edge of regression. One has [3]

$$\lambda_1 = 0, \qquad \lambda_2 = \tau/\kappa d, \tag{66}$$

where d is the distance from the point on the surface to the edge of regression along the tangent straight line passing at this point. As the position of the edge of regression goes to infinity at the critical temperature, the principal curvature λ_2 becomes zero with an exponent α coming from a divergence in distance d. This result requires that τ/κ be finite, which is possible provided $\tilde{\mu}''(\tilde{T})$ is also finite.

Distance d is calculated along the tangent to the edge of regression up to the point with critical density 1. It becomes

$$d = R\left(-1 + \frac{\tilde{P}''(\tilde{T})}{\tilde{\mu}''(\tilde{T})}\right) \tag{67}$$

as expected.

5. THE GEOMETRY OF THE COEXISTENCE CURVE

The coexistence curve has been mentioned many times in the previous section, further discussion of its geometric properties is offered.

Every branch of the coexistence curve is touched by the tangent to the edge of regression along the vector (56) or (52). Furthermore, we note that the divergent part of the edge of regression is parallel to this tangent direction (see Fig. 2).

Position (49) or (50) of one branch of the coexistence curve is thus expressed by the non divergent part of the edge of regression plus a vector in the tangent direction (56)

$$\begin{aligned} \mathbf{r}_\mathrm{A} = (\rho_\mathrm{A}, u_\mathrm{A}, s_\mathrm{A}) &= \big(0,\ \tilde{P}'(\tilde{T}),\ \tilde{P}(\tilde{T}) - \tilde{T}\tilde{P}'(\tilde{T})\big) \\ &\quad + \rho_\mathrm{A}\big(1,\ -\tilde{\mu}'(\tilde{T}),\ \tilde{T}\tilde{\mu}'(\tilde{T}) - \tilde{\mu}(\tilde{T})\big) \qquad (\mathrm{A} = \mathrm{L}, \mathrm{G}). \end{aligned} \tag{68}$$

The position of a point on the coexistence curve is expressed as functions of vapor pressure, chemical potential and density at coexistence. In a change of branch, density is the only function to be changed.

