PHY 770 -- Statistical Mechanics
10-10:50 AM MWF Olin 107

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Lecture 2 -- Chapter 3
Review of Thermodynamics – continued

1. Some empirically obtained equations of state
2. Some properties of entropy
3. Thermodynamic potentials

Equations of state

Variable	Units
T (temperature)	**ºK**
P (pressure)	**Pa**
V (volume)	**m^3**
n (moles)	**$n=N/N_A$**
N (particles)	**$N=nN_A$**

Avogadro's number: N_A=**6.022 141 29 x 10^{23} mol^{-1}**
Boltzmann constant: k=**1.380 6488 x 10^{-23} J K^{-1}**
Molar gas contant: R=N_Ak=**8.314 4621 J mol^{-1} K^{-1}**
http://physics.nist.gov/cuu/Constants/index.html

Equations of State -- examples

	Range of validity
Ideal Gas Law $PV = nRT \equiv NkT$	**dilute limit; ignor particle interactions**
Virial expansion $P = \left(\frac{nRT}{V}\right)\left(1 + \frac{n}{V}B_2(T) + \frac{n^2}{V^2}B_3(T) + \ldots\right)$	**includes effects of higher density in terms of virial coefficients *B_i***
Van der Waals equation of state $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$	**approximates gases and liquids in terms of an excluded volume *nb* and a cohesion parameter *a***

Special properties of entropy

For a reversible process: $dS = \frac{đQ}{T}$

Thermo "laws" involving entropy

2. Heat flows spontaneously from high temperature to low temperature
3. It is not possible to reach the coldest temperature using a finite set of reversible steps

These relationships, together with the notion that entropy is an extensive and additive property leads to the

Fundamental equation of thermodynamics:

$$TS = U - XY - \sum_i \mu_i N_i$$

Fundamental equation of thermodynamics

internal energy; generalized displacement (V); chemical potential

$$TS = U - XY - \sum_i \mu_i N_i$$

generalized force ($-P$); number of particles

Derivation of fundamental equation of thermodynamics:

First law of thermodynamics for a reversible process:

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

$$dS = \frac{1}{T}dU - \frac{Y}{T}dX - \sum_i \frac{\mu_i}{T}dN_i$$

Derivation of fundamental equation of thermodynamics -- continued:

$$dS = \frac{1}{T}dU - \frac{Y}{T}dX - \sum_i \frac{\mu_i}{T}dN_i$$

also:

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

$$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_{X,N_i} = \frac{1}{T} \quad \left(\frac{\partial S}{\partial X}\right)_{U,N_i} = -\frac{Y}{T} \quad \left(\frac{\partial S}{\partial N_i}\right)_{U,X,N_j} = -\frac{\mu_i}{T}$$

$$\Rightarrow S = S(U, X, \{N_i\})$$

Also note because all of these quantities are extensive we can infer the following scaling relationship:

$$S(\lambda U, \lambda X, \{\lambda N_i\}) = \lambda S(U, X, \{N_i\})$$

Derivation of fundamental equation of thermodynamics -- continued:

$$S(\lambda U, \lambda X, \{\lambda N_i\}) = \lambda S(U, X, \{N_i\})$$

$$\frac{d(\lambda S)}{d\lambda} = \left(\frac{\partial S}{\partial(\lambda U)}\right)_{X,N_i} \frac{d(\lambda U)}{d\lambda} + \left(\frac{\partial S}{\partial(\lambda X)}\right)_{U,N_i} \frac{d(\lambda X)}{d\lambda} + \sum_i \left(\frac{\partial S}{\partial(\lambda N_i)}\right)_{U,X,N_j} \frac{d(\lambda N_i)}{d\lambda}$$

$$\Rightarrow S = \left(\frac{\partial S}{\partial(\lambda U)}\right)_{X,N_i} U + \left(\frac{\partial S}{\partial(\lambda X)}\right)_{U,N_i} X + \sum_i \left(\frac{\partial S}{\partial(\lambda N_i)}\right)_{U,X,N_j} N_i$$

$$\Rightarrow S = \frac{1}{T}U - \frac{Y}{T}X - \sum_i \frac{\mu_i}{T} N_i$$

$$\Rightarrow TS = U - YX - \sum_i \mu_i N_i$$

Fundamental equation of thermodynamics

$$TS = U - XY - \sum_i \mu_i N_i$$

Some consequences:

From first law of thermodynamics :

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

$$d(TS) = d\left(U - XY - \sum_i \mu_i dN_i\right)$$

$\Rightarrow$ Gibbs - Duhem equation :

$$SdT + XdY + \sum_i N_i d\mu_i = 0$$

Thermodynamic potentials

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

Differential : $dU = TdS + YdX + \sum_i \mu_i dN_i$

Fundamental equation : $U = TS + YX + \sum_i \mu_i N_i$

Further relationships :

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

Equations of state :

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

Analysis of internal energy continued:

Further relationsh ips :

Equations of state :

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

Maxwell' s relations :

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

Mathematical transformations for continuous functions of several variables & Legendre transforms:

$$z(x,y) \quad \Leftrightarrow \quad x(y,z)???$$

$$z(x,y) \Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$x(y,z) \Rightarrow dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$\text{But}: \left(\frac{\partial x}{\partial y}\right)_z = -\frac{(\partial z/\partial y)_x}{(\partial z/\partial x)_y}$$

Mathematical transformations for continuous functions of several variables & Legendre transforms continued:

$$z(x,y) \Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Let $u \equiv \left(\frac{\partial z}{\partial x}\right)_y$ and $v \equiv \left(\frac{\partial z}{\partial y}\right)_x$

Define new function

$$w(u,y) \Rightarrow dw = \left(\frac{\partial w}{\partial u}\right)_y du + \left(\frac{\partial w}{\partial y}\right)_u dy$$

For $w = z - ux$, $\quad dw = dz - udx - xdu = udx + vdy - udx - xdu$

$$dw = -xdu + vdy \qquad \Rightarrow \left(\frac{\partial w}{\partial u}\right)_y = -x \qquad \left(\frac{\partial w}{\partial y}\right)_u = \left(\frac{\partial z}{\partial y}\right)_x = v$$

For thermodynamic functions:

$$\text{Internal energy}: \quad U = U(S,V)$$

$$dU = TdS - PdV$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$\text{Enthalpy}: \quad H = H(S,P) = U + PV$$

$$dH = dU + PdV + VdP = TdS + VdP = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$\Rightarrow T = \left(\frac{\partial H}{\partial S}\right)_P \qquad V = \left(\frac{\partial H}{\partial P}\right)_S$$

Thermodynamic potentials – Internal Energy

Internal energy	$U(S, X, \{N_j\})$
Total Differential	$dU = T\,dS + Y\,dX + \sum_{j=1}^{r} \mu_j\, dN_j$
Fundamental Equation	$U = TS + YX + \sum_{j=1}^{r} \mu_j N_j$
Equations of State	$T = \left(\frac{\partial U}{\partial S}\right)_{X,\{N_j\}}$
$Y = \left(\frac{\partial U}{\partial X}\right)_{S,\{N_j\}}$	$\mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{S,X,\{N_{i \neq j}\}}$
Maxwell Relations	
$\left(\frac{\partial T}{\partial X}\right)_{S,\{N_j\}} = \left(\frac{\partial Y}{\partial S}\right)_{X,\{N_j\}}$	$\left(\frac{\partial T}{\partial N_j}\right)_{S,X,\{N_{i \neq j}\}} = \left(\frac{\partial \mu_j}{\partial S}\right)_{X,\{N_j\}}$
$\left(\frac{\partial Y}{\partial N_j}\right)_{S,X,\{N_{i \neq j}\}} = \left(\frac{\partial \mu_j}{\partial X}\right)_{S,\{N_j\}}$	$\left(\frac{\partial \mu_j}{\partial N_i}\right)_{S,X,\{N_{l \neq i}\}} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{S,X,\{N_{l \neq j}\}}$

