The Ubiquitous van der Waals Gas

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Under Construction

Abstract: A connection between thermodynamics and dynamical systems is made by recognizing that any three dimensional evolutionary vector field can be made homogeneous by embedding in a projective space of one higher dimension. The Jacobian matrix of such a projectivized vector field always satisfies a Cayley-Hamilton cubic polynomial. By expressing this polynomial in terms of coordinates composed from the similarity invariants of the Jacobian matrix, a correspondence can be made to a universal Gibbs surface of van der Waals gas. It is possible to determine the critical point, the Spinodal line representing the limit of thermodynamic stability, and the ”mixed phase” region for any dynamical system.

Introduction

In 1977, at the Aspen conference on “New Frontiers in Thermodynamics” it was noted by this author that there is a connection between the invariants of the shape matrix of differential geometry, critical behavior (topological transitions) in dynamical systems, and the thermodynamics of a Gibbs equilibrium system. In particular, it was determined that the Spinodal line of a van der Waals gas was given by the condition that the sectional Gauss curvature (the determinant of the shape matrix) of the Gibbs function as a surface constraint in $\{\rho, T, P\}$ space must vanish. The van der Waals Gibbs function is a cubic polynomial which generates the shape of the now classic swallow-tail singularity. (See Figure 1)

The thermodynamic critical point was determined as that point where both the Mean curvature and the Gauss curvature of the Gibbs surface vanished. As the intrinsic Spinodal line in thermodynamics is the limit of single phase stability, the thought, in 1977, was to apply such thermodynamic ideas to the stability analysis of dynamical systems (such as the Brusselator chemical system) in order to gain insight into their behavior. In modern language, the idea recognized that the first law of equilibrium thermodynamics,

$$\omega = dU - TdS + PdV \Rightarrow 0, \qquad 1$$

could be viewed as an integral submanifold of an exterior differential system, with the fundamental group as the projective subgroup of the general linear group. The associated vectors of the 1-form, such that $i(\mathbf{e})\omega = 0$, create a tangent space orthogonal to the adjoint field defined by the covariant components of the 1-form, ω. This vector bundle can be used to define a 3x3 basis frame, whose Cartan matrix of connection coefficients can be used to determine the geometrical properties of the thermodynamic submanifold. The interesting thermodynamic properties turned out to be the zero sets of the similarity invariants of the basis frame.

Turning the idea around, if a dynamical system in 3 dimensions could be used to define a basis frame, then the associated Cartan matrix of connection 1-forms could be used to determine geometrical properties, and the important intrinsic properties would be related to the similarity invariants of the basis frame. As every 3x3 matrix satisfies its Cayley-Hamiltonian polynomial, which in the general case is a cubic polynomial, and as the Jacobian matrix of every 3 dimensional dynamical system is a 3x3 matrix which can be used as a basis frame, then all such systems must have a universal representation as a van der Waals gas.

Indeed, the oscillation frequency of the Brusselator dynamical chemical system was shown by this technique to be related to the square root of the Gauss curvature of the equivalent thermodynamic surface. It is now known that this oscillatory result, in which the square root of the Gauss curvature is an oscillation frequency, is not only a similarity invariant of the dynamical system, but also a projective invariant whereby the dimensionless ratio of the three similarity invariants, MG/K, of a certain three by three Jacobian matrix, is equal to unity. In a 3 dimensional dynamical system, a Hopf bifurcation occurs when a complex conjugate pair of roots has no real part. As M is defined as the sum of the eigenvalues, G as the sum of all pairs of eigenvalues, and K is the product of eigenvalues, the Hopf condition corresponds to the existence of a surface in the three dimensional domain defined by the condition, $MG/K = 1$. Oscillatory limit cycles, if they exist, must reside on the surface defined by the Hopf condition, $MG/K - 1 = 0$, subject to the condition that $G = \omega^2 > 0$. The Hopf bifurcation is not the only set that belongs to the surface constraint, $MG/K - 1 = 0,$ for there is another sheet that belongs to the hyperbolic situation when $G < 0$.

As Tisza points out (Tisza, 1961), it is remarkable that intrinsic subspace curvature properties can have any thermodynamic meaning, as metrical based geometries can not be used to distinguish between the two classes of intensive and extensive thermodynamic variables. However, in the calculus of variations it is known that those extremal principles that are independent of parametric scales lead to projective geometries and Finsler spaces. Indeed, Chern (Chern, 1954) has shown that the key assumption of a Finsler geometry is that the variational integrand be homogeneous of degree 1 in the variables of the tangent space, thereby forming, in his words, a “projectivized” tangent bundle.

