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 3-4* -- Chapter 3
Review of Thermodynamics – continued

1. **Properties of thermodynamic potentials**
2. **Response functions**
3. **Thermodynamic stability**

***Special double lecture, starting at 11 AM on 1/21/2014**

PHY 770 Statistical Mechanics

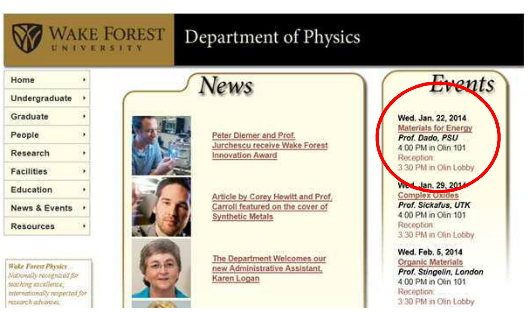
TR 12:30-1:45 PM | OPL 107 | http://www.wfu.edu/~natalie/s14phy770/

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			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



WFU Physics Colloquium

TITLE: Challenges in computational modeling of materials for energy: Understanding energy conversion and storage

SPEAKER: Professor Ismaila Dabo,

Department of Materials Science and Engineering, Penn State University

TIME: Wednesday January 22, 2014 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

Many advances in the understanding and design of nanomaterials have been enabled by spectroscopic methods of increasing spatial and temporal resolution. In electrochemistry, spectroscopy has delivered insight into the processes involved in harvesting, converting, and storing energy. In support to experiment, much progress has been achieved in the simulation of spectroscopic phenomena to shed light into energy conversion at the molecular scale. This understanding is critical to the nanoengineering of electrochemical cells, batteries, dye-sensitized solar cells and water-splitting photosystems. This talk will

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

$$T = \left(\frac{\partial U}{\partial S}\right)_{X,\{N_i\}} \quad Y = \left(\frac{\partial U}{\partial X}\right)_{S,\{N_i\}} \quad \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,X,\{N_j\}}$$

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

$$T = \left(\frac{\partial H}{\partial S}\right)_{Y,\{N_i\}} \quad X = \left(\frac{\partial H}{\partial Y}\right)_{S,\{N_i\}} \quad \mu_i = \left(\frac{\partial H}{\partial N_i}\right)_{S,Y,\{N_j\}}$$

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

$$S = -\left(\frac{\partial A}{\partial T}\right)_{X,\{N_i\}} \quad Y = \left(\frac{\partial A}{\partial X}\right)_{T,\{N_i\}} \quad \mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,X,\{N_j\}}$$

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

$$S = -\left(\frac{\partial G}{\partial T}\right)_{Y,\{N_i\}} \quad X = -\left(\frac{\partial G}{\partial Y}\right)_{T,\{N_i\}} \quad \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,Y,\{N_j\}}$$

Properties of thermodynamic potentials

"Potential" in the sense that energy can be stored and retrieved through thermodynamic work

Equalities ←→ reversible processes
Inequalities ←→ general processes

Entropy $$dS = \frac{đQ}{T} + d_i S$$

Reversible entropy contribution

Entropy production due to irreversible processes $d_i S \geq 0$

$$\Rightarrow dS \geq \frac{đQ}{T}$$

Inequalities associated with thermodynamic potentials – continued

Entropy

$$dS = \frac{đQ}{T} + d_i S$$

For a thermally isolated system: $đQ = 0$

$$dS = d_i S \geq 0$$

➔ At equilibrium when *dS=0* , *S* is a maximum

Inequalities associated with thermodynamic potentials – continued

Internal energy

Since $TdS \geq đQ = dU - YdX - \sum_i \mu_i dN_i$

$$dU \leq TdS + YdX + \sum_i \mu_i dN_i$$

For an isolated system with fixed S, X, and $\{N_i\}$

$$dU \leq 0$$

➔ At equilibrium when *dU=0* , *U* is a minimum (for fixed *S*, *X*, and $\{N_i\}$)

Inequalities associated with thermodynamic potentials – continued

Enthalpy

$$dH \leq TdS - XdY + \sum_i \mu_i dN_i$$

For an isolated system with fixed S, Y, and $\{N_i\}$

$$dH \leq 0$$

➔ At equilibrium when *dH=0* , *H* is a minimum
(for fixed *S*, *Y*, and $\{N_i\}$)

Inequalities associated with thermodynamic potentials – continued

Helmholz free energy

$$dA \leq -SdT + YdX + \sum_i \mu_i dN_i$$

For an isolated system with fixed T, X, and $\{N_i\}$

$$dA \leq 0$$

➔ At equilibrium when *dA=0* , *A* is a minimum
(for fixed *T*, *X*, and $\{N_i\}$)

