I.I Stability Conditions

The conditions derived in section I.G are similar to the well known requirements for mechanical stability. A particle moving in an external potential U settles to a stable equilibrium at a minimum value of U. In addition to the vanishing of the force $-U'$, this is a consequence of the loss of energy to frictional processes. Stable equilibrium occurs at a *minimum* of the potential energy. For a thermodynamic system, equilibrium occurs at the extremum of the appropriate potential, for example at the maximum value of entropy for an isolated system. The requirement that spontaneous changes should *always* lead to an increased entropy, places important constraints on equilibrium response functions, discussed in this section.

Consider a homogeneous system at equilibrium, characterized by intensive state functions $(T, \mathbf{J}, \mu)$, and extensive variables $(E, \mathbf{x}, \mathbf{N})$. Now imagine that the system is arbitrarily divided into two *equal* parts, and that one part spontaneously transfers some energy to the other part in the form of work or heat. The two subsystems, A and B, initially have the same values for the intensive variables, while their extensive coordinates satisfy $E_A + E_B = E$, $\mathbf{x}_A + \mathbf{x}_B = \mathbf{x}$, and $\mathbf{N}_A + \mathbf{N}_B = \mathbf{N}$. After the exchange of energy between the two subsystems, the coordinates of A change to

$$(E_A + \delta E,\ \mathbf{x}_A + \delta\mathbf{x},\ \mathbf{N}_A + \delta\mathbf{N}),\ \text{and}\ (T_A + \delta T_A,\ \mathbf{J}_A + \delta\mathbf{J}_A,\ \mu_A + \delta\mu_A), \tag{I.60}$$

and those of B to

$$(E_B - \delta E,\ \mathbf{x}_B - \delta\mathbf{x},\ \mathbf{N}_B - \delta\mathbf{N}),\ \text{and}\ (T_B + \delta T_B,\ \mathbf{J}_B + \delta\mathbf{J}_B,\ \mu_B + \delta\mu_B). \tag{I.61}$$

Note that the overall system is maintained at constant E, $\mathbf{x}$, and $\mathbf{N}$. Since the intensive variables are themselves functions of the extensive coordinates, to *first order* in the variations of $(E, \mathbf{x}, \mathbf{N})$, we have

$$\delta T_A = -\delta T_B \equiv \delta T, \quad \delta\mathbf{J}_A = -\delta\mathbf{J}_B \equiv \delta\mathbf{J}, \quad \delta\mu_A = -\delta\mu_B \equiv \delta\mu. \tag{I.62}$$

Using eq.(I.48), the entropy of the system can be written as

$$S = S_A + S_B = \left(\frac{E_A}{T_A} - \frac{\mathbf{J}_A}{T_A}\cdot\mathbf{x}_A - \frac{\mu_A}{T_A}\cdot\mathbf{N}_A\right) + \left(\frac{E_B}{T_B} - \frac{\mathbf{J}_B}{T_B}\cdot\mathbf{x}_B - \frac{\mu_B}{T_B}\cdot\mathbf{N}_B\right). \tag{I.63}$$

Since by assumption we are expanding about the equilibrium point, the first order changes vanish, and to second order

$$\delta S = \delta S_A + \delta S_B = 2\left[\delta\left(\frac{1}{T_A}\right)\delta E_A - \delta\left(\frac{\mathbf{J}_A}{T_A}\right)\cdot\delta\mathbf{x}_A - \delta\left(\frac{\mu_A}{T_A}\right)\cdot\delta\mathbf{N}_A\right]. \tag{I.64}$$

(We have used eq.(I.62) to note that the second order contribution of B is the same as A.) Eq.(I.64) can be rearranged to

$$\begin{aligned}\delta S =& -\frac{2}{T_A}\left[\delta T_A\left(\frac{\delta E_A - \mathbf{J}_A\cdot\delta\mathbf{x}_A - \mu_A\cdot\delta\mathbf{N}_A}{T_A}\right) + \delta\mathbf{J}_A\cdot\delta\mathbf{x}_A + \delta\mu_A\cdot\delta\mathbf{N}_A\right]\\ =& -\frac{2}{T_A}\left[\delta T_A\delta S_A + \delta\mathbf{J}_A\cdot\delta\mathbf{x}_A + \delta\mu_A\cdot\delta\mathbf{N}_A\right].\end{aligned} \tag{I.65}$$

The condition for stable equilibrium is that any change should lead to a decrease in entropy, and hence we must have

$$\delta T\delta S + \delta\mathbf{J}\cdot\delta\mathbf{x} + \delta\mu\cdot\delta\mathbf{N} \geq 0. \tag{I.66}$$

We have now removed the subscript A, as the above condition must apply to the whole system as well as to any part of it.

