PHY 770 -- Statistical Mechanics
12:30-1:45 PM TR Olin 107

Instructor: Natalie Holzwarth (Olin 300)
Course Webpage: http://www.wfu.edu/~natalie/s14phy770

Lecture 5 -- Chapter 3
Review of Thermodynamics – continued

1. **Continue the analysis of thermodynamic stability**
2. **Examples**

PHY 770 Statistical Mechanics

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Instructor: Natalie Holzwarth	Phone:758-5510	Office:300 OPL	e-mail:natalie@wfu.edu

Course schedule for Spring 2014

(Preliminary schedule -- subject to frequent adjustment.) Please note that makeup lectures (indicated in red) are scheduled for Tuesdays or Thursdays at 11 AM - 12:15 PM in Olin 107.

	Lecture date	Text Reading	Topic	Assign.	Due date
1	Tue: 01/14/2014	Chap. 3	Review of macroscopic thermodynamics	#1	02/04/2014
2	Thu: 01/16/2014	Chap. 3	Review of macroscopic thermodynamics	#2	02/04/2014
3	Tue: 01/21/2014	Chap. 3	Thermodynamic potentials	#3	02/04/2014
4	Tue: 01/21/2014	Chap. 3	Thermodynamic stability	#4	02/04/2014
5	Thu: 01/23/2014	Chap. 3	Thermodynamic stability	#5	02/04/2014
	Tue: 01/28/2014		NAWH out of town - no class		
	Thu: 01/30/2014		NAWH out of town - no class		
6	Tue: 02/04/2014	Chap. 3			02/06/2014

Summary of thermodynamic potentials

Potential	Variables	Total Diff	Fund. Eq.
U	S,X,N_i	$dU = TdS + YdX + \sum_i \mu_i dN_i$	$U = TS + YX + \sum_i \mu_i N_i$
H	S,Y,N_i	$dH = TdS - XdY + \sum_i \mu_i dN_i$	$H = U - YX$
A	T,X,N_i	$dA = -SdT + YdX + \sum_i \mu_i dN_i$	$A = U - TS$
G	T,Y,N_i	$dG = -SdT - XdY + \sum_i \mu_i dN_i$	$G = U - TS - YX$
Ω	T,X,μ_i	$d\Omega = -SdT + YdX - \sum_i \mu_i dN_i$	$\Omega = U - TS - \sum_i \mu_i N_i$

Derivative relationships of thermodynamic potentials

Internal energy $U(S,X,\{N_i\})$:

$$T=\left(\frac{\partial U}{\partial S}\right)_{X,\{N_i\}} \qquad Y=\left(\frac{\partial U}{\partial X}\right)_{S,\{N_i\}} \qquad \mu_{\mathrm{i}}=\left(\frac{\partial U}{\partial N_i}\right)_{S,X,\{N_j\}}$$

Enthalpy $H(S,Y,\{N_i\})$:

$$T=\left(\frac{\partial H}{\partial S}\right)_{Y,\{N_i\}} \qquad X=\left(\frac{\partial H}{\partial Y}\right)_{S,\{N_i\}} \qquad \mu_{\mathrm{i}}=\left(\frac{\partial H}{\partial N_i}\right)_{S,Y,\{N_j\}}$$

Helmholz free energy $A(T,X,\{N_i\})$:

$$S=-\left(\frac{\partial A}{\partial T}\right)_{X,\{N_i\}} \qquad Y=\left(\frac{\partial A}{\partial X}\right)_{T,\{N_i\}} \qquad \mu_{\mathrm{i}}=\left(\frac{\partial A}{\partial N_i}\right)_{T,X,\{N_j\}}$$

Gibb's free energy $G(T,Y,\{N_i\})$:

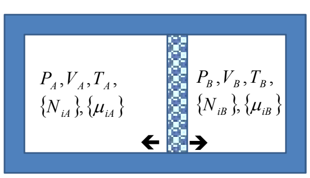
$$S=-\left(\frac{\partial G}{\partial T}\right)_{Y,\{N_i\}} \qquad X=-\left(\frac{\partial G}{\partial Y}\right)_{T,\{N_i\}} \qquad \mu_{\mathrm{i}}=\left(\frac{\partial G}{\partial N_i}\right)_{T,Y,\{N_j\}}$$

