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Matei: mainly pay attention to my arguments in sections 4 and 5, although I'd appreciate feedback on whether my description of the problem was accurate. Thanks!

On the Small Changes in Auxiliary Functions Near Equilibrium

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1 Placing the Problem

For the duration of this study, we will assume that we have an arbitrary composite system consisting of two compartments. The fact that these compartments are defined arbitrarily will become important later in this work – pretend that we are dealing with compartments that are only separated gedanken-experimentally. We will denote which subsystem a quantity refers to be using parenthetical superscripts. Subscripts after a derivative indicate that these quantities are being held constant. We assume that the total volume for the system is fixed, meaning that $\delta V^{(1)} = -\delta V^{(2)}$.

The basic mathematics we will be developing here can be applied to any of the auxiliary functions, or to entropy itself, but we will use the Helmholtz free energy, A, as our example. We note immediately that we have, by the energy minimization principle, that $\Delta A \geq 0$. We expand A as a Taylor series, and we obtain:

$$0 \leq \Delta A = (\delta A)_{T,V,n} + (\delta^2 A)_{T,V,n} + (\delta^3 A)_{T,V,n} + \cdots \tag{1}$$

Each of these terms can, in turn, be written in terms of the relevant derivatives. If we assume that $n_k^{(\alpha)}$ is fixed for all species in all our systems, we can write:

$$\delta^i A = \frac{1}{i!} dA = \frac{1}{i!}\left(\left(\frac{\partial^i A}{\partial V^i}\right)^{(1)}_{T,n}(\delta V^{(1)})^i + \left(\frac{\partial^i A}{\partial V^i}\right)^{(2)}_{T,n}(\delta V^{(2)})^{(i)}\right)$$

However, since $\delta V^{(1)} = -\delta V^{(2)}$, we have can write the above expression as:

$$\delta^i A = \frac{1}{i!}(\delta V^{(1)})^i\left(\left(\frac{\partial^i A}{\partial V^i}\right)^{(1)}_{T,n} + (-1)^i\left(\frac{\partial^i A}{\partial V^i}\right)^{(2)}_{T,n}\right) \tag{2}$$

This expression will be where we depart for the study of each order of the series.

2 Study of the First-Order Term: $(\delta A)_{T,V,n}$

When we have a very small δV, it is obvious that the first-order term will dominate the Taylor series. So from equation 2, we write the case where $i = 1$:

$$\delta A = (\delta V^{(1)})\left(\left(\frac{\partial A}{\partial V}\right)^{(1)}_{T,n} - \left(\frac{\partial A}{\partial V}\right)^{(2)}_{T,n}\right)$$

Assuming that δV is small enough that the first-order term dominates the expression for ΔA, we require that the above expression be positive. Therefore, if we have $\delta V^{(1)} \geq 0$, then $\left(\frac{\partial A}{\partial V}\right)^{(1)}_{T,n} - \left(\frac{\partial A}{\partial V}\right)^{(2)}_{T,n}$ must be positive as well. A similar inequality gives $\left(\frac{\partial A}{\partial V}\right)^{(1)}_{T,n} - \left(\frac{\partial A}{\partial V}\right)^{(2)}_{T,n}$ negative when $\delta V^{(1)} \leq 0$. However, if the direction of the volume change is not constrained, as is the case for our gedanken-experimental system, we have $\left(\frac{\partial A}{\partial V}\right)^{(1)}_{T,n} = \left(\frac{\partial A}{\partial V}\right)^{(2)}_{T,n}$, and $\delta A = 0$.

Another note! IMSM should be listed as a reference at the end, since I took most of my arguments from there. But I didn't want it to go onto a 3rd page.

that's fine.