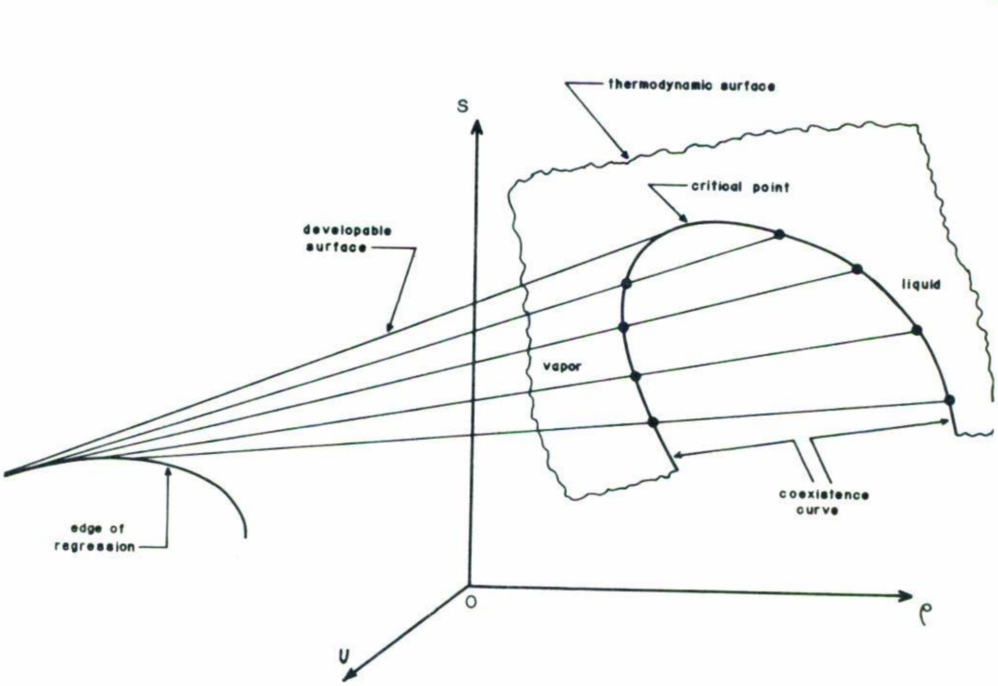

FIGURE 2. Geometric representation of the phase coexistence. The straight lines connect the coexistence liquid and vapor states on the coexistence curve. These lines are tangent to the edge of regression and form a developable surface.

Taking the derivative with respect to temperature $\tilde{T}$ of the position vector (68) one finds

$$\frac{d\mathbf{r}_{\mathrm{A}}}{d\tilde{T}} = \left[\tilde{P}''(\tilde{T}) - \rho_{\mathrm{A}}\tilde{\mu}''(\tilde{T})\right](0,1,-T) \\ + \rho'_{\mathrm{A}}(\tilde{T})\big(1,\ -\tilde{\mu}'(\tilde{T}),\ \tilde{T}\tilde{\mu}'(\tilde{T}) - \tilde{\mu}(\tilde{T})\big). \tag{69}$$

This is a vector tangent to the coexistence curve. According to (63), this vector is expressed with respect to the base (31) in the form

$$\frac{d\mathbf{r}_{\mathrm{A}}}{d\tilde{T}} = \rho'_{\mathrm{A}}\mathbf{e}_{\rho} + u'_{\mathrm{A}}\mathbf{e}_{u} = (\rho'_{\mathrm{A}}, u'_{\mathrm{A}}). \tag{70}$$

Calculating the normal curvature λ_{C} of the tangent direction to the coexistence curve by replacing the vector $\mathbf{n}$, in the definition (37) of normal curvature, by the components (70)

$$\lambda_{\mathrm{C}} = -\frac{1}{R^2(1+\tilde{T}^2+\tilde{\mu}^2)^{1/2}}\left[\left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T + \frac{1}{(\rho'_{\mathrm{A}})^2}\left(\frac{\partial u}{\partial\tilde{T}}\right)_\rho\right]. \tag{71}$$

Dominant terms in this expression go to zero with an exponent γ, showing that the tangent to the coexistence curve must be parallel to the principal direction $\mathbf{n}_1$ as was stated at the end of the Sect. 3.

This conclusion verifies Griffith and Wheeler's suggestion [11] that the preferred direction with a largest divergence is tangent to the coexistence curve.

Furthermore, the Euler equation (48) may be used in a more quantitative form to express the angle $\phi_{\rm C}$ between the tangent to the coexistence curve and the principal direction $\mathbf{n}_1$:

$$\sin^2\phi_{\rm C} = \frac{\lambda_{\rm C} - \lambda_1}{\lambda_2 - \lambda_1}. \tag{72}$$

As this square becomes zero at the critical point, $\phi_{\rm C}$ may be substituted for $\sin\phi_{\rm C}$, and λ_2 can be a negligible curvature as compared to λ_2 in the denominator to obtain the relevant behavior of the angle $\phi_{\rm C}$ at the critical point

$$\phi_{\rm C} = \frac{1}{\rho'_{\rm A} R^2}(1 + \tilde{T}^2 + \tilde{\mu}^2)^{1/2}\left(\frac{\partial u}{\partial \tilde{T}}\right)_{\rho}. \tag{73}$$

This angle disappears with $\Delta\tilde{T}$ according to the correction to scaling exponent $1 - \alpha - \beta$. Both branches of the coexistence curve join smoothly at the critical point. The evidence of this is that $1 - \alpha - \beta$ is positive with a value close to $1/2$ near the critical point. Both branches become parallel to the principal direction $\mathbf{n}_1$ at the junction.