> *It follows that the physical science of thermodynamics, based upon functions which are homogeneous of degree* 1*, is where the theory of projectivized Finsler spaces can be of practical application.*

Recall that a standard feature of projective geometry in the plane is that there exist dual relationships between “points and lines” given by a Legendre transformation, and that these Legendre transforms have special properties for functions which are homogeneous degree 1. In Thermodynamics, it is presumed that there exists a primitive phase function of extensive variables, $\Theta(U, S, V, n),$ which by definition is homogeneous of degree 1 in its variables. The condition of homogeneity can be used to define the conjugate variables (of temperature, pressure and chemical potential) :

$$S(\partial\Theta/\partial S) + V(\partial\Theta/\partial V) + U(\partial\Theta/\partial U) + n(\partial\Theta/\partial n) - \Theta(U, S, V, n) = 0 \qquad 1$$

$$S\,T + V(-P) + U(-\beta) + n(\mu) - \Theta = 0. \qquad 2$$

The constraint that $\Theta \Rightarrow 0$ defines an equilibrium hypersurface in the space of variables (U, S, V, n). If Θ is single valued in U (which implies that $\beta = 1$) then solving for the energy function defines a Monge surface in the space of variables, (S, V, n). Tisza call this solution the primitive energy function. In the equilibrium case, $\Theta \Rightarrow 0,$ the homogeneity condition leads to the Gibbs free energy defined as

$$G := n\mu = -TS + PV + U \qquad 3$$

For fixed n, the result defines a Legendre transformation between $G(T,P)$ and $U(S,V)$. It is important to realize that the Gibbs surface mentioned in the first paragraph for the van der Waals gas is constructed from a Legendre transform of the primitive (Internal) energy function, $U,$ subject to the condition that the internal energy function be single valued. However, the Gibbs (Free) energy function G, is not single valued.

It is also of some importance to note that most textbook treatments of thermodynamics agree with the idea that the phase function (U,S,V,n) must be homogenous of degree 1, but the formulas often presented for the ideal or van der Waals gas do not satisfy the Euler criteria of homogeneity. A correct formulation is presented below. It is a fact that any function can be made homogeneous of degree 1 by merely adding a new variable, and dividing, or renormalizing, each of the old variables by the new variable, and then multiplying the new function by the new variable. For example, consider $f(x,y,z)$. Then $F(x,y,z,s) = sf(x/s,y/s,z/s)$ is homogeneous of degree 1 in the variables, $\{x,y,z,s\}$. This same idea can be extended to vectors: for example, let

$\mathbf{v} = [V^x,V^y,V^z] \Rightarrow \mathbf{V} = [V^x,V^y,V^z,\lambda(V^x,V^y,V^z)] \Rightarrow \mathbf{W} = [V^x/\lambda,V^y/\lambda,V^z/\lambda]$

The key feature of the phase function of thermodynamics is that N, or n, “the number of parts, molecules, or phases” plays the role of the renormalization variable, designated as s in the example. It is to be noted that the Euler criteria for homogeneity is given by the expression, $L = \mathbf{p}\partial H/\partial\mathbf{p} - H(\mathbf{p})$. When $L = 0$, the function H is homogeneous of degree 1 in p. The association to Legendre transformations and Hamiltonian mechanics is obvious. The variational problem when the variational integrand, $L(\mathbf{v})$, is homogeneous of degree 1 in $\mathbf{v}$ is known as the Homogeneous Problem: $\mathbf{v}\partial L/\partial\mathbf{v} - L(\mathbf{v}) = H$. (See Rund). But this format is precisely that used in the theory of special relativity, the theory of minimal surfaces, and in Chern’s version of Finsler geometries built on projective connections.

Based on the concept that different thermodynamic phases represent topological properties, and that a phase change is to be recognized as a signature of a topological evolution, the basic ideas of projective differential geometry mentioned above were utilized (1989) to define certain topological properties of hydrodynamic flows. Different domains of initial conditions for a given hydrodynamic flow could be associated with different phase regions of a thermodynamic substance. A specific example was given for a dynamical system in which the three dimensional flow explicitly induced the Gibbs free energy surface typical for the Van der Waals gas. It then was possible to determine that there were domains of initial conditions for which the system could be put into correspondence with the pure liquid, pure gas, or mixed phase regions of a two phase system. An unstable region would be in the domain which is interior to the spinodal line on the surface representing the equation of state. Although intuition implied that this correspondence was a universal result, no satisfactory argument was known at that time to substantiate the idea of universality, except in specific examples.

