Stability limit of thermodynamic system

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1.1 Le Chatelier's principle.

Maximizing entropy for constant U and all other extensive variables is equivalent to minimizing energy for constant S and all other extensive variables. Denote the extensive variables X_i, which includes entropy S, and their intensive driving force ξ_i. The first law reads

$$\delta U = \sum_i^n \xi_i \, \delta X_i$$

where n is the number of extensive variables. The second law demands that δU vanishes at equilibrium, which sets the equilibrium condition. Choose the convention such as $\xi_i = 0$ at equilibrium.

The second law for local stability further demands

$$\delta^2 U = \frac{1}{2}\sum_{i,j}^n \left(\frac{\partial \xi_i}{\partial X_j}\right)_{X_{k=1,2,\cdots n;k\neq j}} \delta X_i \delta X_j = \frac{1}{2}\sum_{i,j}^n U_{ij} \, \delta X_i \delta X_j > 0$$

for all possible δX_i. So the Jacobian or Hessian U_{ij} needs to positive-definite. The stability against an unimodal fluctuation, i.e., $\delta X_j = 0$ for all $j \neq i$, leads to the requirement that

$$U_{ii} = \left(\frac{\partial \xi_i}{\partial X_i}\right)_{X_{j=1,2,\cdots,n;j\neq i}} > 0 \quad \text{for all } i.$$

These are the familiar results, heat capacity $C_V > 0$, isothermal compressibility $\kappa_T > 0$, and $\partial\mu/\partial N > 0$.

The stability against a bi-modal fluctuation, i.e., $\delta X_j = 0$ for all $j \neq i$ and $j \neq k$, leads to the requirement

$$U_{ii}U_{kk} - U_{ik}^2 > 0$$

for all pairs i and k. The extension to greater numbers of fluctuation modes is given by the Sylvester criterion, treated later.

Within this notation, Le Chatelier's principle amounts to saying that

$$U_{ii} = \left(\frac{\partial \xi_i}{\partial X_i}\right)_{X_{j=1,2,\cdots n;j\neq i}} > \left(\frac{\partial \xi_i}{\partial X_i}\right)_{\xi_{k,k\neq i}, X_{j=1,2,\cdots,n;j\neq i,j\neq k}} > 0.$$

The key distinction being whether the extensive X_j or the intensive ξ_j are fixed. To demonstrate the above result, consider a more general differential (the subscript indices for $X_{j=1,2,\cdots,n;j\neq m,j\neq k}$ implicitly assumed)

$$\left(\frac{\partial \xi_i}{\partial X_m}\right)_{\xi_k} = \frac{\partial\left(\xi_i, \xi_k\right)}{\partial\left(X_m, \xi_k\right)} = \frac{\partial\left(\xi_i, \xi_k\right)/\partial\left(X_m, X_k\right)}{\partial\left(X_m, \xi_k\right)/\partial\left(X_m, X_k\right)} = U_{im} - \frac{U_{ik}U_{km}}{U_{kk}}.$$

Setting $m = i$ gives the Le Chatelier's principle

$$\left(\frac{\partial \xi_i}{\partial X_m}\right)_{\xi_k} = U_{ii} - \frac{U_{ik}U_{ki}}{U_{kk}} = U_{ii} - \frac{U_{ik}^2}{U_{kk}} < U_{ii}.$$

The last step invokes the stability condition $U_{kk} > 0$. The sign $\left(\frac{\partial \xi_i}{\partial X_m}\right)_{\xi_k} > 0$ is fixed by the stability requirement against bi-modal fluctuations, $U_{ii}U_{kk} - U_{ik}^2 > 0$. Physically, an external interaction which disturb the equilibrium bring about processes in the body which tend to reduce the effects of this interaction.

When ξ_i and X_i are set to T and S, the principle leads to a known result, $0 < \frac{1}{C_p} < \frac{1}{C_V}$.

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1.2 Stability criteria.

The sign of Jacobian U_{ij} can be tested by using the **Sylvester's criterion**. A Hermitian matrix M is positive-definite if and only if all the following matrices have a positive determinant: the upper left 1-by-1 corner of M, the upper left 2-by-2 corner of M, $\cdots$, M itself. In other words, all of the leading *principal minors* must be positive.

