SYSTEM STABILITY

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EVOLUTION OF AN ISOLATED SYSTEM

In Chapter 2: Entropy, we have partially developed the fact of Nature that "an isolated system can only evolve towards a unique state called equilibrium state", independent of its initial state, and characterised by a particular internal distribution of conservative magnitudes: that of maximum average uncertainty (i.e. maximum entropy).

For a simple compressible system, characterised by just its internal energy, U, and volume, V, the time evolution of its parts is dictated by the monotonous increase of entropy, S, constrained by the constancy of U and V (a statement of the Second Law of Thermodynamics), namely:

$$\frac{\partial S}{\partial t} \equiv \frac{\partial \sum S_k}{\partial t} > 0, \quad \frac{\partial U}{\partial t} \equiv \frac{\partial \sum U_k}{\partial t} = 0, \quad \frac{\partial V}{\partial t} \equiv \frac{\partial \sum V_k}{\partial t} = 0 \text{ until } \lim_{t \to \infty} \frac{\partial S}{\partial t} = 0 \qquad (1)$$

Furthermore, since, at least for small departures from equilibrium in an isolated system, the dynamics should be proportional to the unbalance force, the entropy function has to be quadratic in the force:

$$\text{(At least when } t \to \infty) \quad \frac{\partial^2 S}{\partial t^2} < 0 \text{ until } \lim_{t \to \infty} \frac{\partial^2 S}{\partial t^2} = 0 \qquad (2)$$
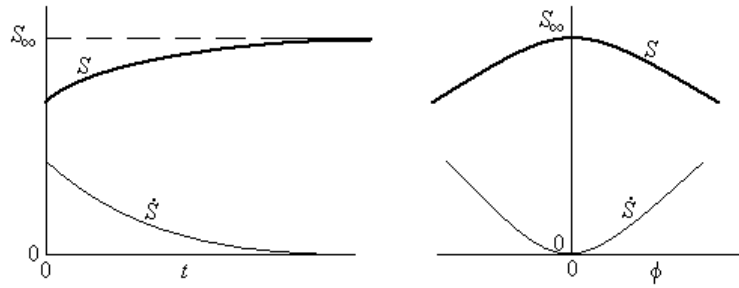
what is shown in Fig. 1.

Fig. 1. Entropy variation with time, $S(t)$, and its rate, $\dot{S}(t)$. ϕ is a characteristic non-equilibrium force (e.g. the averaged temperature gradient in the case of thermal relaxation).

The fact that thermodynamic evolution is governed by a variational principle (the trend towards a stationary value of entropy, under the energy and volume constraints, (1)), is a generic behaviour of Nature, first enunciated by Fermat in the 17th c. for Optics: "light rays travel from one point to another by the path of minimum time of travel", and later developed by Hamilton in the 20th c. for Mechanics: "a body moves in time-space from $(t_1, \vec{r}_1)$ to $(t_2, \vec{r}_2)$ by minimising the action $A \equiv \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t)dt = \min$ " (where L is the Lagrangian function, with units of energy, q are coordinates and p momenta).

In a similar manner as for a mechanical system, thermodynamic systems can be stable or not (consider what a 1 mJ spark can make to a hydrogen-oxygen mixture, or the change in a hot pad when clicking the trigger).

Consequences of equilibrium

In Chapter 2: Entropy, we found the constraints on the distribution of conservative magnitudes at equilibrium. By means of Lagrange multipliers, we find that a first consequence of a system being at equilibrium is the existence of temperature and pressure as common variables shared by all subsystems k (at equilibrium in absence of external fields):

$$\frac{1}{T} \equiv \frac{\partial S_k}{\partial U_k}\bigg|_V = \frac{\partial S}{\partial U}\bigg|_V , \quad \frac{p}{T} \equiv \frac{\partial S_k}{\partial V_k}\bigg|_U = \frac{\partial S}{\partial V}\bigg|_U , \quad \forall k \tag{3}$$

Notice that (3) only apply to systems at equilibrium, contrary to (1) and (2).

