

CHM 421/621

Statistical Mechanics

Lecture 14 Stability of Thermodynamic Systems

Introduction and Review

Lecture Plan

Review of Thermodynamics

Basic Formalism

Conditions of Equilibrium

Equilibrium Relations

Legendre Transformed Representations

Stability of Thermodynamic Systems

Stability of Thermodynamic Systems

Stability criteria

Consider two identical subsystems, each with a fundamental equation $S \equiv S(U, V, N)$ separated by a totally restrictive wall.

We expect, from our considerations before, that even if the wall were made adiabatic the subsystems should be in equilibrium.

Hence, if the transfer of energy (through heat) is allowed then the criterion for stability of the system is

$$S(U + \Delta U, V, N) + S(U - \Delta U, V, N) \leq 2S(U, V, N)$$

i.e. the entropy is concave w.r.t. U

In the limit of the energy transferred being infinitesimal we get the (weaker) condition

$$\left(\frac{\partial^2 S}{\partial U^2} \right)_{V, N} \leq 0$$

Stability of Thermodynamic Systems

Stability criteria

Similarly, if the restrictive wall is made movable then the condition that no volume change occurs is

$$S(U, V + \Delta V, N) + S(U, V - \Delta V, N) \leq 2S(U, V, N)$$

i.e. the entropy is concave w.r.t. V

In the limit of the volume change being infinitesimal we get the (weaker) condition

$$\left(\frac{\partial^2 S}{\partial V^2} \right)_{U, N} \leq 0$$

Stability of Thermodynamic Systems

Local criterion

In general, for arbitrary changes in extensive parameters, for instance in U and V , we have

$$\begin{aligned} S(U + \Delta U, V + \Delta V, N) + S(U - \Delta U, V - \Delta V, N) \\ \leq 2S(U, V, N) \end{aligned}$$

Locally, this translates to the following conditions

$$\left(\frac{\partial^2 S}{\partial U^2} \right)_{V,N} \leq 0$$

$$\left(\frac{\partial^2 S}{\partial V^2} \right)_{U,N} \leq 0$$

$$\frac{\partial^2 S}{\partial U^2} \frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial U \partial V} \right)^2 \geq 0$$

Physically, these local stability conditions ensure that:

- (a) inhomogeneities of either u or v separately do not increase the entropy, and
- (b) also that a coupled inhomogeneity of u and v together does not increase the entropy.

Generally, entropy surface should lie everywhere below its family of tangent planes.

Stability of Thermodynamic Systems

Physical significance of stability criteria

For a thermodynamically stable system the specific heat at constant volume **must** always be positive.

Why?

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} = -\frac{1}{T^2} \left(\frac{\partial T}{\partial U}\right)_{V,N} = -\frac{1}{NT^2 c_v} \leq 0$$
$$\implies c_v \geq 0$$

Stability of Thermodynamic Systems

Isentropic partitioning

An unstable curve could be obtained in experimental measurements, data extrapolation or from statistical mechanics.

