Notes on Quasi-Homogeneous Functions in Thermodynamics

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A special kind of quasi-homogeneity occurring in thermodynamic potentials of standard thermodynamics is pointed out. Some formal consequences are also discussed.

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I. INTRODUCTION

Quasi-homogeneous functions have been introduced in the framework of standard thermodynamics with the aim to studying scaling and universality near the critical point. A common synonymous of “quasi-homogeneous function” is “generalized homogeneous function” [see e.g. [1,2,3]]. We wish to point out here that quasi-homogeneity can be an useful tool in the framework of standard thermodynamics, when one considers intensive variables as independent variables for the equilibrium thermodynamics description of a system. In fact, homogeneity for the fundamental equation in the entropy representation [and in the energy representation] is well-defined in terms of the standard Euler theorem for homogeneous functions. One simply defines the standard Euler operator (sometimes called also Liouville operator) and requires the entropy [energy] to be an homogeneous function of degree one. When the other thermodynamic potentials which are obtained from the entropy [energy] are taken into account by means of suitable Legendre transformations, then part of the independent variables are intensive. The thermodynamic potentials are still homogeneous of degree one in the extensive independent variables, but a different rescaling is appropriate for the independent variables. For example, let us consider the Gibbs potential \( G(T, p, N) \) for a system which is described by means of three independent variables \( T, p, N \). \( G \) is homogeneous of degree one when the system is rescaled by \( \lambda \), such a rescaling corresponding only to a rescaling \( N \rightarrow \lambda N \), because \( T \) and \( p \) are intensive and remain unchanged under rescaling of the system. This is evident because, as it is well known, one has \( G = \mu(p, T)N \), where \( \mu \) is the chemical potential. Actually, one could also define \( G \) as a quasi-homogeneous function of degree one with weights \( (0, 0, 1) \). Then the behavior under scaling is better defined. A mathematical treatment of the same problem is found in Ref. [5]. The approach we present here is characterized by the more general setting allowed by the technology of quasi-homogeneous functions; the sections on the Gibbs-Duhem equation and the on Pfaffian forms contain a further analysis of some formal aspects of standard thermodynamics.

II. QUASI-HOMOGENEOUS FUNCTIONS AND THERMODYNAMICS

Given a set of real coordinates \( x^1, \ldots, x^n \) and a set of weights \( \alpha \equiv (\alpha_1, \ldots, \alpha_n) \in \mathbb{R}^n \), a function \( F(x^1, \ldots, x^n) \) is quasi-homogeneous of degree \( r \) and type \( \alpha \) if, under dilatations by a scale factor \( \lambda > 0 \) one finds

\[
F(\lambda^{\alpha_1} x^1, \ldots, \lambda^{\alpha_n} x^n) = \lambda^r F(x^1, \ldots, x^n).
\]

A differentiable quasi-homogeneous function satisfies a generalized Euler identity:

\[
D F = r F,
\]

where \( D \) is the Euler vector field

\[
D \equiv \alpha_1 x^1 \frac{\partial}{\partial x^1} + \ldots + \alpha_n x^n \frac{\partial}{\partial x^n}.
\]

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Notice that (2) is a necessary and sufficient condition for a differentiable function to be quasi-homogeneous. It is also interesting to define quasi-homogeneous Pfaffian forms. A Pfaffian form

$$\omega = \sum_{i=1}^{n} \omega_i(x) \, dx^i$$

is quasi-homogeneous of degree $r \in \mathbb{R}$ if, under the scaling

$$x^1, \ldots, x^n \to \lambda^{\alpha_1} x^1, \ldots, \lambda^{\alpha_n} x^n$$

one finds

$$\omega \to \lambda^r \omega.$$  

This happens if and only if the degree of quasi-homogeneity $\deg(\omega_i(x))$ of $\omega_i(x)$ is such that $\deg(\omega_i(x)) = r - \alpha_i \forall i = 1, \ldots, n$. For a discussion about quasi-homogeneity and for further references, see [7].

