

PRINCIPAL EQUATIONS OF STATE AND THEIR RELATION TO THE SECOND LAW AND TO THERMODYNAMIC GEOMETRY OPTIMIZATION

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EXTENDED ABSTRACT

Functions, not dynamical equations, are the definitive mathematical objects in equilibrium thermodynamics. However, more than one function is often described as “the” equation of state for any one physical system. Usually these so named equations only capture incomplete physical content in the relationships between thermodynamic variables, while other equations, no less worthy of the name equation of state, go inconsistently by other names. While this approach to terminology can be bewildering to newcomers, it also obscures crucial properties of thermodynamic systems generally. We introduce specific principal equations of state and their complements for ideal gases, photons, and neutrinos that have the complete thermodynamic content from which all other forms can be easily deduced. The Gibbs equation and the Gibbs-Duhem equation,

$$\begin{aligned}dU &= TdS - PdV + \sum_i \mu_i dN_i \\0 &= SdT - VdP + \sum_i \mu_i N_i d\mu_i\end{aligned}$$

can be solved to yield these principal and complementary principal equations of state,

$$\begin{aligned}U &= f(S, V, N_1, N_2, \dots) \\0 &= g(T, P, \mu_1, \mu_2, \dots).\end{aligned}$$

These principal equations of state make properties like the second law of thermodynamics and local thermodynamic equilibrium completely visual (see the figure). The second law requires that the principal equation of state function is convex (bandshell-like surface) and that it scales linearly with the amount of material (green rays). This requirement must obviously also be satisfied by approximate equations of state. Superposition of states ($S(\mathbf{r}_1) + S(\mathbf{r}_2)$) along with the convexity provides the entropy generation resulting from equilibration of the states (short thick vertical red line).

Further, these principal equations of state are the foundation of thermodynamic geometry from which bounds on the exergy lost in a process or the entropy generated in the process can be derived. These bounds, e.g.

$$\Delta A \geq \frac{L^2 \varepsilon}{\tau}$$

are stronger than the conventional bounds stating that the losses must be non-negative, $\Delta A \geq 0$, and they factor nicely into a thermodynamic distance L from initial to final state based on equilibrium quantities, a factor ε describing the relaxation time when the system is disturbed, and finally the duration τ allowed for the process. This is possible only when the complete set of independent extensive variables is used.

Whereas the principal equation of state is given in terms of all the extensive variables of the system, the complementary principal equation of state is formulated in the set of intensive variables only. One loses the property of system scale in these variables, but that makes them naturally suited for envisioning the distinction between global and local thermodynamic equilibrium. All local equilibria of a system would occur at a single point for a particular physical system in global thermodynamic equilibrium. But out of equilibrium, when local equilibrium still makes sense, the local equilibria spread out to become a cloud of points. The extent of that cloud naturally defines a quality for global equilibrium in any system purported to be in equilibrium overall.

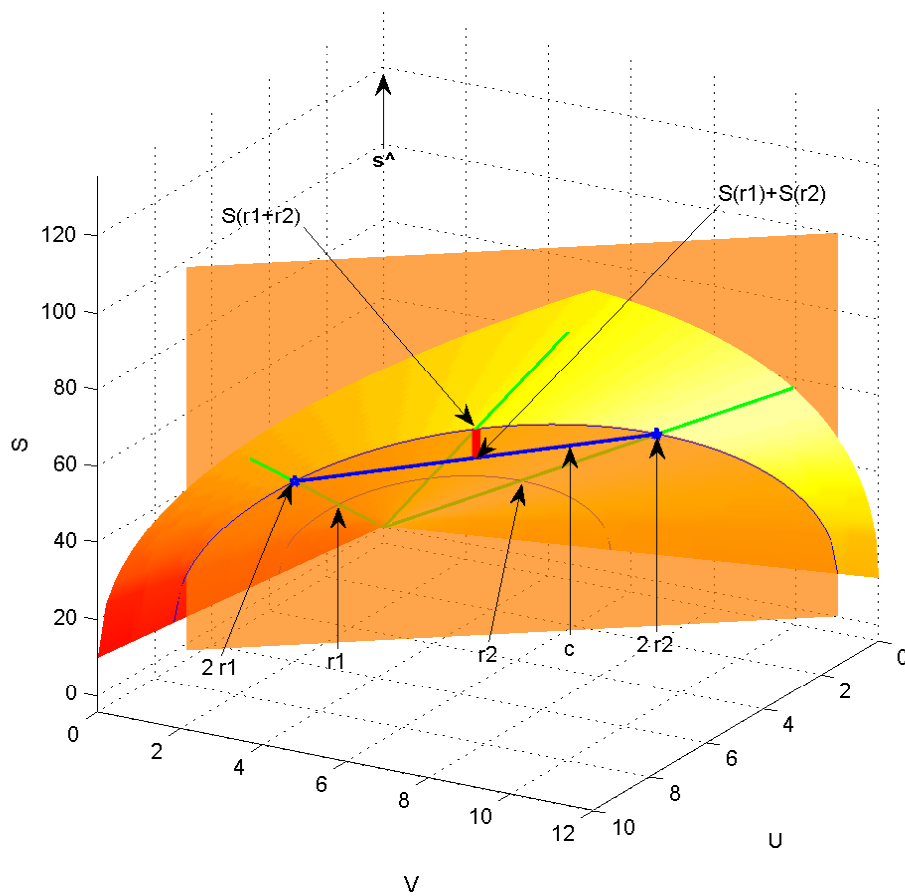


Figure. Equilibrium surface $S(U, V)$ (shaded bandshell-like surface). The green rays emanating from the origin represent equivalent equilibrium states, differing only in magnitude, e.g. states \mathbf{r}_1 and $2\mathbf{r}_1$. The vector \mathbf{c} (thick blue line) is a chord connecting the two equilibrium points $2\mathbf{r}_1$ and $2\mathbf{r}_2$ on the equilibrium surface but otherwise being under the surface and thus passing through non-equilibrium states. The equilibrated mixture of \mathbf{r}_1 and \mathbf{r}_2 is indicated as $S(\mathbf{r}_1 + \mathbf{r}_2)$ and the entropy produced in the equilibration is shown as the thick red line.