It this article it will be demonstrated that the observations described above are indeed universal concepts: Any dynamical system that can be described in terms of a non-linear C1 vector field in three variables can be associated with the thermodynamics of a Van der Waals gas. This universal behavior not only justifies the law of corresponding states in chemistry (Guggenheim 1945), but also yields explicit universal formulas (in terms of cross ratios of similarity invariants) to describe the limits of phase stability that are equivalent to the Spinodal Line and the Binodal line of two phase thermodynamic systems. In addition, the ideas lead to a well defined procedure for treating non-equlibrium thermodynamic systems as complex deviations from the real, or equilibrium, systems.

This claim of universality is not to be treated lightly. For example, it should be remarked that historically many authors, including Thom, have recognized that the cusp catastrophe generated by the cubic fold has many qualitative features of a Van der Waals gas. In 1977 Sewell noted a relationship between Legendre transformations and bifurcation theory, and clearly defined the relationship between the Gibbs free energy surface of a van der Waals gas and its relationship to the swallowtail catastrophe. However, the claims that catastrophe concepts have universal significance have been criticised sharply, both on method and style of presentation and specifically on the grounds that not all dynamical systems have a gradient representation. However, the analysis herein gives credence to some of Thom's claims of universality by demonstrating how the cusp singularity can be constructed in terms of any C1 three dimensional vector field, and the similarity invariants of its Jacobian matrix. Annuling individual similarity invariants (invariants with respect to that special subset of projective transformations, equi-affine transformations, that preserve parallelism and perpendicularity) leads to local bifurcations, and constraining dimensionless cross ratios of similarity invariants leads to global bifurcation diagrams. Then using Sewell's result that the bifurcation set of the swallowtail singularity is related to the Legendre dual of the Cusp singularity completes the universal correspondence.

The example of the van der Waals gas

Consider a thermodynamic system described by an action integral where the integrand can be decomposed in a homogeneous and a non-homogeneous part:

$$\int A = \int [L_0\{\ldots, S, V, n; U\} dU + \omega]. \qquad 4$$

For identification purposes, view the the variables $\{S, V, n)$ as "velocities" and U as the parameter of "time" on the thermodynamic "state" space of extensive variables, $\{\ldots, S, V, n; U\}$. Assume that homogeneous part has the Lagrangian format

$$L_0\{S, V, n; U\} = n\Theta(U/n, S/n, V/n), \qquad 5$$

which is homogenous of degree 1. (It will be presumed that at "equilibrium" the non-homogeneous contribution to the variational integrand is negligible, $\omega \Rightarrow 0$). The Euler equation for homogeneity,

$$S\partial L_0/\partial S + V\partial L_0/\partial V + n\partial L_0/\partial n + U\partial L_0/\partial U - L_0 = 0, \qquad 6$$

permits the intensive variables $(T, P, \mu\}$ to be defined by the canonical (1-jet) conjugate expressions:

$$T = \partial L_0/\partial S, \quad -P = \partial L_0/\partial V, \ \mu = -\partial L_0/\partial n, \beta = -\partial L_0/\partial U. \qquad 7$$

The Lagrange function (for a single valued energy $\supset \beta = 1$) becomes expressible as

$$L_0 = TS - PV - \mu n - U, \qquad 8$$

with a differential,

$$dL_0 = (SdT - VdP - nd\mu) + \{TdS - PdV - \mu dn - dU\} = (SdT - VdP - nd\mu) + \omega. \tag{9}$$

The constraint that dL_0 be transversal to the space $\{S, V, n; U\}$ identifies the vanishing 1-form,

$$\omega = \{TdS - PdV - \mu dn - dU\} = 0, \tag{10}$$

as a constraint which is equivalent to the first law of thermodynamics.

From another point of view, the homogeneity condition may be viewed as a Legendre transformation from the extensive to the intensive variables

$$G(T, P, \mu) = (TS - PV - \mu n) - U(S, V, n) \tag{11}$$

These expressions define a Finsler space for *any* system of ”coordinates”.