The tangent to the edge of regression which connects the two coexistence points can be also expected to become parallel to the principal direction $\mathbf{n}_1$.

Calculating the normal curvature λ_T, using (37), along the tangent direction (57):

$$\lambda_T = -\frac{\left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T + (\rho'_{\rm A})^2\left(\frac{\partial u}{\partial\tilde{T}}\right)_{\rho}^2\left(\frac{\partial\tilde{T}}{\partial u}\right)_{\mu}^2}{[1 + \tilde{\mu}^2 + \tilde{T}^2]^{1/2}R^2}, \tag{74}$$

γ is the dominant exponent as expected.

The angle ϕ_T between $\Delta\mathbf{r}$ and $\mathbf{n}_1$ is deduced in a manner similar to that used for $\phi_{\rm C}$ and to lower order:

$$\phi_T = \frac{1}{R^2}\rho'_{\rm A}\left(\frac{\partial\tilde{\mu}}{\partial\rho}\right)_T [1 + \tilde{\mu}^2 + \tilde{T}^2]^{1/2}, \tag{75}$$

which has a zero limit with exponent $\gamma + \beta - 1$.

These two directions are coupled by a geometric property. They are conjugated directions [3] in the sense that they are orthogonal directions with respect to the second fundamental matrix $\mathbf{B}$:

$$(1,\, \tilde{\mu}')\,\mathbf{B}\begin{pmatrix}\rho'_{\rm A}\\ u'_{\rm A}\end{pmatrix} = 0. \tag{76}$$

Conjugated directions have the characteristic property [3]

$$\tan\phi_{\rm C}\tan\phi_T = \lambda_1/\lambda_2, \tag{77}$$

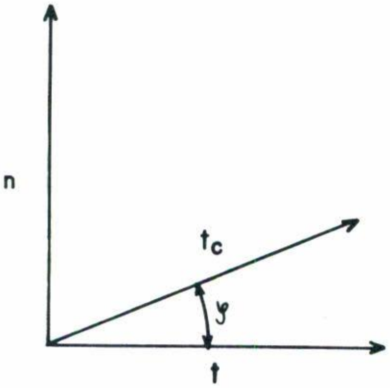

FIGURE 3. The tangent to the coexistence curve $\mathbf{t}_C$ in the plane of the tangent $\mathbf{t}$ and normal $\mathbf{n}$ to the edge of regression form the angle φ between tangents.

which gives a consistency relation between angles and principal curvatures. The trigonometric tangent may be substituted by the angle when it is small.

One more compatibility test was obtained by noting that the vector tangent to the edge of regression and the direction tangent (69) to the coexistence curve form the angle

$$\phi = \phi_C + \phi_T \tag{78}$$

on the plane tangent to the surface.

The vector tangent to the coexistence curve (69) is a divergent vector at the critical point. A parallel finite vector is found by dividing by ρ'_A, which is also divergent.

This tangent vector determines [3] the curvature κ_C of the coexistence curve and to lower order it is

$$\kappa_C = \frac{1}{R^3 \rho'_A}(1 + \tilde{T}^2 + \tilde{\mu}^2)^{1/2} \frac{d}{d\tilde{T}}[(\rho_A \tilde{\mu}'' - \tilde{P}'')/\rho'_A], \tag{79}$$

which is zero at the critical point with the asymptotic exponent $\gamma - 1$.

The unit vector $\mathbf{t}_C$, tangent to the coexistence curve (on any branch), is in the plane formed by unit vectors tangent $\mathbf{t}$ and normal $\mathbf{n}$ associated with the edge of regression in directions (56) and (58), respectively.

From Fig. 3 it is evident that direction $\mathbf{g} = \mathbf{b}$, orthogonal to both $\mathbf{t}$ and $\mathbf{n}$, is also perpendicular to $\mathbf{t}_C$.

