

Generalized Massieu–Planck functions: Geometric representation, extrema and uniqueness properties

Pablo G. Debenedetti

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

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Massieu–Planck functions are thermodynamic transforms closely related to the more familiar Legendre transforms. They arise naturally in the theory of concentration and entropy fluctuations in multicomponent systems. Generalization of the Massieu–Planck transform concept gives rise to a one-to-one correspondence between each thermodynamic potential and an associated Massieu–Planck function having the same uniqueness and extrema properties. The specific Massieu–Planck functions arising in fluctuation theory are particular cases of the transforms whose algebraic and geometric properties are presented here.

I. INTRODUCTION

The measurement and/or calculation of concentration and entropy fluctuations in solutions are of fundamental theoretical and experimental importance. Band broadening by concentration fluctuations, for example, can be used in Raman scattering experiments to investigate cluster sizes and the solvation dependence of the effective intermolecular force range.¹ Light scattering due to concentration fluctuations is also commonly used in the study of binary diffusion in the vicinity of critical endpoints.² Similarly, the increase in specific heat associated with entropy fluctuations is important in the study of cooperative phenomena and lambda transitions.³ The above list is, of course, indicative and by no means exhaustive.

The expressions for concentration and entropy fluctuations can be expressed in terms of Massieu–Planck transforms, or derived from an entropy-explicit formalism⁴ in which Massieu–Planck transforms play a key role. In this paper, we start by deriving the formal properties of generalized Massieu–Planck transforms. This is done by focusing on the representation of functions by means of tangents. The univocal correspondence between thermodynamic potentials and associated Massieu–Planck transforms follows directly from this analysis. Massieu–Planck transforms are then shown to have the same uniqueness and extrema properties as their corresponding thermodynamic potentials. Finally, after establishing the geometric characteristics of Massieu–Planck transforms in the (U, S, V) and (A, T, V) representations, we consider entropy and concentration fluctuations in multicomponent systems, and show how the resulting expressions are particular cases of the type of functions discussed and generalized here.

II. THE TANGENT REPRESENTATION

A function $y = f(x)$ can be represented in terms of its points or in terms of its tangents.⁵ This is shown in Fig. 1. We define $y^{(1)}$, a Legendre transform of y ⁶:

$$y^{(1)} = y - \xi X, \quad (1)$$

$$\xi = \frac{dy}{dX}, \quad (2)$$

and write

$$dy^{(1)} = dy - \xi dX - X d\xi = \xi dX - \xi dX - X d\xi = -X d\xi, \quad (3)$$

or, in other words,

$$y = y(X), \quad (4)$$

$$y^{(1)} = y^{(1)}(\xi). \quad (5)$$

Thorough discussions of Legendre transforms can be found, for example, in Ref. 7; here, we simply summarize the most important properties.

Equation (4) is a representation of the function in terms of its points [Fig. 1(a)], and Eq. (5) is a representation of the same function in terms of its tangents [Fig. 1(b)]: to each value of the slope (ξ), there corresponds an intercept [$y^{(1)}$]. It does not necessarily follow from the fact that y is single valued in terms of X (i.e., we use the word function rigorously) that $y^{(1)}$ should also be single valued in terms of ξ . For $y^{(1)}$ to be single valued, we must also have⁵

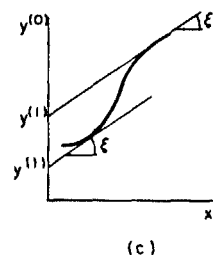
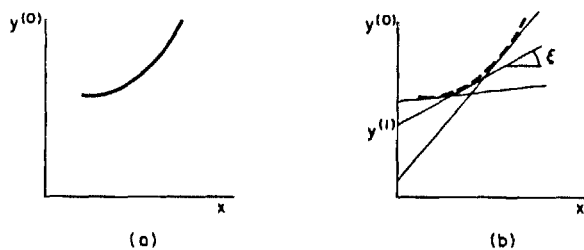


FIG. 1. Representation of a function by means of its points (a) and tangents (b); a multiply defined first transform (c).

$$\frac{d^2y}{dX^2} \neq 0, \tag{6}$$

as can be seen from Fig. 1(c).

We say that a Legendre transformation is information preserving⁷ because both representations [i.e., Eqs. (4) and (5)] are entirely equivalent, and each can be obtained from the other. To obtain Eq. (4) from Eq. (5), we simply write an inverse Legendre transformation:

$$y = y^{(1)} - (-X)\xi = y^{(1)} + X\xi, \tag{7}$$

$$-X = \frac{dy^{(1)}}{d\xi}. \tag{8}$$

A representation of the form

$$y' = \frac{dy}{dx} = g(X), \tag{9}$$

on the other hand, is not information preserving, in that it is only possible to obtain $y = f(X)$ up to an arbitrary constant from knowledge of $y' = g(X)$. Although Eq. (4) is only one of an infinite set of solutions of the form $y = y(X) + c$ which can be obtained from Eq. (9), we call the latter noninformation preserving because, in thermodynamic applications, we are interested in transformations as a result of which a thermodynamic surface in a particular space (U, S, V , for example) can be mapped into an equivalent surface, defined over a different space (H, S, P , for example) without, among other things, introducing additional arbitrary additive constants. An information preserving transformation, therefore, maps a curve (surface) into a single curve (surface), and not into a family of curves (surfaces). Such a transformation, in addition, must have a well defined inverse.