A. quasi-homogeneous potentials in standard thermodynamics

Let us consider a thermodynamic potential $R(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n)$ depending on $k$ intensive variables $y^1, \ldots, y^k$ and $n - k$ extensive variables $x^{k+1}, \ldots, x^n$. $R$ is required to be quasi-homogeneous of degree 1 and its type is

$$\alpha = (0, \ldots, 0, 1, \ldots, 1).$$

Then, one has

$$R = \sum_{i=k+1}^{n} x^i \frac{\partial R}{\partial x^i}.$$  

This expression of the thermodynamic potentials is well-known, it is sometimes referred to as the identity satisfied by the potentials at fixed intensive variables. A treatment on a mathematical ground of the same topic is found in Ref. [5]. It is evident that, in order to ensure that $R$ is a degree one quasi-homogeneous function, the intensive variables can be at most $n - 1$, in which case (cf. also the following section)

$$R = x^n \frac{\partial R}{\partial x^n} \equiv x^n \, r(y^1, \ldots, y^{n-1}),$$

where $r(y^1, \ldots, y^{n-1})$ is of degree zero.
We recall that, given the fundamental equation of thermodynamics in the energy [entropy] representation, one can obtain other fundamental equations by means of the Legendre transform. It is easy to show that:

the Legendre transform with respect to a variable of weight $\alpha$ of a quasi-homogeneous function of degree $r$ is a quasi-homogeneous function of degree $r$ with the weight $\alpha$ changed into the weight $r - \alpha$ of the Legendre-conjugate variable (theorem 2 of [1]). Moreover,

the partial derivative with respect to a variable of weight $\alpha$ of a quasi-homogeneous function $R$ of degree $r$ is a quasi-homogeneous function of degree $r - \alpha$ having the same type as $R$ (theorem 1 of [1]). See also [7].

These results allow to justify easily the following examples.
For the free energy $F(T, V, N)$, one has $F = U - TS$, thus $F$ is a quasi-homogeneous function of degree 1 and of weights $(0, 1, 1)$, and

$$F(T, V, N) = V \frac{\partial F}{\partial V} + N \frac{\partial F}{\partial N}. $$

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Analogously,

\[ S(T, V, N) = V \frac{\partial S}{\partial V} + N \frac{\partial S}{\partial N}. \]  (11)

[In fact, \( S = -\partial F/\partial T \) and theorem 1 of [1] can be applied]. Moreover, given \( S(T, p, N) \), one has

\[ S(T, p, N) = N \frac{\partial S}{\partial N}. \]  (12)

In concluding this section, we point out that the distinction between degree and weights of thermodynamic variables is somehow artificial, a degree becoming a weight if the thermodynamic variable is changed into an independent variable (e.g., the degree zero of the pressure becomes a weight zero when \( p \) is an independent variable).

III. GIBBS-DUHLEM EQUATIONS

Herein we take into account the Gibbs-Duhem equations. Cf. also [5]. Let us define

\[ R_i \equiv \frac{\partial R}{\partial x^i}; \quad R_a \equiv \frac{\partial R}{\partial y^a}. \]  (13)

one has

\[ dR = \sum_{a=1}^{k} R_a \, dy^a + \sum_{i=k+1}^{n} R_i \, dx^i. \]  (14)

On the other hand, one obtains from (8)

\[ dR = \sum_{i=k+1}^{n} R_i \, dx^i + \sum_{i=k+1}^{n} x^i \, dR_i. \]  (15)

The GD equation is then

\[ \sum_{a=1}^{k} R_a \, dy^a - \sum_{i=k+1}^{n} x^i \, dR_i = 0. \]  (16)

This equation is related with the quasy-homogeneity symmetry of the potential. Let us define the Euler operator

\[ X \equiv \sum_{i=k+1}^{n} x^i \frac{\partial}{\partial x^i}. \]  (17)

Let us also define a 1-form

\[ \omega_R \equiv \sum_{a=1}^{k} R_a \, dy^a + \sum_{i=k+1}^{n} R_i \, dx^i \]  (18)

where \( R_a \) are quasi-homogeneous functions of degree one \( X \, R_a = R_a \) and the \( R_i \) are quasi-homogeneous functions of degree zero \( X \, R_i = 0 \). Then \( \omega_R \) is a quasi-homogeneous 1-form of degree one, in the sense that it satisfies \( L_X \, \omega_R = \omega_R \), where \( L_X \) is the Lie derivative associated with \( X \). One can also define a function

\[ R \equiv i_X \omega_R, \]  (19)

where \( i_X \) is the standard contraction operator. As a consequence, one finds

\[ dR = d(i_X \omega_R) = -i_X \, d\omega_R + L_X \, \omega_R = -i_X \, d\omega_R + \omega_R \]  (20)

