Stability criterion for thermodynamic potentials

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Assume the internal energy to have the form

$$U = U(X_1, \ldots, X_N) \,. \tag{1}$$

Let the derived thermodynamic potential P be a Legendre transform of U in the first n parameters:

$$P(y_1, \ldots, y_n, X_{n+1}, \ldots, X_N) = U[y_1, \ldots, y_n](y_1, \ldots, y_n, X_{n+1}, \ldots, X_N) \,. \tag{2}$$

These two potentials are linked by the equation

$$U = P + \sum_{i=1}^{n} y_i X_i \,, \tag{3}$$

where

$$y_i = \frac{\partial U}{\partial X_i} \qquad \text{and} \qquad X_i = -\frac{\partial P}{\partial y_i} \,. \tag{4}$$

For more compact expressions, we denote the remaining non-transformed variables X_k, $k > n$, as y_k. The second variation of the internal energy caused by linear variations of the parameters can be written as

$$\begin{aligned}
\delta^2 U &= \delta^2 P + \sum_{i=1}^{n} 2\delta y_i \delta X_i \\
&= \sum_{i,j=1}^{N} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i + \sum_{i=1}^{n} 2\delta y_i \delta \left(-\frac{\partial P}{\partial y_i} \right) = \sum_{i,j=1}^{N} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i - 2 \sum_{i=1}^{n} \delta y_i \frac{\partial}{\partial y_i} \delta P \\
&= \sum_{i,j=1}^{N} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i - 2 \sum_{i=1}^{n} \delta y_i \frac{\partial}{\partial y_i} \sum_{j=1}^{N} \frac{\partial P}{\partial y_j} \delta y_j = \sum_{i,j=1}^{N} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i - 2 \sum_{i=1}^{n} \sum_{j=1}^{N} \delta y_i \frac{\partial^2 P}{\partial y_i \partial y_j} \delta y_j \\
&= \sum_{i,j=1}^{N} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i - 2 \sum_{i,j=1}^{n} \delta y_i \frac{\partial^2 P}{\partial y_i \partial y_j} \delta y_j - 2 \sum_{i=1}^{n} \sum_{j=n+1}^{N} \delta y_i \frac{\partial^2 P}{\partial y_i \partial y_j} \delta y_j \geq 0 \,.
\end{aligned} \tag{5}$$

In this derivation we started from (3), substituted (4) and used the interchangeability of a variation and a derivative. Now, the first sum can be split into four parts: the n-by-n block that corresponds to the transformed variables, the $(N-n)$-by-$(N-n)$ block that corresponds to the non-transformed variables, and the two off-diagonal blocks. However, due to the symmetry of the Hessian matrix of P (i.e. interchangeability of second mixed partial derivatives), the off-diagonal contribution can be written as twice the same term:

$$\sum_{i,j=1}^{N} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i = \sum_{i,j=1}^{n} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i + \sum_{i,j=n+1}^{N} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i + 2 \sum_{i=1}^{n} \sum_{j=n+1}^{N} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i \tag{6}$$

Altogether, combining (5) and (6), we get

$$\begin{aligned}
\delta^2 U &= -\sum_{i,j=1}^{n} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i + \sum_{i,j=n+1}^{N} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i \\
&= -\sum_{i,j=1}^{n} \delta y_j \frac{\partial^2 P}{\partial y_j \partial y_i} \delta y_i + \sum_{i,j=n+1}^{N} \delta X_j \frac{\partial^2 P}{\partial X_j \partial X_i} \delta X_i \geq 0 \,,
\end{aligned} \tag{7}$$

that is, the Hessian of U, when represented in the natural variables of the potential P (by means of elements of Hessian of P) is a block-diagonal matrix consisting of two blocks only: one of them corresponds to the transformed variables, while the other to the non-transformed. These two blocks are not linked by any further non-zero element. Thanks to this observation, we can formulate the stability criterion for P:

The subset of the Hessian of P that corresponds to the Legendre-transformed variables has to be negative (semi-)definite, while the subset of the Hessian that corresponds to the non-transformed variables has to be positive (semi-)definite.