Legendre transforms can, of course, be generalized to functions of more than one variable.^{6,7} We now summarize the basic concepts of multivariable transforms. For a function $y^{(0)}$ of m variables X_i ($i = 1, \dots, m$),

$$y^{(0)} = y^{(0)}(X_1, \dots, X_m), \tag{10}$$

$$dy^{(0)} = \sum_{i=1}^m \xi_i dX_i, \tag{11}$$

$$\xi_i = \left(\frac{\partial y^{(0)}}{\partial X_i} \right)_{X_{[i]}}, \tag{12}$$

where $X_{[i]}$ denotes constancy of all X 's except X_i , we define its k th Legendre transform as

$$y^{(k)} = y^{(0)} - \sum_{i=1}^k \xi_i X_i, \tag{13}$$

and refer to each ξ_i, X_i pair as conjugate variables.

If we write Eq. (13) in differential form, and substitute Eq. (11), we readily obtain

$$dy^{(k)} = - \sum_{i=1}^k X_i d\xi_i + \sum_{i=k+1}^m \xi_i dX_i, \tag{14}$$

or in other words,

$$y^{(k)} = y^{(k)}(\xi_1, \xi_2, \dots, \xi_k, X_{k+1}, \dots, X_m). \tag{15}$$

The familiar thermodynamic potentials (Helmholtz energy, Gibbs energy, enthalpy, grand potential) can all be obtained from each other through variable reordering and Legendre transformations [this will be illustrated explicitly below

(Table I), when we address the uniqueness-preservation properties of Massieu–Planck transforms].

It follows from the Second Law that the entropy (energy) of a system must be a single-valued function of its energy (entropy) for a given composition, mass, and volume. This means that the relationships

$$U = U(S, V, N_1, \dots, N_n), \tag{16}$$

$$S = S(U, V, N_1, \dots, N_n) \tag{17}$$

are functions in the rigorous sense (boldface denotes extensive properties). We refer to a singly defined function of its arguments as being uniquely (as opposed to multiply) defined, or as possessing uniqueness properties. The potentials obtained from the energy by Legendre transformations (and reordering) are also functions of their arguments in the rigorous sense (see Sec. V). Legendre transforms, in other words, preserve the uniqueness properties which characterize the fundamental equation in its energy representation.

III. SINGLE-VARIABLE MASSIEU–PLANCK TRANSFORMS

As shown in Fig. 2, in describing $y = f(X)$ in terms of its tangents, the pair $[\xi, \phi^{(1)}]$ can be used instead of $[\xi, y^{(1)}]$. Thus to each of Eqs. (1), (3), (5), (7), and (8), there correspond, in the same order, the following relationships:

$$\phi^{(1)} = - \left(\frac{y^{(0)} - \xi X}{\xi} \right) = X - \frac{y^{(0)}}{\xi} = - \frac{y^{(1)}}{\xi}, \tag{18}$$

$$\begin{aligned} d\phi^{(1)} &= dX - \frac{1}{\xi} dy^{(0)} + \frac{y^{(0)}}{\xi^2} d\xi \\ &= \left(\frac{y^{(0)}}{\xi^2} \right) d\xi = -y^{(0)} d(1/\xi), \end{aligned} \tag{19}$$

$$\phi^{(1)} = f(\xi) = g(1/\xi), \tag{20}$$

$$y^{(0)} = \xi X - \xi \phi^{(1)}, \tag{21}$$

$$\frac{y^{(0)}}{\xi^2} = \frac{d\phi^{(1)}}{d\xi}; \quad -y^{(0)} = \frac{d\phi^{(1)}}{d(1/\xi)}, \tag{22}$$

which define a ϕ -type transform for a single-variable function, its total differential, its argument, its inverse transform, and the conjugate of its argument, respectively.

It follows from Fig. 2 that a ϕ -type transform is simply a Legendre transform of the function $X = X(y)$. The generalization of this approach to multivariable functions leads to a

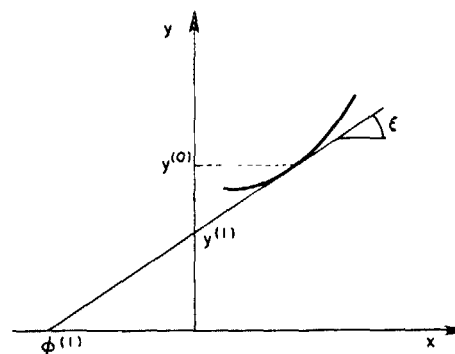


FIG. 2. Legendre (y) and Massieu–Planck (ϕ) transforms of a function of a single variable $y = y(X)$.

formalism in which the independent variables of a ϕ -type transform are quantities such as $1/T$, P/T , etc. This method is mentioned in Gallen's monograph⁴ and outlined in a more recent book by Sychev.⁸ In order to develop the geometric and algebraic properties of ϕ -type transforms, as well as their one-to-one correspondence with Legendre transforms, we find it convenient, in addition, to generalize the relationship between $\phi^{(1)}$ and $y^{(1)}$ [Eq. (18)] to the multivariable case, by expressing each $\{\phi^{(k)}, y^{(k)}\}$ pair as a function of the same arguments. It is obvious that $\phi^{(1)}$ [Eq. (22)] can be regarded both as a function of ξ or as a function of ξ^{-1} : the former approach will be emphasized in the following section.