Why temperature has to be positive

Temperature, defined by (3), can only be positive for a real system at equilibrium, because it is a fact of Nature that the more energy a system has, the more quantum energy levels become accessible and thus the larger the entropy (the number of possible distributions), and temperature is that sensitivity; i.e., $S(U)|_V$ can only be positive and increasing, Fig. 2.
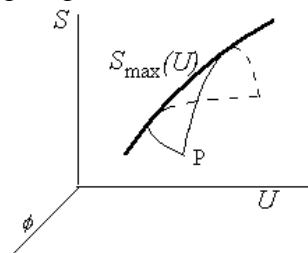

Fig. 2. Entropy variation with internal energy, U (at constant volume), and with an unspecified non-equilibrium parameter, ϕ (e.g. the mean temperature gradient). Notice that from a non-equilibrium

state P, the equilibrium state reached is different if the evolution is at U=constant (maximum entropy) or at S=constant (minimum energy).

The increasing monotony of the function $S(U)|_V$ implies the positiveness of $1/T = \partial S/\partial U|_V$. Furthermore, energy itself has to be also a monotonic increasing function of temperature at constant volume, $\partial U/\partial T|_V > 0$ because otherwise the system would be thermally unstable (energy would flow from colder to hotter parts and entropy would decrease). Thus, the function $S(U)|_V$ is monotonically increasing with monotonically decreasing slope, as represented in Fig. 2.

The reasoning above was based on quantum physics, but a more classical-mechanics reasoning serves the same goal: why temperature has to be positive. The total energy of an isolated system, E (constant), can be composed as the sum of internal energy, U, and kinetic energy of the motion relative to its centre of mass, $E_k = \sum m_i v_i^2/2$, i.e. $E = U + E_k =$ const, and $dE/dt = 0 = dU/dt + dE_k/dt$, but mechanical stability demands $dE_k/dt < 0$ to avoid the system to naturally explode, what forces $dU/dt > 0$ (i.e. the expected conclusion that motion tends to disappear, increasing the system thermal energy), and, since $dS/dt > 0$ for the evolution, it finally implies that $dU/dS > 0$.

Extended mechanical consequences of equilibrium

In , we showed that the consequences of equilibrium can be labelled as follows:

- Thermal equilibrium. At equilibrium, temperature has to be uniform in all subsystems. Sometimes this is called Zero Law of Thermodynamics.
- Mechanical equilibrium. At equilibrium, the only motion possible for the subsystems is as a solid body.
- Chemical equilibrium. At equilibrium, the chemical potential of each species varies proportionally to its molar mass and the energy of the applied field, being uniform in absence of external fields.

But the mechanicistic reasoning used above to show that temperature must be positive can be further extended to an isolated system with total energy E (constant), total linear momentum $\vec{P}$ (constant), total angular momentum $\vec{L}$ (constant), in a constant gravitational field, to yield:

$$E = U + \frac{1}{2}mv_{cm}^2 + \frac{1}{2}I\Omega^2 + mgz = U + \frac{\vec{P}^2}{m} + \frac{\vec{L}^2}{I} + mgz = \text{cont.} \qquad (4)$$

with the traditional mechanical definitions of centre of mass, $\vec{r}_{cm}$, mass-averaged velocity, $\vec{v}_{cm}$, moment of inertia relative to an arbitrary origin, I, inertia-averaged angular speed, $\vec{\Omega}$, linear momentum, $\vec{P}$, and angular momentum, $\vec{L}$:

$$r_{cm} \equiv \frac{\sum m_i \vec{r}_i}{\sum m_i}, \ \vec{v}_{cm} \equiv \frac{\sum m_i \vec{v}_i}{\sum m_i}, \ I \equiv \sum m_i (\vec{r}_i - \vec{r}_{cm})^2, \ \vec{\Omega} \equiv \frac{\sum (\vec{r}_i - \vec{r}_{cm}) \times m_i (\vec{v}_i - \vec{v}_{cm})}{\sum m_i (\vec{r}_i - \vec{r}_{cm})^2},$$

$$\vec{P} \equiv \sum m_i \vec{v}_i = m\vec{v}_{cm}, \quad \text{and} \quad \vec{L} \equiv \sum \vec{r}_i \times m_i \vec{v}_i = I\vec{\Omega} + \vec{r}_{cm} \times \vec{P} \qquad (5)$$

deducing from (4) and from $dU/dS > 0$ that, at equilibrium, the thermal energy tends to a maximum compatible with the constraints (by mechanical energy dissipation by friction), and consequently the mass

should be the highest (but it is constant in this non-relativistic analysis), the moment of inertia should be the highest (i.e. deformable systems tend to rotate around the principal axis of inertia), and the position in the gravity field should be the lowest. As a consequence, at equilibrium, the angular speed is aligned with the angular momentum [2].