Thermodynamic potentials – Enthalpy

Enthalpy	$H(S, Y, \{N_j\})$
Total Differential	$dH = T\,dS - X\,dY + \sum_{j=1}^{r} \mu_j\, dN_j$
Fundamental Equation	$H = U - XY = TS + \sum_{j=1}^{r} \mu_j N_j$
Equations of State	$T = \left(\frac{\partial H}{\partial S}\right)_{Y,\{N_j\}}$
$X = -\left(\frac{\partial H}{\partial Y}\right)_{S,\{N_j\}}$	$\mu_j = \left(\frac{\partial H}{\partial N_j}\right)_{S,Y,\{N_{i \neq j}\}}$
Maxwell Relations	
$\left(\frac{\partial T}{\partial Y}\right)_{S,\{N_j\}} = -\left(\frac{\partial X}{\partial S}\right)_{Y,\{N_j\}}$	$\left(\frac{\partial T}{\partial N_j}\right)_{S,Y,\{N_{i \neq j}\}} = \left(\frac{\partial \mu_j}{\partial S}\right)_{Y,\{N_j\}}$
$\left(\frac{\partial X}{\partial N_j}\right)_{S,Y,\{N_{i \neq j}\}} = -\left(\frac{\partial \mu_j}{\partial Y}\right)_{S,\{N_j\}}$	$\left(\frac{\partial \mu_j}{\partial N_i}\right)_{S,Y,\{N_{l \neq i}\}} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{S,Y,\{N_{l \neq j}\}}$

Thermodynamic potentials – Helmholz Free Energy

Helmholtz free energy	$A(T, X, \{N_j\})$
Total Differential	$dA = -S\,dT + Y\,dX + \sum_{j=1}^{\nu} \mu_j\, dN_j$
Fundamental Equation	$A = U - ST = XY + \sum_{j=1}^{\nu} \mu_j N_j$
Equations of State	$S = -\left(\frac{\partial A}{\partial T}\right)_{X,\{N_j\}}$
$Y = \left(\frac{\partial A}{\partial X}\right)_{T,\{N_j\}}$	$\mu_j = \left(\frac{\partial A}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}}$
Maxwell Relations	
$\left(\frac{\partial S}{\partial X}\right)_{T,\{N_j\}} = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{N_j\}}$	$\left(\frac{\partial S}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j}{\partial T}\right)_{X,\{N_j\}}$
$\left(\frac{\partial Y}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}} = \left(\frac{\partial \mu_j}{\partial X}\right)_{T,\{N_j\}}$	$\left(\frac{\partial \mu_j}{\partial N_i}\right)_{T,X,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,X,\{N_{l\neq j}\}}$

Thermodynamic potentials – Gibbs Free Energy

Gibbs free energy	$G(T, Y, \{N_j\})$
Total Differential	$dG = -S\,dT - X\,dY + \sum_{j=1}^{\nu} \mu_j\, dN_j$
Fundamental Equation	$G = U - TS - YX = \sum_{j=1}^{\nu} \mu_j N_j$
Equations of State	$S = -\left(\frac{\partial G}{\partial T}\right)_{Y,\{N_j\}}$
$X = -\left(\frac{\partial G}{\partial Y}\right)_{T,\{N_j\}}$	$\mu_j = \left(\frac{\partial G}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}}$
Maxwell Relations	
$\left(\frac{\partial S}{\partial Y}\right)_{T,\{N_j\}} = \left(\frac{\partial X}{\partial T}\right)_{Y,\{N_j\}}$	$\left(\frac{\partial S}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j}{\partial T}\right)_{Y,\{N_j\}}$
$\left(\frac{\partial X}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}} = -\left(\frac{\partial \mu_j}{\partial Y}\right)_{T,\{N_j\}}$	$\left(\frac{\partial \mu_j}{\partial N_i}\right)_{T,Y,\{N_{l\neq i}\}} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,Y,\{N_{l\neq j}\}}$