In the earlier work mentioned above, the Gibbs space used in deriving the shape matrix of the equilibrium “surface” was assumed to be a projective geometry of three dimensions, $(U/n, S/n, V/n\}$, on which the projective constraint was that given by the first law of thermodynamics

$$\omega = dU - Q + W = 0. \tag{12}$$

The presumption of classical thermodynamics is that the first law is locally equivalent to a Darboux representation

$$\omega = dU - TdS + PdV + \mu dn \tag{13}$$

equivalent to the constraints on the seven dimensional space $\{U, T, S, P, V, \mu, n\}$ given by the differential system that consists of constraints equivalent to the zero set of a homogeneous of degree 1 function on the extensive variables, $\{U, S, V, n\}$

$$n\Theta(U/n, S/n, V/n) = 0 \tag{14}$$

$$\omega = dU - TdS + PdV + \mu dn \tag{15}$$

$$with \quad d\omega = 0 \quad and \quad \omega \Rightarrow 0$$

The vanishing of the three form, ω^$d\omega = 0,$ insures that the 1-form, $\omega,$ is integrable in the sense of Frobenious, and is at the foundation if Caratheodory’s theory of equilibrium. The existence of this 1-form defines a non-standard, or Cartan surface, for which the shape matrix is not necessarily symmetric, and therefore can have complex eigenvalues. (See appendix A.) In equilibrium thermodynamics the additional constraint that ω is integrable implies the existence of a unique solution function, $n\Theta(U/n, S/n, V/n)$ which is homogeneous of degree1 in the extensive variables $\{U, S, V, n\}$ The partial derivatives of the solution function with respect to the extensive variables, yield the thermodynamic intensities. Whether the 1-form ω is integrable or not, the vanishing of the 1-form constrains the projective shape matrix to be symmetric, and therefore the eigenvalues in the equilibrium case are all real. A point of departure is realized when the projective constraint is chosen such that the shape matrix admits complex eigenvalues. In all projective geometries, the fundamental invariants are constructed from six primitive cross ratios, two of which are bounded by negative infinity and zero, two of which are bounded by zero and one (the probability domain) and two of which are bounded by one and infinity. It will be demonstrated below how this signature of the three projective equivalence classes appear in the relationships that relate envelopes to bifurcations in projective space.

Others have attempted to use differential geometric methods to analyze thermodynamic systems, but almost always these attempts have tried to construct a suitable metric formalism. For example, Tisza mentions that Blashke attempted to deduce a differential geometry that would apply to the metric free Gibbs space, but with only limited success. In Blashke's geometry, the projective space was confined to the equi-affine group, which forces the the shape matrix to be symmetric. Such equi-affine systems admit only real eigen values for the shape matrix, where the richness of non-equilibrium thermodynamics, and its possible application to the theory of dynamical systems, requires the existence of domains of both real and complex eigenvalues. In this article, a projective geometry without metric is presumed to be the natural basis for non-equilibrium thermodynamics.

When the Gibbs primitive phase surface of the van der Waals gas is mapped to its dual by means of a Legendre transformation, the Spinodal line can be interpreted as an edge of regression in the dual surface of "Gibbs free energy". See Figure 1. It is this clue that focuses attention on the theory of envelopes, for the edge of regression is a singularity in an enveloping surface (Struik). It is apparent in the dual surface of Gibbs free energy that, in addition to the edge of regression, there exists another topological feature of singularity, a line of self intersection (which is not an intrinsic property that can be determined locally). This non-metrical feature of self intersection was interpreted as the Binodal line in the earlier work mentioned. Usually, the Binodal line is defined through a heuristic Maxwell construction on the PVT surface representing the equation of state. As Tisza states in reference to the Maxwell procedure,

...a "van der Waals gas" (refering to the equation of state) does not constitute a fully defined thermodynamic system. A complete definition would include the specific heat as a function of say temperature and volume. ... In the concept of a Van der Waals gas a spurious interpolation (the Maxwell construction) through the instable range (of the equation of state) is substituted for the missing (specific heat) information.

In differential geometry, the line of self intersection is a locus of singularities, and as such would offer a projective geometric definition of the Binodal line, without the hueristic Maxwell assumption. Although visually apparent in the equilibrium surface representing the Gibbs free energy, the differential geometry of the extrinsic Binodal line illuded algebraic formulation.