Why pressure has to be positive

Pressure, defined by (3), can only be positive for a real system at equilibrium, because the more volume a system has, the more quantum energy levels become accessible and thus the larger the entropy (the number of possible distributions), and pressure is that sensitivity; i.e., the increasing monotony of the function $S(V)|_U$ implies the positiveness of $p/T = \partial S/\partial V|_U$. Furthermore, since volume has to be also a monotonic decreasing function of pressure at constant energy (or at constant temperature), $\partial V/\partial p|_U$, it follows that the function $S(V)|_U$ is monotonically increasing with monotonically decreasing slope, as represented in Fig. 2 for $S(U)|_V$; in fact, in the case of perfect gases, both functions are quite similar: $S-S_{ref} = mc_v\ln(T/T_{ref}) + mR\ln(V/V_{ref}) = mc_v\ln(U/U_{ref}) + mR\ln(V/V_{ref})$.

From another point of view, pressure can only be positive because, otherwise, the tendency of entropy in isolated systems to increase would mean that its volume would disappear; $dV<0$ if $p<0$ in $p \equiv T\partial S/\partial V|_{U,ni}$). However, contrary to temperature that cannot have negative values because motion would diverge (see above), in liquids, negative pressures can be realised in nature if the appearance of the gas phase implied in the shrinking is hindered, as when the liquid is so pure that no heterogeneous nucleation can occur and a metastable equilibrium exists until the departure from true equilibrium is so large that homogeneous nucleation takes place.

Why thermal capacities have to be positive

The specific thermal capacity at constant volume, c_v, has to be positive because of the thermal stability already explained when analysing why temperature was positive. From its definition, and analysing the evolution of the slope of $S(U)|_V$ in Fig. 2:

$$mc_v \equiv T\left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial U}{\partial T}\right|_V, \quad \frac{\partial}{\partial U}\left.\frac{\partial S}{\partial U}\right|_V = \left.\frac{\partial(1/T)}{\partial U}\right|_V = \frac{-1}{T^2}\left.\frac{\partial T}{\partial U}\right|_V = \frac{-1}{mc_vT^2} < 0 \qquad (6)$$

i.e., from the fact that the slope (always positive, equal to $1/T$) has to decrease when energy increases, it is deduced from (6) that $c_v>0$.

A similar result might be obtained for the thermal capacity at constant pressure, c_p, i.e. $c_p>0$, although extrapolation to other cases is not granted; for instance the thermal capacity along the liquid-vapour saturation line can be negative.

Why compressibilities have to be positive

Compressibility is the effect of pressure on the volume of a system, and two compressibility coefficients may be defined:

$$\kappa \equiv \frac{-1}{V}\frac{\partial V}{\partial p}\bigg|_T \quad \text{and} \quad \kappa_S \equiv \frac{-1}{V}\frac{\partial V}{\partial p}\bigg|_S \tag{7}$$

both of which have to be positive for mechanical stability, based on $\partial^2 S/\partial t^2 < 0$ during the evolution of a system. The explanation is entirely similar to the one developed above for c_v, i.e. to enforce that the equilibrium function $S(V)|_U$ is monotonic, with slope p/T monotonically decreasing with time, entirely similar to function $S(U)|_V$ in Fig. 2:

$$\frac{\partial}{\partial V}\frac{\partial S}{\partial V}\bigg|_U = \frac{\partial(p/T)}{\partial V}\bigg|_U = \frac{-1}{m\kappa}\left(\frac{1}{vT} + \frac{(\kappa p - \alpha T)^2}{c_v \kappa T^2}\right) < 0 \tag{8}$$

what implies that $\kappa > 0$ (κ is sometimes labelled κ_T).