Thermodynamic potentials – Grand Potential

Grand potential	$\Omega(T, X, \{\mu_j\})$
Total Differential	$d\Omega = -S\,dT + Y\,dX - \sum_{j=1}^{\nu} N_j\, d\mu_j$
Fundamental Equation	$\Omega = U - TS - \sum_{j=1}^{\nu} \mu_j N_j = XY$
Equations of State	$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{X,\{\mu_j\}}$
$Y = \left(\frac{\partial \Omega}{\partial X}\right)_{T,\{\mu_j\}}$	$N_j = -\left(\frac{\partial \Omega}{\partial \mu_j}\right)_{T,X,\{\mu_{l\neq j}\}}$
Maxwell Relations	
$\left(\frac{\partial S}{\partial X}\right)_{T,\{\mu_j\}} = -\left(\frac{\partial Y}{\partial T}\right)_{X,\{\mu_j\}}$	$\left(\frac{\partial S}{\partial \mu_j}\right)_{T,Y,\{\mu_{l\neq j}\}} = \left(\frac{\partial N_j}{\partial T}\right)_{X,\{\mu_j\}}$
$\left(\frac{\partial Y}{\partial \mu_j}\right)_{T,X,\{\mu_{l\neq j}\}} = -\left(\frac{\partial N_j}{\partial X}\right)_{T,\{\mu_j\}}$	$\left(\frac{\partial N_j}{\partial \mu_i}\right)_{T,X,\{\mu_{l\neq i}\}} = \left(\frac{\partial N_i}{\partial \mu_j}\right)_{T,X,\{\mu_{l\neq j}\}}$

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$_i$***	$d\Omega = -SdT + YdX - \sum_i \mu_i dN_i$	$\Omega = U - TS - \sum_i \mu_i N_i$

Some examples

Ideal gas with *N* particles of the same type and with

X → *V* *Y* → -*P*

$$k \equiv k_B \quad \text{Boltzmann constant;} \quad \gamma \equiv C_P / C_V$$

$$PV = NkT$$

$$U = \frac{Nk}{\gamma - 1} T = \frac{PV}{\gamma - 1}$$

$$H = U - XY = U + PV$$

$$\Rightarrow H = \frac{Nk\gamma}{\gamma - 1} T$$

Some examples -- continued

Ideal gas with *N* particles of the same type and with

X → *V* *Y* → -*P*

$$k \equiv k_B \quad \text{Boltzmann constant;} \quad \gamma \equiv C_P / C_V$$

$$PV = NkT$$

$$U = \frac{Nk}{\gamma - 1} T = \frac{PV}{\gamma - 1}$$

$$A = U - TS$$

Previously, we have shown :

$$S(T,V) = \frac{Nk}{\gamma - 1} \left(\ln \left(\frac{TV^{\gamma-1}}{T_0 V_0^{\gamma-1}} \right) \right) + S_0$$

Some examples -- continued

Ideal gas with N particles of the same type and with

$X \rightarrow V$ $Y \rightarrow -P$

$$U = \frac{Nk}{\gamma - 1} T \qquad A = U - TS$$

$$\text{with} \quad S(T,V) = \frac{Nk}{\gamma-1}\left(\ln\left(\frac{TV^{\gamma-1}}{T_0 V_0^{\gamma-1}}\right)\right) + S_0$$

$$A = \frac{Nk}{\gamma-1} T\left(1 - \ln\left(\frac{TV^{\gamma-1}}{T_0 V_0^{\gamma-1}}\right)\right) - S_0 T$$

$$= -NkT\left(1 + \ln\left(\frac{T^{\frac{1}{\gamma-1}} V}{T_0^{\frac{1}{\gamma-1}} V_0}\right)\right) - \left(S_0 - \frac{\gamma Nk}{\gamma-1}\right)T$$

1/16/2014 PHY 770 Spring 2014 -- Lecture 2 22