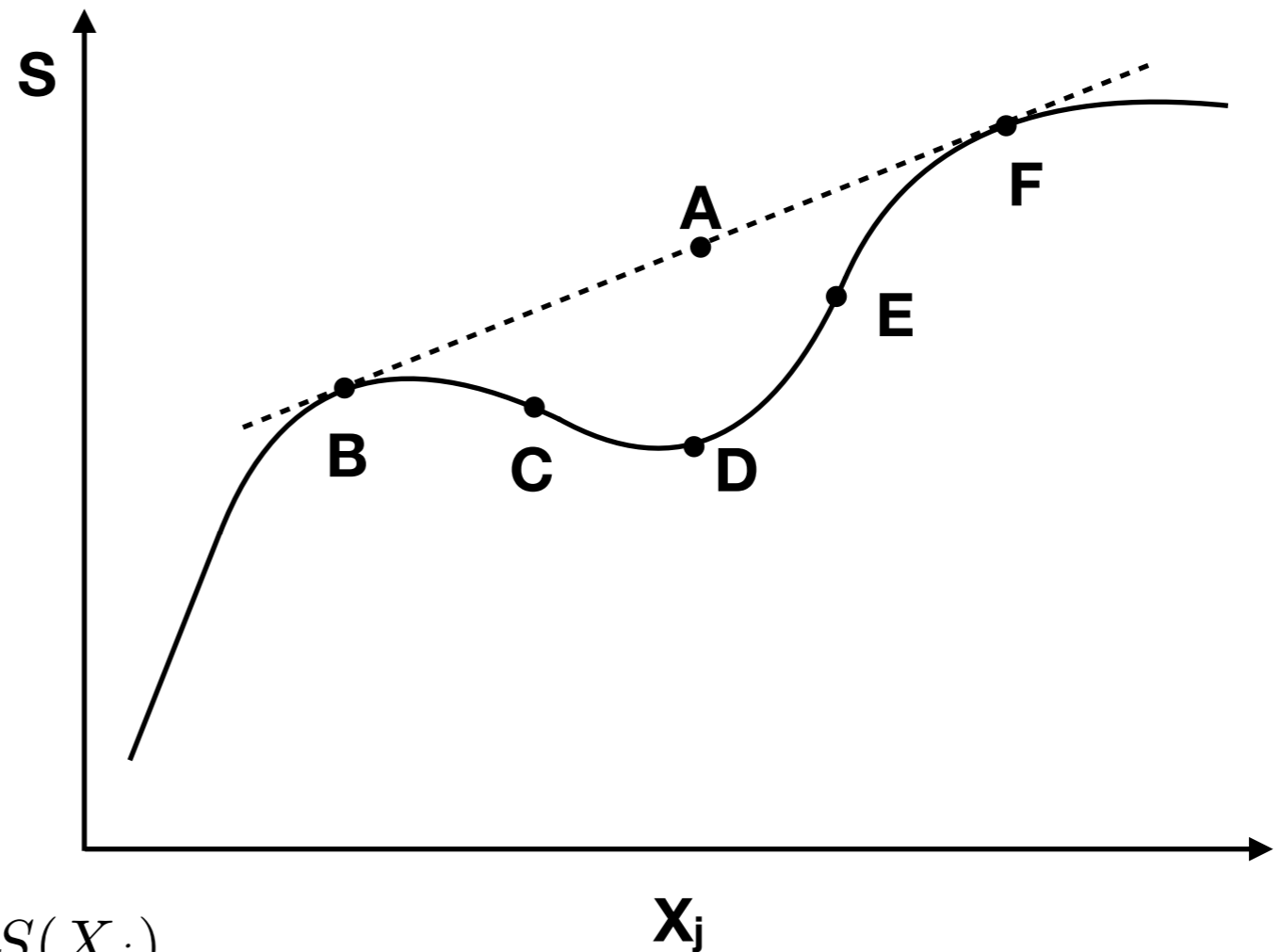
A stable equation can be constructed from these by drawing *superior tangents*.

At any point (A) along these lines

$$S(X_j + \Delta X) + S(X_j - \Delta X) = 2S(X_j)$$

Or, equivalently

$$\left(\frac{\partial^2 S}{\partial X_j^2} \right) = 0 \quad \Rightarrow \text{Phase separation into } \mathbf{B} \text{ and } \mathbf{F}$$



Stability of Thermodynamic Systems

Stability criteria for thermodynamic potentials

Similar criteria can be derived for the other potentials

$$U(S + \Delta S, V + \Delta V, N) + U(S - \Delta S, V - \Delta V, N) \geq 2U(S, V, N)$$

i.e. the stable energy surface should lie above its target planes (convex).

Locally this leads to

$$\begin{aligned}\frac{\partial^2 U}{\partial S^2} &= \frac{\partial T}{\partial S} \geq 0 \\ \frac{\partial^2 U}{\partial V^2} &= -\frac{\partial P}{\partial V} \geq 0 \\ \frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \frac{\partial^2 U}{\partial S \partial V} &\leq 0\end{aligned}$$

Stability of Thermodynamic Systems

Stability criteria for thermodynamic potentials

These results can be extended easily to the Legendre transforms of the energy.

$$P_j = \frac{\partial U}{\partial X_j} \quad X_j = -\frac{\partial U[P_j]}{\partial P_j}$$
$$\implies \frac{\partial X_j}{\partial P_j} = -\frac{\partial^2 U[P_j]}{\partial P_j^2} = 1 / \frac{\partial^2 U}{\partial X_j^2}$$

Thus, the sign of $\frac{\partial^2 U[P]}{\partial P^2}$ is opposite to the sign of $\frac{\partial^2 U}{\partial X^2}$

i.e., if U is a convex function of X then $U[P]$ is a concave function of P .

Stability of Thermodynamic Systems

Stability criteria for thermodynamic potentials

Thus, for Helmholtz potential we have, since $F = U[T]$,

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} \leq 0 \quad \left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} \geq 0$$

For Enthalpy we have, since $H = U[P]$,

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} \geq 0 \quad \left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} \leq 0$$

For Gibbs free energy we have, since $G = U[P, T]$,

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \leq 0 \quad \left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \leq 0$$

Therefore, for constant N , the thermodynamic potentials are concave functions of their extensive variables and convex functions of their intensive variables.

Stability of Thermodynamic Systems

Physical significance of stability criteria

The isothermal compressibility of a stable thermodynamic system **must** always be positive. i.e. $\kappa_T > 0$

Why?

You can also show that

$$c_P \geq c_v \geq 0$$

$$\kappa_T \geq \kappa_S \geq 0$$

Home-work