THE METHOD OF PARTITION RELEASE

Notice that the variable time does not appear explicitly in the consequence of equilibrium, in (3), although it appears in the sense that S in (3) is only the equilibrium state entropy, S_∞ in Fig. 1, whereas in (1) S is entropy at a non-equilibrium state. Classical Thermodynamics renounces to time details and gets ride of the time variable by just focusing on virtual equilibrium states, including non-equilibrium states of a system by considering local equilibrium of its subsystems; i.e. instead of non-equilibrium systems evolving with time, we consider the initial restricted equilibrium of a fine partition within the system, and the final equilibrium reached when the partition is released.

In that way, we write the fundamental relationship for a simple compressible system at equilibrium (based on (3)) as:

$$dS = \frac{\partial S}{\partial U}\bigg|_V dU + \frac{\partial S}{\partial V}\bigg|_U dV = \frac{1}{T}dU + \frac{p}{T}dV \tag{9}$$

We insist that you can no longer look in (9) for $dS/dt > 0$ or $d^2S/dt^2 < 0$, since for an isolated system at equilibrium $dU/dt = dV/dt = dS/dt = 0$; Eq. (9) should be read as: "for a system at equilibrium, there is a surface $S(U,V)$ of possible equilibrium states (corresponding to different energies and volumes), with local slopes $1/T$ and p/T along the axes, indicating the changes in equilibrium entropy due to virtual displacements in the independent variables U and V" (virtual changes refer to considering slightly different system, since U and V cannot changed in an isolated system).

The simplest partition: one small subsystem in a large isolated system

We can simplify the reasoning by considering the universe (the isolated system) to be composed just of two subsystems at equilibrium, a small one that we name without subindex, and a much larger one which we subscript as 0. We now recover the whole meaning of entropy not only as the equilibrium entropy of the subsystem, S, but also as the non-equilibrium entropy of the universe, $S_{univ} = S + S_0$, to relate (1) and (9):

$$\frac{\partial S_{univ}}{\partial t} = \frac{\partial(S + S_0)}{\partial t} > 0, \quad \frac{\partial U_{univ}}{\partial t} = \frac{\partial(U + U_0)}{\partial t} = 0, \quad \frac{\partial V_{univ}}{\partial t} = \frac{\partial(V + V_0)}{\partial t} = 0,$$

$$\frac{\partial S_{univ}}{\partial t} = \frac{\partial (S + S_0)}{\partial t} = \frac{\partial S}{\partial U}\frac{dU}{dt} + \frac{\partial S}{\partial V}\frac{dV}{dt} + \frac{\partial S_0}{\partial U_0}\frac{dU_0}{dt} + \frac{\partial S_0}{\partial V_0}\frac{dV_0}{dt} =$$

$$= \frac{1}{T}\frac{dU}{dt} + \frac{1}{T_0}\frac{dU_0}{dt} + \frac{p}{T}\frac{dV}{dt} + \frac{p_0}{T_0}\frac{dV_0}{dt} = \left(\frac{1}{T} - \frac{1}{T_0}\right)\frac{dU}{dt} + \left(\frac{p}{T} - \frac{p_0}{T_0}\right)\frac{dV}{dt} > 0 \qquad (10)$$

and regain the known consequences of equilibrium, stated in (3): when the whole system reaches its equilibrium state and its entropy can no longer increase ($\partial S_{univ}/\partial t=0$), temperature, and pressure in absence of external force fields, must be the same in all subsystems, i.e. $T=T_0$ and $p=p_0$.

But the inequality in (10) teaches more: it shows that at a non-equilibrium state, the variation of the energy of a system at constant volume, dU/dt, must be of the same sign as its preceding parenthesis in (10); i.e. if $T<T_0$ (i.e. the small subsystem is colder than the larger one) then $dU/dt>0$ (i.e. the small cold system gets energy from the warmest). Similarly, assuming that the system is isothermal, if the small system has more pressure, $p>p_0$, then its volume tends to increase, $dV/dt>0$.

Fluctuations and virtual displacements

Thermodynamic equilibrium is a microscopically dynamic process, with small random local deviations in energy, volume and entropy of the subsystems. We here consider those real fluctuations or similar virtual displacements of the energy and volume of a subsystem in the whole isolated system.

