I. EXTENSIVITY AND THE EULER EQUATION

There are two important equations in Thermodynamics that are a direct consequence of the extensivity of the thermodynamic variables. Consider the internal energy $U = U(S, N, V)$ and imagine that the system is magnified by a factor λ: $N \to \lambda N$ $V \to \lambda V$ $S \to \lambda S$ as they are all extensive. Since the internal energy U is also extensive, it is a homogeneous function of degree one with respect to this transformation

$$U(\lambda S, \lambda N, \lambda V) = \lambda U(S, N, V) \tag{1}$$

Take the derivative with respect to λ of this equation,

$$\frac{\partial U}{\partial \lambda} = \frac{\partial U}{\partial(\lambda S)}\frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda N)}\frac{\partial(\lambda N)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda V)}\frac{\partial(\lambda V)}{\partial \lambda} = \frac{\partial \lambda}{\partial \lambda}U. \tag{2}$$

After taking the derivatives with respect to λ we set $\lambda = 1$ (as it is an arbitrary factor) and arrive at the Euler equation,

$$TS - pV + \mu N = U. \tag{3}$$

Two comments,

1. An analogous equation can be derived for any system described by a different set of thermodynamic variables. The particular form of the Euler equation will be **different** for systems described by a different set of thermodynamic variables.

2. This equation is separate, and does **NOT** follow from $dU = \frac{\partial U}{\partial S}dS + \frac{\partial U}{\partial V}dV + \frac{\partial U}{\partial N}dN$

II. GIBBS-DUHEM EQUATION

Extensivity and the Euler equation lead to another important equation of Thermodynamics. Differentiate Eq. (3):

$$dU = \underbrace{TdS - pdV + \mu dN}_{=dU} + SdT - Vdp + Nd\mu, \tag{4}$$

and the so called Gibbs-Duhem equation results,

$$SdT - Vdp + Nd\mu = 0. \tag{5}$$

Equation (5) indicates that variations of the (in this fluid case) three intensive parameters are not independent, but rather have to satisfy this equation. In other words, whereas the three thermodynamic variables (S, N, V) can be varied independently, the respective three conjugate intensive parameters cannot; rather their variations have to satisfy Eq. (5). Equivalently, the set (p, T, μ) does not constitute a suitable set of independent variables to characterize a state.

Physically, since the system is extensive, a complete description of the state must include at least one extensive variable. Specifying only intensive parameters does not lead to a specification of the system size.

An equivalent way of stating this, is imagining a Legendre transform of U that would eliminate its dependence on the thee thermodynamic variables:

$$U - TS + pV - \mu N. \tag{6}$$

Of course, using Eq. (3), this later equation is identically zero. The Legendre transform does not exist.