It is interesting to note that ϕ -type functions were introduced in thermodynamics before Legendre transforms: in his seminal paper "On the Equilibrium of Heterogeneous Substances," Gibbs⁹ refers to the functions $-A/T$ and $-G/T$, used by Massieu¹⁰: as we shall see, these are particular cases of ϕ -type transforms. The function $-G/T$ was also used by Planck.⁸ It is therefore customary to refer to ϕ -type transforms and their higher order generalizations as Massieu-Planck transforms.⁸

IV. GENERALIZED DEFINITION; GEOMETRIC REPRESENTATION; EXTREMUM PROPERTIES

Given $y^{(0)} = y^{(0)}(X_1, X_2, \dots, X_m)$, we define a k th Massieu-Planck transform ($k < m$):

$$\phi^{(k)} = -\frac{y^{(0)} - \sum_{i=1}^k \xi_i X_i}{\xi_1} = -\frac{y^{(k)}}{\xi_1}, \quad (23)$$

where ξ_i is defined in Eq. (12). As is the case with Legendre transforms, to each ordering of the set there corresponds a different set of transforms. The differential of the k th Massieu-Planck transform is given by

$$d\phi^{(k)} = \left(\frac{y^{(0)} - \sum_{i=2}^k \xi_i X_i}{\xi_1^2} \right) d\xi_1 + \sum_{i=2}^k \left(\frac{X_i}{\xi_1} \right) d\xi_i - \sum_{i=k+1}^m \left(\frac{\xi_i}{\xi_1} \right) dX_i, \quad (24)$$

or, explicitly,

$$d\phi^{(k)} = \begin{cases} \left(\frac{y^{(0)}}{\xi_1^2} \right) d\xi_1 - \sum_{i=2}^m \left(\frac{\xi_i}{\xi_1} \right) dX_i & (k=1), \\ \left(\frac{y^{(0)} - \xi_2 X_2}{\xi_1^2} \right) d\xi_1 + \left(\frac{X_2}{\xi_1} \right) d\xi_2 - \sum_{i=3}^m \left(\frac{\xi_i}{\xi_1} \right) dX_i & (k=2), \\ \left(\frac{y^{(0)} - \sum_{i=2}^k \xi_i X_i}{\xi_1^2} \right) d\xi_1 + \sum_{i=2}^k \left(\frac{X_i}{\xi_1} \right) d\xi_i - \sum_{i=k+1}^m \left(\frac{\xi_i}{\xi_1} \right) dX_i & (2 < k < m), \\ \left(\frac{y^{(0)} - \sum_{i=2}^m \xi_i X_i}{\xi_1^2} \right) d\xi_1 + \sum_{i=2}^m \left(\frac{X_i}{\xi_1} \right) d\xi_i & (k=m). \end{cases} \quad (25)$$

$$(k=1), \quad (25)$$

$$(k=2), \quad (26)$$

$$(2 < k < m), \quad (27)$$

$$(k=m). \quad (28)$$

If, on the other hand, we consider X_1 as a function of $\{y^{(0)}, X_2, \dots, X_m\}$ and apply k Legendre transformations, we readily obtain

$$d\phi^{(k)} = -y^{(0)} d(1/\xi_1) + \sum_{i=2}^k X_i d(\xi_i/\xi_1) - \sum_{i=k+1}^m (\xi_i/\xi_1) dX_i. \quad (29)$$

Thus, as explained above, $\phi^{(k)}$ can be regarded either as a function of $\{\xi_1 \rightarrow \xi_k, X_{k+1} \rightarrow X_m\}$ or of $\{\xi_1^{-1}, \xi_2/\xi_1 \rightarrow \xi_k/\xi_1, X_{k+1} \rightarrow X_m\}$.

Before proceeding further with the formalism, we consider some simple examples. For the ordering

$$U = y^{(0)} = y^{(0)}(S, V, N), \quad (30)$$

we have

$$\phi^{(1)} = -A/T, \quad (31)$$

$$d\phi^{(1)} = -Ud(1/T) + (P/T)dV - (\mu/T)dN = (U/T^2)dT + (P/T)dV - (\mu/T)dN, \quad (32)$$

$$\phi^{(2)} = -G/T, \quad (33)$$

$$d\phi^{(2)} = -Ud(1/T) - Vd(P/T) - (\mu/T)dN = (H/T^2)dT - (V/T)dP - (\mu/T)dN, \quad (34)$$

$$\phi^{(3)} = 0, \quad (35)$$

$$d\phi^{(3)} = 0 = -Ud(1/T) - Vd(P/T) + Nd(\mu/T) = (S/T)dT - (V/T)dP + (N/T)d\mu. \quad (36)$$

If we choose the Helmholtz energy as a basis function, we have, for the ordering $\{V, T, N\}$,

$$y^{(0)} = A = A(V, T, N), \quad (37)$$

$$\phi^{(1)} = -\frac{A + PV}{(-P)} = \frac{G}{P}, \quad (38)$$

$$d\phi^{(1)} = -(A/P^2)dP - (S/P)dT + (\mu/P)dN = Ad(1/P) - (S/P)dT + (\mu/P)dN, \quad (39)$$

$$\phi^{(2)} = -\frac{A + PV + TS}{(-P)} = \frac{H}{P} \quad (40)$$

$$d\phi^{(2)} = -(U/P^2)dP + (T/P)dS + (\mu/P)dN = Ad(1/P) + Td(S/P) + (\mu/P)dN, \quad (41)$$

$$\phi^{(3)} = -\frac{A + PV + TS - \mu N}{(-P)} = \frac{TS}{P}, \quad (42)$$

$$d\phi^{(3)} = -\frac{(TS - PV)}{P^2} dP + \left(\frac{T}{P} \right) dS - \left(\frac{N}{P} \right) d\mu = (A)d(1/P) + Td(S/P) - Nd(\mu/P), \quad (43)$$