Energy and volume fluctuations in the small subsystem, dU and dV, can be positive or negative, and cancel in the whole, $dU+dU_0=0$ and $dV+dV_0=0$, but entropy fluctuations in the whole, $dS+dS_0$, can only be negative in the second approximation (to a first approximation it is zero because there is a local maximum; i.e. $dS_{univ}=0$ but $d^2S_{univ}<0$). Taylor expansion around the maximum, gives:

$$\Delta S_{univ} = \Delta(S + S_0) = (dS + dS_0) + \frac{1}{2!}(d^2S + d^2S_0) + \frac{1}{3!}(d^3S + d^3S_0) + ... =$$

$$= \left(\frac{\partial S}{\partial U}dU + \frac{\partial S}{\partial V}dV + \frac{\partial S_0}{\partial U_0}dU_0 + \frac{\partial S_0}{\partial V_0}dV_0\right) +$$

$$+ \frac{1}{2!}\left(\frac{\partial^2 S}{\partial U^2}(dU)^2 + 2\frac{\partial^2 S}{\partial V \partial U}dUdV + \frac{\partial^2 S}{\partial V^2}(dV)^2 + \frac{\partial^2 S_0}{\partial U_0^2}(dU_0)^2 + 2\frac{\partial^2 S_0}{\partial V_0 \partial U_0}dU_0dV_0 + \frac{\partial^2 S_0}{\partial V_0^2}(dV_0)^2\right) + \frac{1}{3!}...$$

$$= \left[\left(\frac{1}{T} - \frac{1}{T_0}\right)dU + \left(\frac{p}{T} - \frac{p_0}{T_0}\right)dV\right] +$$

$$+ \frac{1}{2!}\left[\left(\frac{\partial \frac{1}{T}}{\partial U} + \frac{\partial \frac{1}{T_0}}{\partial U_0}\right)(dU)^2 + 2\left(\frac{\partial \frac{1}{T}}{\partial V} - \frac{\partial \frac{1}{T_0}}{\partial V_0}\right)dUdV + \left(\frac{\partial \frac{p}{T}}{\partial V} + \frac{\partial \frac{p_0}{T_0}}{\partial V_0}\right)(dV)^2\right] + \frac{1}{3!}... \qquad (11)$$

with the following interpretation. The first bracket, where the relations $dU=-dU_0$ and $dV=-dV_0$ have been introduced, has been described above: it implies that at equilibrium $T=T_0$ and $p=p_0$, and consequently $dS_{univ}=0$. The second bracket, where the relations $dU=-dU_0$, $(dU)^2=(dU_0)^2$, $dV=-dV_0$, and $(dV)^2=(dV_0)^2$ have been introduced, is a quadratic form that must be negative definite because $d^2S_{univ}<0$, what implies in the first term:

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$$\left.\frac{\partial\frac{1}{T}}{\partial U}\right|_V + \left.\frac{\partial\frac{1}{T_0}}{\partial U_0}\right|_V = \left.\frac{-1}{T^2}\frac{\partial T}{\partial U}\right|_V + \left.\frac{-1}{T_0^2}\frac{\partial T_0}{\partial U_0}\right|_{V_0} = \frac{-1}{mc_vT^2} + \frac{-1}{m_0c_vT_0^2} \overset{T=T_0}{=} \frac{-1}{mc_vT^2}\left(1+\frac{m}{m_0}\right) < 0\ (12)$$

and similarly

$$\left.\frac{\partial\frac{p}{T}}{\partial V}\right|_U + \left.\frac{\partial\frac{p_0}{T_0}}{\partial V_0}\right|_U = \frac{-1}{m\kappa}\left(\frac{1}{vT} + \frac{(\kappa p - \alpha T)^2}{c_v\kappa T^2}\right)\left(1+\frac{m}{m_0}\right) < 0 \tag{13}$$

which implies $c_v>0$ and $\kappa>0$, as presented above.

LE CHÂTELIER PRINCIPLE

A general conclusion on system stability can be formulated in terms of a generalised Le Châtelier Principle like that: "if a system is perturbed in one of its state variables, the system responds trying to counterbalance the effect and regain the initial equilibrium" (if the system cannot come back to the initial state, it is said to be unstable; all systems become unstable against large enough perturbations).