Equilibrium properties of thermodynamic potentials

At equilibrium *dS*→*0* and *S*→maximum

At equilibrium *dU*→*0* and *U(S,X,{N$_i$})*→minimum
At equilibrium *dH*→*0* and *H(S,Y,{N$_i$})*→minimum
At equilibrium *dA*→*0* and *A(T,X,{N$_i$})*→minimum
At equilibrium *dG*→*0* and *G(T,Y,{N$_i$})*→minimum
At equilibrium *dΩ*→*0* and *Ω(T,X,{μ$_i$})*→minimum

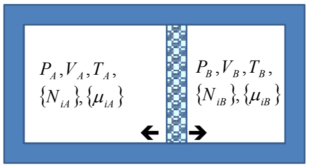
Stability analysis of the equilibrium state



$$\Delta U_A = -\Delta U_B$$
$$\Delta V_A = -\Delta V_B$$
$$\Delta N_{iA} = -\Delta N_{iB}$$

Assume that the total system is isolated, but that there can be exchange of variables *A* and *B*.

Stability analysis of the equilibrium state



If we can assume :

$\Delta U_A = -\Delta U_B$

$\Delta V_A = -\Delta V_B$

$\Delta N_{iA} = -\Delta N_{iB}$

Analysis of entropy fluctuations :

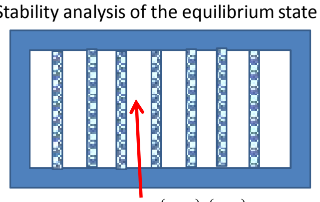
$$\Delta S_{total} = \sum_{\alpha = A,B} \left[\left(\frac{\partial S_\alpha}{\partial U_\alpha} \right) \Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha} \right) \Delta V_\alpha + \sum_i \left(\frac{\partial S_\alpha}{\partial N_{i\alpha}} \right) \Delta N_{i\alpha} \right]$$

$$= \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \Delta U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B} \right) \Delta V_A + \sum_i \left(\frac{\mu_{iA}}{T_A} - \frac{\mu_{iB}}{T_B} \right) \Delta N_{iA}$$

At equilibrium : $T_A = T_B, \quad P_A = P_B, \quad \mu_{iA} = \mu_{iB}$

Note that this result does not hold for non-porous partition.

Stability analysis of the equilibrium state – multi-partioned box



$P_\alpha, V_\alpha, T_\alpha, \{N_{i\alpha}\}, \{\mu_{i\alpha}\}$

Entropy fluctuations in partition α near equilibrium :

$$S_\alpha(U_\alpha, V_\alpha, \{N_{i\alpha}\}) = S_\alpha^0(U_\alpha^0, V_\alpha^0, \{N_{i\alpha}^0\}) +$$
$$+ \text{(first order fluctuations)}$$
$$+ \text{(second order fluctuations)} + \quad .....$$

Stability analysis of the equilibrium state – multi-partioned box

Entropy fluctuations in partition α near equilibrium :

$$S_\alpha(U_\alpha, V_\alpha, \{N_{i\alpha}\}) = S_\alpha^0(U_\alpha^0, V_\alpha^0, \{N_{i\alpha}^0\}) +$$
$$+ \text{(first order fluctuations)}$$
$$+ \text{(second order fluctuations)} + \quad .....$$

(first order fluctuations) =

$$\left(\frac{\partial S_\alpha}{\partial U_\alpha} \right)^0 \Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha} \right)^0 \Delta V_\alpha + \sum_i \left(\frac{\partial S_\alpha}{\partial N_{i\alpha}} \right)^0 \Delta N_{i\alpha}$$

(second order fluctuations) =

$$\frac{1}{2} \left\{ \Delta \left(\frac{\partial S_\alpha}{\partial U_\alpha} \right) \Delta U_\alpha + \Delta \left(\frac{\partial S_\alpha}{\partial V_\alpha} \right) \Delta V_\alpha + \sum_i \Delta \left(\frac{\partial S_\alpha}{\partial N_{i\alpha}} \right) \Delta N_{i\alpha} \right\}$$