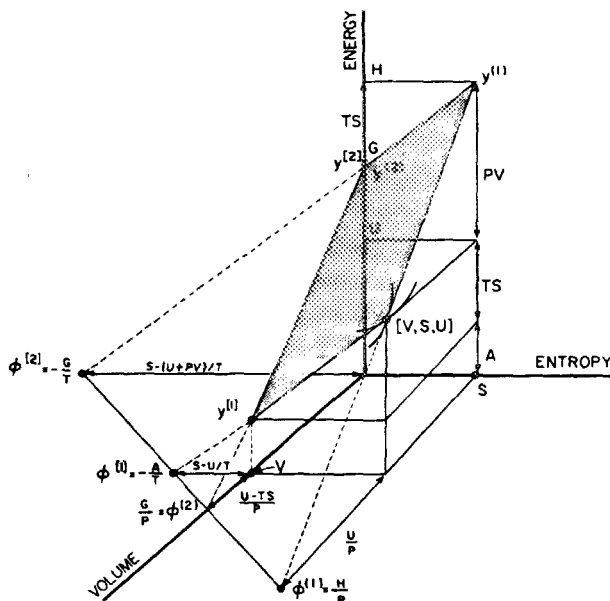


FIG. 3. First- and second-order Legendre and Massieu–Planck transforms in (U, S, V) space.

where all of the above relationships were obtained by straightforward application of Eqs. (23)–(29).

The fundamental equation, in its energy representation, for a closed, single-component system, reads

$$dU = TdS - PdV, \tag{44}$$

or formally,

$$U = U(S, V), \tag{45}$$

where U , S , and V are now intensive variables. The thermodynamics of such a system can be represented in terms of three-dimensional surfaces.¹¹ The geometric representation of all possible Legendre and Massieu–Planck transforms for a unit mass of a closed, single-component system in (U, S, V) and (A, T, V) coordinates is shown in Figs. 3 and 4, where superscript $()$ denotes the orderings (V, S) (Fig. 3) and (T, V) (Fig. 4), and superscript $[]$, the orderings (S, V)

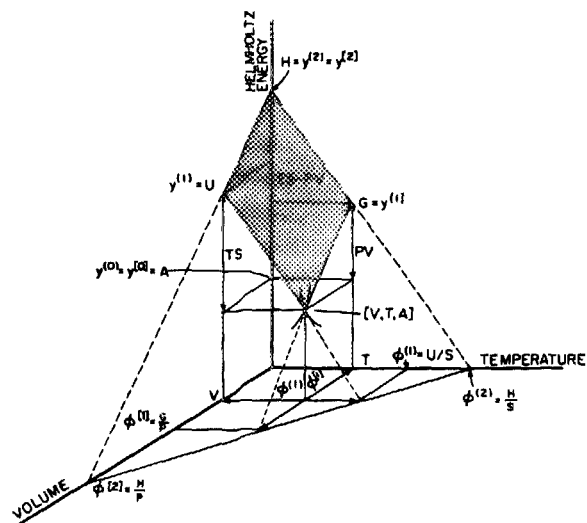


FIG. 4. First- and second-order Legendre and Massieu–Planck transforms in (A, T, V) space.

(Fig. 3) and (V, T) (Fig. 4). The shaded quadrilateral is a plane, tangent to the equilibrium surface at point $[V, S, U]$ (Fig. 3) [or (V, T, A) (Fig. 4)].

The two second-order Massieu–Planck transforms are the intersections of the tangent plane with the coordinate axes on the zero energy (or zero Helmholtz energy) plane. The two first-order Massieu–Planck transforms are obtained by projecting the intersections of constant volume or entropy (temperature, in A, T, V space) planes with the line determined by the two second-order transforms on the entropy (temperature, in A, T, V space) and volume axes, respectively.

At a given temperature and pressure, two (or three) phases of a pure substance can coexist. Under such circumstances the plane shown in Fig. 3 becomes a common tangent plane to the USV surface at the points representing the phases in equilibrium, which must have the same chemical potential. The intersection of this plane with the zero energy plane is therefore the same for all coexisting phases, and so, necessarily, must their second-order Massieu–Planck transforms. The two first-order transforms, on the other hand, are different for each phase but must project on the same line (determined by the two second-order transforms): this follows from the fact that the coexisting phases have different volumes and entropies.

Starting with the fundamental equation in its energy representation, then, we can generate thermodynamic functions which preserve both its information content and its uniqueness properties (i.e., they are functions, in the strict sense, of their arguments): this is done through Legendre transforms (and variable reordering). To each Legendre transform there corresponds a Massieu–Planck transform, which can be expressed as a function of the same arguments and which (as will be shown below), also preserves the uniqueness properties of the basis function: this correspondence is written explicitly in Eq. (23).

To each nonconjugate set of arguments there corresponds a Legendre transform of the energy which is maximized (or minimized) at equilibrium. It follows at once from Eq. (23),

$$\begin{aligned} \phi^{(k)} &= \phi^{(k)}(\xi_1, \dots, \xi_k, X_{k+1}, \dots, X_m) \\ &= - \frac{y^{(k)}(\xi_1, \dots, \xi_k, X_{k+1}, \dots, X_m)}{\xi_1}, \end{aligned}$$

that the corresponding Massieu–Planck transform is also an extremum for all virtual variations at constant $(\xi_1, \dots, \xi_k, X_{k+1}, \dots, X_m)$. This must necessarily be so since $y^{(k)}$ is an extremum and ξ_1 is constant. As an example, the Helmholtz energy [i.e., $y^{(1)}(T, V, N)$] is a minimum with respect to all possible virtual variations at constant volume and temperature about an equilibrium state of a closed system (we consider for simplicity, a pure substance), and it follows at once that $\phi^{(1)} (= -A/T)$ must necessarily be a maximum for virtual variations about the same equilibrium state. This can be summarized by writing

$$\begin{aligned} \Delta\phi^{(k)} \Big|_{\xi_1, \dots, \xi_k, X_{k+1}, \dots, X_m} &= -\xi_1^{-1} \Delta y^{(1)} \Big|_{\xi_1, \dots, \xi_k, X_{k+1}, \dots, X_m} \\ &= -\xi_1^{-1} [\delta y^{(1)} + \frac{1}{2} \delta^2 y^{(1)} + \dots]. \end{aligned} \tag{46}$$

The first-order variation vanishes identically for an equilib-

TABLE I. Legendre and Massieu-Planck transforms of a single-component system.