GENERAL STABILITY OF THERMODYNAMIC SYSTEMS

For generic thermodynamic systems whose fundamental energy equation is $dU=\sum x_i dX_i$, the following relations apply:

- Derivatives of any intensive variable, x_i, with respect to its extensive corresponding variable, X_i, are always positive for any process that keeps constant the rest of extensive variables or their conjugates:

$$\left.\frac{\partial x_i}{\partial X_i}\right|_{X_j \text{ or } x_j} > 0, \quad \text{e.g.:}\quad \left.\frac{\partial T}{\partial S}\right|_V = \frac{T}{mc_V} > 0, \quad \left.\frac{\partial T}{\partial S}\right|_p = \frac{T}{mc_p} > 0, \quad \left.\frac{\partial(-p)}{\partial V}\right|_S = \frac{1}{m\kappa_S} > 0, \quad \left.\frac{\partial(-p)}{\partial V}\right|_T = \frac{1}{m\kappa} > 0$$

$$(14)$$

- From the two analogue derivatives, i.e. the ones that only differ in the conjugate variable kept constant, the one where the extensive variable is kept constant is larger than the other:

$$\left.\frac{\partial x_i}{\partial X_i}\right|_{X_j} > \left.\frac{\partial x_i}{\partial X_i}\right|_{x_j} > 0, \quad \text{e.g.:}\quad \left.\frac{\partial T}{\partial S}\right|_V > \left.\frac{\partial T}{\partial S}\right|_p > 0 \to c_p > c_V > 0, \quad \left.\frac{\partial(-p)}{\partial V}\right|_S > \left.\frac{\partial(-p)}{\partial V}\right|_T > 0 \to \kappa > \kappa_S > 0$$

$$(15)$$

In fact, it can easily be demonstrated that:

$$\gamma \equiv \frac{c_p}{c_V} = \frac{\kappa}{\kappa_S} \tag{16}$$

As example of $dU=\sum x_i dX_i$ equations, a list of terms are here added to the thermal and compressibility terms, TdS and $-pdV$: $dU=TdS-pdV+\sum\mu_i dn_i+\sigma dA+FdL-Md\theta+EdP+HdM+VdQ+\sum\tau_i d(V_0\varepsilon_i)$; i.e. the chemical terms for each species $\sum\mu_i dn_i$, a surface tension term σdA, a linear stretching term FdL, a torsional twisting term $-Md\theta$, an electrical polarization term EdP, a magnetic induction term HdM, an electrical capacitance term VdQ, and the elastic terms $\sum\tau_i d(V_0\varepsilon_i)$, where τ_i and ε_i are the six components of the stress and strain tensors (that are symmetric), and V_0 the volume of the undeformed solid..

The consequences of system stability can be then stated as follows:

- Thermal stability. At equilibrium, T, c_v, c_p and γ have to be positive, with $c_p>c_v$ and $\gamma>1$.
- Mechanical stability. At equilibrium, p, κ and κ_S have to be positive, with $\kappa>\kappa_S$.
- Chemical stability. At equilibrium, the chemical potential of each species increases monotonically with its concentration, since from (9) $\partial\mu_i/\partial n_i|_{U,V}>0$.

A statement of the stability criteria is second differential of equilibrium entropy in terms of its main variables has a negatively-defined quadratic form:

$$d^2s=\begin{bmatrix}du & dv\end{bmatrix}\begin{bmatrix}s_{uu} & s_{uv}\\ s_{vu} & s_{vv}\end{bmatrix}\begin{bmatrix}du\\ dv\end{bmatrix}<0 \quad\rightarrow\quad \begin{bmatrix}\dfrac{-1}{c_vT^2} & \dfrac{\alpha T-\kappa p}{c_v\kappa T^2}\\[3mm] \dfrac{\alpha T-\kappa p}{c_v\kappa T^2} & \dfrac{-1}{\kappa}\left(\dfrac{1}{vT}+\dfrac{(\alpha T-\kappa p)^2}{c_v\kappa T^2}\right)\end{bmatrix}<0\ (17)$$