Inequalities associated with thermodynamic potentials – continued

Gibbs free energy

$$dG \leq -SdT - XdY + \sum_i \mu_i dN_i$$

For an isolated system with fixed T, Y, and $\{N_i\}$

$$dG \leq 0$$

➔ At equilibrium when *dG=0* , *G* is a minimum
(for fixed *T*, *Y*, and $\{N_i\}$)

Inequalities associated with thermodynamic potentials – continued

Grand potential

$$d\Omega \leq -SdT + YdX + \sum_i N_i d\mu_i$$

For an isolated system with fixed T, X, and $\{\mu_i\}$

$$d\Omega \leq 0$$

➔ At equilibrium when $d\Omega = 0$, Ω is a minimum (for fixed T, X, and $\{\mu_i\}$)

Example:

Consider a system having a constant electrostatic potential ϕ at fixed T and P containing a fixed number of particles $\{N_i\}$ for $i=1,\ldots \nu-1$. Find the change in the Gibbs free energy when dN_ν particles, each with charge q_ν are reversibly added to the system.

$$dG = -SdT - VdP + \sum_{i=1}^{\nu-1} \mu_i dN_i + q_\nu \phi dN_\nu + \mu_\nu dN_\nu$$

For constant $T, P, \{N_i\}$:

$$dG = (q_\nu \phi + \mu_\nu) dN_\nu$$

Thermodynamic response functions -- heat capacity

$$C = \frac{đQ}{dT}$$

$$đQ = dU - YdX - \sum_i \mu_i dN_i$$

Assuming $U = U(T, X, \{N_i\})$:

$$đQ = \left(\frac{\partial U}{\partial T}\right)_{X,N_i} dT + \left(\left(\frac{\partial U}{\partial X}\right)_{T,N_i} - Y\right) dX + \sum_i \left(\left(\frac{\partial U}{\partial N_i}\right)_{T,X,N_j} - \mu_i\right) dN_i$$

For heat capacity at constant $X, \{N_i\}$:

$$C_{X,\{N_i\}} = \left(\frac{\partial U}{\partial T}\right)_{X,N_i}$$

Thermodynamic response functions -- heat capacity -- continued

$$C = \frac{đQ}{dT}$$

$$đQ = dU - YdX - \sum_i \mu_i dN_i$$

Assuming $U = U(T, X, \{N_i\})$:

$$đQ = \left(\frac{\partial U}{\partial T}\right)_{X,N_i} dT + \left(\left(\frac{\partial U}{\partial X}\right)_{T,N_i} - Y\right) dX + \sum_i \left(\left(\frac{\partial U}{\partial N_i}\right)_{T,X,N_j} - \mu_i\right) dN_i$$

For heat capacity at constant $Y, \{N_i\}$:

Note that : $dX = \left(\frac{\partial X}{\partial T}\right)_{Y,N_i} dT + \left(\frac{\partial X}{\partial Y}\right)_{T,N_i} dY + \sum_i \left(\frac{\partial X}{\partial N_i}\right)_{T,Y,N_j} dN_i$

At constant $Y, \{N_i\}$: $dX = \left(\frac{\partial X}{\partial T}\right)_{Y,N_i} dT$

$$đQ = \left(\frac{\partial U}{\partial T}\right)_{X,N_i} dT + \left(\left(\frac{\partial U}{\partial X}\right)_{T,N_i} - Y\right)\left(\frac{\partial X}{\partial T}\right)_{Y,N_i} dT$$

$$\Rightarrow C_{Y,\{N_i\}} = C_{X,\{N_i\}} + \left(\left(\frac{\partial U}{\partial X}\right)_{T,N_i} - Y\right)\left(\frac{\partial X}{\partial T}\right)_{Y,N_i}$$

Example: Heat capacity of ideal gas : $U = \sum_i \frac{N_i}{\gamma_i - 1} kT$

$$PV = \sum_i N_i kT$$

For heat capacity at constant $X \Leftrightarrow V, \{N_i\}$

$$C_{V,\{N_i\}} = \left(\frac{\partial U}{\partial T}\right)_{V,N_i}$$

$$\Rightarrow C_{V,\{N_i\}} = \sum_i \frac{N_i}{\gamma_i - 1} k$$

For heat capacity at constant $Y \Leftrightarrow -P, \{N_i\}$:

$$C_{P,\{N_i\}} = C_{V,\{N_i\}} + \left(\left(\frac{\partial U}{\partial V}\right)_{T,N_i} + P\right)\left(\frac{\partial V}{\partial T}\right)_{P,N_i}$$

$$= \sum_i \frac{N_i}{\gamma_i - 1} k + \sum_i N_i k = \sum_i \frac{\gamma_i N_i}{\gamma_i - 1} k$$

Thermodynamic response functions -- heat capacity -- continued

Alternate analysis in terms of S: $đQ = TdS$

Assuming $S = S(T, X, \{N_i\})$:

$$đQ = T\left(\left(\frac{\partial S}{\partial T}\right)_{X,N_i} dT + \left(\frac{\partial S}{\partial X}\right)_{T,N_i} dX + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{T,X,N_j} dN_i\right)$$

