Thermodynamic stability

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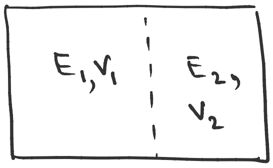
Thermodynamic stability and le Chatelier Principle

Consider a microcanonical system: In a homogeneous state, thermodynamics



is given by the entropy $S(E,V,N)$, where E is total energy V is total volume and N is total number of particles.

Imagin two subsystems of volume $V_1 = \alpha V$ and $V_2 = (1-\alpha)V$.

In the equilibrium state, Energy is homogeneously distributed and the entropy density of the total system $s(e) = \frac{1}{V} S(E,V)$ [We ignore N for simplicity]

Imagin an inhomogeneous state where energy density $e_1 = \frac{E_1}{V_1} \neq e_2 = \frac{E_2}{V_2}$ in the two subsystems are not same. Entropy corresponding to that inhomogeneous state is

$$\boxed{V_1 s(e_1) + V_2 s(e_2) \leq V s(\underbrace{\alpha e_1 + (1-\alpha) e_2}_{E/V \text{ with } E = E_1 + E_2.})}$$

This is because entropy in the homogeneous equilibrium state is maximum.

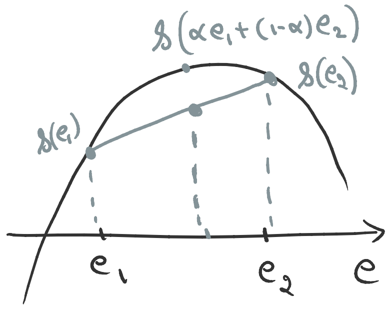
Rewriting the equation we get

$$\boxed{\alpha s(e_1) + (1-\alpha) s(e_2) \leq s\left(\alpha e_1 + (1-\alpha) e_2\right)}$$

This means entropy is a concave function of energy density.

An immediate consequence of this is that

$$s''(e) \leq 0$$



By definition, $s'(e) = \frac{1}{T}$

and $s''(e) = -\frac{1}{T^2} \cdot \frac{\partial T}{\partial e} = -\frac{1}{T^2 c_v}$

gives $\boxed{c_v \geq 0}$

This result came out from a therodynamic consideration that any spontaneous fluctuation does not destabilize a homogeneous equilibrium state.

If a fluctuation makes energy density in a subsystem increase, then $c_v > 0$ means temp is higher, and energy flows out to decrease the temp. Had c_v was negative energy difference would have constantly grown, making the homogeneous state unstable. Similar statement applies for other response functions like compressibility, susceptibility etc.

The stability of thermodynamic state is summarized in the following statement.

le Chatelier's principle: "If a system is in a stable equilibrium, then spontaneous change of its parameters must bring about processes which tend to restore system to equilibrium."

[for you to think: the argument uses statistical independance of two subsystems. What happens near criticality, or for systems with long range interactions?]