Another similar statement can be cast in terms of the internal energy variations for a constant entropy and constant volume system:

$$d^2u=\begin{bmatrix}ds & dv\end{bmatrix}\begin{bmatrix}u_{ss} & u_{sv}\\ u_{vs} & u_{vv}\end{bmatrix}\begin{bmatrix}ds\\ dv\end{bmatrix}>0 \quad\rightarrow\quad \begin{bmatrix}\dfrac{T}{c_v} & \dfrac{-\alpha T}{c_v\kappa}\\[3mm] \dfrac{-\alpha T}{c_v\kappa} & \dfrac{\gamma}{\kappa v}\end{bmatrix}>0 \qquad\qquad (18)$$

However, extrapolation to other thermodynamic potentials may be chocking. For instance, for a subsystem undergoing an evolution at constant temperature and pressure in the presence of a much larger subsystem, the whole being isolated, the potential that governs the process is Gibbs function of the small system, $G(T,p)=U+pV-TS$, with $dG=-SdT+Vdp$. If the small system is displaced from equilibrium, the evolution, constrained as always by increasing the entropy of the universe, $dS_{univ}=dS+dS_0>0$, now is equivalent to $dG<0$, as can be easily demonstrated since $dS_{univ}=dS+dS_0=dS+(dU_0+p_0dV_0)/T_0=dS-(dU_0+pdV_0)/T=-dG/T>0$. But, contrary to the former potentials S and U, now it is $dG/dt<0$ and $d^2G/dt^2<0$, instead of e.g. $dU/dt<0$ and $d^2U/dt^2>0$, as shown in Fig. 3, i.e. $dG=-TdS_{univ}<0$ but also $d^2G=TdS^2_{univ}<0$.
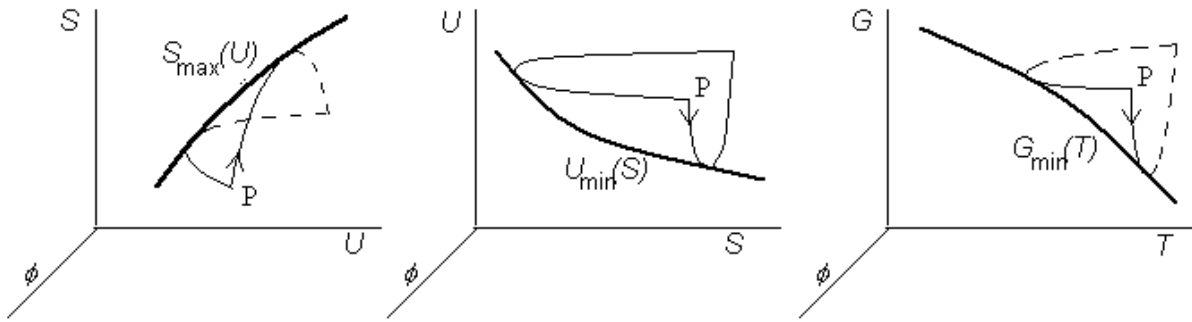
Fig. 3. Differences between 'extremisation' of different thermodynamic potentials. ϕ is an unspecified non-equilibrium parameter (e.g. the mean temperature gradient). The arrow shows the direction of evolution with time from a non-equilibrium state, P, towards the equilibrium state (a extremum in the potential).

and consequently, the second variation is now:

$$d^2 g = \begin{bmatrix} dT & dp \end{bmatrix} \begin{bmatrix} g_{TT} & g_{Tp} \\ g_{pT} & g_{pp} \end{bmatrix} \begin{bmatrix} dT \\ dp \end{bmatrix} < 0 \quad \rightarrow \quad \begin{bmatrix} -\dfrac{c_p}{T} & \alpha v \\ \alpha v & -\kappa p \end{bmatrix} < 0 \tag{19}$$

REFERENCES

1. Kondepudi, D., Prigogine, I., "Modern Thermodynamics", John Wiley & Sons, 1998.
2. Callen, H.B., "Thermodynamics", John Wiley and Sons, 1960.
3. Diu, B., Guthmann, C., Kederer, D., Roulet, B., "Macroscopic motion of a totally isolated system in statistical equilibrium", Am. J. Phys. 58 (10), 1990.

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