The first condition leads to $U_{11} > 0$. The second condition leads to

$$\frac{\partial(\xi_1,\xi_2)}{\partial(X_1,X_2)} = \frac{\partial(\xi_1,\xi_2)/\partial(\xi_1,X_2)}{\partial(X_1,X_2)/\partial(\xi_1,X_2)} = \frac{(\partial\xi_2/\partial X_2)_{\xi_1}}{1/U_{11}} > 0 \quad \Rightarrow \quad \left(\frac{\partial\xi_2}{\partial X_2}\right)_{\xi_1} > 0.$$

Note that, since the ordering is arbitrary, the index '2' may refer to any degree of freedom other than '1'. Likewise, the first condition implies that $U_{ii} > 0$ for all i. The third condition leads to a similar result

$$\frac{\partial(\xi_1,\xi_2,\xi_3)}{\partial(X_1,X_2,X_3)} = \frac{\partial(\xi_1,\xi_2,\xi_3)/\partial(\xi_1,\xi_2,X_3)}{\partial(X_1,X_2,X_3)/\partial(\xi_1,\xi_2,X_3)} = \left(\frac{\partial\xi_3}{\partial X_3}\right)_{\xi_1,\xi_2}\frac{\partial(\xi_1,\xi_2)}{\partial(X_1,X_2)} > 0 \quad \Rightarrow \quad \left(\frac{\partial\xi_3}{\partial X_3}\right)_{\xi_1,\xi_2} > 0.$$

The higher order conditions lead to

$$\left(\frac{\partial\xi_k}{\partial X_k}\right)_{\xi_1,\xi_2,\cdots,\xi_{k-1},X_{k+1},\cdots,X_n} > 0, \text{ for } k = 1,2,\cdots,n-1.$$

The last condition at $k = n$ gives

$$\left(\frac{\partial\xi_n}{\partial X_n}\right)_{\xi_1,\xi_2,\cdots,\xi_{n-1}},$$

which vanishes because of the Gibbs-Duhem relation—this is the only physical condition used so far; everything else applies generally to a Hermitian matrix. An example is given in the one-component systems for which $(\partial\mu/\partial N)_{T,P} = 0$. Physically, this means when all the independent $n-1$ intensive variables e.g., T and P, are fixed. Growing the remaining extensive N leads to the overall growth of system size, such that the other extensive variables V and S grows in proportion, which results in no change in the conjugate intensive variable. An alternative path can be taken and leads to

$$\frac{\partial(\xi_1,\xi_2)}{\partial(X_1,X_2)} = \frac{\partial(\xi_1,\xi_2)/\partial(X_1,\xi_2)}{\partial(X_1,X_2)/\partial(X_1,\xi_2)} = \left(\frac{\partial\xi_1}{\partial X_1}\right)_{\xi_2} U_{22} > 0 \quad \Rightarrow \quad \left(\frac{\partial\xi_1}{\partial X_1}\right)_{\xi_2} > 0,$$
$$\frac{\partial(\xi_1,\xi_2,\xi_3)}{\partial(X_1,X_2,X_3)} = \frac{\partial(\xi_1,\xi_2,\xi_3)/\partial(X_1,X_2,\xi_3)}{\partial(X_1,X_2,X_3)/\partial(X_1,X_2,\xi_3)} = \left(\frac{\partial(\xi_1,\xi_2)}{\partial(X_1,X_2)}\right)_{\xi_3} U_{33} > 0 \quad \Rightarrow \quad \left(\frac{\partial(\xi_1,\xi_2)}{\partial(X_1,X_2)}\right)_{\xi_3} > 0.$$

The pattern clearly can be generalized. And many alternative conditions may be constructed.

Since indexing is arbitrary, the thermodynamic stability implies

$$\left(\frac{\partial\xi_i}{\partial X_i}\right)_{X_{k,k\neq i},(\xi \text{ or } X)_{j;j\neq i,j\neq k}} > 0,$$

where i is any degree of freedom of interest, k is a needed extensive constraint, and j are all remaining degrees of freedom which may be intensive or extensive. The number of such inequalities is $n\left(2^{n-1}-1\right)$: n represents the stability mode, i; 2^{n-1} counts the number of intensive or extensive choices for k and j modes; '-1' eliminates the choice of all intensive parameters.

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1.3 Stability limit.