The above condition was obtained assuming that the overall system was kept at constant E, $\mathbf{x}$, and $\mathbf{N}$. In fact, since all coordinates appear symmetrically in this expression, the same result is obtained for any other set of constraints. For example, variations in δT and $\delta\mathbf{x}$ with $\delta\mathbf{N} = 0$, lead to

$$\begin{cases}\delta S = \left.\dfrac{\partial S}{\partial T}\right|_{\mathbf{x}}\delta T + \left.\dfrac{\partial S}{\partial x_i}\right|_T\delta x_i\\ \delta J_i = \left.\dfrac{\partial J_i}{\partial T}\right|_{\mathbf{x}}\delta T + \left.\dfrac{\partial J_i}{\partial x_j}\right|_T\delta x_j\end{cases}. \tag{I.67}$$

Substituting these variations into eq.(I.66) leads to

$$\left.\frac{\partial S}{\partial T}\right|_{\mathbf{x}}(\delta T)^2 + \left.\frac{\partial J_i}{\partial x_j}\right|_T\delta x_i\delta x_j \geq 0. \tag{I.68}$$

Note that the cross terms proportional to $\delta T\delta x_i$ cancel due to the Maxwell relation in eq.(I.56). Eq.(I.68) is a *quadratic from*, and must be positive for *all choices* of δT and $\delta\mathbf{x}$. The resulting constraints on the coefficients are independent of how the system was initially partitioned into subsystems A and B, and represent the conditions for stable equilibrium.

If only δT is non-zero, eq.(I.66) requires $\partial S/\partial T|_{\mathbf{x}} \geq 0$, implying a positive heat capacity, since

$$C_{\mathbf{x}} = \left.\frac{đQ}{dT}\right|_{\mathbf{x}} = T \left.\frac{\partial S}{\partial T}\right|_{\mathbf{x}} \geq 0. \tag{I.69}$$

If only one of the δx_i in eq.(I.66) is non-zero, the corresponding response function $\partial x_i/\partial J_i|_{T,x_{j\neq i}}$ must be positive. However, a more general requirement exists since all $\delta\mathbf{x}$ values may be chosen non-zero. The general requirement is that the matrix of coefficients $\partial J_i/\partial x_j|_T$ must be *positive definite*. A matrix is positive definite if all of its eigenvalues are positive. It is necessary, but not sufficient, that all the diagonal elements of such a matrix (the inverse response functions) be positive, leading to further constraints between the response functions. Including chemical work for a gas, the appropriate matrix is

$$\begin{bmatrix} -\frac{\partial P}{\partial V}\Big|_{T,N} & -\frac{\partial P}{\partial N}\Big|_{T,V} \\ \left.\frac{\partial \mu}{\partial V}\right|_{T,N} & \left.\frac{\partial \mu}{\partial N}\right|_{T,V} \end{bmatrix}. \tag{I.70}$$

In addition to the positivity of the response functions $\kappa_{T,N} = -V^{-1}\,\partial V/\partial P|_{T,N}$ and $\partial N/\partial \mu|_{T,V}$, the determinant of the matrix must be positive, requiring

$$\left.\frac{\partial P}{\partial N}\right|_{T,V} \left.\frac{\partial \mu}{\partial V}\right|_{T,N} - \left.\frac{\partial P}{\partial V}\right|_{T,N} \left.\frac{\partial \mu}{\partial N}\right|_{T,V} \geq 0. \tag{I.71}$$

Another interesting consequence of eq.(I.66) relates to the critical point of a gas where $\partial P/\partial V|_{T_c,N} = 0$. Assuming that the critical isotherm can be analytically expanded as

$$\delta P(T = T_c) = \left.\frac{\partial P}{\partial V}\right|_{T_c,N} \delta V + \frac{1}{2} \left.\frac{\partial^2 P}{\partial V^2}\right|_{T_c,N} \delta V^2 + \frac{1}{6} \left.\frac{\partial^3 P}{\partial V^3}\right|_{T_c,N} \delta V^3 + \cdots, \tag{I.72}$$

the stability condition $-\delta P \delta V \geq 0$ implies that $\partial^2 P/\partial V^2|_{T_c,N}$ must be zero, and the third derivative negative, if the first derivative vanishes. This condition is used to obtain the critical point of the gas from mean-field approximations to the isotherms (such as the van der Waals isotherms). In fact, it is usually not justified to make a Taylor expansion around the critical point as in eq.(I.72), although the constraint $-\delta P \delta V \geq 0$ remains applicable.