Stability analysis of the equilibrium state – multi-partioned box

(second order fluctuations) =

$$\frac{1}{2}\left\{ \Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)\Delta U_\alpha + \Delta\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)\Delta V_\alpha + \sum_i \Delta\left(\frac{\partial S_\alpha}{\partial N_{i\alpha}}\right)\Delta N_{i\alpha} \right\}$$

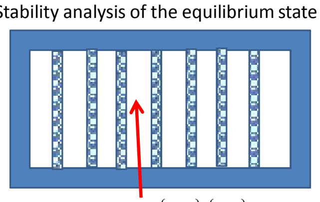
notation :

$$\Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right) \equiv \left(\frac{\partial^2 S_\alpha}{\partial U_\alpha{}^2}\right)^0 \Delta U_\alpha + \left(\frac{\partial^2 S_\alpha}{\partial V_\alpha \partial U_\alpha}\right)^0 \Delta V_\alpha + \sum_i \left(\frac{\partial^2 S_\alpha}{\partial N_{i\alpha}\partial U_\alpha}\right)^0 \Delta N_{i\alpha}$$

$$\Delta\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right) \equiv \left(\frac{\partial^2 S_\alpha}{\partial V_\alpha{}^2}\right)^0 \Delta V_\alpha + \left(\frac{\partial^2 S_\alpha}{\partial U_\alpha \partial V_\alpha}\right)^0 \Delta U_\alpha + \sum_i \left(\frac{\partial^2 S_\alpha}{\partial N_{i\alpha}\partial V_\alpha}\right)^0 \Delta N_{i\alpha}$$

$$\Delta\left(\frac{\partial S_\alpha}{\partial N_{i\alpha}}\right) \equiv \left(\frac{\partial^2 S_\alpha}{\partial V_\alpha \partial N_{i\alpha}{}^2}\right)^0 \Delta V_\alpha + \left(\frac{\partial^2 S_\alpha}{\partial U_\alpha \partial N_{i\alpha}}\right)^0 \Delta U_\alpha + \sum_j \left(\frac{\partial^2 S_\alpha}{\partial N_{j\alpha}\partial N_{i\alpha}}\right)^0 \Delta N_{j\alpha}$$

Stability analysis of the equilibrium state – multi-partioned box



$P_\alpha, V_\alpha, T_\alpha, \{N_{i\alpha}\}, \{\mu_{i\alpha}\}$

Entropy fluctuations total box near equilibrium :

ΔS_{total} = (first order fluctuations) + (second order fluctuations) + ...

0

(second order fluctuations) =

$$\sum_\alpha \frac{1}{2}\left\{ \Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)\Delta U_\alpha + \Delta\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)\Delta V_\alpha + \sum_i \Delta\left(\frac{\partial S_\alpha}{\partial N_{i\alpha}}\right)\Delta N_{i\alpha} \right\}$$

Stability analysis of the equilibrium state – multi-partioned box

Entropy fluctuations total box near equilibrium :

ΔS_{total} = (second order fluctuations) + ...

(second order fluctuations)

$$= \sum_\alpha \frac{1}{2}\left\{ \Delta\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)\Delta U_\alpha + \Delta\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)\Delta V_\alpha + \sum_i \Delta\left(\frac{\partial S_\alpha}{\partial N_{i\alpha}}\right)\Delta N_{i\alpha} \right\}$$

$$= \sum_\alpha \frac{1}{2}\left\{ \Delta\left(\frac{1}{T}\right)_\alpha \Delta U_\alpha + \Delta\left(\frac{P}{T}\right)_\alpha \Delta V_\alpha + \sum_i \Delta\left(\frac{\mu_i}{T}\right)_\alpha \Delta N_{i\alpha} \right\}$$

Noting that : $T\Delta S = \Delta U + P\Delta V - \sum_i \mu_i \Delta N_i$

$$\Rightarrow \Delta S_{total} = -\frac{1}{2T}\sum_\alpha \left\{ \Delta T_\alpha \Delta S_\alpha - \Delta P_\alpha \Delta V_\alpha + \sum_i \Delta\mu_{i\alpha}\Delta N_{i\alpha} \right\}$$