For heat capacity at constant $X, \{N_i\}$:

$$đQ = T\left(\frac{\partial S}{\partial T}\right)_{X,N_i} dT$$

$$C_{X,\{N_i\}} = T\left(\frac{\partial S}{\partial T}\right)_{X,\{N_i\}} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{X,\{N_i\}}$$

For heat capacity at constant $Y, \{N_i\}$:

(After some algebra --)

$$C_{Y,\{N_i\}} = T\left(\frac{\partial S}{\partial T}\right)_{Y,\{N_i\}} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{Y,\{N_i\}}$$

Thermodynamic response functions -- mechanical response
Results stated here without derivation:

Isothermal susceptiblity: $\chi_{T,\{N_i\}} = \left(\frac{\partial X}{\partial Y}\right)_{T,\{N_i\}} = -\left(\frac{\partial^2 G}{\partial Y^2}\right)_{T,\{N_i\}}$

Adiabatic susceptiblity: $\chi_{S,\{N_i\}} = \left(\frac{\partial X}{\partial Y}\right)_{S,\{N_i\}} = -\left(\frac{\partial^2 H}{\partial Y^2}\right)_{S,\{N_i\}}$

Thermal expansivity: $\alpha_{Y,\{N_i\}} = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_i\}}$

Relationships between response functions: $\frac{\chi_{T,\{N_i\}}}{\chi_{S,\{N_i\}}} = \frac{C_{Y,\{N_i\}}}{C_{X,\{N_i\}}}$

$$\chi_{T,\{N_i\}}\left(C_{Y,\{N_i\}} - C_{X,\{N_i\}}\right) = T\left(\alpha_{Y,\{N_i\}}\right)^2$$
$$C_{Y,\{N_i\}}\left(\chi_{T,\{N_i\}} - \chi_{T,\{N_i\}}\right) = T\left(\alpha_{Y,\{N_i\}}\right)^2$$

Thermodynamic response functions -- mechanical response
Typical parameters:

Isothermal susceptiblity ←→ isothermal compressibility

$$\kappa_{T,\{N_i\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\{N_i\}} = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,\{N_i\}}$$

Adiabatic susceptiblity ←→adiabatic compressibility

$$\kappa_{S,\{N_i\}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,\{N_i\}} = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,\{N_i\}}$$

Thermal expansivity←→ Thermal expansivity

$$\alpha_{P,\{N_i\}} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,\{N_i\}}$$

Example: mechanical responses for an ideal gas

For ideal gas: $U = \frac{N}{\gamma - 1}kT$

$PV = NkT$

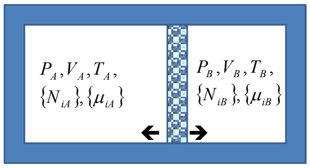
Isothermal compressibility: $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\{N_i\}} = \frac{1}{P}$

Adiabatic compressibility: $\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$

Note that: $PV^\gamma = P_0 V_0^\gamma \quad \Rightarrow \kappa_S = \frac{1}{\gamma P}$

Thermal expansivity: $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T}$

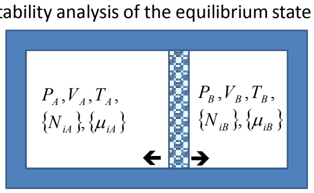
Stability analysis of the equilibrium state



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

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 fluctuatio ns :

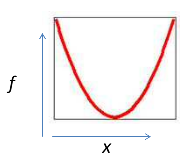
$$\Delta S_{total} = \sum_{\alpha=A,B}\left[\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)\Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)\Delta V_\alpha + \sum_i \left(\frac{\partial S_\alpha}{\partial N_{i\alpha}}\right)\Delta N_{i\alpha}\right]$$
$$= \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\Delta U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)\Delta V_A + \sum_i \left(\frac{\mu_{iA}}{T_A} - \frac{\mu_{iB}}{T_B}\right)\Delta N_{iA}$$

At equilibriu m : $T_A = T_B$, $P_A = P_B$, $\mu_{iA} = \mu_{iB}$

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

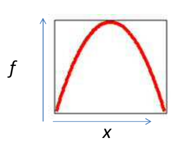
Stability analysis of the equilibrium state – continued

Note that the equilibrium condition can be a *stable* or *unstable* equilibrium.



Stable function (convex)

$$\frac{d^2 f}{dx^2} \geq 0$$



Unstable function (concave)

$$\frac{d^2 f}{dx^2} < 0$$

Stability analysis of the equilibrium state -- continued

Extending the analysis of entropy fluctuations in a multi - partitioned system :
analyzing leading second order terms

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

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

Using the first law relation and other identities :

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

the second order expansion becomes :

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