$y^{(0)}$	$y^{(1)}$	$\phi^{(1)}$	$y^{(2)}$	$\phi^{(2)}$	$y^{(3)}$	$\phi^{(3)}$
$U(S,V,N)$	$A(T,V,N)$	$-\frac{A}{T}(T,V,N)$	$G(T,-P,N)$	$-\frac{G}{T}(T,-P,N)$	0	0
$U(V,S,N)$	$H(-P,S,N)$	$\frac{H}{P}(-P,S,N)$	$G(-P,T,N)$	$\frac{G}{P}(-P,T,N)$	0	0
$A(T,V,N)$	$U(-S,V,N)$	$\frac{U}{S}(-S,V,N)$	$H(-S,-P,N)$	$\frac{H}{S}(-S,-P,N)$	$TS(-S,-P,\mu)$	$T(-S,-P,\mu)$
$A(V,T,N)$	$G(-P,T,N)$	$\frac{G}{P}(-P,T,N)$	$H(-P,-S,N)$	$\frac{H}{P}(-P,-S,N)$	$TS(-P,-S,\mu)$	$\frac{TS}{P}(-P,-S,\mu)$
$H(S,P,N)$	$G(T,P,N)$	$-\frac{G}{T}(T,P,N)$	$A(T,V,N)$	$-\frac{A}{T}(T,V,N)$	$-PV(T,V,\mu)$	$\frac{PV}{T}(T,V,\mu)$
$H(P,S,N)$	$U(V,S,N)$	$-\frac{U}{V}(V,S,N)$	$A(V,T,N)$	$-\frac{A}{V}(V,T,N)$	$-PV(V,T,\mu)$	$P(V,T,\mu)$
$G(T,P,N)$	$H(-S,P,N)$	$\frac{H}{S}(-S,P,N)$	$U(-S,V,N)$	$\frac{U}{S}(-S,V,N)$	$[TS-PV](-S,V,\mu)$	$\left[\frac{TS-PV}{S}\right](-S,V,\mu)$
$G(P,T,N)$	$A(V,T,N)$	$-\frac{A}{V}(V,T,N)$	$U(V,-S,N)$	$-\frac{U}{V}(V,-S,N)$	$[TS-PV](V,-S,\mu)$	$-\left[\frac{TS-PV}{V}\right](V,-S,\mu)$

rium state (equilibrium criteria), and the sign of the second-order variations (stability criteria) of a Massieu-Planck transform and its corresponding Legendre transform are opposite (equal), if ξ_1 is positive (negative).

V. UNIQUENESS PRESERVATION

The uniqueness properties of Massieu-Planck transforms follow from those of the corresponding Legendre transforms [here, the word "corresponding" denotes the one-to-one relationship defined by Eq. (23)]. In what follows, we consider single-component systems for simplicity: we will start by deriving the uniqueness properties of thermodynamic potentials from those of U ; subsequently, we consider the uniqueness of Massieu-Planck transforms.

The familiar thermodynamic potentials A , H , and G can be obtained from U by variable reordering and Legendre transformations (Table I). In order to prove that these and the other potentials shown in Table I are, indeed, singly defined functions of their arguments, it is necessary to invoke, as a postulate, the following empirical observation: the equilibrium states of a closed system of given mass and composition with no internal barriers to the attainment of mechanical or thermal equilibrium or to the flow of mass, and in the absence of gravitational or other potential fields are uniquely defined by specifying the values of two independently variable nonconjugate properties.

The axiomatics associated with the formulation of the Second Law being beyond the scope of this paper, we simply state that the above mentioned postulate (though without the important specification that the two properties be nonconjugate) is one of four from which the Second Law has been "derived" in a consistent postulatory approach.⁷ If U is everywhere singly defined, and, in addition, $\delta^2 U > 0$ everywhere, the uniqueness properties of A , H , G , and the other potentials to be discussed below follow trivially from those of U [this is the straightforward generalization of Eq. (6)]. We therefore address specifically (see below) the significance of the convexity condition in the light of the above mentioned postulate.

For closed, single-component systems, N is a trivial variable. Ordering the (nontrivial) variables which define U as (S,V) or (V,S) gives rise, upon application of a single

Legendre transformation, to A and H (Table I): G can be obtained as a first-order transform of either one of these potentials, after reordering. Therefore, we will first prove that A and H are functions of their arguments, and then extend the proof to G , considered as a first-order transform of A or H . In this way, we need only consider the uniqueness-preservation properties associated with first-order transformations, taken one at a time.

Consider the basis function $U = y^{(0)}(X_1, X_2)$ ($X_3 = N$ is a trivial variable, as explained above), which is not multiply defined in terms of X_1 and X_2 . Then, its first Legendre transform is

$$y^{(1)} = y^{(0)} - \xi_1 X_1 = y^{(1)}(\xi_1, X_2), \quad (47)$$

and let us assume that there exist values of ξ_1 and X_2 (i.e., ξ_1^* , X_2^*) for which $y^{(1)}$ is not singly defined. This implies

$$y^{(1)}(\xi_1^*, X_2^*) = a = y^{(0)}(X_1, X_2^*) - \xi_1^* X_1, \quad (48)$$

$$y^{(1)}(\xi_1^*, X_2^*) = b = y^{(0)}(X_1', X_2^*) - \xi_1^* X_1'. \quad (49)$$

In other words, for $a \neq b$, we must have $X_1 \neq X_1'$ (recall that $y^{(0)}$ is singly defined, by hypothesis). We conclude that the only possible way for $y^{(1)}$ to be multiply defined is to have different values of X_1 at constant X_2 and ξ_1 . This can happen in five different ways and is illustrated in Fig. 5.