The coexistence curve also determines two unit vectors $\mathbf{n}_C$ and $\mathbf{b}_C$, normal and binormal to the curve in corresponding order. The three vectors $\mathbf{t}_C$, $\mathbf{n}_C$ and $\mathbf{b}_C$ form an orthonormal basis associated with the coexistence curve in the same way that vector $\mathbf{n}, \mathbf{t}$, and $\mathbf{b} = \mathbf{g}$ corespond to the edge of regression.

Since vector $\mathbf{b} = \mathbf{g}$ is in the plane orthogonal to $\mathbf{t}_C$, it is in the plane containing vectors $\mathbf{n}$ and $\mathbf{b}_C$. Let θ denote the angle between the directions $\mathbf{g}$ and $\mathbf{b}_C$ (see Fig. 4).

The curvature κ_C of the coexistence curve is a function of the normal curvature λ_C and the angle θ by the Meusnier theorem [3]

$$\lambda_C = \kappa_C \sin\theta \tag{80}$$

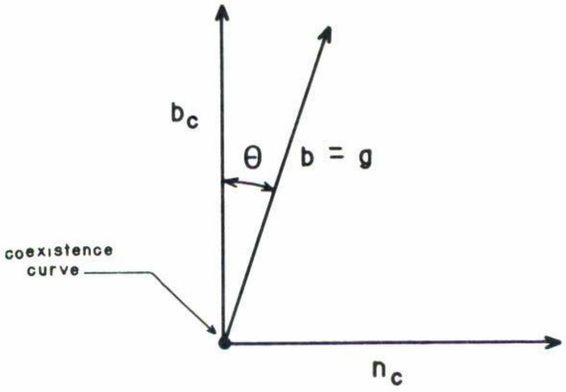

FIGURE 4. The normal $\mathbf{n}_C$ and binormal $\mathbf{b}_C$ to the coexistence curve are in the same plane as the normal to the surface $\mathbf{g}$. This is equal to the binormal to the edge of regression. θ is the angle between binormals.

Note that λ_C is smaller than κ_C near the critical point this theorem can be used to determine how the angle θ goes to zero. Therefore,

$$\frac{R}{\theta} = (1 + \tilde{T}^2 + \tilde{\mu}^2)\frac{d}{d\tilde{T}} \ln \left[\left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T \rho'_A + \frac{1}{\rho'_A} \left(\frac{\partial u}{\partial \tilde{T}} \right)_\rho \right], \tag{81}$$

which shows θ approaches zero as $\Delta\tilde{T}$.

Note this is an integer exponent in a one component system, found for a non classical system.

It is interesting to note that angles ϕ and θ are the Euler angles which rotate the $\mathbf{t}, \mathbf{n}, \mathbf{b}$ frame into the $\mathbf{t}_C, \mathbf{n}_C, \mathbf{b}_C$ frame. The third Euler angle is zero. In this form it is possible to calculate the torsion of the coexistence curve up to the relevant term

$$\tau_C = \frac{1}{\rho'_A(1 + \tilde{T}^2 + \tilde{\mu}^2)} \left\{ 1 + \frac{d}{d\tilde{T}} \left[1 \Big/ \frac{d}{d\tilde{T}} \ln \left(\left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T \rho'_A + \frac{1}{\rho'_A} \left(\frac{\partial u}{\partial \tilde{T}} \right)_\rho \right) \right] \right\}, \tag{82}$$

which has an exponent $1 - \beta$ associated with it. This ends the calculations made of the geometric properties of the coexistence curve.

Some of the accepted geometric properties are based on the finiteness of the second derivative of the chemical potential at coexistence. This second derivative may be written in terms of discontinuities on the liquid and vapor branches of the coexistence curve.