The van der Waals Gas

In the classical development of thermodynamics, the van der Waals gas is often used as a cornerstone example. However, the phase function, Θ, given in many textbook treatments is not explicitly homogeneous of degree 1 in the extensive variables. A homogenously correct formulation, to within a constant, is given by the relation:

$$\Theta\{...S,V,n;U\} = n[e^{\frac{S}{nCv}}(\frac{V}{n}-b)^{-\frac{R}{Cv}} - \frac{a}{(\frac{V}{n}+cb)} - \frac{U}{n}]. \qquad 16$$

This equation for $\Theta\{S,V,n;U\}$ satisfies the Euler condition for homogeneity of degree 1,

$$U\partial\Theta/\partial U + V\partial\Theta/\partial V + S\partial\Theta/\partial S + n\partial\Theta/\partial n - \Theta = 0. \qquad 17$$

The partial derivatives with respect to the extensive variables may be used to define intensive variables,

$$(P = -\partial\Theta/\partial V,\ T = \partial\Theta/\partial S,\ \mu = -\partial\Theta/\partial n, \beta = -\partial\Theta/\partial U) \qquad 18$$

such that the fundamental equation expressing homogeneity of degree 1 becomes

$$-\beta U - VP + ST - n\mu = \Theta(S, V, n; U..P, T, \mu) \qquad 19$$

When is assumed to be the fundamental equation of constraint, the internal energy becomes a function of the variables $\{S, V, n\}$. Subject to the constraint of the first law,

$$dU - TdS + PdV + \mu dn = 0, \qquad 20$$

the Gibbs free energy can be deduced as a Legendre transformation between the intensive and extensive variables,

$$G(P, T, \mu) = VP - ST - n\mu - U(S, V, n) \qquad 21$$

Note that a correction factor, cb, has been added to the collision term $(a/(V/n + cb)$ in order to account for the finite size (or wavelength cb) of the colliding molecules. The coefficient c will be of the order of unity, and can be adjusted to give a better fit of the van der Waals gas equation to the experimental data of (RT/PV) at the critical point.

. The temperature equation may be inverted to yield an expression for the entropy. The partial of S with respect to T at constant V and n leads to the expected expression involving the specific heat $(\partial U/\partial S)/T = nC_v/T$. When the expression for the temperature in terms of entropy and volume is inserted into the pressure equation, the usual van der Waals equation of state is retrieved. From the phase function

$$T = \frac{\partial}{\partial S}(\Theta) = (e^{\frac{S}{nC_v}}(\frac{V}{n} - b)^{-\frac{R}{C_v}})/C_v \qquad 22$$

$$P = -\frac{\partial}{\partial V}(\Theta) = \frac{nRT}{V - bn} - a\frac{n^2}{(V + cbn)^2} \qquad 23$$

Differentiating P with with respect to V yields

$$\partial P/\partial V = -\frac{nRT}{(-V + bn)^2} + 2a\frac{n^2}{(V + cbn)^3} \qquad 24$$

and

$$\partial^2 P/\partial V^2 = -2\frac{nRT}{(-V + bn)^3} - 6a\frac{n^2}{(V + cbn)^4} \qquad 25$$

The classic argument to determine the cricital point sets these relations to zero. It will be demonstrated below, that these relations are obtained by finding the point on the Gibbs surface where the mean curvature and the Gauss curvature vanish simultaneously. The values of the thermodynamic variables at the critical point are:

$$V_c = bn(2c + 3), \quad T_c = \frac{8a/27}{bR(c + 1)}, \quad P_c = \frac{a/27}{b^2(c + 1)^2} \qquad 26$$

which leads to the universal constant independent from the geometrical parameters $\{a, b\}$:

$$nRT_c/(P_cV_c) = 8\frac{c+1}{2c+3}. \tag{27}$$

For c = 0, the universal constant is 8/3, the usual value given for the van der Waals gas; but when the “wavelength” of the molecules is included, the effective collision cross-section is increased, such that at a value of c = 1, the universal critical point constant becomes 3.2. This value is in much better agreement with typical experimental values.