Cases (a) and (b) violate the hypothesis of uniqueness for $y^{(0)}$ in terms of its arguments (i.e., the Second Law). Cases (c) and (d) violate the postulate whereby any two nonconjugate properties uniquely specify an equilibrium state: in case (c), the system under question can exist in two different forms having the same temperature and density but different entropy ($X_1 = S$), or the same entropy and pressure but different density ($X_1 = V$). In case (d), in addition, the system can have two different temperatures ($X_1 = S$) or pressures ($X_1 = V$) for a given entropy, volume, and energy [point (a)]. Case (e) is also a violation of the above mentioned postulate: we can, however, show that this alternative is impossible without invoking this postulate, by noting that Fig. 5(e) implies, at point (b),

$$\left(\frac{\partial^2 U}{\partial X_1^2}\right)_{X_2, N} = 0 = \left(\frac{\partial \xi_1}{\partial X_1}\right)_{X_2, N}. \quad (50)$$

The necessary and sufficient condition for the stability

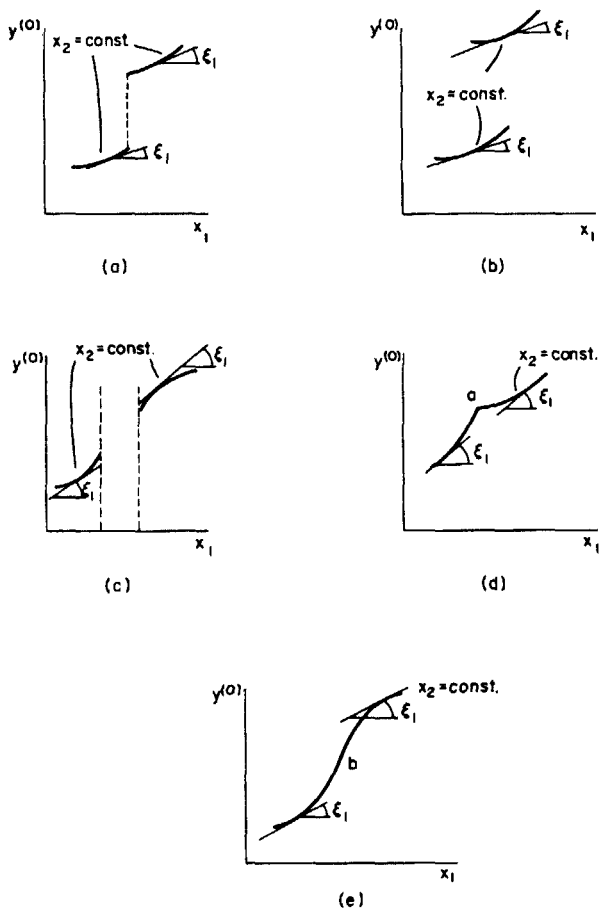


FIG. 5. Possible violations of the uniqueness of a first-order Legendre transform: violation of the uniqueness of the basis function [(a),(b)]; nonconjugate properties do not uniquely specify equilibrium states [(c),(d)]; violation of a stability condition (e).

of an equilibrium state of an n -component system, however, can be written as¹²

$$U_{11} > 0, \tag{51}$$

$$\begin{vmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{vmatrix} > 0, \tag{52}$$

$$\begin{vmatrix} U_{11} & \dots & U_{1,n+1} \\ \vdots & & \vdots \\ U_{n+1,1} & \dots & U_{n+1,n+1} \end{vmatrix} > 0, \tag{53}$$

where

$$U_{ij} = \frac{\partial^2 U}{\partial X_i \partial X_j} \tag{54}$$

and

$$U = U(X_1, \dots, X_{n+2}). \tag{55}$$

An equilibrium state of an n -component system, in other words, is stable if, and only if, the above determinants are all positive. We also point out, parenthetically, that, from the above stability criterion we can derive the stronger condition⁷

$$\left(\frac{\partial \xi_{n+1}}{\partial X_{n+1}} \right)_{\xi_1 \rightarrow \xi_n, X_{n+2}} > 0, \tag{56}$$

which is necessarily violated before any of the above determinants vanishes [the partial derivative in Eq. (56) is called a stability coefficient]. Therefore, in case (e) the part of the curve where $(\partial \xi_1 / \partial X_1) < 0$ is unphysical, and no two stable (or metastable) equilibrium states exist on the (U, S, V) surface such that $X_1 \neq X_1'$ if X_2 and ξ_1 are constant.