The system loses stability when one of the $n\left(2^{n-1}-1\right)$ inequalities is violated. The stability limit is reached when, starting from within the stability window, the first such inequality becomes 0.

(a) *The differentials with $n-2$ intensive constraints are more susceptible.*

This is a consequence of the Le Chatelier's principle. The response $(\partial\xi_i/\partial X_i)_j$ is smaller when the constraint on the j-th mode is changed from extensive to intensive, *i.e.*, $(\partial\xi_i/\partial X_i)_{\xi_j} < (\partial\xi_i/\partial X_i)_{X_j}$. Consecutive extension to greater number of j modes results in the following chain of inequalities.

$$\left(\frac{\partial\xi_{n-1}}{\partial X_{n-1}}\right)_{X_1,\cdots,X_{n-1},X_n} > \left(\frac{\partial\xi_{n-1}}{\partial X_{n-1}}\right)_{X_1,\cdots,X_{n-2},\xi_{n-2},X_n} > \left(\frac{\partial\xi_{n-1}}{\partial X_{n-1}}\right)_{X_1,\cdots,X_{n-4},\xi_{n-3},\xi_{n-2},X_n} > \cdots$$
$$> \left(\frac{\partial\xi_{n-1}}{\partial X_{n-1}}\right)_{\xi_1,\cdots,\xi_{n-2},X_n} > 0.$$

Thus, to analyze the limit of stability, only the differential involving the greatest $(n-2)$ number of intensive constraints need to considered. The stability conditions is reduced to the set of inequalities

$$\left(\frac{\partial\xi_{n-1}}{\partial X_{n-1}}\right)_{\xi_1,\cdots,\xi_{n-2},X_n} > 0 \quad \text{(susceptible modes).}$$

Since the ordering of indices is arbitrary, there are $n(n-1)$ such conditions, or "susceptible" modes.

(b) *The $n(n-1)$ susceptible modes vanish simultaneously at the stability limit.*

The previous section analyzed the sign of Jacobian by using the Sylvester's criterion. For each particular ordering of degrees of freedom, the criterion for positive-definiteness leads to a set of $n-1$ conditions,

$$\left(\frac{\partial\xi_1}{\partial X_1}\right) > 0, \quad \left(\frac{\partial\xi_2}{\partial X_2}\right)_{\xi_1} > 0, \quad \left(\frac{\partial\xi_3}{\partial X_3}\right)_{\xi_1,\xi_2} > 0, \quad \cdots, \quad \left(\frac{\partial\xi_{n-1}}{\partial X_{n-1}}\right)_{\xi_1,\xi_2,\cdots,\xi_{n-2}} > 0.$$

For notational simplicity, the extensive constraints are not specified explicitly. Reordering indices results in different, yet **equivalent**, sets of conditions. And there are obviously $n(n-1)$ such sets.

The stability limit is defined when, moving along any path within—this is essential—the stability window, the Jacobian loses stability by violating any such constraint. But the Le Chatelier's principle implies that the constraints with $n-2$ intensives are more susceptible. Therefore, right at the stability limit, it is only possible that certain "susceptible" mode vanishes. Since each of the $n(n-1)$ sets of conditions obtained can be used, since each of them contains one "susceptible" mode, and since they are equivalent criteria for the sign of Jacobian, the only possible scenario is that **all the susceptble modes vanish simultaneously**.

Therefore, the stability condition can be equivalently stated and stability limit equivalently constructed by referring to any of the $n(n-1)$ condition

$$\left(\frac{\partial\xi_{n-1}}{\partial X_{n-1}}\right)_{\xi_1,\cdots,\xi_{n-2},X_n} > 0.$$

For one-component system, this could be any of the following six conditions: $\left(\frac{\partial T}{\partial S}\right)_{p,N} > 0$, $\left(\frac{\partial T}{\partial S}\right)_{V,\mu} > 0$, $\left(\frac{\partial p}{\partial V}\right)_{T,N} > 0$, $\left(\frac{\partial p}{\partial V}\right)_{S,\mu} > 0$, $\left(\frac{\partial \mu}{\partial N}\right)_{T,V} > 0$, and $\left(\frac{\partial \mu}{\partial N}\right)_{S,p} > 0$.

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1.4 Example: single-component substance.