I.J The Third Law

Differences in entropy between two states can be computed using the second law, from $\Delta S = \int đQ_{\rm rev}/T$. Low temperature experiments indicate that $\Delta S(\mathbf{X}, T)$ vanishes as T goes to zero for any set of coordinates $\mathbf{X}$. This observation is independent of the other laws of thermodynamics, leading to the formulation of a third law by Nernst, which states

- *The entropy of all systems at zero absolute temperature is a universal constant that can be taken to be zero.*

The above statement actually implies that

$$\lim_{T\to 0} S(\mathbf{X}, T) = 0, \tag{I.73}$$

which is a stronger requirement than the vanishing of the differences $\Delta S(\mathbf{X}, T)$. This extended condition has been tested for metastable phases of a substance. Certain materials such as sulphur or phosphine can exist in a number of rather similar crystalline structures (*allotropes*). Of course, at a given temperature only one of these structures is truly stable. Let us imagine that as the high temperature equilibrium phase A, is cooled slowly, it makes a transition at a temperature T^* to phase B, releasing *latent heat* L. Under more rapid cooling conditions the transition is avoided, and phase A persists in metastable equilibrium. The entropies in the two phases can be calculated by measuring the heat capacities $C_A(T)$ and $C_B(T)$. Starting from $T = 0$, the entropy at a temperature slightly above T^* can be computed along the two possible paths as

$$S(T^* + \epsilon) = S_A(0) + \int_0^{T^*} dT' \frac{C_A(T')}{T'} = S_B(0) + \int_0^{T^*} dT' \frac{C_B(T')}{T'} + \frac{L}{T^*}. \tag{I.74}$$

Such measurements have indeed verified that $S_A(0) = S_B(0) \equiv 0$.

Consequences of the third law:

(1) Since $S(T = 0, \mathbf{X}) = 0$ for all coordinates $\mathbf{X}$,

$$\lim_{T\to 0} \left.\frac{\partial S}{\partial \mathbf{X}}\right|_T = 0. \tag{I.75}$$

(2) Heat capacities must vanish as $T \to 0$ since

$$S(T, \mathbf{X}) - S(0, \mathbf{X}) = \int_0^T dT' \frac{C_{\mathbf{X}}(T')}{T'}, \tag{I.76}$$

and the integral diverges as $T \to 0$ unless

$$\lim_{T\to 0} C_{\mathbf{X}}(T) = 0. \tag{I.77}$$

(3) Thermal expansivities also vanish as $T \to 0$ since

$$\alpha_J = \frac{1}{x}\left.\frac{\partial x}{\partial T}\right|_J = \frac{1}{x}\left.\frac{\partial S}{\partial J}\right|_T. \tag{I.78}$$

The second equality follows from the Maxwell relation in eq.(I.56). The vanishing of the latter is guaranteed by eq.(I.75).

(4) It is impossible to cool any system to absolute zero temperature in a finite number of steps. For example, we can cool a gas by an adiabatic reduction in pressure. Since the curves of S versus T for different pressures must join at $T = 0$, successive steps involve progressively smaller changes, in S and in T, on approaching zero temperature. Alternatively, the unattainability of zero temperatures implies that $S(T = 0, P)$ is independent of P. This is a weaker statement of the third law which also implies the equality of zero temperature entropy for different substances.

In the following sections, we shall attempt to justify the laws of thermodynamics from a microscopic point of view. The first law is clearly a reflection of the conservation of energy, which also operates at the microscopic level. The zeroth and second laws suggest an irreversible approach to equilibrium, a concept that has no analog at the particulate level. It is justified as reflecting the collective behavior of large numbers of degrees of freedom. In statistical mechanics the entropy is calculated as $S = k_B \ln g$, where g is the degeneracy of the states (number of configurations with the same energy). The third law of thermodynamics thus requires that $g = 1$ at $T = 0$, i.e. that the ground state of any system is unique. This condition *does not hold* within the framework of classical statistical mechanics, as there are examples of both non-interacting (such as an ideal gas), and interacting (the frustrated spins in a triangular antiferromagnet) systems with degenerate ground states, and a finite zero temperature entropy. However, classical mechanics is inapplicable at very low temperatures and energies where quantum effects become important. The third law is then equivalent to the statement that the ground state of a quantum mechanical system is unique. While this can be proved for a non-interacting system, there is no general proof of its validity with interactions. Unfortunately, the onset of quantum effects (and other possible origins of the breaking of classical degeneracy) are system specific. Hence it is not a priori clear how low the temperature must be, before the predictions

of the third law can be observed. Another deficiency of the law is its inapplicability to glassy phases. Glasses results from the freezing of supercooled liquids into configurations with extremely slow dynamics. While not truly equilibrium phases (and hence subject to all the laws of thermodynamics), they are effectively so due to the slowness of the dynamics. A possible test of the applicability of the third law to glasses, is discussed in test #1 review problems.

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Fall 2013

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