Projective Invariants

Klein established the idea of defining geometry in terms of its invariants with respect to equivalence classes of transformations. At an elementary level, euclidean geometry can be defined as that class of transformations that preserves the ”rigid” body properties of size and shape; i.e., the invariants of translations and rotations define what is meant by Euclidean geometry . Cayley looked at the problem from the matrix point of view, and considered transformations of the general linear group, subjected to certain constraints. For example, if the Jacobian matrix of transformations on a 4 dimensional space are constrained by a single (holonomic) function on the 16 elements of the Jacobian matrix, then the space defines a projective geometry. The single constraint can be formulated in several ways and still yield a group structure to the Jacobian representation.

The invariance of a linear constraint on the domain will lead to the Affine group of transformations (which preserve parallelism in subspaces but can accomodate shears of translation.). A quadratic constraint on the domain will lead to the conformal group, with many special cases depending upon the signature of the quadratic form. The constraint of absolute involution leads to the symplectic group, and if the involution is elliptic then perpendicularity can be defined. The two constraints of invariant line and invariant involution lead to the domain of similarity transformations. If the further constraint of an invariant cubic form is imposed as a equi-volume consideration, then the three constraints lead to euclidean geometry. Note that these ideas correspond for a 3x3 matrix to the invariance of the three symmetry invariants of the matrix, the trace, the determinant, and the trace of the adjoint matrix.

Many interesting formulas can be obtained by considering the ”projectivized” vector space of homogeneous coordinates. Projectivized vectors are constructed by a map from the original space of dimension N in to a space of dimension N+1, where the new N+1 ”coordinate” is a homogeneous function of the N original coordinates. The original ”coordinates” may be the component functions of the original vector field, itself. Then, construct the map from N+1 dimensions back down to N dimensions, constructing a new vector field whose components have bee ”renormalized” by the homogeneous function.

For example consider the ”projectivized position” vector

$$\mathbf{R} = \begin{bmatrix} U, & V, & W, & S \end{bmatrix}/\lambda \doteq (U^k/\lambda) \tag{28}$$

with the scaling or renormalization factor in the form of a Holder norm

$$\lambda = (aU^p + bV^p + cW^p + eS^p)^{N/p}. \tag{29}$$

The Jacobian matrix

$$J = [\partial(U^m/\lambda)/\partial U^n]$$

of such a position vector with respect to the ”coordinate” variables $\{U, V, W, S\}$ has certain invariant properties for various values of the polynomial exponent p and the homogeneity exponent, N, and for arbitrary an-isotropy constants with arbitrary signatures $\{a, b, c, e\}$, of the renormalization function, λ.

The Jacobian matrix (any p) has

1. zero trace when λ is homogeneous of degree 4 ($N = 4$),
2. has zero determinant when λ is homogeneous of degree 1 ($N = 1$),
3. is in conformal involution for $N = 2$, with the conformal factor equal to λ^2
4. has the trace of the adjoint matrix equal to zero when $N = 4/3$

Dynamical Systems

Examples

The Brusselator

The Lorenz attractor

The Dynamo

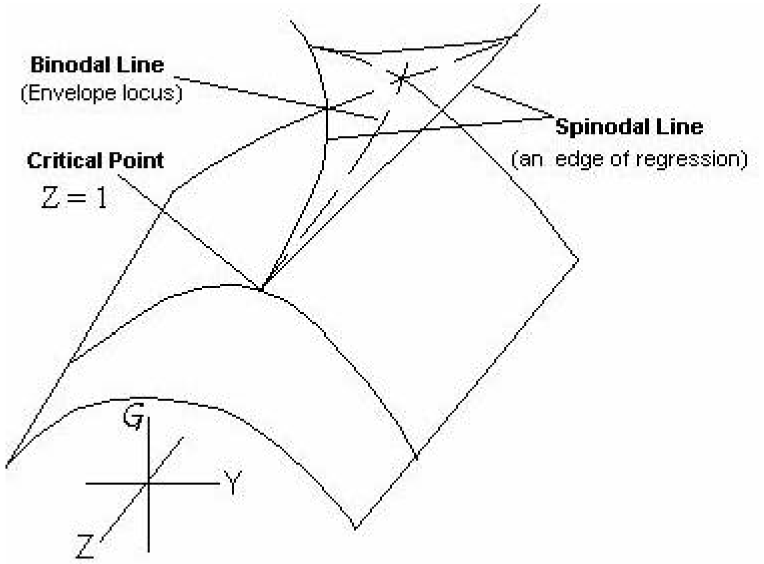

Fig. 1 A Universal Thermodynamic Swallowtail