If \( \omega_R \) is a closed 1-form (and then, exact in the convex thermodynamic domain), then \( d\omega_R = 0 \) and \( dR = \omega_R \), i.e. \( R \) is the potential associated with \( \omega_R \). Notice also that in the latter case one finds
\[-i_X \, d\omega_R = 0 \]  \hfill (21)

which corresponds to the Gibbs-Duhem equation. In fact, one has

\[
d\omega_R = \sum_{a=1}^{k} dR_a \wedge dy^a + \sum_{i=k+1}^{n} dR_i \wedge dx^i  \hfill (22)
\]

and

\[
i_X \, d\omega_R = \sum_{a=1}^{k} (i_X \, dR_a) \, dy^a - \sum_{a=1}^{k} dR_a \, (i_X \, dy^a) + \sum_{i=k+1}^{n} (i_X \, dR_i) \, dx^i - \sum_{i=k+1}^{n} dR_i \, (i_X \, dx^i) \hfill (23)
\]

where \(i_X \, dR_a = X \cdot R_a = R_a\), and \(i_X \, dR_i = X \cdot R_i = 0\).

The converse is also true, i.e., if (21) is satisfied then from (20) follows that \(\omega_R\) is closed.

The GD equation is then satisfied because of the equality of the mixed second derivatives of \(R\) (Schwartz theorem) and because of the quasi-homogeneous symmetry. In fact, by defining \(Q_{\alpha\beta}\) the matrix of the second partial derivatives of \(R\), one finds

\[
\sum_{i=k+1}^{n} x^i \, dR_i = \sum_{a=1}^{k} \sum_{i=k+1}^{n} x^i \, Q_{ia} \, dy^a + \sum_{j=k+1}^{n} \sum_{i=k+1}^{n} x^i \, Q_{ij} \, dx^j. \hfill (24)
\]

Then the Gibbs-Duhem equation (16) is equivalent to

\[
\sum_{a=1}^{k} \sum_{i=k+1}^{n} x^i \, Q_{ia} \, dy^a = \sum_{a=1}^{k} R_a \, dy^a \hfill (25)
\]

\[
\sum_{j=k+1}^{n} \sum_{i=k+1}^{n} x^i \, Q_{ij} \, dx^j = 0. \hfill (26)
\]

The former formula (25) is implemented if both Schwartz theorem and the quasi-homogeneous symmetry are implemented. In fact,

\[
\sum_{a=1}^{k} \sum_{i=k+1}^{n} x^i \, Q_{ia} \, dy^a = \sum_{a=1}^{k} \sum_{i=k+1}^{n} x^i \left( \frac{\partial}{\partial x^i} \frac{\partial}{\partial y^a} R \right) \, dy^a = \sum_{a=1}^{k} \frac{\partial R}{\partial y^a} \, dy^a = \sum_{a=1}^{k} R_a \, dy^a. \hfill (27)
\]

Also (26) is implemented, in fact

\[
\sum_{j=k+1}^{n} \sum_{i=k+1}^{n} x^i \, Q_{ij} \, dx^j = \sum_{j=k+1}^{n} \sum_{i=k+1}^{n} x^i \left( \frac{\partial}{\partial x^j} \frac{\partial}{\partial x^i} R \right) \, dx^j = \sum_{j=k+1}^{n} \left( \sum_{i=k+1}^{n} x^i \frac{\partial R}{\partial x^i} \frac{\partial R}{\partial x^j} \right) \, dx^j, \hfill (28)
\]

and the latter is zero because \(\partial R/\partial x^i\) are functions of degree zero for all \(i = k + 1, \ldots, n\).  

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IV. PFAFFIAN FORM $\delta Q_{\text{rev}}$

Let us consider the Pfaffian form $\delta Q_{\text{rev}}$ for a system described by $(T, V, N)$, where $T$ is the absolute temperature; one has

$$\delta Q_{\text{rev}} = C_{VN}(T)dT + a(T, V, N)dV + b(T, V, N)dN. \quad (30)$$