Stability analysis of the equilibrium state

Note that at equilibrium, S_{total} = *maximum*

➔ $\Delta S_{total} \leq 0$

$$\Delta S_{total} = -\frac{1}{2T}\sum_{\alpha}\left\{\underbrace{\Delta T_\alpha \Delta S_\alpha - \Delta P_\alpha \Delta V_\alpha + \sum_i \Delta\mu_{i\alpha}\Delta N_{i\alpha}}_{\geq 0}\right\}$$

After a few more steps --

$$\Delta S_{total} = -\frac{1}{2T}\sum_{\alpha}\left\{\left(\frac{\partial S}{\partial T}\right)^0_{V,\{N_i\}}\Delta T_\alpha^2 - \left(\frac{\partial P}{\partial V}\right)^0_{T,\{N_i\}}\Delta V_\alpha^2 + \sum_{i,j}\left(\frac{\partial \mu_j}{\partial N_i}\right)^0_{T,P,\{N_i\}}\Delta N_{i\alpha}\Delta N_{j\alpha}\right\}$$

Stability analysis of the equilibrium state -- continued

Le Chatelier's principle: If a system is in stable equilibrium, then any spontaneous charge in its parameters must bring about processes which tend to restore the system to equilibrium.

$$\Delta S_{total} = -\frac{1}{2T}\sum_{\alpha}\left\{\left(\frac{\partial S}{\partial T}\right)^0_{V,\{N_i\}}\Delta T_\alpha^2 - \left(\frac{\partial P}{\partial V}\right)^0_{T,\{N_i\}}\Delta V_\alpha^2 + \sum_{i,j}\left(\frac{\partial \mu_j}{\partial N_i}\right)^0_{T,P,\{N_i\}}\Delta N_{i\alpha}\Delta N_{j\alpha}\right\}$$

By assumption, the fluctuations of each variable is independent so that we can examine each term separately.

$$\left(\frac{\partial S}{\partial T}\right)^0_{V,\{N_i\}} \geq 0 \qquad \Rightarrow C_{V,\{N_i\}} = T\left(\frac{\partial S}{\partial T}\right)_{V,\{N_i\}} \geq 0$$

$$\left(\frac{\partial P}{\partial V}\right)^0_{T,\{N_i\}} \leq 0 \qquad \Rightarrow \kappa_{T,\{N_i\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\{N_i\}} \geq 0$$

Stability analysis of the equilibrium state -- continued

$$\Delta S_{total} = -\frac{1}{2T}\sum_{\alpha}\left\{\left(\frac{\partial S}{\partial T}\right)^0_{V,\{N_i\}}\Delta T_\alpha^2 - \left(\frac{\partial P}{\partial V}\right)^0_{T,\{N_i\}}\Delta V_\alpha^2 + \sum_{i,j}\left(\frac{\partial \mu_j}{\partial N_i}\right)^0_{T,P,\{N_i\}}\Delta N_{i\alpha}\Delta N_{j\alpha}\right\}$$

Contributions from fluctuations in the chemical potentials

$$\sum_{i,j}\left(\frac{\partial \mu_j}{\partial N_i}\right)^0_{T,P,\{N_i\}}\Delta N_{i\alpha}\Delta N_{j\alpha} \geq 0$$

$$\text{Define:}\quad \mathbf{M} \equiv \begin{pmatrix} m_{11} & m_{12} & \cdots & m_{1\nu} \\ m_{21} & m_{22} & \cdots & m_{2\nu} \\ \vdots & \vdots & \cdots & \vdots \\ m_{\nu 1} & m_{\nu 2} & \cdots & m_{\nu\nu} \end{pmatrix} \qquad \Rightarrow \mathbf{M} \text{ must be positive definite}$$

$$\text{where:}\quad m_{ij} \equiv \left(\frac{\partial \mu_j}{\partial N_i}\right)_{T,P,\{N_i\}} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,P,\{N_i\}}$$

Example 3.10 from Reichl:

Consider a system at constant *P,T* containing two kinds of particles A and B with the following form for the Gibbs free energy:

$$G(T,P,N_A,N_P) = N_A\mu_A^0 + N_B\mu_B^0 + kTN_A \ln\left(\frac{N_A}{N_A+N_B}\right) + kTN_B \ln\left(\frac{N_B}{N_A+N_B}\right) + \lambda\frac{N_A N_B}{N_A+N_B}$$