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3 Study of the Second-Order Term: $(\delta^2 A)_{T,V,n}$

In the case where the first-order term is null, we the positivity of ΔA can be used to determine the sign of the second-order term from the Taylor expansion in equation 1. By plugging the value $i = 2$ into equation 2, we obtain the following expression:

$$\delta^2 A = \frac{1}{2}(\delta V^{(1)})^2 \left(\left(\frac{\partial^2 A}{\partial V^2} \right)^{(1)}_{T,n} + \left(\frac{\partial^2 A}{\partial V^2} \right)^{(2)}_{T,n} \right)$$

Since $(\delta V^{(1)})^2$ is positive for all real $\delta V^{(1)}$, the positivity of ΔA gives us

$$\left(\frac{\partial^2 A}{\partial V^2} \right)^{(1)}_{T,n} + \left(\frac{\partial^2 A}{\partial V^2} \right)^{(2)}_{T,n} \geq 0$$

Since the division into subsystems is arbitrary, this is equivalent to saying

$$\left(\frac{\delta^2 A}{\delta V^2} \right)_{T,n} \geq 0$$

To give this equation physical significance, we note that $\left(\frac{\delta^2 A}{\delta V^2} \right)_{T,n} = -\left(\frac{\partial p}{\partial v} \right)_{T,n}$. We define the isothermal compressibility as $K_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p} \right)$, and note that the positivity of ΔA requires that it also be positive.

4 Study of the Odd Higher-Order Terms: $(\delta^{2m+1} A)_{T,V,n}$

All the odd terms can be analyzed in a manner parallel to that of the first-order term. Since $\delta V^{(1)}$ can be made arbitrarily small, the lowest-order non-null term dominates the Taylor series for ΔA. When that term is odd, i.e. $i = 2m + 1$, $m \in \mathbb{N}$, equation 2 is of the form:

$$\delta^{2m+1} A = \frac{1}{(2m+1)!}(\delta V^{(1)})^{2m+1} \left(\left(\frac{\partial^{2m+1} A}{\partial V^{2m+1}} \right)^{(1)}_{T,n} - \left(\frac{\partial^{2m+1} A}{\partial V^{2m+1}} \right)^{(2)}_{T,n} \right)$$

Since $\delta^{2m+1} A$ dominates the expansion of ΔA, we have the positivity of the expression. Since $(\delta V^{(1)})^{2m+1}$ is of the same sign as $\delta V^{(1)}$, we have the requirement that $\left(\frac{\partial^{2m+1} A}{\partial V^{2m+1}} \right)^{(1)}_{T,n} - \left(\frac{\partial^{2m+1} A}{\partial V^{2m+1}} \right)^{(2)}_{T,n}$ be of the same sign as $\delta V^{(1)}$. Since the sign of $\delta V^{(1)}$ is not constrained, and the compartments are defined arbitrarily, we find that $\left(\frac{\partial^{2m+1} A}{\partial V^{2m+1}} \right)_{T,n} = 0$.

5 Study of the Even Higher-Order Terms: $(\delta^{2m} A)_{T,V,n}$

Just as the odd terms were analyzed using the same arguments as for the first-order term, the even terms will be analyzed using the arguments for the second-order term. We now look at the case where the $(\delta^{2m} A)$ dominates the Taylor expression, and therefore is positive. Returning again to equation 2:

$$\delta^{2m} A = \frac{1}{(2m)!}(\delta V^{(1)})^{2m} \left(\left(\frac{\partial^{2m} A}{\partial V^{2m}} \right)^{(1)}_{T,n} + \left(\frac{\partial^{2m} A}{\partial V^{2m}} \right)^{(2)}_{T,n} \right)$$

Since $(\delta V^{(1)})^{2m}$ is positive for any real $\delta V^{(1)}$, we have the requirement that the term $\left(\frac{\partial^{2m} A}{\partial V^{2m}} \right)^{(1)}_{T,n} + \left(\frac{\partial^{2m} A}{\partial V^{2m}} \right)^{(2)}_{T,n}$ be positive. Since the compartments are defined arbitrarily, we have $\left(\frac{\partial^{2m} A}{\partial V^{2m}} \right)_{T,n} > 0$.