Stumbling in the thermodynamic dance

a. Attempting to take a step in the thermodynamic dance, we try a Legendre transformation to variables T, p, and μ by defining

$$\Phi = G - \mu N.$$

But $\mu = G/N$, so $\Phi = 0$ and any attempt to say, for example,

$$\left.\frac{\partial \Phi}{\partial \mu}\right)_{T,p} = -N,$$

is bound to fail. The source of the problem is that T, p, and μ are all *intensive*. While it takes three variables to specify a fluid (for example T, p, and N), these specify the fluid's *size* as well as it "substance" (intensive) properties. If you only want to specify its intensive properties, then only two variables are needed. The three variables T, p, and μ over-specify the system — they are not all independent.

Also, it is clear that given T, p, and μ — all intensive quantities — we cannot find any extensive quantity such as N, V, or E.

b. So we want a description in terms of two intensive variables and one intensive master function. Starting with

$$dG = -S\,dT + V\,dp + \mu\,dN$$

and $G = \mu N$, whence

$$dG = \mu\,dN + N\,d\mu,$$

we have

$$N\,d\mu = -S\,dT + V\,dp.$$

Using the definitions for intensive quantities

$$s = \frac{S}{N} \quad \text{and} \quad v = \frac{V}{N},$$

we obtain

$$d\mu = -s\,dT + v\,dp.$$