$\delta Q_{\text{rev}}$ has to be integrable, i.e., it satisfies $\delta Q_{\text{rev}} \wedge d(\delta Q_{\text{rev}}) = 0$, and it is known that $T$ is an integrating factor for $\delta Q_{\text{rev}}$, with

$$\frac{\delta Q_{\text{rev}}}{T} = dS. \quad (31)$$

Then, one finds that

$$\frac{\delta Q_{\text{rev}}}{T} = \frac{C_{VN}(T)}{T}dT + \frac{a(T, V, N)}{T}dV + \frac{b(T, V, N)}{T}dN \quad (32)$$

is exact and a potential is given by

$$S = \frac{a(T, V, N)}{T} V + \frac{b(T, V, N)}{T} N. \quad (33)$$

Notice that the quasi-homogeneity of degree one of $S$ is the tool allowing to obtain this result. It is “trivial” that $S$ is the potential associated with $\delta Q_{\text{rev}}/T$; it is less trivial that its “homogeneity” leads to (33). For a proof, see the appendix. $\delta Q_{\text{rev}}$ is quasi-homogeneous of degree one and weights $(0, 1, 1)$. From the theory of quasi-homogeneous integrable Pfaffian forms [7], it is known that an integrating factor is also given by

$$f = a(T, V, N) \frac{V}{T} + b(T, V, N) \frac{N}{T}. \quad (34)$$

The proof is found in Ref. [7]. It is evident that

$$f = TS. \quad (35)$$

Analogously, one can consider $(T, p, N)$ as independent variables

$$\delta Q_{\text{rev}} = C_{pN}(T)dT + \eta(T, p, N)dp + \zeta(T, p, N)dN, \quad (36)$$

in which case

$$f = \zeta(T, p) \frac{N}{T} = TS. \quad (37)$$

APPENDIX A: POTENTIALS OF EXACT QUASI-HOMOGENEOUS PFAFFIAN FORMS

We show that, if

$$\omega = \sum_{a=1}^{k} B_a(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dy^a + \sum_{i=k+1}^{n} B_i(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dx^i \quad (A1)$$

is a $C^2$ exact quasi-homogeneous Pfaffian form of degree one, with $B_a, x^i$ quasi-homogeneous of degree one and $B_i, y^a$ quasi-homogeneous of degree zero with respect to the Euler operator

$$Y = \sum_{i=k+1}^{n} x^i \frac{\partial}{\partial x^i} \quad (A2)$$

then

$$P(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) = \sum_{i=k+1}^{n} B_i(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \frac{x^i}{x^i} \quad (A3)$$
is a potential associated with $\omega$. In fact, let us consider

$$
dP = \sum_{i=k+1}^{n} B_i(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dx^i + \sum_{i=k+1}^{n} x^i \, dB_i(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n)
$$

(A4)

$$
= \sum_{i=k+1}^{n} B_i(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dx^i + \sum_{i=k+1}^{n} x^i \sum_{j=k+1}^{n} \frac{\partial B_i}{\partial x^j}(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dx^j
$$

(A5)

$$
+ \sum_{i=k+1}^{n} x^i \sum_{a=1}^{k} \frac{\partial B_i}{\partial y^a}(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dy^a.
$$

(A6)

The exactness of the Pfaffian form $\omega$ implies that $d\omega = 0$ and, in particular

$$
\frac{\partial B_i}{\partial y^a} = \frac{\partial B_a}{\partial x^i} \quad a = 1, \ldots, k; \ i = k + 1, \ldots, n,
$$

(A7)

$$
\frac{\partial B_i}{\partial x^j} = \frac{\partial B_j}{\partial x^i} \quad i, j = k + 1, \ldots, n
$$

(A8)

Then, one obtains

$$
\sum_{i=k+1}^{n} x^i \sum_{a=1}^{k} \frac{\partial B_i}{\partial y^a}(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dy^a = \sum_{i=k+1}^{n} x^i \sum_{a=1}^{k} \frac{\partial B_a}{\partial x^i}(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dy^a
$$

(A9)

$$
= \sum_{a=1}^{k} \left( \sum_{i=k+1}^{n} x^i \frac{\partial}{\partial x^i} B_a(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \right) \, dy^a
$$

(A10)

$$
= \sum_{j=1}^{k} B_a(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dy^a,
$$

(A11)

because each $B_a$ is quasi-homogeneous of degree one. On the other hand, one has

$$
\sum_{i=k+1}^{n} x^i \sum_{j=k+1}^{n} \frac{\partial B_i}{\partial x^j}(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dx^j = \sum_{i=k+1}^{n} x^i \sum_{j=k+1}^{n} \frac{\partial B_i}{\partial x^j}(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \, dx^j
$$

(A12)

$$
= \sum_{j=k+1}^{n} \left( \sum_{i=k+1}^{n} x^i \frac{\partial}{\partial x^i} B_j(y^1, \ldots, y^k, x^{k+1}, \ldots, x^n) \right) \, dx^j
$$

(A13)

$$
= 0,
$$

(A14)

because each $B_i$ is quasi-homogeneous of degree zero.

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