The Clausius-Clapeyron equation follows from parallelism between the directions (52) and (56):

$$\tilde{\mu}' = -\frac{u_L - u_G}{\rho_L - \rho_G}. \tag{83}$$

The second derivative of this function may be written as

$$\tilde{\mu}'' = -[(u'_L - u'_G) + (\rho'_L - \rho'_G)\tilde{\mu}']/(\rho_L - \rho_G). \tag{84}$$

The sum $u' + \rho'\tilde{\mu}'$ on the right hand side of this equation was seen in (63) and is also equal to (65):

$$u'_{\mathrm{A}} + \rho'_{\mathrm{A}}\tilde{\mu}' = \left(\frac{\partial \tilde{\mu}_{\mathrm{A}}}{\partial \rho}\right)_T (\rho'_{\mathrm{A}})^2 + \left(\frac{\partial u_{\mathrm{A}}}{\partial \tilde{T}}\right)_\rho \qquad (\mathrm{A} = \mathrm{G}, \mathrm{L}), \tag{85}$$

where the subindex A denotes the branch on which the partial derivative has been calculated. Substitution of this equation in (84) gives

$$\tilde{\mu}'' = -\frac{1}{\rho_{\mathrm{L}} - \rho_{\mathrm{G}}} \left\{ \left[\left(\frac{\partial \tilde{\mu}_{\mathrm{L}}}{\partial \rho}\right)_T (\rho'_{\mathrm{L}})^2 - \left(\frac{\partial \tilde{\mu}_{\mathrm{G}}}{\partial \rho}\right)_T (\rho'_{\mathrm{G}})^2 \right] - \left[\left(\frac{\partial u_{\mathrm{L}}}{\partial \tilde{T}}\right)_\rho - \left(\frac{\partial u_{\mathrm{G}}}{\partial \tilde{T}}\right)_\rho \right] \right\}, \tag{86}$$

and after rearranging this equation it follows that

$$\begin{aligned}\tilde{\mu}'' = &-\frac{1}{\rho_{\mathrm{L}} - \rho_{\mathrm{G}}} \left\{ \left[\left(\frac{\partial \tilde{\mu}_{\mathrm{L}}}{\partial \rho}\right)_T - \left(\frac{\partial \tilde{\mu}_{\mathrm{G}}}{\partial \rho}\right)_T \right] \frac{1}{2} \left[(\rho'_{\mathrm{L}})^2 + (\rho'_{\mathrm{G}})^2 \right] - \left[\left(\frac{\partial u_{\mathrm{L}}}{\partial \tilde{T}}\right)_\rho - \left(\frac{\partial u_{\mathrm{G}}}{\partial \tilde{T}}\right)_\rho \right] \right\} \\ &- \left[\left(\frac{\partial \tilde{\mu}_{\mathrm{L}}}{\partial \rho}\right)_T + \left(\frac{\partial \tilde{\mu}_{\mathrm{G}}}{\partial \rho}\right)_T \right] \frac{1}{2} (\rho'_{\mathrm{L}} + \rho'_{\mathrm{G}}) \frac{d}{d\tilde{T}} \ln(\rho_{\mathrm{L}} - \rho_{\mathrm{G}}). \end{aligned} \tag{87}$$

The exponent of the density difference is $\Delta\tilde{T}^\beta$ and the derivative of the density diameter has a $\Delta\tilde{T}^{-\alpha}$ limit. Hence, the last term on the right hand side of Eq. (87) has the relevant exponent $\gamma - \alpha - 1$.

Other terms on the right hand side could have a divergence with exponent $-\alpha - \beta$ if different values for the partial derivatives could be obtained on each branch of the coexistence curve at the critical point. Assuming that the behavior of $\tilde{\mu}''$ is finite at the critical point leads to some cancellation which implies that the relevant contribution of the partial derivatives should be the same, independent of which branch is followed to reach the critical point.

If a correction to scaling exponent $1 - \alpha - \beta$ is assumed, the resulting exponent for the first term on the right hand side is $1 - 2\alpha - 2\beta$ which equals the exponent $\gamma - \alpha - 1$ found in last term. A finite second derivative also predicts that this exponent is zero, or that some cancellation of terms should occur.