Thus, both **A** and **H** are functions of their arguments. The derivation of the uniqueness properties of **G** is similar, though there is an important difference that must be taken into account, as will be shown below. Because **G** is a first-order transform of **A** (or **H**), both of which are (singly defined) functions of their arguments, cases (a) and (b) (Fig. 5) are also impossible. Similarly, the second derivatives

$$\left(\frac{\partial^2 \mathbf{A}}{\partial \mathbf{V}^2} \right)_{T,N} = - \left(\frac{\partial P}{\partial \mathbf{V}} \right)_{T,N} = \frac{1}{\mathbf{V}K_T}, \tag{57}$$

$$\left(\frac{\partial^2 \mathbf{A}}{\partial T^2} \right)_{\mathbf{V},N} = - \left(\frac{\partial S}{\partial T} \right)_{\mathbf{V},N} = - \frac{NC_V}{T}, \tag{58}$$

$$\left(\frac{\partial^2 \mathbf{H}}{\partial \mathbf{S}^2} \right)_{P,N} = \left(\frac{\partial T}{\partial \mathbf{S}} \right)_{P,N} = \frac{T}{NC_P}, \tag{59}$$

$$\left(\frac{\partial^2 \mathbf{H}}{\partial P^2} \right)_{S,N} = \left(\frac{\partial \mathbf{V}}{\partial P} \right)_{S,N} = \frac{-1}{\frac{1}{\mathbf{V}K_T} + \frac{NC_V}{T} (\partial T / \partial \mathbf{V})_{S,N}^2} \tag{60}$$

are all nonzero, and therefore case (e) (Fig. 5) is impossible. However, because T and P are *not* independently variable when two (or three) phases of a pure substance are in equilibrium, we cannot apply the postulate (see above) which we used for the first-order transforms of **U** to cases (c) or (d) (Fig. 5) if $y^{(0)}$ is **A** or **H**.

In this case, however, \mathbf{G}/N is equal in all phases in equilibrium. Thus, although

$$\mathbf{G}(-P, T, N) = \mathbf{A}(\mathbf{V}, T, N) + P\mathbf{V} = y^{(0)} - \xi_1 X_1, \tag{61}$$

$$\mathbf{G}(T, -P, N) = \mathbf{H}(\mathbf{S}, -P, N) - T\mathbf{S} = y^{(0)} - \xi_1 X_1, \tag{62}$$

and it is entirely possible to have different values of X_1 (\mathbf{V} or \mathbf{S}) at constant X_2 and ξ_1 (T and P , in both cases), the potential \mathbf{G} is still uniquely defined in terms of its arguments.

Because of the one-to-one correspondence between Legendre and Massieu–Planck functions [Eq. (23)], the uniqueness properties of the latter are necessarily identical to those of the former. Equation (23), in other words, implies that, if $y^{(k)}$ is a single-valued function of its arguments $(\xi_1 \rightarrow \xi_k; X_{k+1}, \dots, X_m)$, then $\phi^{(k)}$ must necessarily be so, too, because, for given $(\xi_1 \rightarrow \xi_k; X_{k+1}, \dots, X_m)$ and a singly defined $y^{(k)}$, the ratio $y^{(k)}(\xi_1 \rightarrow \xi_k; X_{k+1}, \dots, X_m) / \xi_1$ is also single valued.

We illustrate this in Table I, where we show all possible Legendre and Massieu–Planck transforms of the four thermodynamic potentials corresponding to the ordering $X_3 = N$. The only cases that merit special attention are the third transforms of the Helmholtz energy, Gibbs energy, and enthalpy, since the Legendre transforms $(T\mathbf{S}, -P\mathbf{V},$ and $T\mathbf{S} - P\mathbf{V})$ are not among the functions we discussed so far (the third transform of the enthalpy is, of course, the familiar grand potential of statistical mechanics). We must show, in other words, that $T\mathbf{S}, -P\mathbf{V},$ and $T\mathbf{S} - P\mathbf{V}$ are single-valued functions of $(\mathbf{S}, P, \mu), (T, \mathbf{V}, \mu),$ and $(\mathbf{S}, \mathbf{V}, \mu),$ re-

spectively. This is easily done by writing

$$TS(S, P, \mu) = H(S, P, N) - N\mu, \quad (63)$$

$$-PV(T, V, \mu) = A(T, V, N) - N\mu, \quad (64)$$

$$[TS - PV](S, V, \mu) = U(S, V, N) - N\mu, \quad (65)$$

and noting that, for single-valued H , A , and U , the functions on the left-hand side can only be multivalued if the conditions

$$\left(\frac{\partial \mu}{\partial N}\right)_{P,S} = \left(\frac{\partial^2 H}{\partial N^2}\right)_{S,P} = 0, \quad (66)$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,V} = \left(\frac{\partial^2 A}{\partial N^2}\right)_{T,V} = 0, \quad (67)$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{S,V} = \left(\frac{\partial^2 U}{\partial N^2}\right)_{S,V} = 0 \quad (68)$$

are satisfied [i.e., Eqs. (66)–(68) are the conditions under which N can have different values on the equilibrium surface in (H, S, P, N) , (A, T, V, N) , and (U, S, V, N) space, when (S, P, μ) , (T, V, μ) or (S, V, μ) , respectively, are prescribed].

The above conditions are never satisfied, the first two being stability coefficients (and therefore positive), and the last being of the form U_{11} (for the orderings N, S, V , or N, V, S) which [see Eq. (51)] is also positive and cannot vanish, even at a stability limit.

In all cases, therefore, Massieu-Planck transforms are, indeed, singly defined functions of the same set of arguments as the corresponding Legendre transform [here, again, “corresponding” denotes the univocal relationship defined in Eq. (23)].

VI. MASSIEU-PLANCK TRANSFORMS AND FLUCTUATIONS

Having developed the formalism, we now show how Massieu-Planck transforms arise naturally in the theory of fluctuations in solutions.