Two convenient differentials to use are thermal and mechanical responses.

$$\left(\frac{\partial T}{\partial S}\right)_{p,N} = \frac{T}{C_p}, \qquad C_p = C_V + \frac{VT\alpha_p^2}{\kappa_T};$$
$$-\left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{1}{V\kappa_T}, \qquad \kappa_T = \kappa_S + \frac{VT\alpha_p^2}{C_p}.$$

Inside the stable window, the following inequalities are satisfied:

$$0 < \frac{T}{C_p} < \frac{T}{C_V}, \qquad 0 < \frac{1}{V\kappa_T} < \frac{1}{V\kappa_S}.$$

The stability limit is found by demanding either $T/C_p \to 0$ or $1/(V\kappa_T) \to 0$; or, alternatively, $C_p \to \infty$ or $\kappa_T \to \infty$. Eliminating the dependence on $VT\alpha_p^2$ leads to

$$(C_p - C_V)\,\kappa_T = (\kappa_T - \kappa_S)\,C_p \quad \Rightarrow \quad \frac{\kappa_T}{\kappa_S} = \frac{C_p}{C_V}.$$

The first 2-by-2 entries of the Jacobian reads

$$\mathbf{J} = \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} \\ \frac{\partial^2 U}{\partial V \partial S} & \frac{\partial^2 U}{\partial V^2} \end{pmatrix} = \begin{pmatrix} \frac{T}{C_V} & -\frac{\alpha_p}{\kappa_T}\frac{T}{C_V} \\ -\frac{\alpha_p}{\kappa_T}\frac{T}{C_V} & \frac{C_p}{C_V}\frac{1}{V\kappa_T} \end{pmatrix} = \begin{pmatrix} \frac{T}{C_V} & -\frac{\alpha_p}{\kappa_T}\frac{T}{C_V} \\ -\frac{\alpha_p}{\kappa_T}\frac{T}{C_V} & \frac{1}{V\kappa_S} \end{pmatrix}$$

which has a determinant (the last step used the identity $\kappa_T C_V = \kappa_S C_p$)

$$\det(\mathbf{J}) = \frac{TC_p}{V\kappa_T C_V^2} - \frac{\alpha^2 T^2}{\kappa_T^2 C_V^2} \quad \Rightarrow \quad \det(\mathbf{J}) = \frac{T}{V}\frac{1}{C_V\kappa_T} = \frac{T}{V}\frac{1}{C_p\kappa_S}.$$

The stability condition may be one of the following two.

(1) $J_{11} > 0$ & $\det(\mathbf{J}) > 0$:

$$C_V > 0 \quad \& \quad C_V\kappa_T > 0 \quad \Longrightarrow \quad C_V > 0 \quad \& \quad \kappa_T > 0.$$

(2) $J_{22} > 0$ & $\det(\mathbf{J}) > 0$:

$$\kappa_S > 0 \quad \& \quad C_p\kappa_S > 0 \quad \Longrightarrow \quad C_p > 0 \quad \& \quad \kappa_S > 0.$$

Condition (1) implies condition (2) in that $C_p > C_V$ and

$$\kappa_S = \kappa_T \frac{C_V\kappa_T}{C_V\kappa_T + VT\alpha_p^2} = \frac{\kappa_T}{1 + \alpha_p^2 V^2 \det(\mathbf{J})}.$$

Condition (2) implies condition (1) in that $\kappa_T > \kappa_S$ and

$$C_V = C_p \frac{C_p\kappa_S}{C_p\kappa_S + VT\alpha_p^2} = \frac{C_p}{1 + \alpha_p^2 V^2 \det(\mathbf{J})}.$$

Thus the two sets of conditions are equivalent. Given that $C_p > C_V$ and $\kappa_T > \kappa_S$, the stability limit is equivalently given by $\kappa_T = \infty$ or $C_p = \infty$.

Exactly what happens in the vicinity of the stability limit? Since condition set (1) and (2) are equivalent, we focus on set (1). Obviously, $\kappa_T \to \infty$ and $C_p \to \infty$ is expected. A finite C_V would have led to a finite C_p for finite (true for vdW) α_p, so C_V diverges as well. The divergence rate is $\frac{C_V}{C_p} = \frac{\kappa_S}{\kappa_p} = 1 - \frac{VT\alpha_p^2}{C_p\kappa_T}$.

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