In the last section the behavior of geometric objects near the critical point is reassessed.

6. DISCUSSION

A geometric study of the vapor liquid phase equilibrium was undertaken with classical differential geometry in the ρ, u, s space similar to Gibbs' space.

The one-phase region is an elliptic surface expressing the stability of the system. The two-phase region is a developable surface, tangent to its edge of regression, determined only by the vapor pressure and the chemical potential at coexistence. Both the one-phase and the two-phase surfaces are in tangent contact at the coexistence curve formed by two branches, the liquid and the vapor, which join smoothly at the critical point. Frenet's equations of the edge of regression and the coexistence curve were considered in detail and curvatures and torsions were calculated up to relevant terms near the critical temperature.

At the critical point all the curvatures and torsions involved become zero. Tangents to the coexistence curve and the edge of regression become parallel to a principal direction on the surface. This direction is associated with the flatest one and also with an exponent γ in agreement with a Griffiths and Wheeler suggestion.

At the beginning, a deviation from Tisza's prescription for the association of an affine geometry with thermodynamics was made. At the end of the calculations the geometric results can be listed to see if they are in agreement with a generalized geometry.

Some relevant results are expressed in terms of affine invariant properties like tangency, parallel direction, flatness, etc. The concept of orthogonality between the g vector and the tangent directions precluded by affine geometry was seen to be important.

Most of the results could be obtained using an affine geometry. However, the classical differential geometry, was a particular class of affine geometry because the results are easier and the language more intuitive.

Using only the chain rule for partial differentials, $\gamma - \alpha$ was found as the correction exponent. The same correction exponent was also found when principal curvature and directions were considered beyond the first relevant term.

Half the value of this exponent was obtained as the correction exponent when the chain rule was applied to calculate u' or $\tilde{\mu}'$. In addition, it was also obtained when $\tilde{\mu}''$ was a finite quantity at the critical temperature. The same correction exponent was consistent with the divergence of the derivative of the density diameter. This exponent was assumed to be the correction to scaling exponent by Green, Cooper and Sengers using Griffiths and Wheeler's suggestion. This exponent is important when geometrically representing the critical behaviour for the angles ϕ_C, ϕ_T and ϕ, which express parallelism among the coexistence curve, the tangent to the edge of the regression and the flatest principal direction.

The principal curvature λ_2 has an exponent α and the curvature λ_1 an associated exponent γ. Both curvatures may be considered with an exponent α and adding corrections with exponent $\gamma - \alpha$.

These arguments strongly suggest that the correction to scaling exponents should be

$$1 - \alpha - \beta = \gamma + \beta - 1 = \frac{\gamma - \alpha}{2} \tag{88}$$

or a multiple of this number.

The corrected exponents α_i, β_i, and γ_i, introduced by Sengers and Sengers [9] in revised and extended scaling, obey the equations

$$\begin{aligned} \alpha_i + \beta_i &= \alpha + \beta, \\ \gamma_i + \beta_i &= \gamma + \beta, \\ \gamma_i - \alpha_i &= \gamma - \alpha, \end{aligned} \tag{89}$$

in agreement with the idea that the correcting exponent (88) could be valid with effective exponents [8].

The exponents of the curvatures found were $\gamma, \alpha, 1+\alpha$ and $\gamma - 1$. The exponent $1-\beta$ associated with torsion on the coexistence curve is the average of these exponents of curvatures

$$1-\beta = \frac{\gamma+\alpha}{2} = \frac{1+\alpha+\gamma-1}{2}. \tag{90}$$

The integer exponent 1 associated to angle θ was a surprise for a non classical behaviour.

By returning to Gibbs' coordinates V, S and U, many results can be recovered. The main change is the replacement of ρ, u and $\tilde{P}$ by V, P and μ, respectively. Geometrically, the most relevant difference is that the edge of regression remains finite at the critical temperature.

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