In addition to the applications mentioned in the Introduction, the study of fluctuations in solutions is of fundamental theoretical importance as a consequence of the pioneering work of Kirkwood and Buff¹³ who derived relationships between solution properties (partial molar volumes, compressibility) and pair correlation integrals (or, equivalently, fluctuation covariances). These relationships have since been applied to a variety of systems of practical interest,¹⁴ and in addition, have served as a basis for much theoretical work.¹⁵

For an n -component mixture, the partial derivative

$$\left(\frac{\partial^2 y^{(n)}}{\partial X_{n+1}^2}\right)_{\xi_1 \rightarrow \xi_n; X_{n+2}} = \left(\frac{\partial^2 \xi_{n+1}}{\partial X_{n+1}^2}\right)_{\xi_1 \rightarrow \xi_n; X_{n+2}} \quad (69)$$

is called a stability coefficient. The vanishing of a stability coefficient can be shown⁶ to be the mathematical condition for which the quadratic form $\delta^2 U$ loses its positive-definite character: thus, the locus of points satisfying the condition

$$\left(\frac{\partial^2 \xi_{n+1}}{\partial X_{n+1}^2}\right)_{\xi_1 \rightarrow \xi_n; X_{n+2}} = 0 \quad (70)$$

is the locus of limits of stability, or spinodal curve. Because $(n+2)$ variables can be ordered in $(n+2)!$ ways, there are

$(n+2)!/n!$ stability coefficients for an n -component system, all of which vanish along a spinodal curve. To each stability coefficient there corresponds a principal fluctuation, which we define¹⁶ as a fluctuation of an extensive variable (S, V, N_i) within a subsystem whose size is defined by a single extensive parameter (X_{n+2}) . The relationship¹⁶ is

$$\langle (\delta X_{n+1})^2 \rangle_{X_{n+2}} = (kT) / \left(\frac{\partial^2 \xi_{n+1}}{\partial X_{n+1}^2} \right)_{\xi_1 \rightarrow \xi_n; X_{n+2}} \quad (71)$$

Density and concentration fluctuations are of particular interest, since they are readily associated with an operational definition.¹⁶ The general density or concentration fluctuation is one in which both X_{n+1} and X_{n+2} are either V or N_i , and only these variables. Thus, for a binary mixture, we have

$$\langle (\delta N_1)^2 \rangle_{N_2} = kT / \left(\frac{\partial \mu_1}{\partial N_1} \right)_{T, P, N_2}, \quad (72)$$

$$\langle (\delta N_1)^2 \rangle_V = kT / \left(\frac{\partial \mu_1}{\partial N_1} \right)_{T, \mu_2, V}. \quad (73)$$

Invoking Eq. (29) we readily derive the Massieu-Planck-explicit form for the general density or concentration fluctuation:

$$\langle (\delta X_{n+1})^2 \rangle_{X_{n+2}} = (-k) / \left(\frac{\partial^2 \phi^{(n)}}{\partial X_{n+1}^2} \right)_{1/\xi_1 \rightarrow \xi_n/\xi_1; X_{n+2}}, \quad (74)$$

where we require that $X_1 = S$ (i.e., $\xi_1 = T$), and the basis function is U (i.e., X_{n+1} and $X_{n+2} = V$ or N_i). Principal fluctuations involving entropy either as a fluctuating quantity ($X_{n+1} = S$) or as an extent-defining parameter ($X_{n+2} = S$) can be expressed in terms of Massieu-Planck functions. In the former case (fluctuating entropy), we have

$$\langle (\delta S)^2 \rangle_{X_{n+2}} = -k(\xi_{n+1}/\xi_1) / \left[\frac{\partial^2 \phi^{(n)}}{\partial X_{n+1}^2} \right]_{1/\xi_1 \rightarrow \xi_n/\xi_1; X_{n+2}}, \quad (75)$$

an example of which is

$$\begin{aligned} \langle (\delta S)^2 \rangle_V &= kT / \left(\frac{\partial T}{\partial S} \right)_{\mu, V} \\ &= -k(T/\mu) / \left[\frac{\partial(-T/\mu)}{\partial S} \right]_{1/\mu; V}. \end{aligned} \quad (76)$$

In the latter case (entropy extent defining), we write

$$\begin{aligned} \langle (\delta X_{n+1})^2 \rangle_S &= -k(\xi_{n+2}/\xi_1) / \left[\frac{\partial^2 \phi^{(n)}}{\partial X_{n+1}^2} \right]_{1/\xi_1 \rightarrow \xi_n/\xi_1; X_{n+2}}, \end{aligned} \quad (77)$$

an example of which is

$$\begin{aligned} \langle (\delta V)^2 \rangle_S &= -kT / \left(\frac{\partial P}{\partial V} \right)_{\mu, S} \\ &= -k(T/\mu) / \left[\frac{\partial(P/\mu)}{\partial V} \right]_{1/\mu; S}, \end{aligned} \quad (78)$$

and where the basis function is U , in all cases. We note that, in fluctuation theory, Massieu-Planck transforms are naturally expressed as functions of $\xi_1^{-1}, \xi_2/\xi_1, \dots$, etc.

VII. CONCLUSION

The generalized Massieu-Planck transform defined in Eq. (23) gives rise to a set of functions of the same argu-

ments, and with the same uniqueness and extrema properties (the latter to within an unimportant sign difference) that characterize the corresponding Legendre transforms. For a closed, single-component system, there exist eight basic Massieu–Planck transforms [AT^{-1} ; AV^{-1} ; HP^{-1} ; HS^{-1} ; US^{-1} ; UV^{-1} ; GT^{-1} , and GP^{-1}]; additional transforms (arising from the inclusion of N , the system's mass, among the transformed variables) are possible, and are shown in Table I. Any plane which is tangent to the equilibrium surface in (USV) or (ATV) space intersects the zero energy (or Helmholtz energy) plane along a line: the four first- and second-order Massieu–Planck functions which correspond to the choice $X_3 = N$ project on such a line.

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